PRECISE ATOMIC MASSES AND MASS DIFFERENCES FOR Hf, Ta, W and Re

by

Kumar Satish Sharma, B.Sc.(Hon.)

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AUTHOR: Kumar Satish Sharma, B.Sc.(Hon.), University of Manitoba

SUPERVISOR: Professor R.C. Barber

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SCOPE AND CONTENTS:

The stability of operation and the sensitivity of the Manitoba II spectrometer have been significantly improved through changes and modifications of the instrumentation. This has made it possible to redetermine the results for two doublets involving the rare nuclides ^{180}W and ^{174}Hf. The mass difference $^{181}Ta - ^{180}Ta$ has also been determined for the first time by a mass spectrometric technique.

A total of 16 new doublet spacings have been determined in this work. These new results, when combined with a few other precise measurements, constitute for the first time a completely over determined set of mass differences between the naturally occurring isotopes of Hf, Ta, W and Re. A set of self consistent masses and mass differences was derived from these data and the systematic properties of the calculated S_{2n} values have been interpreted in terms of Nilsson single particle levels. The data are also used to determine the groundstate energy level structure at A = 180.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

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CHAPTER 1

INTRODUCTION

1-0. INTRODUCTION

The atomic view of matter began as a result of speculations by the ancient Greek philosophers. Empedocles (430 B.C.) and later Democritus (400 B.C.) attempted to construct a doctrine which explained the many and varied properties of materials in terms of a set of tiny indivisible particles. This theory, though briefly revived by Roman philosophers, lay dormant until the 1800's. At this time it was once again revived by Dalton and other chemists in an attempt to explain the law of proportions in chemistry. Dalton proposed that in a chemical reaction a fixed number of identical particles of one type combine with a fixed number of particles of another type to produce a composite particle. The law of proportions then reflected the numbers of particles involved and their masses. This theory represents a fairly accurate model of chemical reactions in terms of interactions between atoms, except that the possibility of the existence of isotopes was not considered.

In the chemist's view, the atom was no more than a convenient model to explain certain chemical phenomena. It was generally accepted that atoms were microscopic indivisible particles that could not be created, destroyed or changed in any manner. As a result of investigations by Goldstein (1886), Wien (1898) and Thomson (1913), features like the charge to mass ratio and the first details of the structure of atoms began to emerge.

The current view of the atom as a physical particle having the properties of mass, charge and extension in space and a fairly complex structure has developed over roughly the last 100 yrs. It is with the property of mass that this work is mainly concerned.

1-1. STANDARDS OF MASS

Mass, like the quantities of length and time, escapes definition except in terms of a prescription for its measurement. This prescription usually takes the form of comparing the mass of the object in question with the mass of a second object which is taken to be the standard. Similar prescriptions are used in the definitions of length and time.

The mass of an object may be compared to the standard by examining the accelerations of the object and the standard when subjected to a particular force. The property measured in this case is called "inertial mass". Comparisons between the object and standard may also be made on the basis of the gravitational interaction between each of them and a third mass. In this case the "gravitational mass" is said to be measured. The equality between inertial and gravitational mass has been established by Eotvos and Dicke (as described by Roll, 1964) to an accuracy of $1/10^{11}$.

A standard of mass, in the form of a solid, platinum - iridium (90/10) alloy, cylinder with height equal to its diameter has been defined as 1 kilogram and is kept at the Bureau International des poids et mesures in France. Copies of the standard kilogram may be compared to the original to a precision of $1/10^{8}$.

The sheer size of the kilogram, which is approximately 10^{25} times the mass of an atom, coupled with the difficulty in designing experiments to compare masses of atoms with the standard kilogram makes this mass standard an unsuitable one for use in atomic mass determinations. Moreover this standard is not universally available to all experimenters. Therefore, a second standard of mass has been adopted for use in the atomic domain.

Before 1960 two scales of atomic mass were in use: the chemical scale in which the gram atomic weight of Oxygen (of natural isotopic composition) was chosen to be exactly 16 g. and the physical scale in which the atomic mass of ^{16}O was chosen to be exactly 16 atomic mass units (16 amu). These two scales were replaced by a single scale (Mattauch, 1960 and Wichers, 1962) in which a single atom of ^{12}C has a mass of exactly 12 mass units (12 u). This standard has the advantage of being available to any investigator and in particular facilitates the determination of atomic masses by mass spectrometric methods.

Thus, one may express the unit of atomic mass as

$$1 \text{ u} = 1/12 \text{ (mass of } ^{12}C). \qquad (1\text{-}1)$$

Combining this definition with the definition of a gram-atomic weight and Avogadro's number, N_A, it is possible to define the atomic mass unit in terms of the standard kilogram as follows

$$1 \text{ u} = 1/N_A \text{ g}. \qquad (1\text{-}2)$$

A connection between the atomic mass scale and the energy scale (electron volts) may be established by means of the now well known relation between mass and energy presented by Einstein in 1905 viz.

$$E = mc^2. \qquad (1\text{-}3)$$

Combining Eqns. 1-2 and 1-3 with the definition of an electron volt yields,

$$1\ u = c^2/N_A e \quad eV \tag{1-4}$$

where e is the charge of the electron (in coulombs) and c is the speed of light (in m/sec).

Recently Avogadro's number has been determined to a precision of 1 part per million, in a beautiful experiment, by Deslattes (1974, 1976). A standard value for general metrological use has been recommended by the Consultative Committee on the Definition of the Metre (Cohen, 1976) which gives the speed of light with a precision of $4/10^9$. These results and others have been combined in a least squares adjustment by Cohen (1976) and a self consistent set of fundamental constants obtained. The quantities in equations 1-2 and 1-4 may be calculated from the results of this adjustment as,

$$1\ u = 1.660\ 565\ 5 \pm 86\ X10^{-27}\ kg \tag{1-5a}$$

$$1\ u = 931.501\ 6 \pm 26\ MeV \tag{1-5b}$$

1-2. THE IMPORTANCE OF ATOMIC MASS DETERMINATIONS

Inasmuch as a knowledge of the mass of macroscopic objects is useful in understanding their nature and behaviour so also it is with atoms. It is found that the masses of atoms (measured on the ^{12}C scale) differ from whole numbers by less than 0.1 u. This is a good indication that atoms are composite structures made up of the same constituent parts. Moreover the magnitude of this deviation from whole numbers provides a wealth of information about the binding energies of the constituent parts of the atom. Many modern techniques exist (some

of which are discussed below) which allow the experimenter to evaluate atomic masses and mass differences to a precision of ~ 1 keV. While this is not enough to study effects involving atomic electrons, nuclear binding energy effects which are typically of the order of several MeV may be easily investigated. In particular, the variation in these binding energies from one nuclide to another provides a picture of the interactions between the nucleons in the nucleus. A few of the methods used to determine atomic masses and mass differences are outlined below.

1-3. METHODS OF ATOMIC MASS DETERMINATION

A. <u>α - decay</u>: The α - decay of a nucleus may be represented by the reaction

$$ {}^{A}_{z}X \rightarrow {}^{A-4}_{z-2}Y + {}^{4}_{2}He + Q \qquad (1\text{-}6) $$

By measuring the energy of the α - particle and calculating the related recoil energy of the parent nucleus, the mass difference between X and Y may be determined. Such energy measurements are usually performed with a magnetic analyser which is calibrated by means of α - particles of a known energy (α - particles emitted in the decay of isotopes of polonium are commonly used). This type of measurement is responsible for the determination of most of the atomic mass differences among nuclei heavier than Pb. Uncertainties as low as 50 eV have been reported by Rytz (1972) in the determination of the energies of some of the standards used. In addition to magnetic analysers surface barrier detectors may also be employed to measure α - particle energies. In this case the uncertainty of a typical measurement is ~ 20 keV.

B. β - decay: The β - decay of a nucleus involves one of the following reactions

$$^{A}_{z}X \rightarrow {}^{A}_{z+1}Y + \beta^{-} + \bar{\nu} + Q \qquad (1\text{-}7a)$$

$$^{A}_{z}X \rightarrow {}^{A}_{z-1}Y + \beta^{+} + \nu + Q \qquad (1\text{-}7b)$$

$$^{A}_{z}X + e^{-} \rightarrow {}^{A}_{z-1}Y + Q \qquad (1\text{-}7c)$$

In the first two cases (Eqns. 1-7a,b) the energy released in the decay is shared by the β - particle and the neutrino. The β - particles are therefore seen to have a continuous spectrum of energies. The Q-value must therefore be estimated as the maximum possible β - particle energy from the observed energy spectrum. This is called the end-point of the β - particle spectrum. A knowledge of the energies of any accompanying γ - rays is also essential. Precisions of ~ 0.1 keV have been attained in some cases (e.g. with the large iron free magnetic spectrometer at Chalk River) but typical uncertainties are ~ 10 keV.

The energy released in the third process (Eqn. 1-7c) is difficult to measure accurately. In this process an atomic electron (usually from the inner shell) is captured by the nucleus and one or more X-rays are emitted. The energy released in the course of this reaction is deduced from the sum of the energies of the X-rays observed. The low energies and the number of X-rays involved make it difficult to measure accurately the energy released in this process.

C. Nuclear reactions: Nuclear reactions induced by charged particle beams and neutrons are also used to determine mass differences. In this method a target nucleus (X) is bombarded by a projectile (a) resulting in the formation of a product nucleus (Y) and an outgoing

projectile (b). Such reactions are customarily written in the form X (a,b) Y. In this case the energy released or Q-value is defined as

$$Q = (M_x + M_a - M_y - M_b)\ c^2 \qquad (1.8)$$

This quantity may be evaluated experimentally by measuring the energies of a, b and Y. The most precise measurements of this type are in (n, γ) reactions involving thermal neutrons, for which uncertainties < 1 keV are frequently attained. Other reactions yield results ranging from 1-10 keV.

D. Mass spectrometric methods: In this method the absolute mass of an atom X may be determined directly by comparing the mass of the atom with the mass of a hydrocarbon fragment in a mass spectrometer. The resulting mass difference enables a direct calculation of the mass of X. The absolute masses of a number of nuclides have been determined to a high degree of precision (uncertainties of ~ 100 eV) in this manner. These masses, some of which are listed in Table 4-2, may be used as secondary standards for mass determinations. Uncertainties of 1 - 5 keV are typically obtained.

Ionic species containing atoms X and Y as part of their constituents may also be compared using this technique. By selecting ions constituted of atoms whose masses are known precisely and X and Y and measuring the mass difference between them the mass difference between X and Y can be determined. This method, which has been in use at many laboratories, yields results whose precision approaches 1 keV in most cases. Precisions as high as 65 eV have been attained by some investigators.

Until recently mass spectrometric determinations have been

carried out only among the naturally occurring nuclides while data on the unstable nuclides was obtained through nuclear reaction and decay Q-values. More recently Klapisch and his associates (Thibault et al, 1975) at Orsay and Wollnik (1975) at Lohengrin have utilized mass spectrometric techniques to study short-lived, unstable nuclides produced in charged particle reactions. In this laboratory (Manitoba I and II) a helium jet transport system is currently under construction (Venkatasubramanian et al, 1979). This system will be used to transport short-lived nuclides, produced by (p, xn) reactions, in the University of Manitoba cyclotron vault, to the mass spectrometry laboratory, some 100 m away, for analysis.

1-4. TABLES OF ATOMIC DATA

The results from the various laboratories represent a large number of determinations of atomic mass differences and a much smaller number of absolute mass determinations. These data usually provide several ways of evaluating any particular mass difference, not all of which will agree with other data. All of these measurements may be written as a linear combination of the atomic masses. Thus a system of linear equations, each equation representing a mass or mass difference, with the set of atomic masses representing the unknown quantities may be set up. This system of equations is overdetermined for many nuclides as the number of measurements greatly exceeds the number of nuclides considered. A least squares solution for this system of equations is extracted in a manner originated by Mattauch (1965) and continued to recent years by Wapstra and his collaborators Gove (1971)

and Bos (1977). The resulting set of self-consistent masses and mass differences is published approximately every 5 yrs. in the form of the so-called Mass Evaluations. These compilations have the advantage that in the course of the calculation grossly inconsistent data may be recognized and removed to further enhance the reliability of the calculated results.

CHAPTER 2

HISTORY AND DEVELOPMENT OF MASS SPECTROMETRY

2-0. INTRODUCTION

In 1886, while working with discharge tubes, Goldstein discovered positive rays. These rays were subsequently deflected by Wien (1898) with electric and magnetic fields and shown to have an e/m ratio that was much smaller than that of the electron. In order to investigate further the nature of these rays Thomson (1913) built his famous positive ray parabola apparatus at Cambridge. This device, which consisted of parallel, coterminous electric and magnetic fields, analysed the ion beam presented to it into a family of parabolas, each parabola corresponding to a particular e/m. With this apparatus Thomson (1912) was able to identify the constituents of the positive rays as ionized molecules of the discharge tube gas and found strong evidence that neon exists in two isotopic forms.

2-1. EARLY INSTRUMENTS

Under the encouragement of Thomson, Aston, then a research student at Cambridge, designed and built an instrument, which he called a "mass spectrograph", to be used in the study of stable isotopes (Aston, 1919). This instrument had many of the characteristics of the deflection instruments which came later.

In general, in a deflection instrument, an ion source is used to illuminate an entrance or object slit. This slit is used as the object for an arrangement of electric and magnetic fields which

produce a set of images, each of which corresponds to a different e/m value at a photographic plate or at an exit slit which selects a particular mass for detection. The sharpness of each image, and hence the resolution of the apparatus, depends on the focussing properties of the apparatus, the variations in the velocities of the ions and the angular divergence of the ion beam used.

In Aston's instrument a highly collimated beam of ions was deflected first by an electric field and then by a magnetic field (in the same plane) and then detected on a photographic plate. The instrument had the property of "velocity focussing" i.e. that ions having different velocities did not contribute to the broadening of the image at the photographic plate.

At almost the same time Dempster (1918) built an instrument at Chicago to perform the same function. This instrument did not have the velocity focussing property but instead had a direction focussing property. That is, the apparatus focussed a monoenergetic ion beam, which initially diverged in direction, at an exit slit, and thereby greatly reduced the need for collimating the ion beam. In this instrument, different mass spectral lines were brought to a focus at the exit slit by changing the magnetic field. Bainbridge (1933) added a Wien velocity filter to a Dempster type instrument to reduce the effects caused by variations in the ionic velocity.

Herzog (1934) presented a general analysis of the focussing properties of electric and magnetic fields which lead to the construction of several instruments having both velocity and direction focussing. A summary of the ion optical properties of the two major

constituent fields used in mass spectrometers is briefly presented below.

2-2. POSITIVE ION OPTICS

The trajectories of ions of mass, m and charge, q as they traverse electric (E) and magnetic (B) fields are defined by the Lorentz force equation.

$$F = q\ (E + V \times B) \qquad (2\text{-}1)$$

where V is the velocity of the ion considered. This relationship was applied to the particular field geometries and yielded the results summarized below.

A. Magnetic Analysers: One of the major components of mass spectrometers is the sector shaped homogenous magnetic field (see Fig. 2-1). If the magnetic field is constant and perpendicular to the velocity of an ion entering it, then the trajectory of the ion is a circle of radius a_m such that

$$a_m = \frac{MV}{qB} \qquad (2\text{-}2)$$

in a plane perpendicular to the applied field.

Suppose that ions of mass M_o and velocity V_o emerge from an object point, O (Fig. 2-1) with a half angular spread, α ($\alpha << 1$). An ion, following the median path, enters the magnetic field normally after traversing a distance l_m, where it follows a circular path of radius a_m. It emerges from the field normally and proceeds to an image point, I, a distance l'_m away from the field boundary, where the ion beam is focussed to a point. For normal entry and exit, the

points O, C and I all lie on the same straight line as stated in a rule by Barber (1933). A more complete geometrical method for locating O, C and I for cases of non-normal incidence and exit was given later by Cartan (1937).

An analysis of this situation, using methods commonly used in ion optics was presented by Herzog (1934). He considered displacements of the image b_m' resulting from small displacements of the object, b_m, a change in ionic mass from M_o to M_o $(1+\gamma)$ and change in ionic velocity from V_o to V_o $(1+\beta)$. He found that when β and γ are small $(\beta, \gamma << 1)$ this displacement is given by:

$$b_m' = a_m (\beta+\gamma) B_1 - b_m B_2 \qquad (2\text{-}3)$$

where B_1 and B_2 are constants dependent on the geometry of the apparatus (Table 2-1).

B. Electrostatic Analysers: Another common component of deflection type mass spectrometers is the electrostatic analyser. This analyser usually consists of a sector of a cylindrical condensor. A radial electric field is generated by applying a potential V between a pair of concentric cylindrical electrodes of radii $a_e + k$ and $a_e - k$ respectively (Fig. 2-2). The magnitude of this electric field E is given by

$$E \approx \frac{V}{2k} \qquad (2\text{-}4a)$$

for $k << a_e$. As in the case of the magnetic analyser, discussed above, ions of mass M_o and velocity V_o start from an object point O (Fig. 2-2) with a half angular spread α $(\alpha << 1)$. An ion following the median path traverses a distance l_e before entering the field normally where it follows a circular path of radius a_e such that

$$a_e = \frac{2k\ M_o\ V_o^2}{q\ V} \qquad (2\text{-}4b)$$

The ion exits the field normally and proceeds to an image point I at a distance l_e' where the ion beam is brought to a focus. The displacement of the image, b_e' as a result of small displacements of the object, b_e, a change in the ionic mass from M_o to $M_o\ (1 + \gamma)$ and change in the ionic V_o to $V_o\ (1 + \beta)$ has been given by Herzog as

$$b_e' = a_e\ (\beta + \tfrac{1}{2}\ \gamma)\ E_1 - b_e\ E_2 \qquad (2\text{-}5)$$

where E_1 and E_2 are constants, dependent on the geometry of the apparatus (Table 2-1), and $\beta, \gamma << 1$.

C. Double focussing: It will be noticed that in Eqn. 2-5 the coefficient for γ differs from the coefficient for β. This is not the case for the isolated magnetic analyser (Eqn. 2-3). It is therefore possible to design a compound system using an electrostatic analyser and a magnetic analyser in which the velocity dispersions cancel while a mass dispersion remains.

Let us consider a compound system in which the image formed by the electrostatic analyser is presented as the object to the magnetic analyser which subsequently forms an image at the detector. Using Eqn. 2-3 and 2-5 we describe displacements of the final image, b', for small displacements of the object b, changes in ionic mass from M_o to $M_o\ (1 + \gamma)$ and changes in ionic velocity from V_o to $V_o\ (1 + \beta)$ by

$$b' = a_m\ (\beta + \gamma)\ B_1 - \left[a_e\ (\beta + \tfrac{1}{2}\ \gamma)E_1 - b\ E_2\right] B_2 \qquad (2\text{-}6)$$

This expression can be rewritten as

$$b' = \gamma\ (a_m\ B_1 - \tfrac{1}{2}\ a_e\ E_1\ B_2) + \beta\ (a_m\ B_1 - a_e\ E_1\ B_2) + b\ E_2\ B_2 \qquad (2\text{-}7)$$

Therefore by choosing

$$a_m B_1 = a_e E_1 B_2 \qquad (2\text{-}8)$$

we can construct an instrument which not only has direction focussing properties but also one in which the image is not broadened by small variations in the ionic velocities. Such an instrument is said to have double focussing properties.

It should be emphasized at this point that Herzog's analysis is accurate only to first order terms in β and γ. Many instruments, based on Herzog's theory have been constructed, the earliest and most notable ones by Dempster (1935) in Chicago, Bainbridge and Jordan (1936) at Harvard and Mattauch and Herzog (1934) in Vienna.

The 1950's saw the construction of several large double focussing mass spectrometers, an order of magnitude larger in size than their predecessors. These instruments were capable of attaining high resolving powers (10^5). Such instruments were built by Johnson and Nier (1953) at Minnesota, Duckworth (1957) at McMaster (subsequently moved to Manitoba and referred to as Manitoba I), Ogata and Matsuda (1957) at Osaka (referred to as Osaka I), Collins and Bainbridge (1957) at Harvard, Hintenberger (1957) at Mainz and Stevens (1960) at Argonne, the latter three of which incorporated at least partial second order corrections to the ion-optics (see Table 2-2).

Herzog's theory was extended to include second order terms in β, γ and α by Hintenberger and König (1959) who used a slightly different approach to the problem. Using methods similar to ones used in geometrical optics Hintenberger and König expressed the deviation of a ray, Y, from the optic axis (which in Figs. 2-1 and 2-2 is the

same as the median ray) as function of α and β as follows,

$$Y = a_m (B_{10} \alpha + B_{20}\beta + B_{11} \alpha^2 + B_{12} \alpha \beta + B_{22} \beta^2) \quad (2\text{-}9)$$

where the five coefficients B_{ij} may be expressed in terms of the eight geometrical parameters of the compound system, viz., ϕ_m, ϕ_e (the angles of deflection in the magnetic and electric fields respectively), ε' and ε'' (the angles that the entrance and exit boundaries of the magnetic field make with the normals to the ion path), $\frac{a_e}{a_m}$ (the ratio of the radius of curvature in the electric field to that in the magnetic field), $\frac{l_e}{a_m}$, $\frac{l_m'}{a_m}$ and $\frac{d}{a_m}$ (where l_e is the distance from the object slit to the electric field, l_m' is the distance from the magnetic field to the object slit and d is the distance separating the two fields). Second order double focussing is achieved by the requirement that all the B_{ij} vanish simultaneously for a particular geometry, i.e.,

$$B_{10} = B_{20} = B_{11} = B_{12} = B_{22} = 0 \quad (2\text{-}10)$$

Hintenberger and König selected values for three of the geometrical parameters and solved the system of equations (Eqn. 2-10) to obtain unique solutions for the values of the five remaining geometrical parameters, using a digital computer. In this manner a list of possible geometries for second order double focussing mass spectrometers was generated and published by Hintenberger and König (1959).

An instrument based on one of the geometries suggested in these lists was built by Barber et al (1967) at the University of Manitoba. This spectrometer, on which the work for this thesis was done, will be referred to as Manitoba II.

A second order double focussing mass spectrometer was also constructed at Osaka (referred to as Osaka II) by Matsuda et al (1966). This instrument utilizes the large mass dispersions achieved by using a non uniform (1/R) magnetic field to obtain high resolutions (1/500,000). In addition to deflection type instruments very significant contributions have also been made by a mass synchrometer designed by the late L.G. Smith. Using this instrument Smith (1967) carried out some of the most precise mass determinations made among the light elements (eg. H, D, T, ^{14}N, ^{16}O, ^{35}Cl, ^{37}Cl). This spectrometer has since been transferred from Princeton to Delft where modifications are being carried out by Koets (1975) under the direction of A.H. Wapstra.

D. Fringe Fields: In the above discussion the effects of fringing fields have been neglected. In most cases the effects on the focussing properties of instruments are far from negligible.

In the electrostatic cases effective field boundaries may be accurately established at the physical boundaries of the electrodes by the use of grounded diaphragms positioned according to theory given by Herzog (1935).

The effects of magnetic fringe fields on focussing has been elaborated by Kerwin (1963). For the Manitoba II spectrometer the approximate correction necessary to compensate for the fringe field was that advocated by Nier (1940). He suggested that the effects of the magnetic fringe field may be approximated by extending the field one gap width past the physical boundary of the pole pieces of the magnet. This rule works well, especially with narrow gaps.

In addition, the magnetic fringe field has the property of focussing the ion beam in the vertical plane, viz. z focussing (Cross, 1951). This property is instrumental in enhancing the transmission of Manitoba II.

2-3. ELEMENTS OF MASS SPECTROMETRY

The analysis of Herzog may be used to describe further the properties of double focussing instruments. Eqn. 2-7 may be rewritten as

$$b' = D\gamma + \mathfrak{M}b \qquad (2\text{-}11)$$

It will be seen from Eqn. 2-11 that a displacement, b, of the object produces a displacement of b' of the image. Thus $\mathfrak{M}$ can be readily identified as the magnification of the instrument. Similarly, in Eqn. 2-11, the coefficient D is a measure of the displacement of the image when the ionic mass is changed ($\gamma = 1$). This quantity is called the dispersion of the instrument.

Two commonly used methods of ion detection in mass spectrometry are the photographic and the electronic method. The performance of a given instrument differs according to the techniques used. In both cases the object of the ion-optical system is a slit of width S_o illuminated by an ion beam. A series of images of width, $\mathfrak{M}\ S_o$, corresponding to the different mass constituents are formed at some focus point where they are recorded in some manner.

With the photographic technique the images are recorded on a photographic plate in a manner similar to that in optical spectrographs. Since the spectral lines have a width W given by

$$W = \mathfrak{M} S_o \tag{2-12}$$

the images corresponding to the two masses must be separated by at least this amount to be resolved as separate lines. Thus

$$\gamma D = M S_o \tag{2-13}$$

Therefore the resolution, R, of the instrument for a slit width S_o is given by

$$R = \gamma = \frac{\Delta M}{M_o} = \frac{\mathfrak{M} S_o}{D} \tag{2-14}$$

In the case of electrical detection the image of the object slit is usually swept across a slit of width S_i, placed at the focus of the instrument, by a small sweep field. This has the effect of broadening the image width, W, as seen by a detector placed behind the image slit in such a way that

$$W = \mathfrak{M} S_o + S_i \tag{2-15}$$

Therefore the resolution, R, is given in this case by

$$R = \gamma = \frac{\Delta M}{M_o} = \frac{\mathfrak{M} S_o + S_i}{D} \tag{2-16}$$

When the photographic technique is used the mass difference between a pair of lines is readily obtained from a knowledge of the spacing between the lines and the dispersion of the instrument. In practice however difficulties arise in the precise determination of these quantities. To further complicate matters double focussing, in most cases, is only obtained for one particular value of a_m (as a consequence of Eqn. 2-8) since a_e is fixed. However this is not a serious problem as the focussing characteristics change slowly with displacements from the optic axis.

In the case of electronic detection only one value for a_m is

used as different masses are brought successively to the same image point, by changing the fields in the instrument. By measuring the amount that these fields are changed to bring two lines into focus successively, one can determine the mass difference between the two ion-groups. This technique, which is called peak matching, is the cornerstone of high-precision mass spectrometry.

The width of an image at the detector of a mass spectrometer is given by

$$W = R\ M \tag{2-17}$$

where R is the resolution and M is the ionic mass. If it is possible to locate the position of the spectral line within some fraction, f of the line width, then the uncertainty in the mass determination, δm, will be

$$\delta_m = f\ R\ M. \tag{2-18}$$

The corresponding precision of the determination is then given by

$$\frac{\delta_m}{M} = f\ R \tag{2-19}$$

For the photographic technique f is approximately 1/50. For peak matching techniques f ranges from 1/500, where visual techniques are used to judge peak coincidence, to 1/5000 when this method is augmented with digital data acquisition and processing techniques. This gain in precision more than offsets the loss in resolution (usually a factor of 2) that arises with electrical detection methods as predicted by Eqn. 2-16.

A. Peak matching: The peak matching technique is based on a theorem by Swann (1931) and by Bleakney (1936). Starting with the Lorentz

force equation (Eqn. 2-1) Bleakney showed that an ion of mass M' can be made to follow exactly the same trajectory as an ion of mass M through a series of constant electric and magnetic fields if all the magnetic fields are held constant and if all the electric fields E_i are changed to E_i' such that

$$M' E_i' = M E_i \tag{2-20}$$

Eqn. 2-20 may also be written as

$$\frac{\Delta M}{M'} = \frac{\Delta E_i}{E_i} \tag{2-21}$$

where $\Delta M = M' - M$ and $\Delta E_i = E_i - E_i'$.

Thus if the magnetic fields used in a spectrometer are held constant and if the electric fields are all changed as prescribed by Eqn. 2-21 then the second member of a mass spectroscopic doublet may be brought to the position where the first member had been initially focussed.

This technique was first developed by Smith and Damm (1953, 1956) and subsequently applied to a deflection type instrument by the group at the University of Minnesota (Giese and Collins, 1954, Quissenberry, 1956). A mass spectral peak is generated by sweeping the ion beam across the collector slit S_c. This sweep is synchronized with the sweep of an oscilloscope which is used to display the transmitted ion current as a function of time. If, on alternate traces of the oscilloscope, the potentials applied to the instrument (and hence the electric fields) are changed according to Eqn. 2-21, the two peaks in question will appear to coincide on the display oscilloscope screen. This is known as the matched condition.

Accordingly Eqn. 2-21 is rewritten in the form

$$\frac{\Delta M}{M'} = \frac{\Delta V_i}{V_i} \qquad (2\text{-}22)$$

Thus from a measurement of $\frac{\Delta V}{V}$ at a convenient electrode and the mass of one of the peaks the mass difference ΔM may be calculated. In a double focussing mass spectrometer, the peak position is most sensitive to the potential applied to the plates of the electrostatic analyser, V_e. Then the mass difference is determined by

$$\Delta M = M \frac{\Delta V_e}{V_e} \qquad (2\text{-}23)$$

Extensive use has been made of digital techniques to facilitate the detection of the matched condition and to remove possible operator and instrumental biases. Some of these methods will be described in detail later. A comprehensive treatment of the details of this method may be found in Meredith (1972).

B. Systematic errors: One of the critical requirements of peak matching is that Eqn. 2-22 be satisfied faithfully. It is possible, however, for potentials to arise in the instrument that are beyond the control of the operator. When this happens small, but persistent, systematic errors appear in the masses determined. These errors, which are proportional to the doublet width, ΔM, have been investigated in detail for Manitoba II by Southon (1973, 1977). It was believed that the dominant mechanism for producing these errors was the collection of charges on insulating films that were formed on the electrostatic analyser plates. The phenomenon of surface charges accumulating on relatively clean metal plates has been investigated by Petit-Clerc and Carette (1968, 1970) who found that it was possible for potentials of

up to 0.5 V to develop and persist for several hours when the plates were subjected to electron or ion-bombardment.

The magnitude of the systematic error, E, is determined by measuring the spacing between two widely spaced mass spectral peaks whose separation is well known. By comparing the measured mass difference, ΔM_{meas}, with the well known value for the mass difference, ΔM, it is possible to calculate E as follows,

$$E = \frac{\Delta M - \Delta M_{meas}}{\Delta M} \qquad (2\text{-}24)$$

Then if $\Delta M'$ is the mass difference determined for a narrow doublet the corrected value, ΔM, is given by

$$\Delta M = \Delta M' \ (1 + E) \qquad (2\text{-}25)$$

For Manitoba II E is approximately 150 parts per million and has shown very little change from day to day.

TABLE 2-1

Ion Optical Coefficients (1st order focussing)

Coefficient	Definitions
B_1	$1 + \frac{f_m}{l_m - g_m}$
B_2	$\frac{f_m}{l_m - g_m}$
E_1	$1 + \frac{f_e}{l_e - g_e}$
E_2	$\frac{f_e}{l_e - g_e}$
f_m	$\frac{a_m}{\mathrm{Sin}\phi_m}$
g_m	$f_m \mathrm{Cos}\phi_m$
f_e	$\frac{a_e}{\sqrt{2}\ \mathrm{Sin}(\sqrt{2}\ \phi_e)}$
g_e	$fe\ \mathrm{Cos}(\sqrt{2}\ \phi_e)$

Table 2-2 Current high resolution mass spectrometers

Location	B^*_{11}	B^*_{12}	B^*_{22}	Resolving Power**	Latest Measurements	Description of Instrument
Mainz	0	-11.5	-10.2	70,000		Hintenberger (1957)
Osaka II	0	0	0	300,000	Nakabushi (1970)	Matsuda (1966)
Argonne	0	-6.69	-10.33	200,000	Stevens (1970)	Stevens et al (1960)
Harvard	0	-6.1	-1.4	100,000	Kerr (1971)	Collins and Bainbridge (1957)
Osaka I	4.54	-13.2	+2.93	150,000	Katakuse (1972)	Ogata and Matsuda (1957)
Princeton/Delft	-	-	-	150,000	Smith (1975)	Smith (1967)
Manitoba I	0.70	-0.37	-2.12	100,000	Barnard (1977)	Duckworth et al (1957)
Manitoba II	0	0	0	200,000	Kozier (1979)	Barber et al (1967)
Minnesota	0	-2.4	1.4	80,000	Halverson (1979)	Johnson and Nier (1953)

* from Williams and Duckworth (1972).

** estimated at the "base" (i.e. at ~ 5% peak height).

Fig. 2-1 Magnetic Analyser

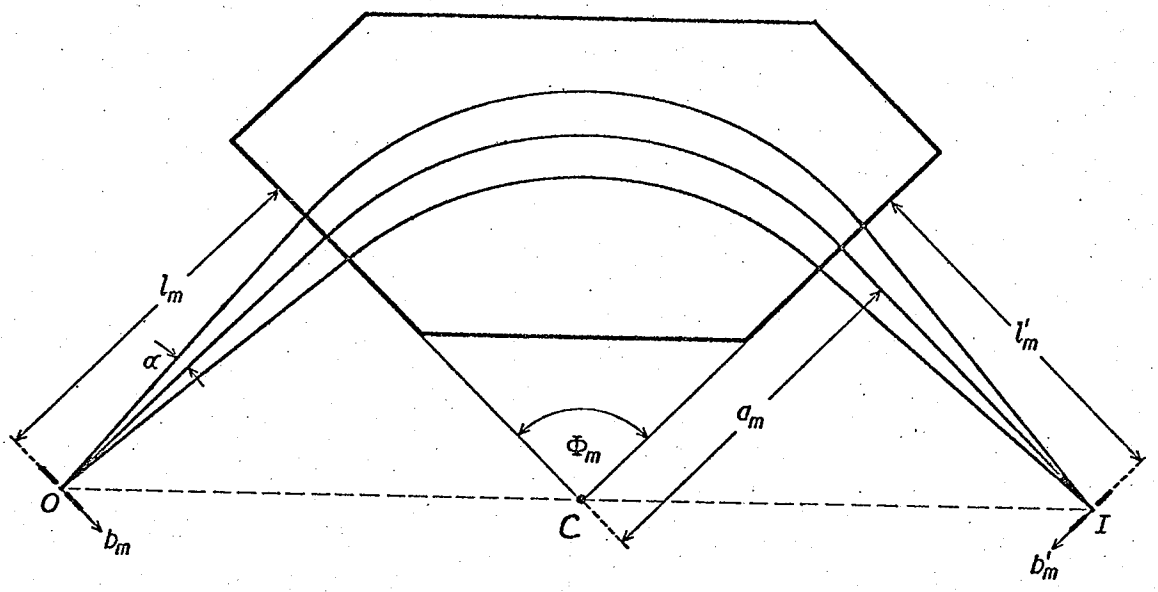
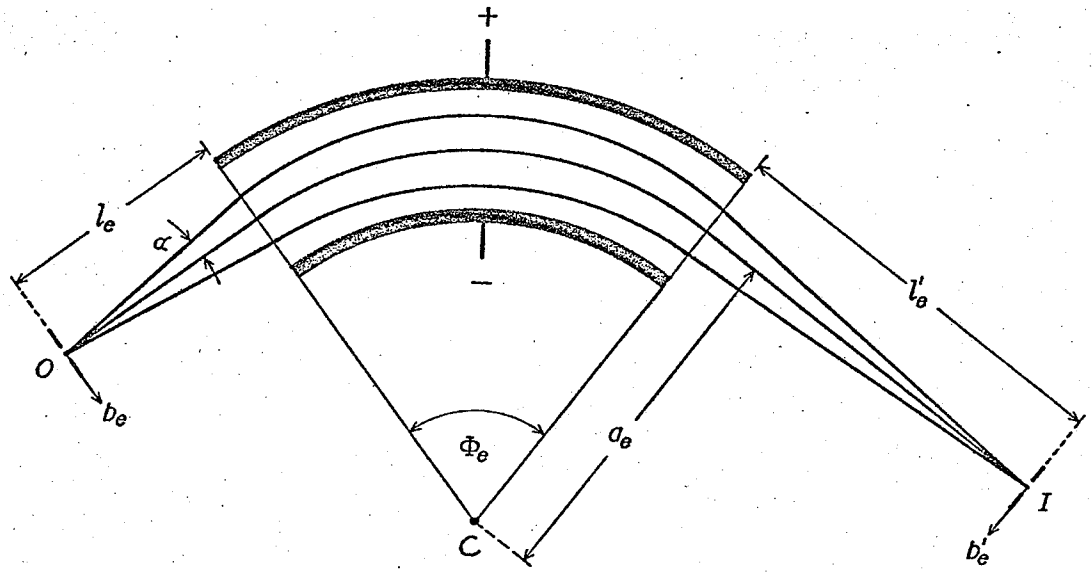

l_m
α
Φ_m
a_m
l'_m
O
C
I
b_m
b'_m

Fig. 2-2 Electrostatic Analyser


+
−
l_e
α
O
b_e
Φ_e
a_e
C
l'_e
I
b'_e

CHAPTER 3

THE MANITOBA II MASS SPECTROMETER

3-0. INSTRUMENT GEOMETRY

The Manitoba II mass spectrometer was constructed according to one of the many instrument geometries proposed by Hintenberger and König (1959) which possess complete second order double focussing properties (see also Appendix 1). Detailed descriptions of this instrument have been presented before by Bishop (1969) and Barber (1968, 1971). A summary of the more important features of the instrument is presented below.

The size of the spectrometer is fairly compact for a high resolution mass spectrometer. The geometry calls for relatively small values for l_e/a_e, d/a_e and l'_m/a_e (see Fig. 3-2) so that the total length of the ion path is only 4.59 m when a_e is chosen to be 1 m. This short pathlength reduces effects resulting from the scattering of ions by the residual gases in the vacuum.

The compact size of the instrument has made it possible to mount it on a 5 x 12 foot steel table that is constructed of 2" steel plate reinforced by 8" steel I-beams. This table is mounted on 8 pneumatic mounts which serve to isolate the spectrometer from building vibrations.

This design calls for straight, rather than curved, magnetic field boundaries and thereby simplifies, considerably, the construction, assembly and alignment of the magnet. The z-focussing properties, resulting from the inclined boundaries, greatly enhance the transmission

of the instrument (see also Sec. 3-3 and Appendix I).

An intermediate direction focus, located between the electric and magnetic fields enables the use of an energy defining slit (S_β) which controls the range of energies transmitted. The intermediate direction focus also simplifies the procedures used to focus and align the instrument.

The overall magnification of the instrument is 0.5 so that less stringent demands are placed on the quality of the object slit. This slit is subject to intense ion bombardment (roughly 10 μA at 20 kV) which causes it to deteriorate over a period of several weeks. The dispersion of the instrument is 53 cm. Therefore, for a resolution of $1/10^5$ the calculated slit widths are, S_o = 5.4 μ and S_i = 2.7 μ. The highest resolution attained so far has been $1/5.5 \times 10^5$ (Kozier, 1977) and the instrument operates at a resolution of $1/2 \times 10^5$ on a routine basis.

3-1. THE ION SOURCE REGION

The ion source used on this instrument is an electron bombardment type similar to one described by Von Ardenne (1962) and is shown schematically in Fig. 3-3. It has been described in detail by Bishop (1969), Meredith (1971) and Barber (1971) and is used here in a slightly modified form.

The ions are produced by electron bombardment in the vicinity of a small hole in a stainless steel tube (ionization chamber) which contains the sample vapour. The sample is held outside the source in a copper tube which is heated by passing a current through a nichrome

ribbon wrapped around the outside of the tube. The sample vapours thus produced are introduced into the ionization chamber through a gas inlet consisting of a nickel tube which is electrically isolated from the source casing. In some cases a short length of stainless steel tubing was added to the copper tube to provide some degree of thermal isolation between the sample and the source.

The electrons are provided by a rhenium filament (approximately 0.050" x 0.375" in size) which was heated by a current of approximately 15 A. During our studies of tungsten, tantalum and rhenium the thickness of the filament increased with use because of the decomposition of the sample material on the filament. This made it necessary to increase the current handling capacity of the filament current supply to 25 A. The filament is held at a potential of approximately -150 V with respect to the ionization chamber.

A repeller electrode placed directly behind the filament is maintained at a potential of approximately -400 V with respect to the ionization chanber. The repeller and the source casing (which are electrically connected) form the polepieces of an electromagnet which provides a strong axial magnetic field (approximately 1 k G) in the vicinity of the ionization chamber. The electromagnet is energized by a current of 10 A flowing through a copper coil wound around the source body. The effect of the magnetic field is to cause the electrons, emitted by the filament, to follow tight helical trajectories and to oscillate back and forth along the axis of the source in the vicinity of the hole in the ionization chamber. A blue glow associated with the plasma may be seen in this region when the source is

in operation.

An accelerating potential, V_a, of 19,400 V is applied directly to the ionization chamber to provide a good definition of the energy of the ion beam. This potential is provided by a Universal Voltronics corporation model BRE 30-2 (30 k V, 2 mA) power supply which has a short term stability of 0.5 V. This voltage may be switched according to Eqn. 2-22 by adding to it an additional voltage, Δ Va, derived from a Kepco model ABC power-supply. Details about this scheme have been presented in detail by Southon (1973). The beam is extracted from the source by a grounded electrode placed just outside the source and is presented to a focussing and steering system.

The extracted ions may be steered horizontally and vertically by two separate pairs of deflection plates. The ions are then focussed on the principal slit (S_o) by a pair of quadrupole lenses. Details of the focussing and steering system have been presented before by Southon (1973). The potentials applied to the quadrupoles and deflection plates are derived from a pair of Kepco ABC power supplies with the aid of voltage dividers. These potentials may also be switched according to Eqn. 2-22 (Southon, 1973).

The principal slit is variable in width and in orientation about the optic axis. Two lathe slides are used to locate the slit with respect to the electrostatic analyser. A rotary table is also available to adjust the angle of entry of the ion beam into the electrostatic analyser.

The ion source region is evacuated by two 100 l/s diffusion pumps. The pressure in this region is approximately

1×10^{-6} torr. As described by Kozier (1977), an attempt was made to replace the oil diffusion pumps with an oil free pumping system. It was suspected that oil vapour from the pumps was responsible for the formation of insulating layers on the electrodes of the electrostatic analyser. Surface charges residing on these layers would produce systematic errors (Sec. 2-3 B). The results of this experiment were somewhat inconclusive. Moreover the ion-pumps were unsatisfactory in handling the gas load in this region. In the light of larger gas loads (mostly He) anticipated with the projected He - jet transport system we have returned to oil diffusion pumps.

3-2. THE ELECTROSTATIC ANALYSER REGION

The geometry and construction of the electrostatic analyser have been described in detail by Bishop (1969). The two cylindrical electrodes are made of gold plated Armco iron and are located with respect to each other by means of carefully ground quartz spacers and inconel springs. A high degree of uniformity in the electric field was obtained by careful machining and positioning procedures. The mean radius of the analyser, a_e, is 1 m ($\pm$ 10 μ) with a 2 cm gap between the plates. The angle of deflection, ϕ_e, is 94.65^o. The field is terminated at either end by grounded blocks positioned according to the theory of Herzog (1935). The entrance aperture to the analyser is controlled by a variable slit, S_α, which limits the angular divergence of the accepted beam to approximately $\pm$ 2 x 10^{-3} rad. A second variable slit, S_β, positioned at the intermediate direction focus is used to limit the range of velocities transmitted, β, to approximately

$\pm$ 8 x 10^{-4}.

The electrostatic analyser is enclosed in a vacuum vessel having 12.5 mm stainless steel walls and metal gaskets (the main gasket is a gold wire). The entire chamber is evacuated by means of a 140 l/s ion-pump. Three lathe slides located directly beneath the intermediate direction focus may be used to position the analyser with respect to the magnetic analyser. The source and principal slit assembly are supported by a 20 cm steel I-beam which is rigidly attached to the vacuum chamber. The main vacuum chamber is isolated from the source region by means of a 5.25 cm gate valve. This structure, which weighs approximately a ton, is supported by 3 ball bearings so that it may be moved about a pivot point located directly below the intermediate direction focus.

A potential, V_e, of approximately 780 V is applied across the plates of the analyser. This potential is derived from eight 97.2 V mercury batteries (each of which, in turn, consists of 73, 1.35 V mercury cells spot welded together in series). As can be seen from Fig. 3.4 the eight batteries together with two 200 Ω resistors are connected in a chain consisting of 4 batteries in series followed by the two 200 Ω resistors in series followed by the remaining 4 batteries in series. The chain is grounded in between the two resistors. Two Guildline choppers are used to switch this potential according to Bleakney's theorem (Eqn. 2-22) by applying a voltage across the two 200 Ω resistors. These choppers are driven by synchronous motors using O-ring drives and have been described in detail by Meredith (1971) and Southon (1973). A few modifications were made and

will be discussed later (Sec. 3-5). The potentials applied to the plates are measured with a precision potentiometer that has been described previously (Bishop, 1969; Barber, 1971). The batteries, precision potentiometer and one of the choppers, are housed in a temperature controlled environment. Details about the measurement techniques will be presented later (Sec. 3-4).

3-3. MAGNETIC ANALYSER REGION

The sector angle, ϕ_m is 90^o and the ions follow a path whose mean radius, a_m, is 62.74 cm. The field is uniform to 1/5000 over the entire gap for a wide range of fields ($\gtrsim$ 3 k G). It is generated by six coils, connected in parallel and arranged in pairs on 3 C-shaped yokes.

The magnet coils were water cooled until a leak developed in one of the water lines inside one coil. Attempts were made to repair this leak by circulating a radiator repair fluid through the cooling lines using a closed loop cooling system. This method proved unsuccessful. However the coils are now operating satisfactorily with no cooling for currents of $\lesssim$ 30 A.

The magnet current supply, first described by Southon (1973) is capable of supplying 60 A with a stability of 1 ppm over a period of a few minutes. A six phase transformer coupled with a full wave rectifying system and choke and capacitor filtering system produces the "raw" current. A regulating circuit (Fig. 3.5a), consisting of two sets of sense amplifiers which control a pass bank of transistors, is used to regulate precisely this current. The circuitry as described by

Southon (1973) has been transferred to a printed circuit board, with a few minor changes, so that more reliable operation is obtained (primarily through the reduction of the amount of noise picked up at the inputs of the amplifiers). The pass bank has also been rebuilt, with silicon transistors (Motorola type MJE 2955) replacing the germanium transistors. A new circuit (Fig. 3-5b) has been developed which improves the short term stability (0.02 sec. and less) by a factor of 100. The potential developed across 52 turns of #30 wire wound around the polepieces of the magnet is amplified using a state of the art operational amplifier (Burr Brown 3440 K). This signal which is proportional to the rate of change of the flux through the sense coils is then used in conjunction with a power amplifier to drive a correction current through a single turn of #22 wire wound around the upper polepiece. Thus the device keeps constant the total flux through the magnet gap and the related magnetic field. In this way the field within the working gap is regulated against small changes originating for any reason.

The image or collector slit, S_C, is similar in construction to the principal slit. The position of the collector slit may be changed by the use of two screw drives. In a reappraisal of the focussing properties of the spectrometer using a ray tracing technique (see Appendix 1) it was noted that the z - focus (i.e. the focus in the vertical plane) was located some 2 m away from the magnetic field boundary. The sensitivity of the instrument was subsequently improved by increasing the length of the collector slit from 1 mm to 5 mm. A height slit, S_H, is located at the entrance to the magnet should it be

desirable to limit the height of the ion beam in the vertical direction. However it has been our experience that the axial aberrations are sufficiently small that the instrument can be operated at very high resolutions with S_H fully open.

The ion beam is swept across the collector slit by a sawtooth magnetic field generated by a pair of Helmholtz coils located in the drift space between the magnet and the collector slit. The sawtooth magnetic field is derived from the sweep voltage of the display oscilloscope. In the past, the sweep field was swept linearly from a value of 0 to some value B_o. This method has the disadvantage that when the peak for a particular group of ions is centered on the oscilloscope screen, the ions experience a small deflection in the sweep field and the focussing properties of the spectrometer are thereby altered slightly. Moreover when changing from forward to reverse sweep (i.e. reversing the sweep direction) the magnetic field must be adjusted to keep the same peak at the center of the viewing field. These problems have been eliminated by replacing the sweep amplifier described by Southon (1973) with a new circuit shown in Fig. 3-6. Here the sweep signal from the display oscilloscope is offset by a small voltage and presented to a (Kepco model 36-5M) bipolar operational power supply (essentially an operational amplifier with large power handling capacity) which is used as a voltage to current converter and energizes the sweep coils. This results in the magnetic field being swept from some value $-B_o$ to $+B_o$ through zero. The ions that are centered on the screen experience little or no deflection in additional magnetic fields.

The ions transmitted through the collector slit are detected

by a (Mullard model B 419 AL) channel electron multiplier placed approximately 2 cm behind the slit. This electron multiplier replaces the magnetic strip electron multiplier used before. Each ion produces a pulse of electrons, at the output of the electron multiplier, which is then amplified by a fast preamplifier (Fig. 3-7). The preamplifier tailors each pulse into an output pulse that is 2V high and 180 ns in duration. At this stage either the pulses are presented to the pulse counting input of a multichannel analyser (for use in the computer assisted peak matching process) or they are processed further. The pulses are further amplified, by a slower amplifier, and used for display purposes and for the visual null method of peak matching.

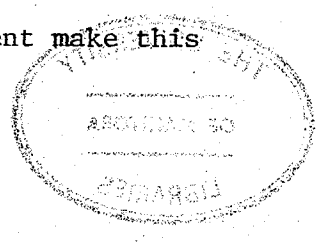
3-4. PEAK MATCHING ON MANITOBA II

Three variations of the peak matching procedure, briefly outlined in Chapter 2, are currently used in this laboratory for the determination of the separation of two mass spectral peaks. The procedures and apparatus used with these techniques have been described in detail by Bishop (1969), Meredith (1972), Southon (1973) and Kozier (1977). A brief description, together with details on some major changes, of these methods is presented below.

A. The visual method: The first of the peak matching procedures is very similar to the early method described by Giese and Collins (1954). In this method the alternate traces of the oscilloscope are split (by the addition of a small D.C. voltage) in a manner similar to dual beam oscilloscopes. During alternate sweeps the potentials applied to the instrument are changed from V to V'; this results in a lateral

displacement of the spectrum displayed on one of the two traces. If the potentials are changed as prescribed by Bleakney's theorem (Eqn. 2-22) then the spectrum is displaced in such a manner that a peak on the lower trace will be lined up with another peak on the upper trace. This is called the matched condition and the masses of the ions corresponding to the two peaks and the changes in the potentials are related by Eqn. 2-22.

In practice, the approximate values for the changes of various potentials are calculated from a prior knowledge of the masses corresponding to the peaks in question. The change in the electrostatic analyser voltage (ΔV_e) is then varied around the calculated value to obtain, more precisely, the matched condition. Only ΔV_e is adjusted since the instrument is relatively insensitive to changes in the other potentials. If the approximations for the potentials are found to be relatively poor (i.e. ΔV_e has to be adjusted by more than 10%) then the change in the accelerating voltage (ΔV_a) may be adjusted as well to ensure that the condition of identical trajectories required by Bleakney's theorem is being satisfied as accurately as possible. This is achieved by adjusting ΔV_a in such a manner that both the displaced and the reference spectrum are blocked by the β-slit at the same time when the accelerating potential is varied over the range of approximately 100 V. Peaks may be matched to a precision of 1/1000 of a peak width in this method. While this level of precision is hardly acceptable for the precise determination of atomic mass differences, the speed and facility of measurement make this method a boon for the identification of spectra.



In addition to this, one may change only the accelerating potential by about 10V while keeping the other potentials constant. In this case the displacement of the spectra between the two traces corresponds to an estimate of the velocity dispersion of the instrument. One can subsequently adjust the instrument in such a manner that, simultaneously, a direction focus and a negligible velocity dispersion are attained.

B. Visual null method: In order to improve the sensitivity and accuracy of the method described above, a signal averaging technique for the detection of the matched condition was developed by Benson and Johnson (1966). This method was quickly adopted by other researchers (e.g. Macdougall, 1966; Stevens and Moreland, 1967; Barber, 1967). A modified version, as described by Bishop (1969) is used on Manitoba II as one of two possible systems for the precise determination of mass differences.

In this method the oscilloscope traces are not split and the display signals for the alternate traces are routed through two separate amplifiers. The relative gains of the amplifiers are adjusted such that the amplitudes of the two peaks of interest are equal. The signals are then presented to a Nicolet model 535 multichannel analyser (M.C.A.), operating in the signal averaging mode, whose sweeps are synchronized to the sweeps of the Helmholtz coils. This M.C.A. replaces the Fabritek 1052 analyser described in previous work and will be described in greater detail later.

The input signal to the signal averager is digitized point by point and data from alternate sweeps are added and subtracted from

the memory of the M.C.A. Thus a digital signal consisting of the sum of the differences, point by point, between the two spectra is accumulated. If the potentials are not switched in such a manner that a matched condition is obtained, an S-shaped error signal is accumulated (Fig. 3-8a). When the peaks are matched, both with respect to position and amplitude, a completely symmetric noise signal (null signal) is accumulated (Fig. 3-8b). Since data are generally accumulated over many sweeps, small differences in the relative positions of the peaks may be detected. This method also makes it possible to determine the spacing between peaks when one or more members of the doublet are weak.

The rough values for the changes in the potentials are calculated from existing data about the masses involved (usually one of the mass evaluations discussed in Chapter 1) and ΔV_e is then varied around the rough value to achieve the matched condition as described above. In order to minimize the effects of biases that may occur in any one particular configuration of the instrument, an unweighted average of eight matches, corresponding to each of the possible configurations, is taken as the result of one "run". The eight possible configurations are permutations based on the following choices:

(a) The ΔV_i may be added or subtracted from the reference potentials i.e. the lighter or the heavier member of the doublet may be displaced. (This is termed the "add" or "subtract" mode.)

(b) The direction of the sweep of the Helmholtz coils may be reversed, i.e. one may sweep from the heavier masses toward the lighter masses or vice versa ("forward"/"reverse" mode).

(c) The reference peak may be routed through either of the two

amplifiers.

C. Computer-assisted peak matching: Inasmuch as the detection of the matched condition in the above methods involves a judgement on the part of the operator, a technique to detect the matched condition through the use of a digital computer was developed by Stevens and Moreland (1967) in an attempt to escape the possible effects of biases introduced by the operator. Similar methods were later developed by Kayser (1972) at Minnesota and Meredith (1972) for use on Manitoba II.

In this method the memory of the M.C.A. is divided into quadrants and four separate spectra accumulated in each quadrant (Fig.3-9). Thus, each complete sweep of the M.C.A. corresponds to 4 sweeps of the Helmholtz coils and the display oscilloscope. On the first sweep the potentials on the instrument are changed in such a manner as to satisfy Eqn. 2-22 approximately (i.e. the spectrum is displaced by approximately one doublet width) and the resulting spectrum is recorded in quadrant 1 of the M.C.A. During the second sweep the potentials are returned to their normal values except for the electrostatic analyser potential, V_e, which is changed by a small amount δV_1 (approximately $V_e/5 \times 10^5$) and the resulting spectrum is accumulated in quadrant 2. The spectrum recorded in quadrant 3 (third sweep) corresponds to the spectrum generated when all the potentials applied to the instrument are at their normal values. On the sweep through the fourth quadrant the potential applied to the electrostatic analyser is once again changed by a small amount δV_2 ($\delta V_2 \simeq -\delta V_1$) and the resulting spectrum

recorded. This cycle is repeated many times until sufficient data have been accumulated (usually about 3000 sweeps). The data are then stored on magnetic tape for subsequent analysis using an I.B.M. 370/158 digital computer.

A detailed description of the computer analysis has been presented previously by Meredith (1972). In his analysis Meredith uses the relative positions of the peaks in quadrants 2, 3 and 4 and the values of δV_1 and δV_2 to estimate the relation of peak position to small changes in the electrostatic analyser potential. This relation may then be used to calculate the precise value of ΔV_e for the matched condition.

The centroids of the peaks in the various quadrants are taken to represent the position of the peaks. The centroids are calculated by considering all points in the peak above 15% of the peak height. The peak height is estimated by means of a 7 point quadratic fit among points near the top of the peak. A baseline (having a quadratic form) is estimated on the basis of points far away from the peak and is subtracted from the spectrum before analysis. The changes in V_e, viz. ΔV_e, δV_1 and ΔV_2 are measured with the precision potentiometer. Changes in V_e that may occur during sweeps through quadrant 3 are monitored and subtracted if necessary from ΔV_e, δV_1 and δV_2. The magnitudes of δV_1 and δV_2 are chosen such that the peaks in quadrants 1 and 3 are bracketed by the peaks in quadrants 2 and 4. The results of a least squares fit between the positions of the peaks in quadrants 2, 3 and 4 and δV_1 and δV_2 are used to estimate the changes necessary in ΔV_e in order that the position of the peak in quadrant 1 matches

the position of the peak in quadrant 3. This information, together with less precise information about the masses of the two ion groups involved, may be used with Eqn. 2-23 to determine the mass separation between the two peaks.

More recently Kozier (1977) developed a technique of evaluating the relative separation of two peaks (recorded in different quadrants) by means of a least squares technique. In this method the sum of the squares of the differences of the two spectra is minimized as a function of two variables viz. the separation between the peaks and their relative amplitudes. This method seems to perform at least as well as the centroid method for determining separations between the peaks, but produces somewhat erratic results when the data have an unfavourable signal-to-noise ratio. For this reason only the centroid method and the visual null methods were used to obtain the data for this work.

In the computer assisted method, as in the visual null method, there are eight possible configurations arising from the following choices:

(a) ΔV_e may be added or subtracted.

(b) Forward or reverse sweep.

(c) The potentials changed during quadrants 2 and 3 may be interchanged (the "normal"/"backwards" mode).

The unweighted average of eight matches, each made for a different configuration, is accepted as the result of a single measurement or run.

3-5. HARDWARE ASSOCIATED WITH PEAK MATCHING

Until recently, data for the computer assisted peak matching process was accumulated in the M.C.A. by using it in the signal averaging mode. In this configuration the input signal is digitized point by point and added to the memory. Noise, which is added during the digitizing process, and baseline modulations tend to obscure weak signals when processed in this manner. Particularly with weak signals low frequency baseline modulations tend to modulate the position of the centroids of the peaks with disastrous effects on the results of the measurement. A new method, in which each pulse from the electron multiplier is recorded as a single event in the memory of the M.C.A., has been implemented and used to obtain much of the data in this work. This technique greatly improves the sensitivity of the spectrometer while reducing the stringent requirements placed on the baseline. In particular, attention is drawn to the results obtained for measurements involving the rare isotopes of hafnium, tungsten and tantalum (see Chap. 4), in this work, which differ significantly from results obtained earlier by this group using the signal averaging technique.

The power supplies and the various mechanisms for adding and subtracting the changes in the quiescent operating voltages remain largely as described by Southon (1973). Mercury relays are used to switch the accelerating potential, the potentials applied to the quadrupole lenses and the deflection plates. These potentials are changed in synchronization with a timing signal derived from the flyback of the oscilloscope sweep. The potentials applied to the electrostatic

analyser are switched by means of one of two Guildline choppers driven by O ring drives and synchronous motors. These choppers have gold-plated contacts mounted on spring steel arms driven by cams. Here contact resistances are reproducible to a higher degree than are those in mercury-wetted relays.

Two timing signals, A and B (see Fig. 3-10 a,b), are also generated by the choppers (only A is used for the visual null method). In the past A and B were generated directly by the choppers. Since there is always a tendency for mechanical contacts to bounce, a sharp edge on either of these signals and hence, precise synchronization was hard to achieve. This problem was solved by using the choppers as a trigger for a pair of R-S flip-flops which then produced the timing signals. A new trigger synthesizer was built (Fig. 3-11) incorporating this feature.

The timing signals generated by this circuit and their relationship to changes in the other potentials applied to the instrument are shown in Fig. 3-10 a,b. Briefly, a trigger pulse is generated approximately 500 μs after A or B changes. The potentials applied to the electrostatic analyser are switched slightly before A or B changes. Thus a period of greater than 500 μs is allowed for the applied voltages to settle before the spectrum is recorded. The trigger pulse is used to initiate the sweeps of the oscilloscope and the M.C.A. The M.C.A. was modified to accept a pulse which would reset the memory address scalar. This pulse is generated by the synthesizer in synchronization with the falling edge of A thereby ensuring that the right spectrum would be recorded in the proper quadrant. Additionally,

start and stop commands are generated by the circuit and accepted by the M.C.A., thereby ensuring that each data acquisition cycle starts and ends in the appropriate memory address.

The signal averager was also modified to perform the add/subtract function required in the visual null method. The M.C.A. was further modified to stop after a sweep through a given quadrant and wait for a trigger pulse before sweeping through the next quadrant.

The frequency of the chopped signals was chosen to be approximately 20 hz. This avoids the problem of unwittingly synchronizing the data acquisition cycle with the line frequency (60 hz) and thereby opening the door to biases in peak position. At this frequency it is only possible to use half of the memory (2048 channels) for the visual null method (with a dwell time of 23 μs per point). The use of larger sections of the memory implies proportionately faster dwell times. This is not possible since the memory may be viewed ("live") only when dwell times greater than 20 μs per point are used. For the quadrant method, however, the entire memory (4096 channels) is used with a dwell time of 10 μs per point.

Fig. 3-1 The Manitoba II Mass Spectrometer

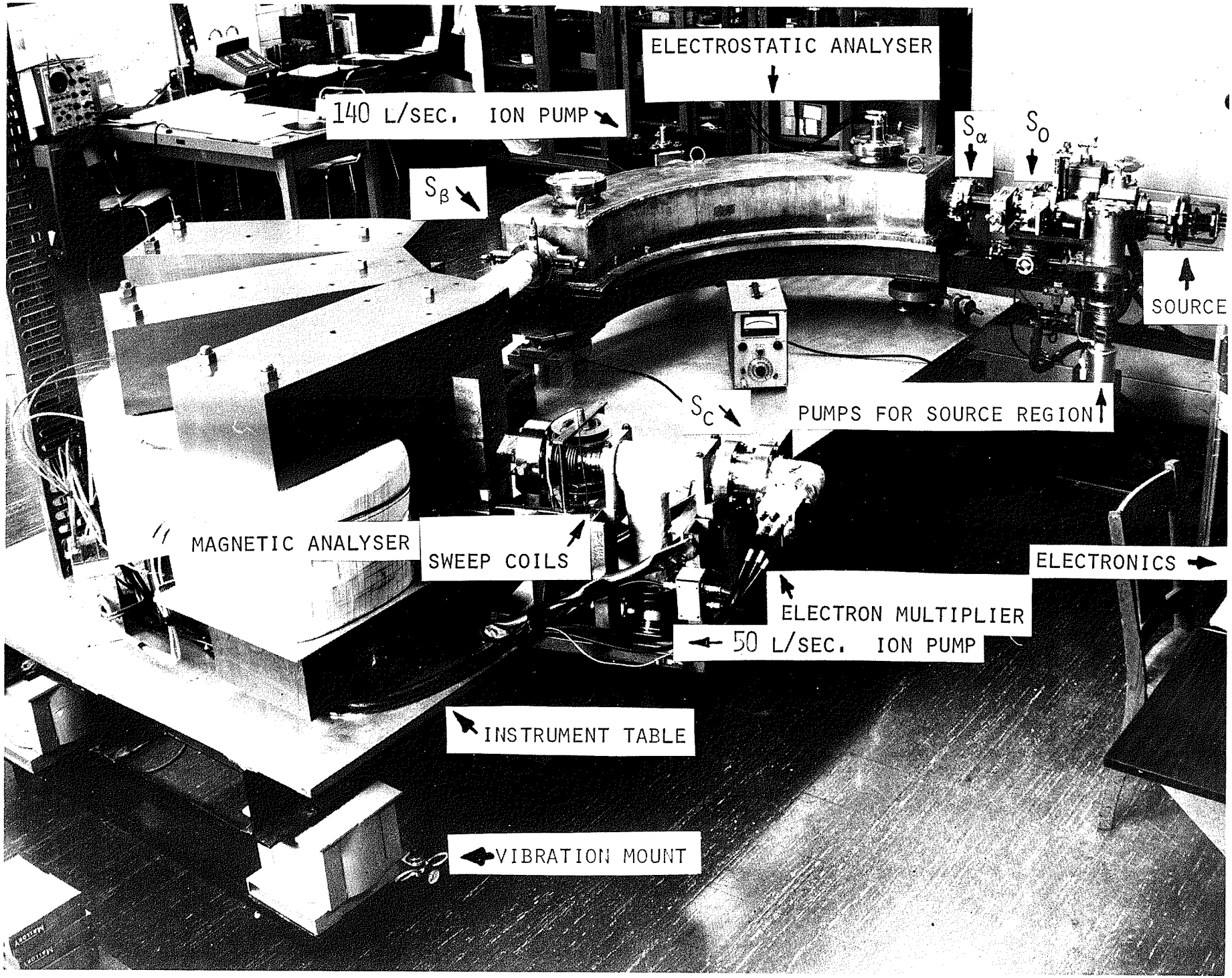

ELECTROSTATIC ANALYSER
140 L/SEC. ION PUMP
S_α
S_0
S_β
SOURCE
S_C
PUMPS FOR SOURCE REGION
MAGNETIC ANALYSER
SWEEP COILS
ELECTRONICS
ELECTRON MULTIPLIER
50 L/SEC. ION PUMP
INSTRUMENT TABLE
VIBRATION MOUNT

Fig. 3-2 Geometry of the Manitoba II Spectrometer

a_e = 100·00 cm.
Φ_e = 94·65°
a_m = 62·74 cm.
Φ_m = 90°
l_e = 44·45 cm.
l'_e = 17·63 cm.
l_m = 82·49 cm.
l'_m = 59·46 cm.
ϵ' = 27°
ϵ'' = 15°
$2k$ = 2·000 cm.

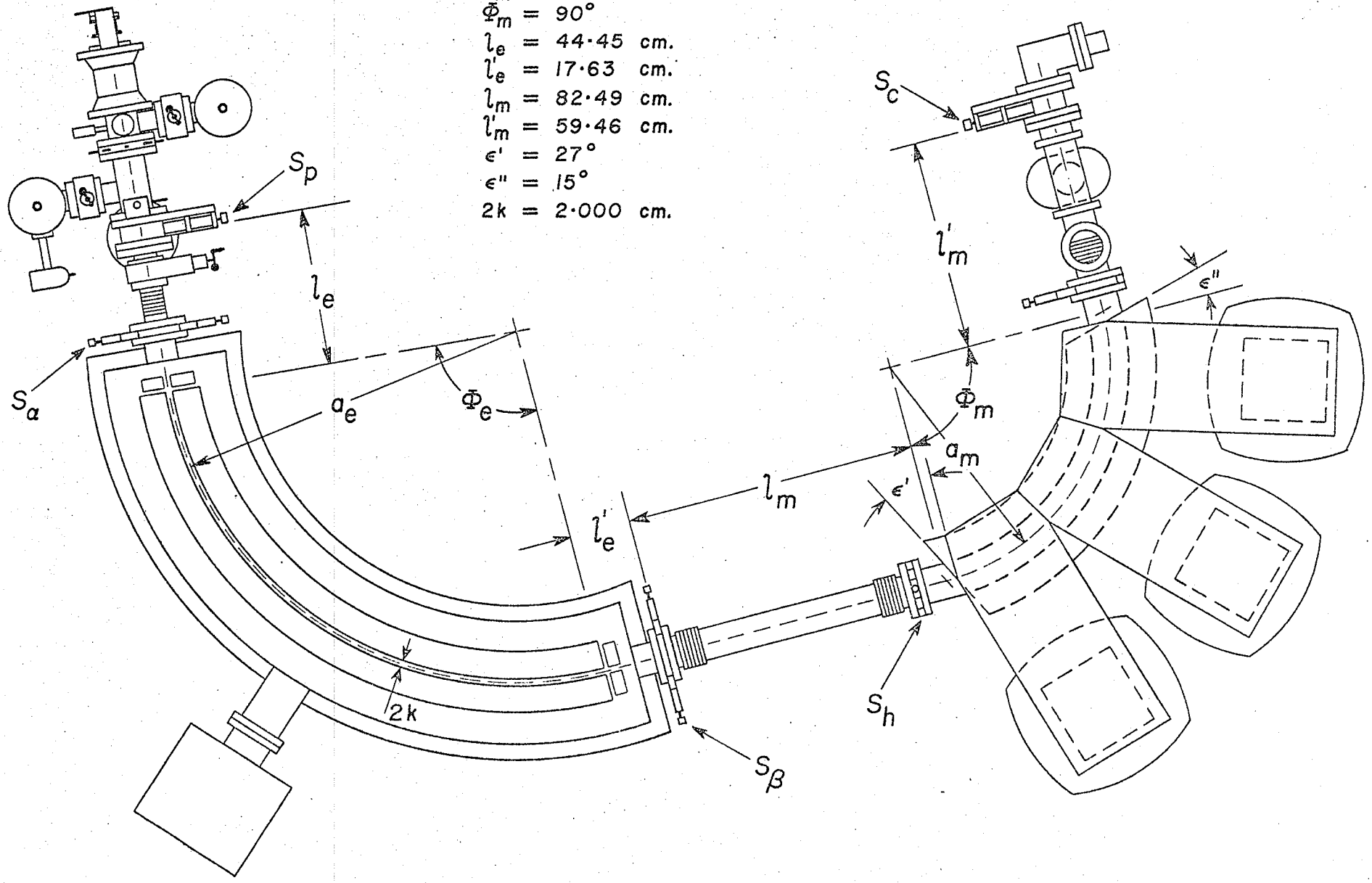
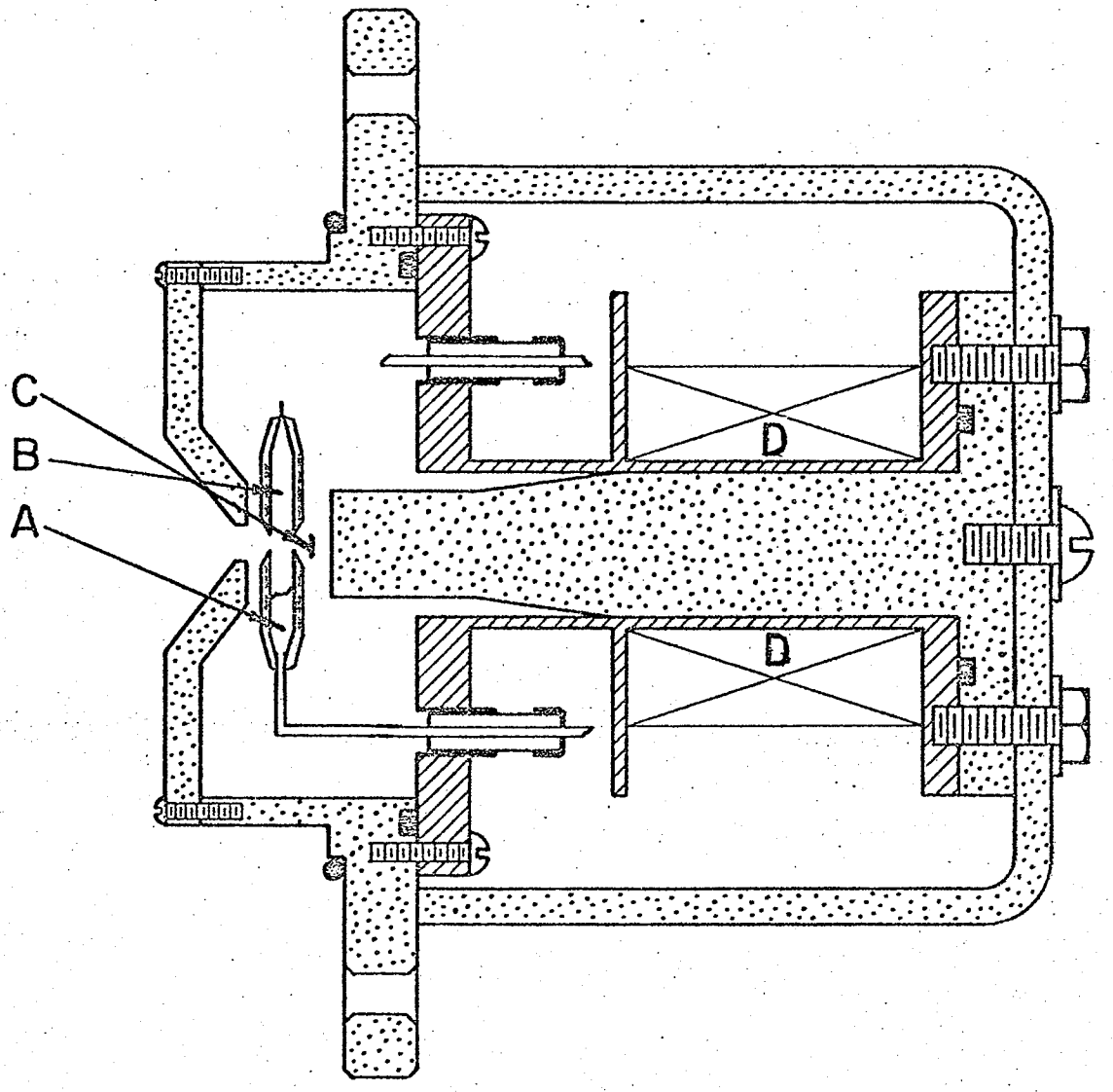


Fig. 3-3 Ion Source



E

BRASS

IRON

A SAMPLE

B OVEN (stainless steel)

C Re FILAMENT (coated with LaB_6)

D Cu WINDINGS FOR $\vec{B}$

E 5 cm

Fig. 3-4 Electrostatic Analyser Supply System

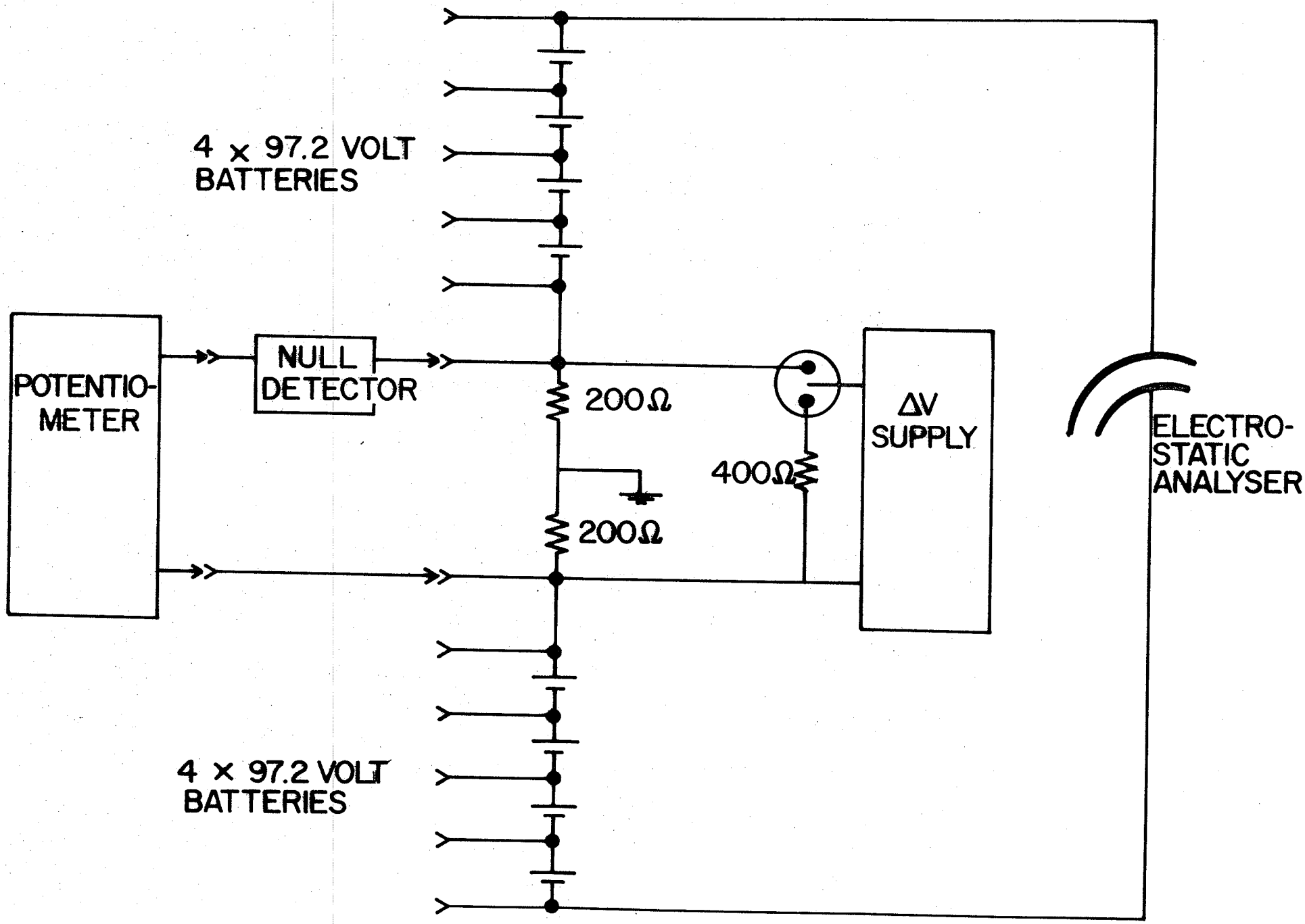

4 x 97.2 VOLT
BATTERIES
POTENTIO-
METER
NULL
DETECTOR
200Ω
400Ω
200Ω
ΔV
SUPPLY
ELECTRO-
STATIC
ANALYSER
4 x 97.2 VOLT
BATTERIES

Fig. 3-5a Current Supply for the Magnetic Analyser

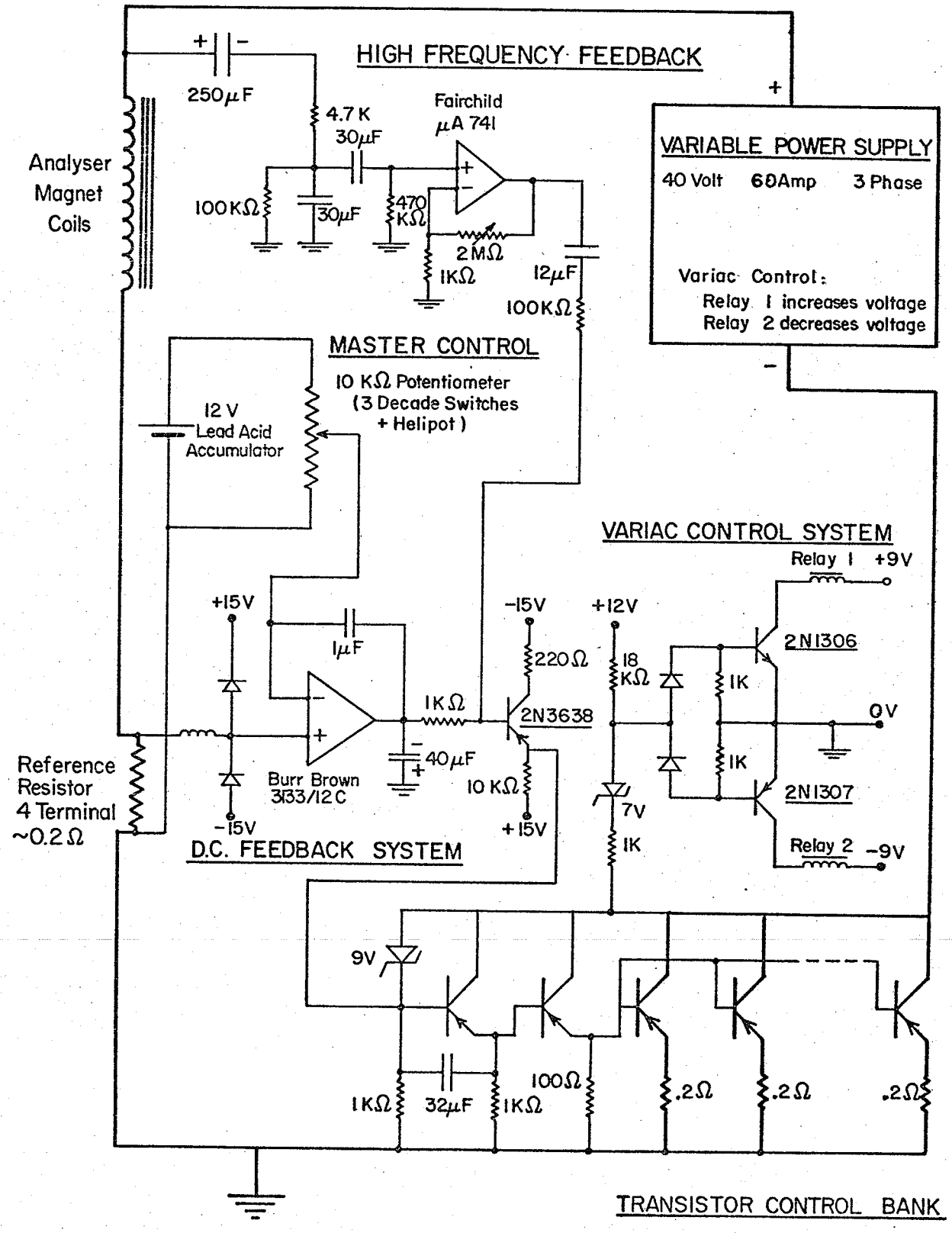

HIGH FREQUENCY FEEDBACK
250μF
4.7 K
30μF
Fairchild
μA 741
Analyser
Magnet
Coils
100KΩ
30μF
470
KΩ
2MΩ
1KΩ
12μF
100KΩ
VARIABLE POWER SUPPLY
40 Volt 60Amp 3 Phase
Variac Control:
Relay 1 increases voltage
Relay 2 decreases voltage
MASTER CONTROL
10 KΩ Potentiometer
(3 Decade Switches
+ Helipot)
12 V
Lead Acid
Accumulator
VARIAC CONTROL SYSTEM
Relay 1 +9V
+15V
1μF
-15V
+12V
220Ω
18
KΩ
2N1306
1K
1KΩ
2N3638
0V
40μF
10 KΩ
Burr Brown
3133/12C
1K
2N1307
7V
-15V
+15V
1K
Relay 2 -9V
Reference
Resistor
4 Terminal
~0.2Ω
D.C. FEEDBACK SYSTEM
9V
1KΩ
32μF
1KΩ
100Ω
.2Ω
.2Ω
.2Ω
TRANSISTOR CONTROL BANK

Fig. 3-5b Regulator for short term variations in the Magnetic Field

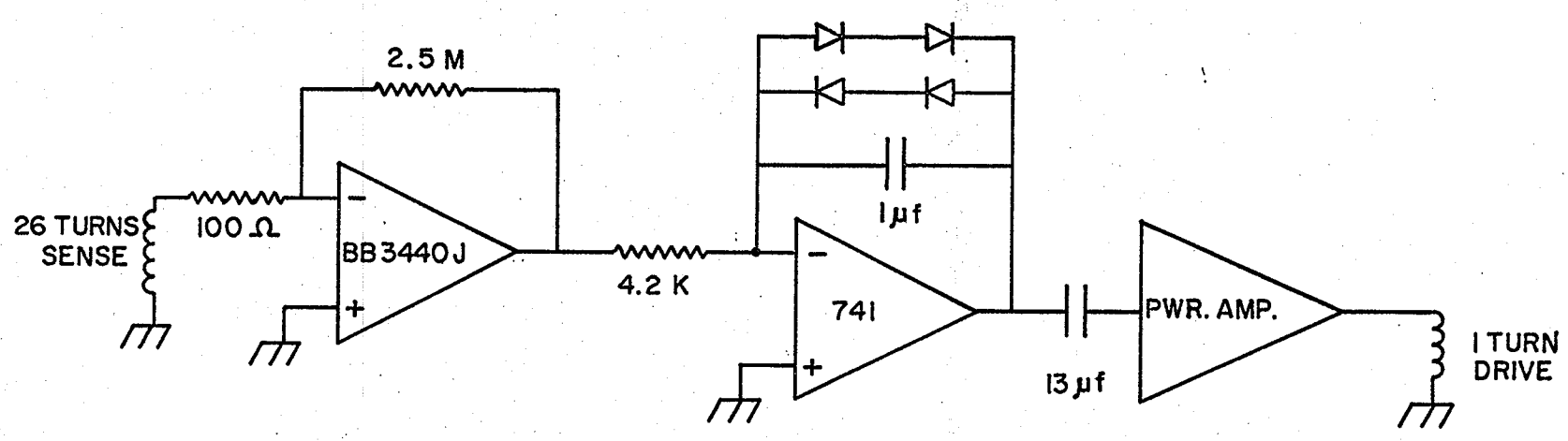
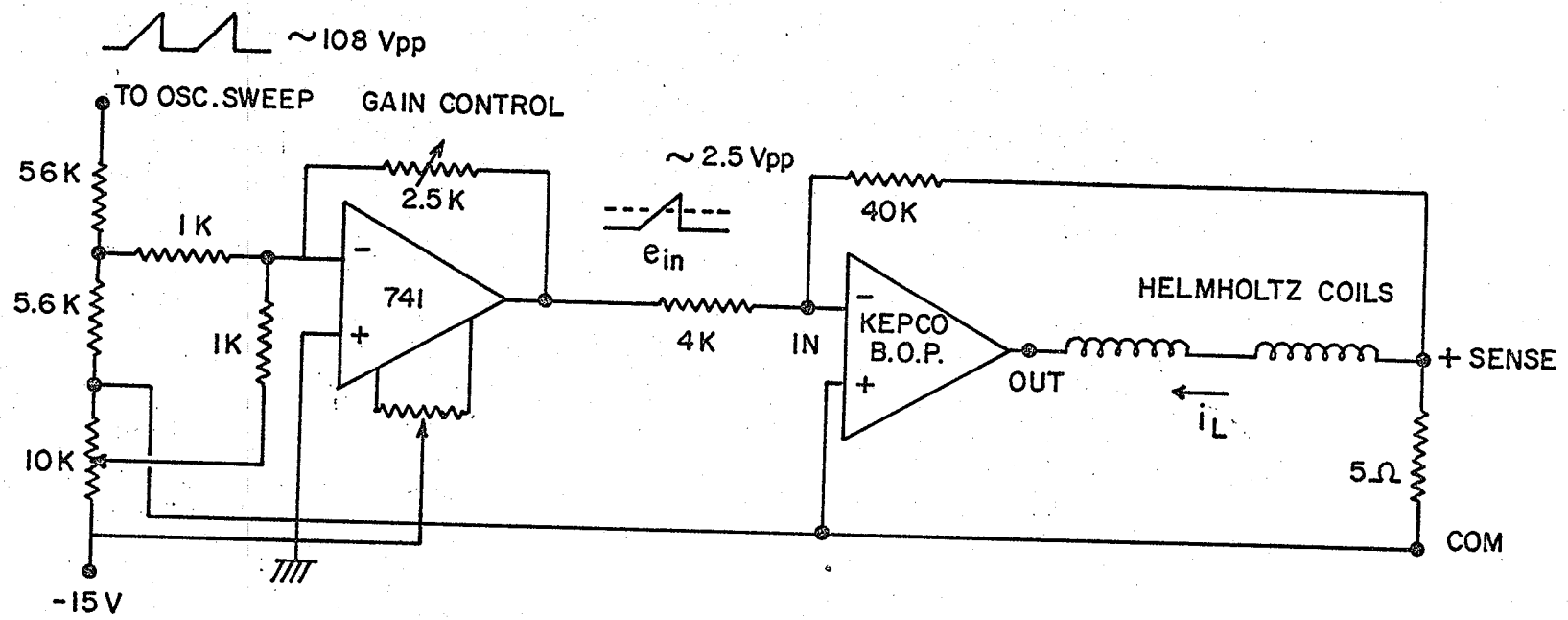

2.5 M
26 TURNS
SENSE
100 Ω
BB3440J
4.2 K
1 µf
741
PWR. AMP.
13 µf
1 TURN
DRIVE

Fig. 3-6 Sweep Amplifier



$$i_L = \frac{e_{in}}{4K}\left(1 + \frac{40K}{5}\right) \simeq 2\,e_{in}$$

Fig. 3-7 Electron Multiplier Preamplifier

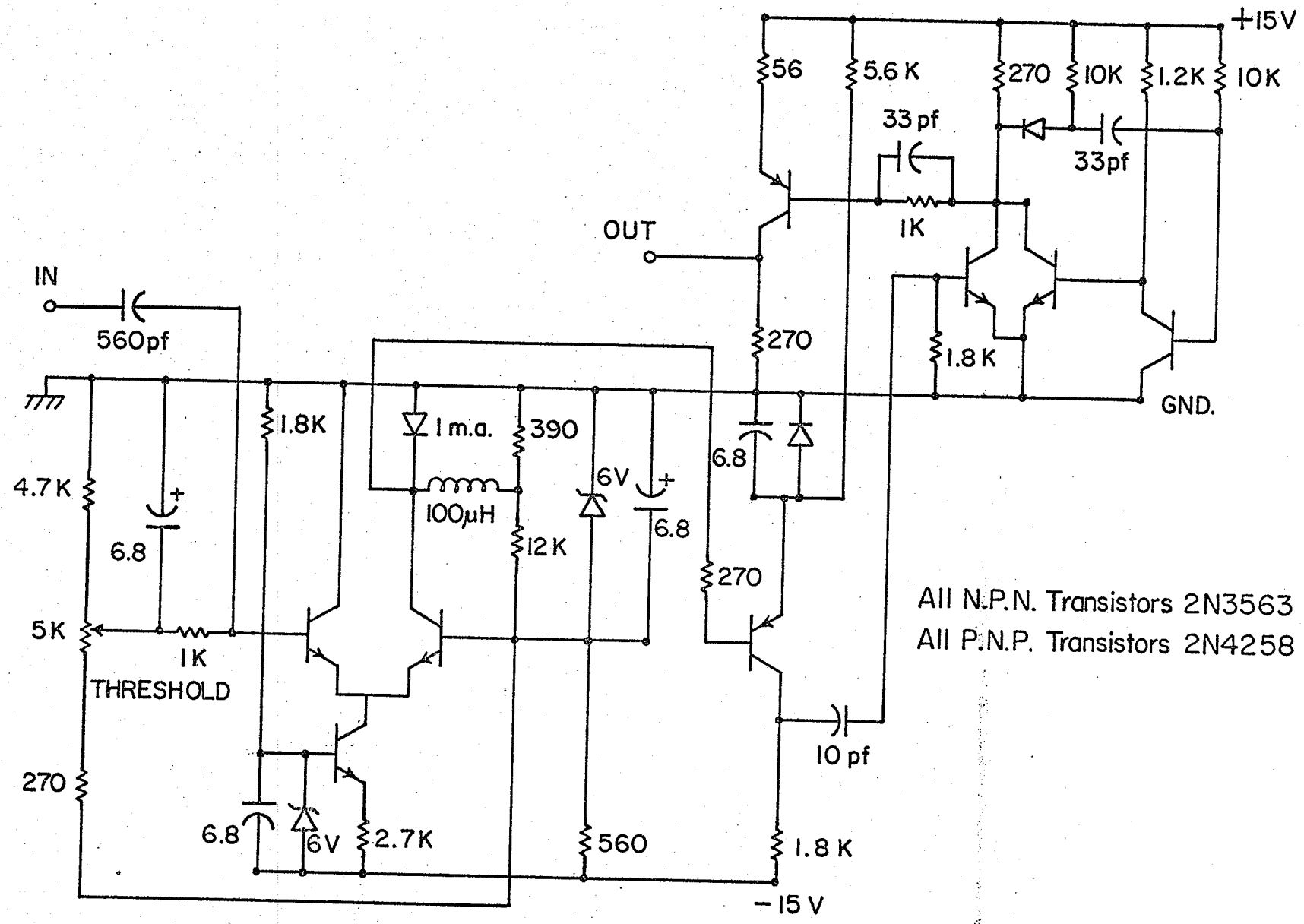
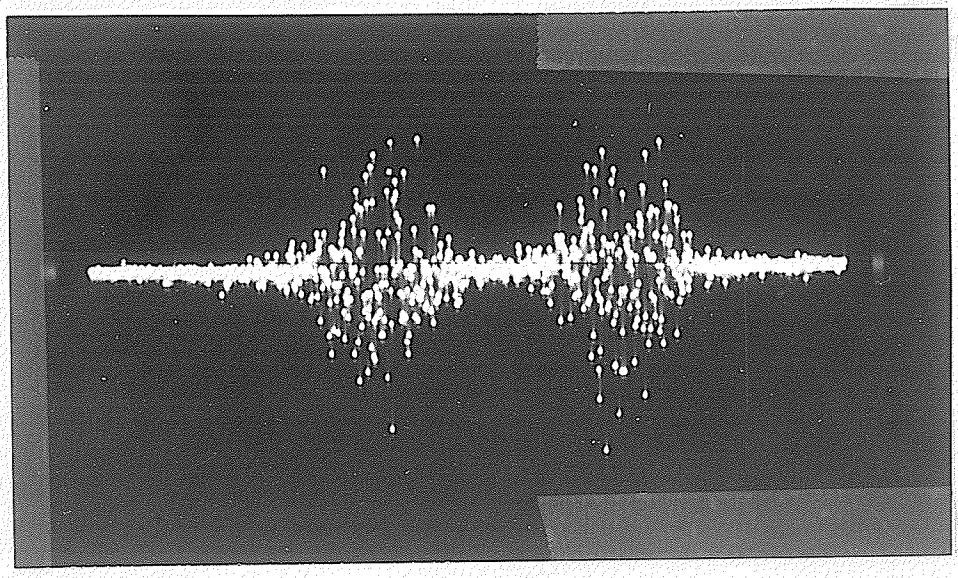

+15V
56
5.6 K
270
10K
1.2K
10K
33 pf
33pf
1K
OUT
IN
560pf
270
1.8 K
GND.
1.8K
1 m.a.
390
6.8
4.7 K
6.8
100μH
12 K
6V
6.8
270
All N.P.N. Transistors 2N3563
All P.N.P. Transistors 2N4258
5K
1K
THRESHOLD
10 pf
270
6.8
6V
2.7K
560
1.8 K
-15 V

Fig. 3-8 Error Signal generated with the Visual Null Method:

(a) when a peak is matched to itself.

(b) when a peak is mismatched to itself by a displacement of $1/4 \times 10^6$.



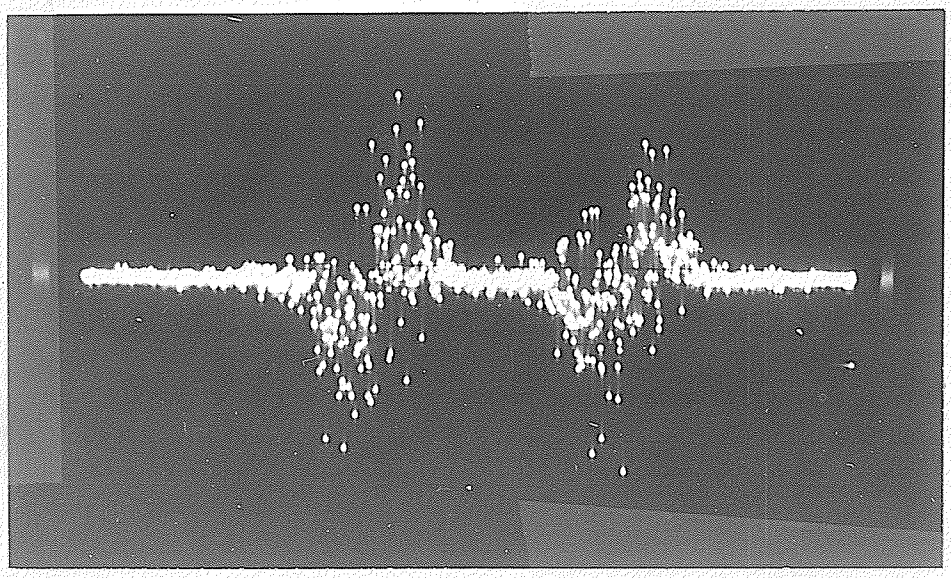


Fig. 3-9 Relative positions of the peaks collected in each quadrant for the Centroid Method (normal, add, forward mode).

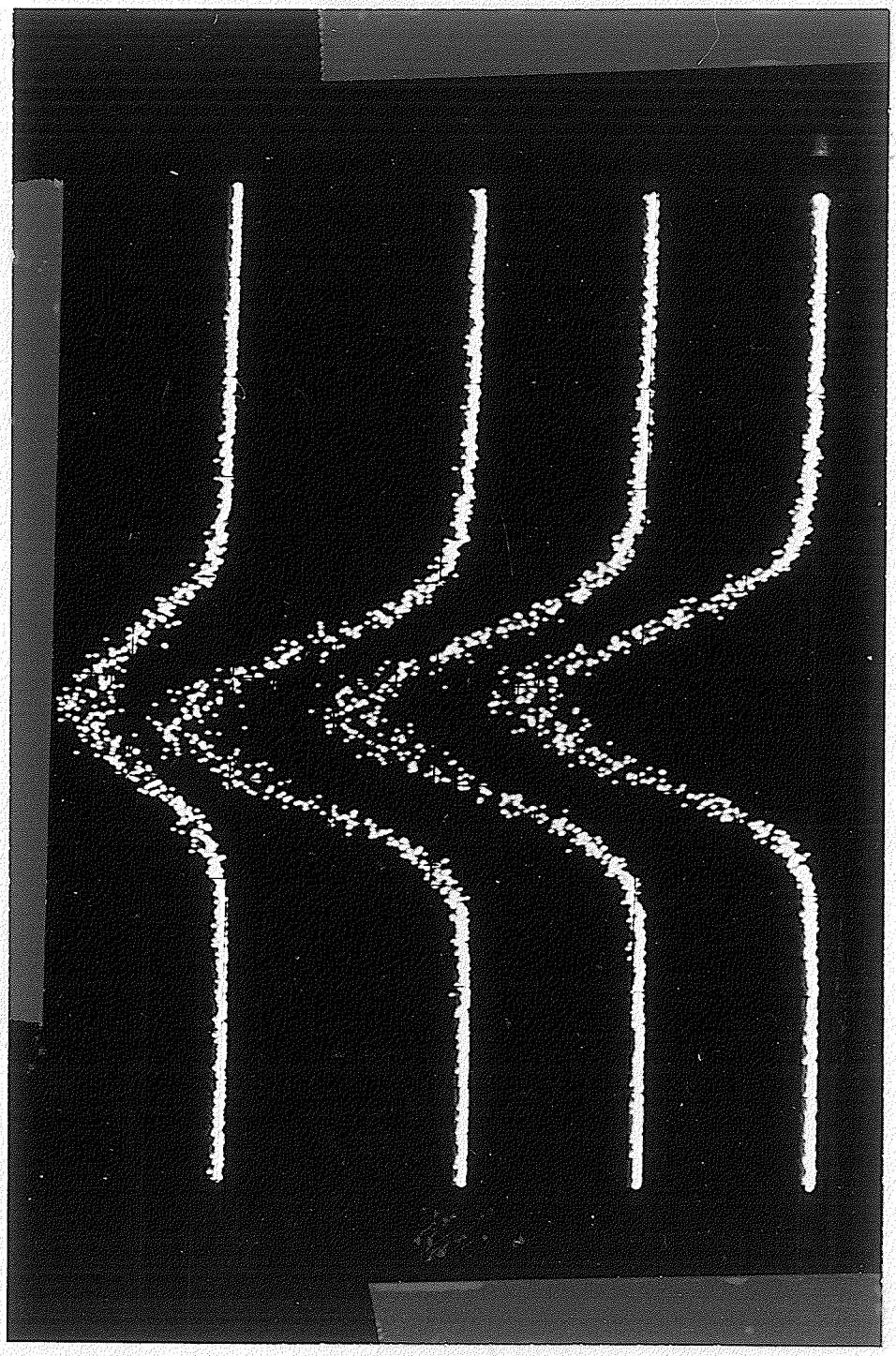


Fig. 3-10a Waveforms for the Visual Null Method

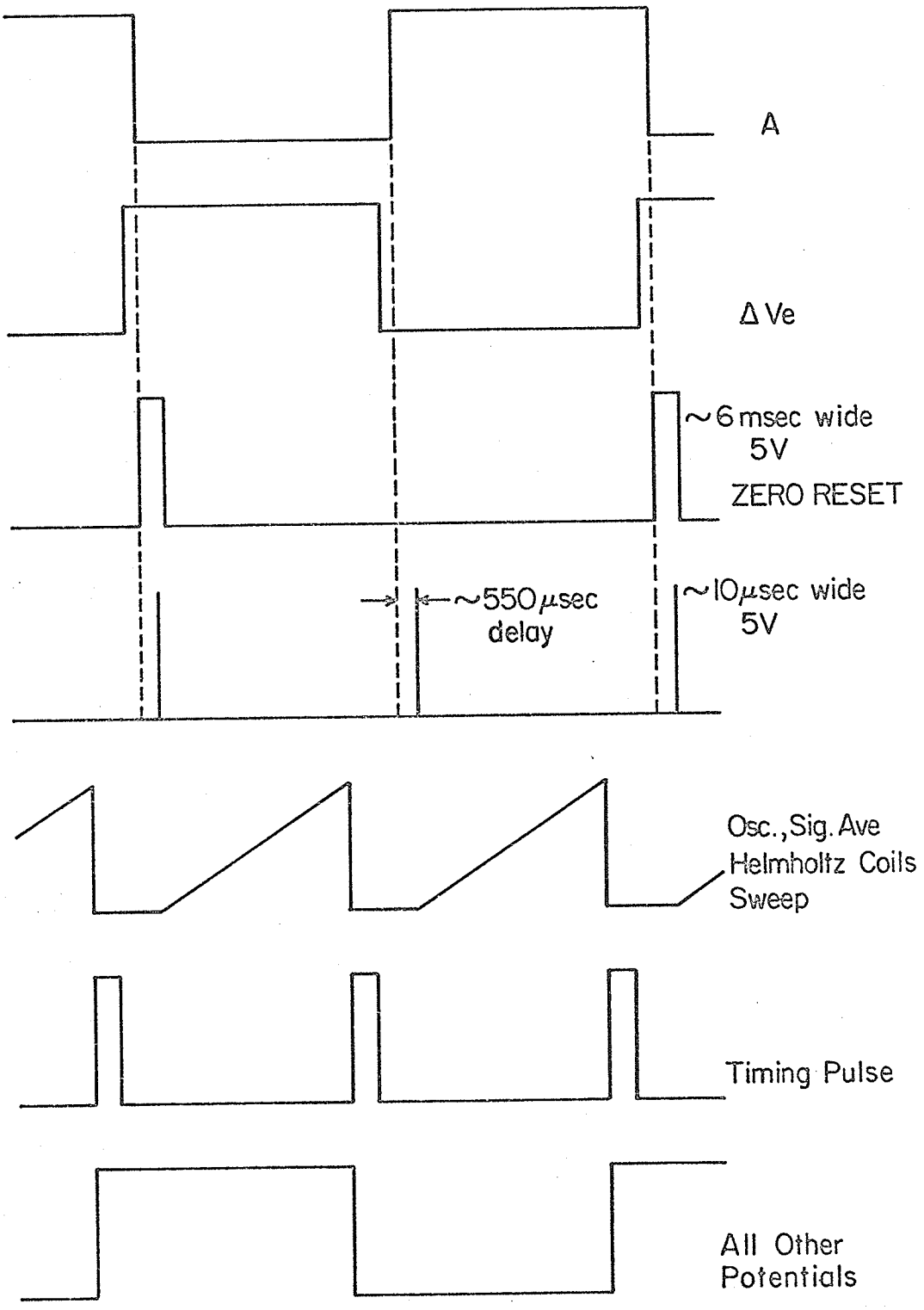

A
ΔVe
~6 msec wide
5V
ZERO RESET
~550 μsec
delay
~10 μsec wide
5V
Osc., Sig. Ave
Helmholtz Coils
Sweep
Timing Pulse
All Other
Potentials

Fig. 3-10b Waveforms for the Centroid Method

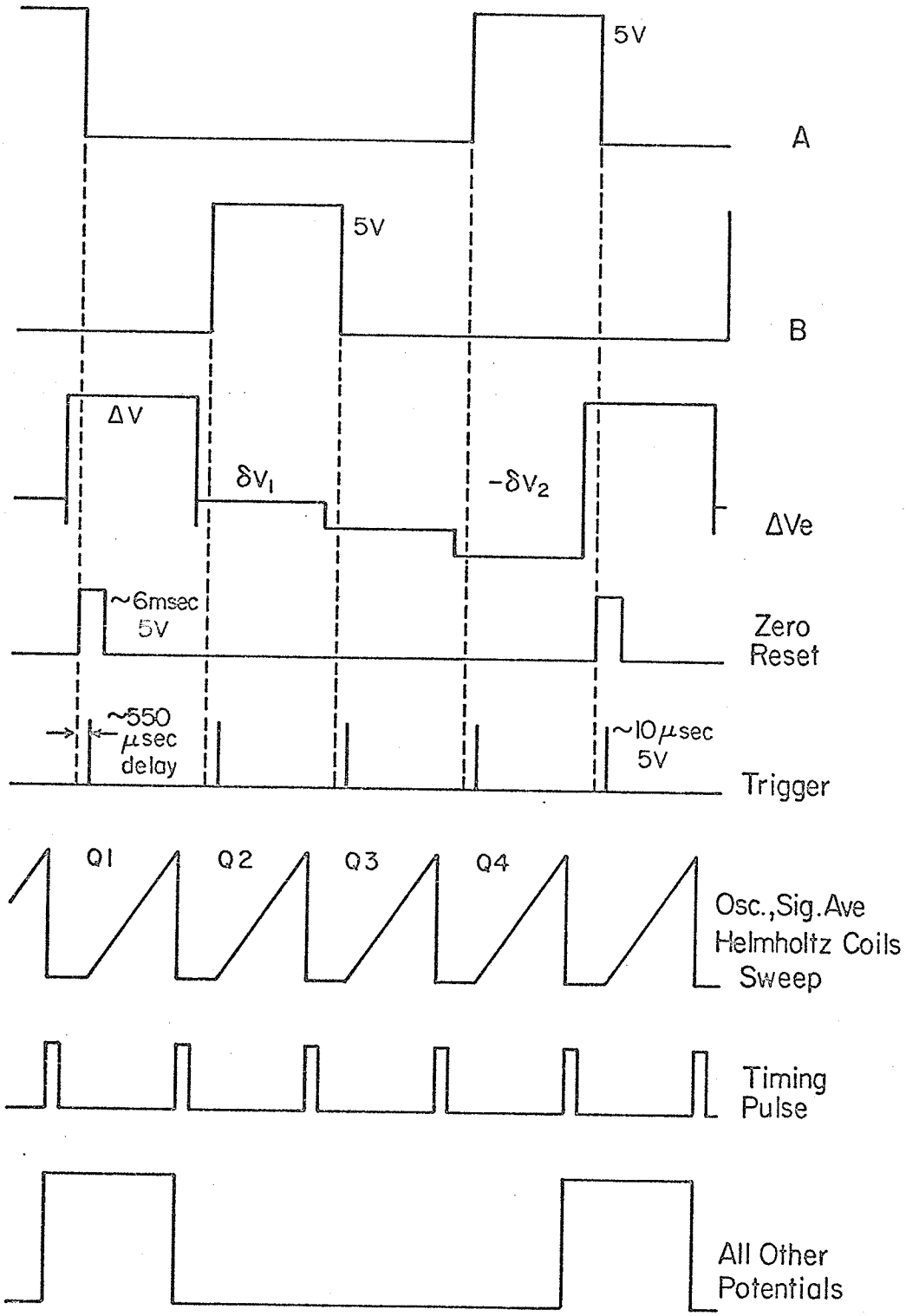
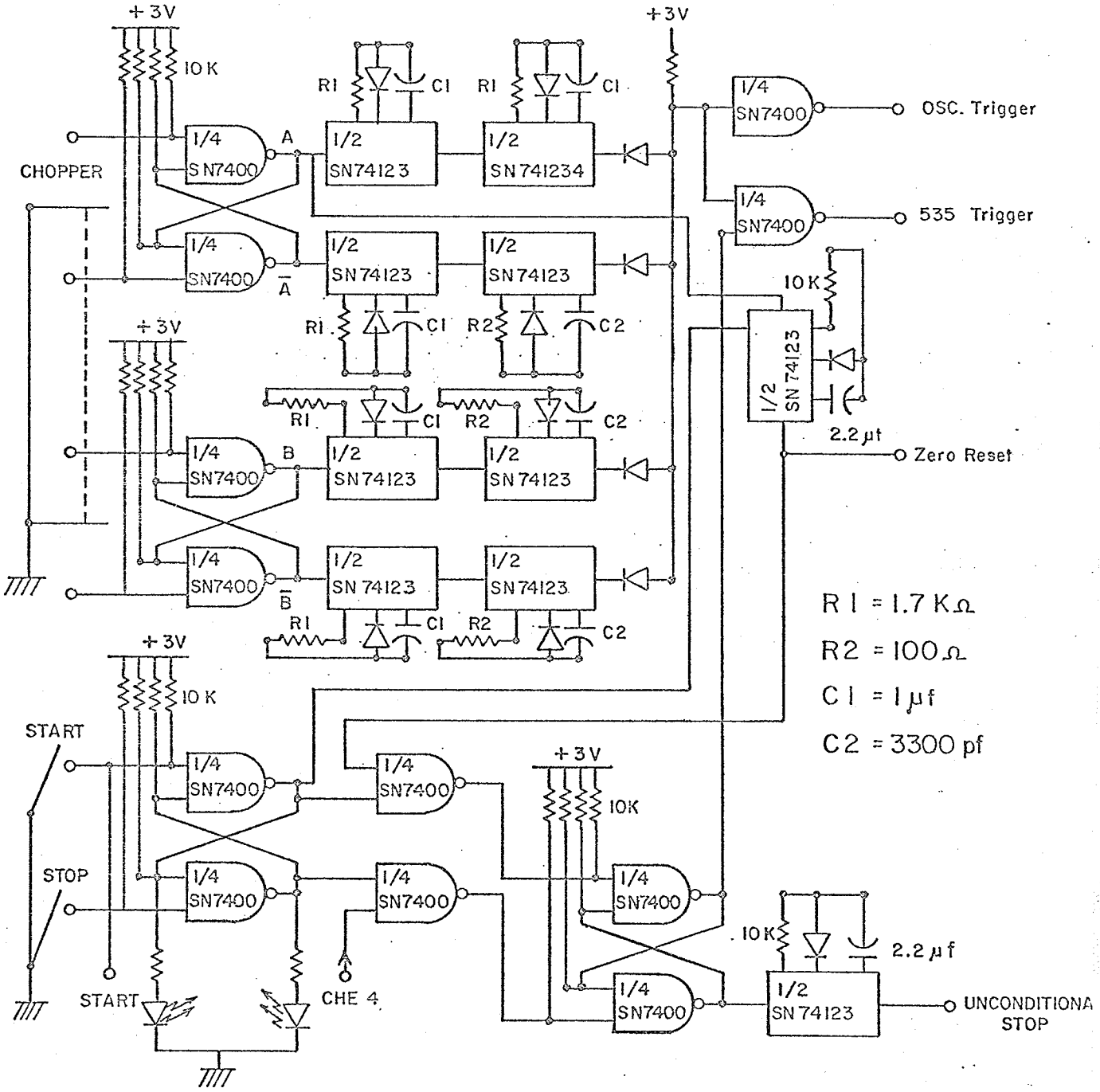

5V
A
5V
B
ΔV
δV1
-δV2
ΔVe
~6msec
5V
Zero
Reset
~550
μsec
delay
~10μsec
5V
Trigger
Q1
Q2
Q3
Q4
Osc.,Sig.Ave
Helmholtz Coils
Sweep
Timing
Pulse
All Other
Potentials

Fig. 3-11 Synchronization and Control System


+3V
10K
CHOPPER
1/4 SN7400
A
$\bar{A}$
B
$\bar{B}$
R1
C1
R2
C2
1/2 SN74123
1/2 SN741234
OSC. Trigger
535 Trigger
Zero Reset
2.2 μf
R1 = 1.7 KΩ
R2 = 100Ω
C1 = 1 μf
C2 = 3300 pf
START
STOP
CHE 4
UNCONDITIONA
STOP

CHAPTER 4

NEW ATOMIC MASS DETERMINATIONS

4-0. INTRODUCTION

In this work the Manitoba II, second order double focussing mass spectrometer has been used to determine 16 new doublet spacings among the mass spectra of hafnium, tantalum, tungsten and rhenium chlorides and oxy-chlorides. These measurements are part of a continuing systematic study of precise atomic mass differences in the region of $60 \leq z \leq 76$ (Barber, 1972, 1973, 1974, 1976 and Sharma, 1977 a,b).

4-1. EXPERIMENTAL DETAILS

The mass differences were determined by means of doublets of the types

$$\text{I} \qquad A + 2 \times {}^{35}Cl - {}^{A}Y\ {}^{37}Cl = \Delta M_1$$

$$\text{II} \qquad A + 3 \times {}^{16}O_2 - {}^{A}Y\ {}^{35}Cl = \Delta M_2$$

$$\text{III} \qquad A + 5 \times {}^{16}O_2 - {}^{A}Y\ {}^{37}Cl = \Delta M_3$$

$$\text{IV} \qquad A + 1 \times {}^{16}O_2\ {}^{37}Cl - {}^{A}Y\ {}^{35}Cl_2 = \Delta M_4$$

$$\text{V} \qquad A + 1 \times {}^{17}O\ {}^{35}Cl - {}^{A}Y\ {}^{16}O\ {}^{37}Cl = \Delta M_5$$

where X and Y may or may not be the same element. Doublet spacings range from 1/38,000 to 1/9000, with doublets of type I being the closest and those of types II and III the widest in spacing.

The ionic species used in these measurements were obtained through the dissociation of the molecules of the appropriate chloride or oxy-chloride in the source. The sample material was contained in a

copper tube outside the source and the vapour introduced into the ionizing region as described in Sec. 3-1. For measurements involving more than one element, either the compounds of each element were mixed together and loaded into the sample tube or they were placed in two sample tubes connected to the source by means of a T-joint. The relative intensities of the two members of the doublet could be controlled in the first case by changing the ratio of the amounts of each compound in the mixture and in the latter case by controlling the temperatures of the sample tubes. The first method works well when the two compounds involved have similar vapour pressures at a given temperature and is used wherever possible because of its simplicity. The dual sample tube method usually provides better control and is used when the first method fails.

Each of the doublet spacings reported here is a result of approximately 10 runs done on different days over the period of a month. Each run consists of eight matches (see Chapter 3), each match corresponding to a determination of the doublet separation under a different configuration of the apparatus. A straight average of the results of each of the constituent eight runs is taken to be result of one run. The weighted average of the results from all of the relevant runs is then accepted as the final calue for the doublet spacing.

If $a_i \pm \sigma_i$ is the result from a particular run then the weighted average of the results a_i is calculated as follows

$$\langle a \rangle = \left(\sum_i a_i/\sigma_i^2\right) \Big/ \left(\Sigma 1/\sigma_i^2\right) \qquad (4\text{-}1)$$

The uncertainity in this average is taken to be the larger of the two quantities σ_{ext} and σ_{int} defined below,

$$\sigma^2_{int} = 1/(\sum_i 1/\sigma_i^2) \qquad (4\text{-}2)$$

$$\sigma^2_{ext} = \sum_i (\langle a \rangle - a_i)^2/\sigma_i^2/(\sum_i 1/\sigma_i^2)\ (N\text{-}1) \qquad (4\text{-}3)$$

The average precision for this group of measurements is $1/10^8$. While this is not as good as in some measurements made by this group it reflects the low natural abundance of some of the nuclides involved, as well as the difficulties encountered in the measurement of mass differences between chemically different ionic species. This dissimilarity leads to difficulties in establishing stable intensity ratios and may also result in anomalously large energy spreads. A similar tendency has also been discussed by Kozier (1977).

The sixteen doublet spacings determined in this work are presented in Table 4-1. Doublets of type I may be combined with the well known $^{37}Cl - ^{35}Cl$ mass difference to yield the atomic mass difference between X and Y. Similarly the results from types II and III may be combined with the $^{35}Cl - ^{16}O_2$ and the $^{37}Cl - ^{16}O_2$ mass differences to yield the corresponding differences. The $^{37}Cl - ^{35}Cl$ mass difference as well as the $^{35}Cl - ^{16}O_2$ mass difference is required for the type IV doublets. The fifth type of doublet requires the $^{17}O - ^{16}O$ mass difference in addition to the chlorine difference. The auxilliary data required to calculate the atomic mass difference between the nuclides X and Y for the various types of doublets is listed in Table 4-2. An examination of Table 4-1 will show that some of the doublets listed differ from the types listed above. This difference is usually in the addition of extra chlorine or oxygen atoms to both members of the doublet and does not change the comments made above.

In addition to the 16 doublet spacings reported above 4

doublets of type I among the spectra of $HfCl_5$ and 2 doublets of the type

$$^{A}X^{16}O_2 - C_2\ Cl_5 = \Delta M_6$$

have been investigated by other members of this group (Southon, 1973 and Kozier, 1977). The results from doublets of type VI may be combined with the well known masses of ^{13}C, ^{16}O, ^{35}Cl and ^{37}Cl (see Table II) to obtain the absolute value for the mass of nuclide ^{A}X. In this way the atomic masses of ^{183}W and ^{186}W were determined by Kozier (1977). The results for these additional doublets are listed in Table 4-3.

As described in Chapter 3, the procedure for accumulating data with the multichannel analyser has been improved through the use of pulse counting techniques. These new techniques have been used in this work to redetermine the results for two doublets involving the relatively rare isotopes ^{180}W (0.13%) and ^{174}Hf (0.17%). The new results for these doublets (presented in Table 4-1) differ significantly from those reported earlier by Barber (1973). In particular the original values for these doublet spacings:

$$^{183}W\ ^{16}O_2 - {}^{180}W^{35}Cl = 24\ 421 \pm 9\ \mu u \qquad (4\text{-}1)$$

$$^{176}Hf^{35}Cl - {}^{174}Hf^{37}Cl = 4\ 106 \pm 16\ \mu u \qquad (4\text{-}2)$$

have been redetermined in this work as

$$^{183}W^{16}O_2 - {}^{180}W^{35}Cl = 24\ 509 \pm 6\ \mu u \qquad (4\text{-}3)$$

$$^{176}Hf^{35}Cl - {}^{174}Hf^{37}Cl = 4\ 314.2 \pm 0.9\ \mu u \qquad (4\text{-}4)$$

In the light of the large change in these values the hafnium doublet spacing was measured at three widely different masses using the fragments $HfCl_2$, $HfCl_3$ and $HfCl_4$ as a check on the integrity of the results.

The values for the doublet spacing were found to be consistent with each other. The changes in the results may be attributed to the improvements in the quality of the baseline as described in Chapter 3.

The pulse counting technique also made it possible to determine the spacing of a doublet involving the rare isotope of tantalum viz. ^{180}Ta (0.015%). In this measurement the spacing of the doublet $^{181}Ta^{17}O^{35}Cl_2$ - $^{180}Ta^{16}O^{35}Cl^{37}Cl$ was determined. The intensity of both peaks of the doublet was approximately $1/10^4$ of the parent peak ($^{181}Ta^{16}O^{35}Cl_2$) intensity. This represents an extension of the sensitivity of the instrument by at least an order of magnitude.

4-2. DESCRIPTION OF THE LEAST SQUARES EVALUATION

The results from the 21 mass spectral doublets listed in Tables 4-1 and 4-3 may be used to determine 21 atomic mass differences among the 15 stable nuclides of rhenium, tungsten, tantalum and hafnium. These determinations are shown schematically in Fig. 4-1. The experimental data discussed above may be expressed as a linear combination of the 15 atomic masses, M_j so that each of the 22 observations may be expressed in the following manner:

$$\Sigma A_{Ij} M_j = Y_I \pm S_I \text{ where } I = 1, \ldots, 24 \text{ and } j=1,\ldots,15. \quad (4\text{-}5)$$

and S_I is the standard deviation associated with the measured value Y_I. The elements of the matrix A_{Ij} are chosen in such a manner as to generate the appropriate differences between the atomic masses for each observational equation.

It is possible to calculate estimates for the values of the

observed values (Y_I) based on a set of estimates for the masses M_j^* such that:

$$Y_I^* = \Sigma A_{Ij} M_j^* \qquad j = 1, \ldots, 15 \qquad (4\text{-}6)$$

From this one defines the residual r_I as

$$r_I = Y_I^* - Y_I \qquad (4\text{-}7)$$

as has been discussed in Sharma (1977b) the best estimates for the masses M_j^* may be obtained by minimizing the weighted sum of the squares of the residuals i.e.

$$\chi^2 = \Sigma \omega_I r_I^2 \quad \text{or} \quad \Sigma (r_I / S_I)^2 \qquad (4\text{-}8)$$

In a calculation such as this one expects the quantity $\chi^2/2f$ to be equal to $1 \pm 1/2f$ where f is the number of degrees of freedom of the system. This type of analysis has been used by Wapstra and Gove (1971) and Wapstra and Bos (1977) in the generation of the Atomic Mass Evaluations and on a smaller scale by Meredith and Barber (1972).

4-3. SUPPLEMENTARY DATA

The above procedure works best when all of the masses concerned are linked to at least two other masses by means of measurements in such a manner that a particular mass may be calculated in at least two different ways from a knowledge of one other mass and the set of measurements. This condition reduces the chances of a systematic bias in one measurement influencing our choices for the M_j^*. The 21 doublets discussed above fall short of this requirement in 3 areas:

1) There exists only one measurement connecting ^{174}Hf to the main body of data viz. doublet a (Fig. 4-1)

2) The even-A and odd-A isotopes of hafnium are only linked in one

place (through doublets b, c and e).

3) There exists only one datum linking ^{180}Ta with the main body of data viz. doublet d.

Other mass spectral or reaction data that could provide supplementary links for ^{174}Hf do not exist. However the mass differences between the even and odd isotopes of hafnium may be completed by the addition of a precise (n,γ) value between ^{177}Hf and ^{178}Hf (this link is labelled v in Fig. 4-1). listed in Table 4-4.

The mass differences involving ^{180}Ta warrant special attention. The decay scheme proposed by Greenwood (1975) in Nuclear Data Sheets is shown in Fig. 4-2a. This indicates that there are two relatively close energy levels for ^{180}Ta, one with a lifetime of 8.1 hr and the other with a lifetime of 10^{13} yrs. Wapstra (1977) has recently suggested the scheme shown in Fig. 4-2b in which the 8.1 hr state is identified as the groundstate and the 10^{13} yr state is a long-lived, naturally occurring isomeric state.

The β-decay energy from the 8.1 hr state has been measured by Brown (1951) and Gallagher (1962) and the weighted average of these two measurements (see Table 4-4) yields

$$^{180}\text{Ta}^{8.1\text{ hr}} - {}^{180}\text{W} = 762 \pm 12\ \mu\text{u} \qquad (4\text{-}9)$$

In addition to this value Lanier (1972) has determined a relatively precise ^{180}Ta(n,γ)Q-value for ^{180}Ta (see Table 4-4) using a natural tantalum sample. This measurement gives the following mass difference

$$^{181}\text{Ta} - {}^{180}\text{Ta} = n - 8215.8 \pm 4.0\ \mu\text{u} \qquad (4\text{-}10)$$

The difference may also be calculated from a ^{181}Ta(γ,n) threshold measurement by Barkman (1977) as

$$^{181}Ta - {}^{180}Ta = n - 8137 \pm 5 \text{ μu} \qquad (4\text{-}11)$$

In this work the mass difference may be calculated from doublet d as

$$^{181}Ta - {}^{180}Ta = n - 8259 \pm 21 \qquad (4\text{-}12)$$

The measurement of the β-decay energy (Eqn. 4-9) may be compared to the quantities in equations 4-10, 4-11 and 4-12 by combining the β-decay energy with the results of doublets e and g (Table I). This procedure results in

$$^{181}Ta - {}^{180}Ta^{8.1\ hr} = n - 8121 \pm 13 \text{ μu} \qquad (4\text{-}13)$$

An examination of the above results reveals that the numbers in Eqn. 4-13 and 4-11 agree within their stated errors. This leads to the suggestion that the ^{181}Ta (γ,n) threshold measurement by Barkman (Eqn. 4-11) was made from the groundstate of ^{181}Ta to the 8.1 hr state of ^{180}Ta. Furthermore the two measurements made with natural ^{180}Ta (Eqns. 4-10 and 4-12) yield significantly lower values for the mass difference between ^{180}Ta and ^{181}Ta. This is consistent with Wapstra's proposed scheme, in which the 10^{13} yr state of ^{180}Ta is a naturally occurring, isomeric state.

In an effort to obtain a better picture of the energy levels the β-decay value (Eqn. 4-9) and the (γ,n) threshold measurements (Eqn. 4-11) were included in the least-squares evaluation. This increased the number of equations to 24 and changed the number of masses being calculated to 16. A discussion of the results of the calculation with reference to A = 180 is deferred until the next section.

4-4. RESULTS OF THE LEAST SQUARES EVALUATION

The resulting χ^2, when the above system of equations was solved, was 10.1. Inasmuch as there are 8 degrees of freedom for this system of equations, the generalized Birge ratio ($\chi^2/2f$) has a value of 1.12 which compares favourably with the expected value of 1 ± 0.25. This is an indication that none of the data used are in gross disagreement with each other and that the errors assigned to each datum have been realistically estimated.

The input and output values together with the residuals and contributions to χ^2 (i.e. $(r_I/S_I)^2$) are shown in Table 4-5. The largest contributions to χ^2 arise from 5 doublets (b, e, f, h and m) associated with the nuclides of ^{183}W and ^{184}W. This probably reflects the large number of measurements that connect these nuclides.

A. Comparison of calculated masses with other data: The set of self-consistent masses obtained through the calculation are compared with the output values from the 1977 Mass Evaluation (Wapstra and Boss, 1977) in Table 4-6. A systematic difference between the values for the masses from the two sources of 34.8 μu exists. This is an improvement over the comparison made earlier (Sharma, 1977a) when the output of a similar least squares evaluation, using only the tungsten and rhenium data was compared with the masses listed in the 1971 Mass Evaluation (Wapstra and Gove, 1971). Since the masses presented here are not significantly different from those presented earlier (Sharma, 1977a) this may be taken as an indication that the changes in the input data for the 1977 Mass Evaluation are instrumental in moving the output

values closer to the values presented here. In particular new data, in the form of mass differences, have become available linking the nuclides in this region with more reliable absolute mass measurements in the neodymium region.

The absolute masses for ^{179}Hf and ^{180}Hf may also be compared with recent results for atomic mass determinations at the University of Minnesota by Halverson and Johnson (1979). In this case a systematic disagreement of ~15 μu exists, a discrepancy somewhat outside the stated errors (see Table 4-6). Some time ago this group (Sharma, 1977b) published an extensive least squares evaluation involving all available reaction and mass spectrometric data for nuclides in the region $68 \leq z \leq 72$. Here the masses of the nuclides considered were calculated on the basis of the mass differences and a single absolute mass measurement of ^{162}Er based on measurements made by Benson and Johnson (1966) at Minnesota. These calculated masses are also presented for comparison with values from this work in Table 4-6. It will be seen that in this case the masses agree within their stated errors.

B. Comparison of the calculated mass differences with other data: The mass differences between the nuclides may be compared with the mass differences derived in the 1977 Mass Evaluation by comparing the single neutron (S_n) and double neutron (S_{2n}) separation energies defined below

$$S_n = n - M(z, N+1) - M(z, N) \qquad (4\text{-}14)$$

$$S_{2n} = 2n - M(z, N+2) - M(z,N) \qquad (4\text{-}15)$$

where n is the mass of the neutron and M (z,N) is the mass of the nuclide $^{z+N}_{N}X$. These quantities represent the binding energies of the last neutron or the last pair of neutrons in the nucleus of the heavier

nuclide. The S_n and S_{2n} values calculated from the output of this least squares adjustment are compared with values obtained from the 1977 Mass Evaluation in Table 4-7. Additional data from the 1977 Mass Evaluation were used, whenever necessary, to make the list more complete. Here, in contrast with the situation shown in Table 4-6, the values are seen to be generally in very good agreement with the 77 mass evaluation. Comparison is also possible with the results of a mass doublet from Halverson and Johnson (1979) which yields:

$$^{180}Hf - ^{179}Hf = n - 7390.69 \pm 4.38 \text{ keV}, \qquad (4\text{-}16)$$

a value which agrees with the S_n value for ^{180}Hf presented in Table 4-7.

C. Results of the calculation for A = 180: The relative positions of the groundstate energy levels for the nuclides at A = 180 are presented in Fig. 4-2b. The naturally occurring, long lived, isomeric state of ^{180}Ta is also shown. The (n,γ) value by Lanier and the results from doublet d, may be used in a weighted average to determine the spacing between ^{181}Ta and the long lived isomer of ^{180}Ta. A fairly substantial discrepancy (43 ± 21 μu) exists between these two values with the mass spectral doublet yielding a lower value for the mass of the isomer. Such a discrepancy between mass spectral data and precise (n,γ) measurements has not been characteristic of results obtained in recent work by this group and is taken to reflect the difficulty in studying this doublet (viz. low intensities). Although it carries lower precision than the γ-ray measurement this result is here interpreted as distinguishing in an unequivocal and independent manner,

the states which are involved in the energy measurements. None of the present mass spectrometric measurements supports the ordering of states given by Nuclear Data Sheets.

Inasmuch as both measurements locate the isomeric state some 100 keV above the 8.1 hr state it was decided that a weighted average of these two values would fairly represent the best value. Note that the weight given to the (n,γ) value is accordingly much larger than the weight given to the doublet. This yields a separation between the isomeric and the groundstate of 77 ± 9 keV with the 10^{13} yr state appearing above the groundstate.

D. S_{2n} systematics: As noted in previous work (Duckworth et al, 1969; Meredith, 1972; Barber, 1973 and Sharma, 1977), certain systematic properties of S_{2n} values become apparent when S_{2n} values for even - N nuclides are plotted against N (the neutron number). Such a plot is presented in Fig. 4-3. Wherever possible data from this work is used; the remaining data were obtained from the 1977 Mass Evaluation. In particular, segments of adjacent curves are seen to be parallel when viewed over a range of 2 neutrons at particular values of N. Attention is especially drawn to a well defined break in the curves at N = 108. This break is similar to changes following major shell closures (Barber, 1973) though on a smaller scale. This feature indicates that the energy difference between the groundstates at N = 108 and N = 110 are greater than those of their nearest even - N neighbors. The nuclei in this region are known to be deformed and the energies of the single-particle states are given by the Nilsson single-particle levels

(Ogle, 1972). Thus one may consider the above results as an indication of a relatively large gap above the $9/2^+$ (624) level (N = 108). The theoretical levels appear in the correct order with a larger gap than usual above N = 108 when a spheroidal deformation ($\varepsilon_2 = 0.025$) together with a small tetroidal deformation is assumed.

4-5. CONCLUSION

The stability of operation and the sensitivity of the Manitoba II spectrometer have been significantly improved through changes and modifications of the instrumentation. This improvement has made it possible to redetermine the results for two doublets involving the rare nuclides ^{180}W and ^{174}Hf. The precision of the new results is comparable to or superior to available data involving these two nuclides. In addition to this, the mass difference $^{181}Ta - ^{180}Ta$ has also been determined. While the precision associated with this measurement is not as high as that in reaction Q-value data, this measurement helps to determine unequivocally the groundstate energy level structure at A = 180.

A total of sixteen new doublets have been determined in this work extending the region of our systematic study of atomic mass differences (viz. $60 \leq z \leq 72$) to $60 \leq z \leq 76$. These sixteen mass differences, when combined with a few other precise measurements, form, for the first time, a completely overdetermined set of mass differences between the stable isotopes of hafnium, tantalum, tungsten and rhenium. A set of self-consistent masses and mass-differences has been derived from these data and the systematic properties of the calculated S_{2n} values

have been interpreted in terms of Nilsson single-particle levels.

Table 4-1 New atomic mass differences

Code	Doublet	Mass Difference (μu)
a	$^{176}Hf^{35}Cl - {}^{174}Hf^{37}Cl$	4314.2 ± 0.9
b	$^{183}W^{16}O_2{}^{35}Cl - {}^{178}Hf^{35}Cl^{37}Cl$	30455.7 ± 5.0
c	$^{181}Ta^{35}Cl_2 - {}^{179}Hf^{35}Cl^{37}Cl$	5128.6 ± 2.1
d	$^{181}Ta^{17}O^{35}Cl_2 - {}^{180}Ta^{16}O^{35}Cl^{37}Cl$	7571.8 ± 21
e	$^{183}W^{35}Cl - {}^{181}Ta^{37}Cl$	5177.2 ± 1.2
f	$^{184}W^{16}O_2 - {}^{181}Ta^{35}Cl$	23917.5 ± 2.8
g	$^{183}W^{16}O_2 - {}^{180}W^{35}Cl$	24509 ± 6
h	$^{186}W^{16}O_2 - {}^{183}W^{35}Cl$	25122 ± 5
i	$^{184}W^{35}Cl - {}^{182}W^{37}Cl$	5676.3 ± 2.2
j	$^{186}W^{35}Cl - {}^{184}W^{37}Cl$	6382.0 ± 1.4
k	$^{183}W^{16}O_2{}^{37}Cl - {}^{182}W^{35}Cl_2$	20045.6 + 1.8
l	$^{184}W^{16}O_2{}^{37}Cl - {}^{183}W^{35}Cl_2$	18734.7 ± 3.0
m	$^{187}Re^{16}O_2 - {}^{184}W^{35}Cl$	25797.4 ± 3.5
n	$^{185}Re^{35}Cl - {}^{183}W^{37}Cl$	5678.7 ± 1.0
o	$^{187}Re^{35}Cl - {}^{185}Re^{37}Cl$	5744.2 ± 1.2

Table 4-2 Auxiliary data

1u	931.5016 ± 26 MeV
$^{37}Cl - ^{35}Cl$	1.997049895 ± 100 u
^{35}Cl	34.968852729 ± 68 u
^{37}Cl	36.965902624 ± 105 u
^{16}O	15.99491464 ± 5 u
^{17}O	16.9991306 ± 8 u
^{13}C	13.033354839 ± 17 u
n	1.008664967 ± 34 u
^{1}H	1.007825037 ± 10 u
^{3}H	3.016049286 ± 32 u

N.B. The errors shown effect the last decimal places shown.

Table 4-3 Other relevant doublets measured by this group

Code	Doublet	Mass Difference (μu.)	Ref.
p	$^{180}Hf^{35}Cl_2 - {}^{176}Hf^{37}Cl_2$	11036.1 ± 3.0	1
q	$^{179}Hf^{35}Cl - {}^{177}Hf^{37}Cl$	5544.4 ± 0.7	1
r	$^{178}Hf^{35}Cl - {}^{176}Hf^{37}Cl$	5239.5 ± 1.3	1
s	$^{180}Hf^{35}Cl - {}^{178}Hf^{37}Cl$	5798.4 ± 0.7	1
t	$^{186}W^{16}O - {}^{13}C^{12}C^{35}Cl_4{}^{37}Cl$	104592.7 ± 3.2	2
u	$^{183}W^{16}O - {}^{12}C_2{}^{35}Cl_5$	100858.0 ± 2.7	2

1) Southon (1973)

2) Kozier (1977), Sharma (1977a)

Table 4-4 Additional data used for the calculation

Code	Reaction	Q-value or threshold energy	Ref.
v	$^{177}Hf(n,\gamma)^{178}Hf$	7625.5 ± 1.0 keV	Faler (1969)
w	$^{180}Ta(\beta^-)^{180}W$	705 ± 15 keV	Brown(1951)
		710 ± 15 keV	Gallagher(1961)
		708 ± 11 keV	wt. average
x	$^{180}Ta(n,\gamma)^{181}Ta$	7653 ± 4 keV	Lanier(1972)
y	$^{181}Ta(n,\gamma)^{180}Ta$	7580 ± 5 keV	Barkman(1977)

Table 4-5 Input/output from adjustment

Mass Difference	Input value	Output value	r_I	wr_I^2
$^{180}Hf - ^{176}Hf$	4n - 29523.9 ± 3.0	29522.4 ± 1.3	1.46	0.24
$^{178}Hf - ^{177}Hf$	n - 8186.7 ± 1.2	8186.9 ± 1.2	-0.29	0.06
$^{179}Hf - ^{177}Hf$	2n - 14735.6 ± 0.7	14735.5 ± 0.7	0.10	0.02
$^{176}Hf - ^{174}Hf$	2n - 15965.8 ± 0.9			
$^{178}Hf - ^{176}Hf$	2n - 15040.5 ± 1.3	15040.8 ± 1.2	-0.27	0.04
$^{180}Hf - ^{178}Hf$	2n - 14481.6 ± 0.7	14481.7 ± 0.7	-0.08	0.01
$^{183}W - ^{178}Hf$	5n - 36795.7 ± 5.0	36800.6 ± 2.4	-4.99	1.01
$^{181}Ta - ^{179}Hf$	2n - 15151.4 ± 2.1	15150.5 ± 2.0	0.92	0.19
$^{181}Ta - ^{180}Ta^*$	n - 8137.4 ± 5.4	8135.4 ± 5.0	1.99	0.14
$^{180}Ta^* - ^{180}W$	762 ± 12	772 ± 7	9.93	0.69
$^{181}Ta - ^{180}Ta$	n - 8218 ± 9			
$^{183}W - ^{181}Ta$	2n - 15102.8 ± 1.2	15101.6 ± 1.1	1.16	0.94
$^{184}W - ^{181}Ta$	3n - 23053.9 ± 2.8	23058.1 ± 1.6	-4.20	2.25
$^{183}W - ^{180}W$	3n - 22462.4 ± 6.0	22464.9 ± 5.5	-2.48	0.17
$^{186}W - ^{183}W$	3n - 21849.4 ± 5.0	21854.2 ± 1.8	-4.83	0.93
$^{184}W - ^{182}W$	2n - 14603.7 ± 2.2	14602.8 ± 1.6	0.86	0.15
$^{186}W - ^{184}W$	2n - 13898.0 ± 1.4	13897.7 ± 1.3	0.23	0.03
$^{183}W - ^{182}W$	n - 6645.8 ± 1.8	6646.4 ± 1.5	-0.58	0.10
$^{184}W - ^{183}W$	n - 7956.7 ± 3.0	7956.5 ± 1.4	0.22	0.01
$^{187}Re - ^{184}W$	3n - 21174.0 ± 3.5	21179.5 ± 1.9	-5.53	2.50
$^{185}Re - ^{183}W$	2n - 14601.3 ± 1.0	14600.8 ± 1.0	0.45	0.20
$^{187}Re - ^{185}Re$	2n - 14535.8 ± 1.2	14535.1 ± 1.2	0.65	0.29
^{186}W	185.9543464 ± 3.2	347.2 ± 2.3	0.77	0.06
^{183}W	182.9502071 ± 1.7	206.6 ± 2.2	-0.55	0.04

* Denotes the 8.1 hr state.

Table 4-6 Calculated masses and comparison values

Nuclide	This work	1977 mass table	Sharma (1977b)	Halverson and Johnson (1977)
^{174}Hf	173.9400293 ± 3.6	173.940065 ± 8	173.940037 ± 7	
^{176}Hf	175.9413934 ± 3.5	175.941420 ± 6	175.941401 ± 7	
^{177}Hf	176.9432045 ± 3.1	176.943233 ± 6	176.943213 ± 7	
^{178}Hf	177.9436825 ± 3.2	177.943710 ± 6	177.943691 ± 7	
^{179}Hf	178.9457989 ± 3.1	178.945827 ± 6	178.945807 ± 7	178.9458150 ± 1.7
^{180}Hf	179.9465307 ± 3.3	179.946561 ± 6	179.946540 ± 7	179.9465448 ± 3.5
^{180}Ta*	179.9474487 ± 5.5	179.947489 ± 14		
^{180}Ta	179.947531 ± 9			
^{181}Ta	180.9479783 ± 2.4	180.948014 ± 7		
^{180}W	179.9466766 ± 5.9	179.946727 ± 8		
^{182}W	181.9481880 ± 2.6	181.948225 ± 7		
^{183}W	182.9502066 ± 2.2	182.950245 ± 7		
^{184}W	183.9509150 ± 2.3	183.950953 ± 7		
^{186}W	185.9543472 ± 2.3	185.954377 ± 7		
^{185}Re	184.9529356 ± 2.4	184.952977 ± 7		
^{187}Re	186.9557304 ± 2.6	186.955765 ± 7		

* Denotes the 8.1 hr state.

Table 4-7 S_{2n}, S_n values in comparison with 77 Mass Evaluation

	S_{2n} (keV)	S_n (keV)	Comparison Values	
^{174}Hf				
^{176}Hf	14872.13 ± 0.81	8082 ± 10[a]	14880 ± 5	8090 ± 8
^{177}Hf	14466.55 ± 10[a]	6384.36 ± 1.56	14474 ± 8	6383.3 ± 2.1
^{178}Hf	14010.48 ± 1.12	7626.15 ± 1.09	14009.6 ± 2.0	7626.3 ± 0.9
^{179}Hf	13726.11 ± 0.65	6099.99 ± 1.26	13726.1 ± 1.1	6099.8 ± 0.8
^{180}Hf	13489.69 ± 0.64	7389.75 ± 1.42	13487.9 ± 0.9	7388.11 ± 0.39
^{180}Ta				
^{181}Ta		7578.12 ± 4.65		7583 ± 12
^{180}W				
^{182}W	14735.00 ± 5.66	8050 ± 9[b]	14747 ± 4	8062 ± 7
^{183}W	14241.04 ± 8.65[b]	6191.09 ± 1.41	14253 ± 7	6190.6 ± 1.5
^{184}W	13602.54 ± 1.53	7411.45 ± 1.32	13602.3 ± 1.5	7411.68 ± 0.30
^{186}W	12945.77 ± 1.21	7191.87 ± 1.57[c]	12953.3 ± 2.6	7199.4 ± 2.6
^{185}Re	14156.69 ± 8.06[d]	7685.28 ± 6.22[e]	14154 ± 8	7682 ± 6
^{187}Re	13539.49 ± 1.07	7370.80 ± 3.37[f]	13545.8 ± 2.3	7366.7 ± 2.2

calculated using:

a) $S_n(^{175}Hf)$ = 6790 ± 10 keV

b) $S_n(^{181}W)$ = 6685 ± 7 keV

c) $S_n(^{185}W)$ = 5753.9 ± 1.0 keV

d) $Q_\beta(^{183}W)$ = -556 ± 8 keV

e) $Q_\beta(^{184}W)$ = -1496 ± 6 keV

f) $Q_\beta(^{180}W)$ = -587.8 ± 2.6 keV

from the 1977 Mass Evaluation.

Fig. 4-1 Input Data

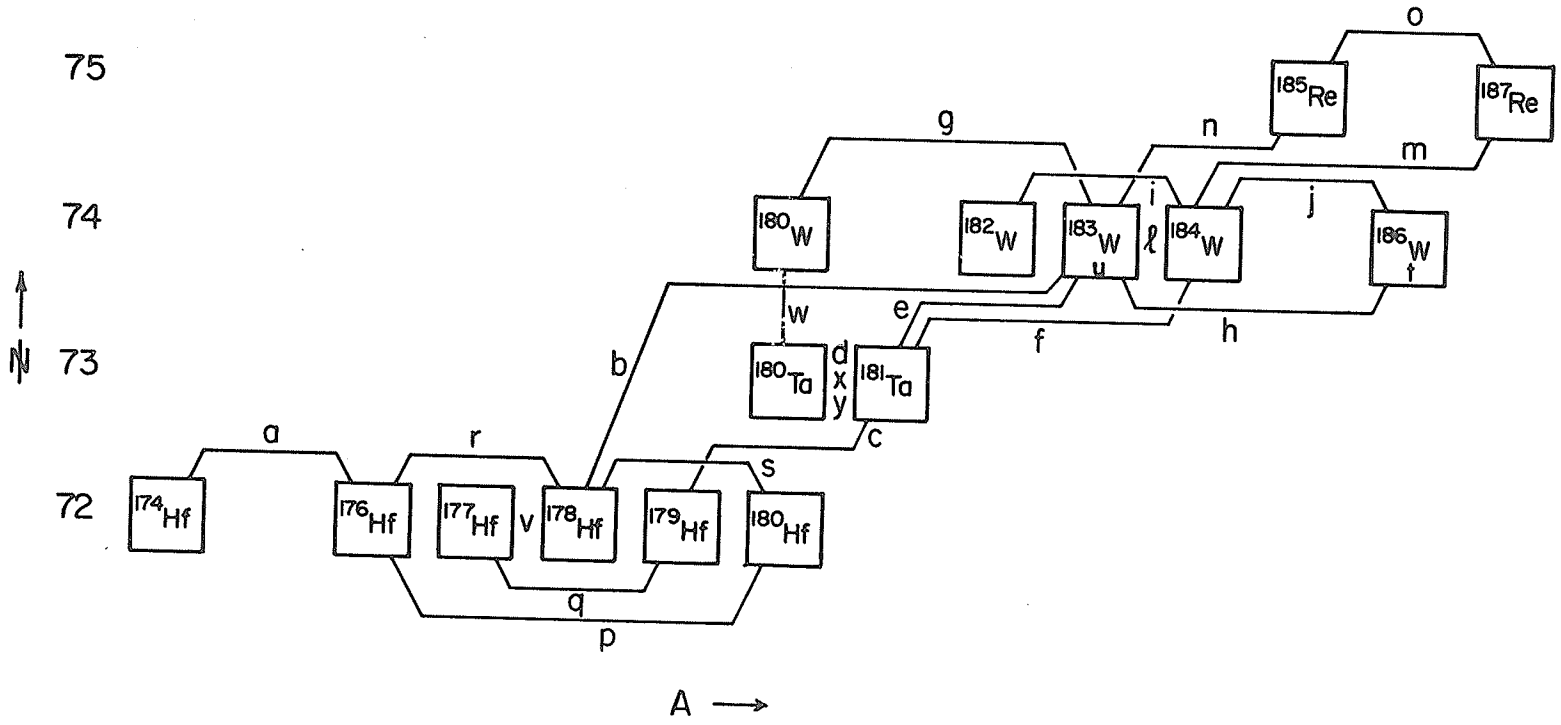

75
74
73
72
N
A
^{174}Hf
^{176}Hf
^{177}Hf
^{178}Hf
^{179}Hf
^{180}Hf
^{180}Ta
^{181}Ta
^{180}W
^{182}W
^{183}W
^{184}W
^{186}W
^{185}Re
^{187}Re
a
b
c
d
e
f
g
h
i
j
k
l
m
n
o
p
q
r
s
t
u
v
w
x
y

Fig. 4-2a Groundstate energy levels at A = 180 as given by Greenwood (1975) from Wapstra and Gove (1973).

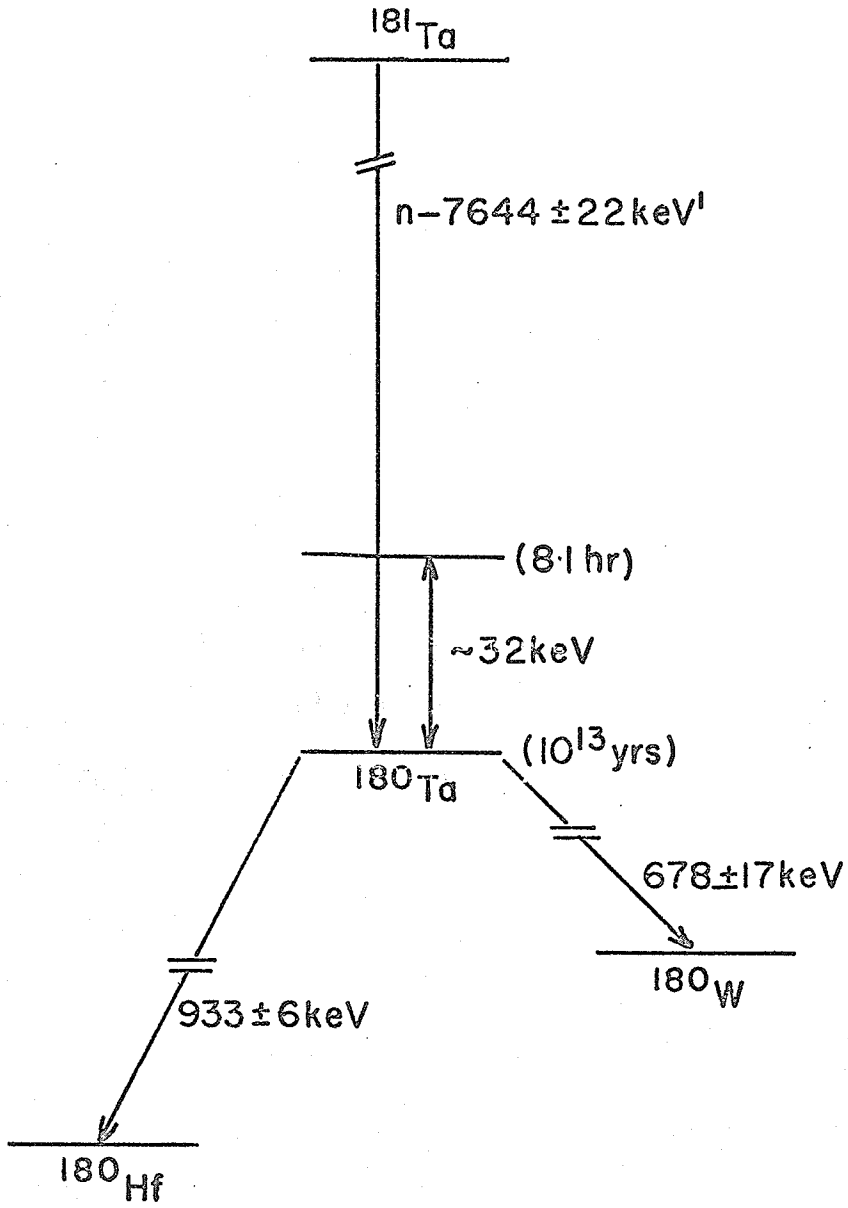

181Ta
n-7644±22keV
(8·1 hr)
~32keV
(10^13 yrs)
180Ta
678±17keV
180W
933±6keV
180Hf

Fig. 4-2b Groundstate energy levels at A = 180 as determined by these results

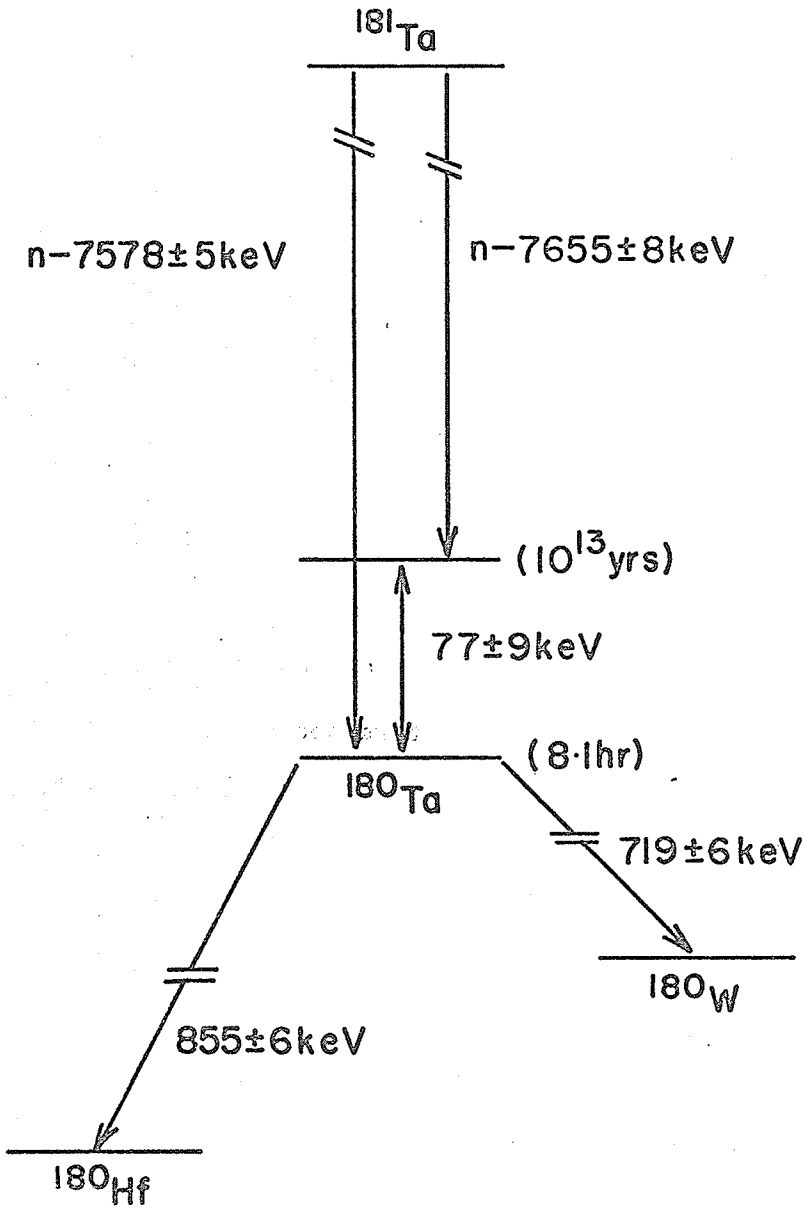
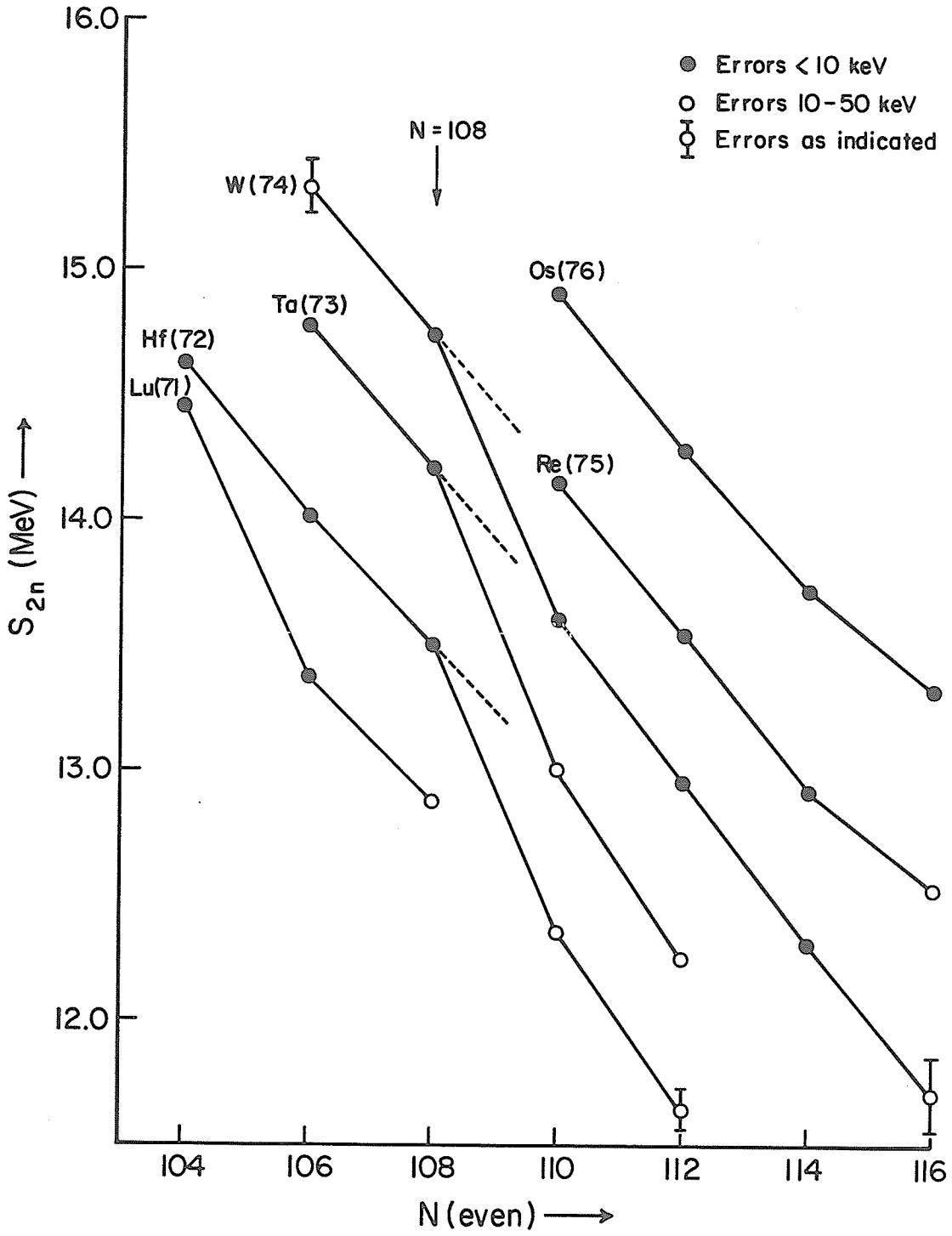

^{181}Ta
n-7578±5keV
n-7655±8keV
(10^{13}yrs)
77±9keV
($8\cdot1$hr)
^{180}Ta
719±6keV
^{180}W
855±6keV
^{180}Hf

Fig. 4-3 S_{2n} Systematics


16.0
15.0
14.0
13.0
12.0
S_{2n} (MeV) ⟶
Errors < 10 keV
Errors 10-50 keV
Errors as indicated
N = 108
W(74)
Os(76)
Ta(73)
Hf(72)
Lu(71)
Re(75)
104
106
108
110
112
114
116
N (even) ⟶

APPENDIX 1

The ion optical properties of a mass spectrometer may be investigated with a second-order ray tracing technique described by Wollnik (1967). In this method the effect of each part of the instrument on a ray is simulated with a linear transformation of a vector describing the incident ray. The matrix which is used to transform this initial vector into a vector describing the exit ray is termed a "transfer matrix). In this manner, several transfer matrices may be utilized to represent each individual component in the instrument (viz. field free regions, electric fields, magnetic fields and fringe fields). The transfer matrix, which describes the effect of the instrument, as a whole, on the incident ray, is obtained from the product of all the individual transfer matrices used.

The above technique forms the basis for a computer program developed by Kaiser (1969) at the Argonne National Laboratory. This program was used to evaluate the ion-optical properties of the Manitoba II spectrometer. In all, 7 matrices were necessary to describe this instrument corresponding to the following parts:

(a) the field free region between the principal slit and the electric field,

(b) the electric field,

(c) the field free region between the electric and magnetic fields,

(d) the fringe field at the entrance of the magnet,

(e) the magnetic field,

(f) the fringe field at the exit of the magnet and

(g) the field free region between the magnet and the collector slit.

The coefficients B_{ij} described before in Eqn. 2-9 and other properties of the spectrometer were calculated and are presented in Table A1 - 1. Note that the values of the B_{ij}'s are small as expected, since the geometry is designed to produce second order focussing. The focus point for the axial direction (z-focus) occurrs some 200 cm from the edge of the magnet and the α-focus and the β-focus occur at the same point (59.45 cm from the edge of the magnet).

Table A1 - 1

Summary of the ion-optical parameters of Manitoba II

B_{10} = 0.000

B_{20} = 2.126×10^{-4}

B_{11} = -6.865×10^{-4}

B_{12} = 1.302×10^{-3}

B_{22} = 8.010×10^{-4}

Magnification = 0.4951

Mass Dispersion = 53.13 cm

z-focus = 193.09 cm (measured from the boundary of the magnetic field)

α-focus = 59.45 cm (measured from the boundary of the magnetic field)

β-focus = 59.45 cm (measured from the boundary of the magnetic field)

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BY

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Precise atomic masses and mass differences for W and Re[1]

K. S. SHARMA, K. S. KOZIER, J. W. BARNARD, R. C. BARBER, AND S. S. HAQUE
Department of Physics, University of Manitoba, Winnipeg, Man., Canada R3T 2N2
AND
H. E. DUCKWORTH[2]
University of Winnipeg, Winnipeg, Man., Canada R3B 2E9
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The 1 m radius, second order double focusing mass spectrometer at the University of Manitoba has been used to obtain atomic mass differences for eleven mass doublets. These data are combined with well known values for the atomic masses of ^{13}C, ^{16}O, ^{35}Cl, and ^{37}Cl to derive both atomic masses and mass differences for all of the naturally-occurring isotopes of W and Re.

Le spectromètre de masse de 1 m de rayon, à double focalisation au second ordre, de l'Université du Manitoba a été utilisé pour obtenir des différences de masse atomique pour onze doublets. Ces données sont combinées avec des valeurs bien connues des masses atomiques de ^{13}C, ^{16}O, ^{35}Cl et ^{37}Cl, afin d'obtenir à la fois les masses atomiques et les différences de masse pour tous les isotopes naturels de W et Re.

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Introduction

The 1.00 m radius, second order double focusing mass spectrometer ('Manitoba II') (Barber *et al.* 1971) has been used in a continuing systematic investigation of precise atomic mass differences. In particular, a large number of atomic mass differences in the region from Nd to Hf have been determined (Barber *et al.* 1972, 1973, 1974, 1976) by means of doublets of the types:

$$[1] \qquad {}^{A}X - {}^{A}Y = \Delta M_1$$

$$[2] \qquad {}^{A+2}X^{35}Cl - {}^{A}Y^{37}Cl = \Delta M_2$$

$$[3] \qquad {}^{A+4}X^{35}Cl_2 - {}^{A}Y^{37}Cl_2 = \Delta M_3$$

where X and Y may or may not be the same element.

In the present work, which is a continuation of this project, 11 new doublet spacings in the mass spectra of tungsten and rhenium oxychlorides, have been determined. The doublets studied were of the types [2] and [3] as well as of the following types:

$$[4] \qquad {}^{A+1}X^{16}O_2{}^{37}Cl - {}^{A}Y^{35}Cl_2 = \Delta M_4$$

$$[5] \qquad {}^{A+3}X^{16}O_2 - {}^{A}Y^{35}Cl = \Delta M_5$$

$$[6] \qquad {}^{A}X^{16}O - C_2Cl_5 = \Delta M_6$$

[1]Work supported by the National Research Council of Canada.
[2]Adjunct Professor of Physics, University of Manitoba, Winnipeg, Man., Canada.

Doublet spacings are in the range of 1/38 000 to 1/1 900. Doublets of types [2] and [3] can be combined with the $^{37}Cl - {}^{35}Cl$ mass difference to yield atomic mass differences between X and Y. Doublets of types [4] and [5] require this difference as well as the $^{35}Cl - {}^{16}O_2$ mass difference. The sixth type of doublet can be combined with the well known masses for ^{16}O, ^{13}C, ^{35}Cl, and ^{37}Cl to yield the absolute mass of nuclide ^{A}X. Two of the eleven doublets reported here are of this type.

Experimental

The mass difference between two different ionic species is measured by some variation of the peak matching technique which has been discussed in detail elsewhere (Benson and Johnson 1966; Barber *et al.* 1964, 1968, 1971, 1976; Meredith *et al.* 1972; Southon *et al.* 1977). In this method, a peak corresponding to a particular mass is generated by sweeping the ion beam across the collector slit with a sawtooth magnetic field. This magnetic field is applied in a part of the drift space between the magnetic analyser and the collector slit. The ion current is then amplified by an electron multiplier and displayed on the oscilloscope from which the sawtooth was derived.

The peak matching method is based on a theorem given by Bleakney (1936). If an ion of mass M, initially at rest, traverses a particular path through the mass spectrometer, then an ion

of mass M', also initially at rest at the same point, will traverse exactly the same path through the instrument, if all magnetic fields remain unchanged and all potentials V_i applied to the various electrodes are changed to V_i', such that

$$[7] \qquad MV_i = M'V_i'$$

In particular, by changing the potentials applied to the electrostatic analyser, on alternate sweeps, from V to $V' = V + \Delta V$, such that the peak for M' falls at the same point as the peak for M on the display oscilloscope trace, $\Delta M = M - M'$ can be calculated from

$$[8] \qquad \Delta M/M' = \Delta V/V$$

Once ΔV is set, the ratio of ΔV to V is determined by apparatus that has been previously described (Bishop and Barber 1970).

The signal for a peak is accumulated over many sweeps, in a single averager, to improve the signal to noise ratio.

The coincidence of the peaks for M and M' may be detected by one of two methods. In the first, the 'visual null' method, the input signal to the signal averager is alternatively added and subtracted from the memory of the signal averager (Benson and Johnson 1966; Barber *et al.* 1971). The matched condition is determined by letting the two peaks cancel each other in the memory.

More recently, we have used a computer assisted method of peak matching (Meredith *et al.* 1972). The signal averager's memory is divided into four quadrants corresponding to four sweeps. A reference peak is accumulated in the first quadrant and the 'unknown' peak is accumulated in the remaining three quadrants at positions corresponding to three different voltages which bracket the matched position. The computer is used in a least squares fit of the centroid positions of the peaks and the applied voltages. This least squares fit is then used to calculate the voltage corresponding to the matched condition.

Until recently, in the 'computer' method, the input signal to the signal averager was converted, point by point, to digital information and then added to the memory. In this mode, low frequency variations in the baseline and noise, which is intentionally added to the digitizer of the averager, tended to obscure weak signals. Moreover the low frequency variations in the baseline had the effect of falsely modulating the peak position. These deficiencies have been corrected by modifying the detection electronics so that each ion pulse from the electron multiplier is recorded as one event directly in the averager memory. This removes the stringent requirements on baseline variation and greatly improves the overall sensitivity for weak peaks.

Results and Discussion

The 11 mass differences determined in this study are presented in Table 1. In particular we note that the value reported here for the doublet $^{183}W^{16}O_2 - {}^{180}W^{35}Cl$ is significantly different from the value given by us in previous work (24 421 ± 9 μu, Barber *et al.* 1973). In both cases the sample material contained ^{180}W only in natural abundance (0.13%), making the doublet unfavourable. As suggested above, it is believed that, in the signal averaging mode which was used in the earlier determination, the information about the peak was degraded substantially. All of the present measurements were made using the pulse counting procedure.

The new data may be combined with the auxiliary data summarized in Table 2. Where possible we have preferred to use values in the 1971 atomic mass evaluation which include the data of Smith (1971) (from Wapstra and Gove (1971), p. 368) as indicated in Table 2. In the case of the $^{37}Cl - {}^{35}Cl$ mass difference, the values are from three virtually independent sources. The weighted mean of these values has been adopted in this work.

Absolute masses for ^{183}W and ^{186}W may be derived from two of the doublet values. As is evident in Fig. 1, these values with the remaining nine doublets form an overdetermined set of mass differences for the isotopes of tungsten and rhenium. The measurements were combined in

TABLE 1. New atomic mass differences

Code	Doublet	Atomic mass differences (μu)
A	$^{183}W^{16}O_2 - {}^{180}W^{35}Cl$	24 509 ± 6
B	$^{186}W^{35}Cl - {}^{184}W^{37}Cl$	6 382.0 ± 1.4
C	$^{184}W^{35}Cl - {}^{182}W^{37}Cl$	5 676.3 ± 2.2
D	$^{184}W^{16}O_2{}^{37}Cl - {}^{183}W^{35}Cl_2$	18 734.7 ± 3.0
E	$^{183}W^{16}O_2{}^{37}Cl - {}^{182}W^{35}Cl_2$	20 045.6 ± 1.8
F	$^{186}W^{16}O_2 - {}^{183}W^{35}Cl$	25 122 ± 5
G	$^{187}Re^{35}Cl - {}^{185}Re^{37}Cl$	5 744.2 ± 1.2
H	$^{187}ReO_2 - {}^{184}W^{35}Cl$	25 797.4 ± 3.5
I	$^{185}Re^{35}Cl - {}^{183}W^{37}Cl$	5 678.7 ± 1.0
J	$^{186}W^{16}O - {}^{13}C^{12}C^{35}Cl_4{}^{37}Cl$	104 592.7 ± 3.2
K	$^{183}W^{16}O - {}^{12}C_2{}^{35}Cl_5$	100 858.0 ± 2.7

TABLE 2. Auxiliary data (u)

Atomic mass	Value	Reference
$^{37}Cl - {}^{35}Cl$	1.997 049 85 ± 13	Wapstra and Gove (1971), including Smith (1971)
	1.997 050 11 ± 30	Katakuse and Ogata (1972)
	1.997 049 74 ± 10	Barber *et al.* (1976)
	1.997 049 802 ± 76	Weighted mean
$^{35}Cl - {}^{16}O_2$	2.979 023 79 ± 11	Wapstra and Gove (1971), including Smith (1971)
^{13}C	13.003 355 08 ± 23	Wapstra and Gove (1971), including Smith (1971)
^{35}Cl	34.968 852 76 ± 7	Wapstra and Gove (1971), including Smith (1971)
^{37}Cl	36.965 902 61 ± 12	Wapstra and Gove (1971), including Smith (1971)
n	1.008 665 02 ± 4	Wapstra and Gove (1971), including Smith (1971)
$^{3}He - D$	1.001 927 30 ± 12	Wapstra and Gove (1971), including Smith (1971)
1u	931.4934 ± 28 MeV	*e* from Cohen and Taylor (1973)
		N_A from Deslattes (1976)
		c from Cohen (1976)

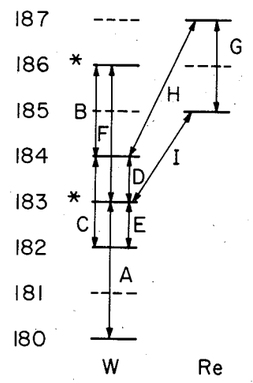

FIG. 1. Schematic diagram of atomic mass differences in W and Re. The letters refer to the doublets in Table 1. The symbol * indicates a doublet by which an absolute mass is determined.

a least squares adjustment in order to obtain a set of self consistent values for the masses and single and double neutron separation energies (S_n, S_{2n}). The results of the calculation are given in Tables 3 and 4.

It is evident in Table 3 that the new values for the masses are substantially more precise than, and differ in a systematic way from, the 1971 atomic mass evaluation by ~65 μu and from the 1975 midstream atomic mass evaluation (Wapstra and Bos 1976) by ~35 μu. This is not surprising, inasmuch as the input data in both mass evaluations for the absolute masses are generally much less precise than the data for the mass differences. Accordingly, in both evaluations, the derived mass differences amongst the W and Re isotopes are relatively precise and are seen to be in good agreement with the present values. In contrast, the corresponding absolute masses are only weakly determined by doublets in this region. Instead they primarily reflect the presence of precise absolute masses some distance away to which the W and Re masses are connected by a chain of mass differences. The accumulation of small systematic errors in this chain of differences may cause the absolute values so derived to differ from the present values by amounts well outside the stated uncertainties.

We also note that the errors shown in Table 3 for S_{2n} from the 1975 mass evaluation are taken from the errors on the masses. The errors actually calculated in this least squares adjustment will generally be smaller, but are only available from the correlation matrix and were not given by Wapstra and Bos (1976) in this work.

A further comparison of the 'best' values of mass differences from the present work with other precise determinations may be made through the S_n values for tungsten as given in Table 4. The new S_n values for ^{183}W and ^{184}W are derived solely from this work and the data in Table 2, and are seen to be in excellent agreement with previous precise (n,γ) Q values. As indicated, it is necessary to combine the mass spectroscopic differences with Q_β for ^{185}W and ^{187}W to derive the S_n values given for ^{185}W, ^{186}W, and ^{187}W.

Unfortunately a similar comparison cannot be made in rhenium inasmuch as a *direct* determination of the Q value for $^{186}Re(e.c.)^{186}W$ is not available. One may, however, combine our value for the difference

[9] $^{186}W \rightarrow {}^{185}Re = n - 6757.5 \pm 2.1$ keV

TABLE 3. Atomic masses and double neutron separation energies

	Mass (u) (errors in μu)		S_{2n} (keV)	
Nuclide	This work	Comparison values	This work	Other work
^{180}W	179.946 674 3 ± 6.2	179.946 700 ± 210[a]	—	—
		179.946 724 ± 12[d]		15 339 ± 101[d]
^{182}W	181.948 188 0 ± 2.6	181.948 248 ± 13[a]	14 732.9 ± 5.6	14 700 ± 200[a]
		223 ± 11[d]		14 755 ± 7[b]
				14 743 ± 10[c]
				14 747 ± 11[d]
^{183}W	182.950 207 3 ± 2.2	182.950 266 ± 13[a]	—	—
		241 ± 9[d]		14 254 ± 11[d]
^{184}W	183.950 914 3 ± 2.4	183.950 975 ± 13[a]	13 603.2 ± 1.6	13 602.5 ± 1.9[a]
		950 ± 9[d]		13 609 ± 7[b]
				13 606 ± 5[c]
				13 603 ± 11[d]
^{185}Re	184.952 936 3 ± 2.4	184.953 007 ± 14[a]	—	—
		952 973 ± 9[d]		14 154 ± 14[d]
^{186}W	185.954 346 9 ± 2.4	185.954 402 ± 14[a]	12 945.4 ± 1.4	12 951.8 ± 3.4[a]
		372 ± 9[d]		12 956 ± 5[c]
				12 955 ± 11[d]
^{187}Re	186.955 730 8 ± 2.6	186.955 791 ± 14[a]	13 539.7 ± 1.0	13 550.4 ± 3.4[a]
		759 ± 9[d]		13 548 ± 11[d]

[a]1971 mass table (Wapstra and Gove 1971).
[b]Casten *et al.* (1976).
[c]Oothoudt and Hintz (1973).
[d]1975 midstream atomic mass evaluation (Wapstra and Bos 1976).

TABLE 4. Single neutron separation energies (keV)

Nuclide	This work	Mass table input[a]	Nuclear data tables[b]	Other
^{183}W	6190.4 ± 1.4	6190.8 ± 1.5	6191.0 ± 2.5	6201 ± 15[c]
				6204 ± 10[e]
^{184}W	7412.8 ± 1.5	7411.0 ± 1.5	7413.0 ± 3.5	7411.1 ± 0.6[d]
				7412 ± 8[c]
^{185}W	5755.4 ± 2.1[e]	5749.0 ± 5.0		5758 ± 10[c]
^{186}W	7190.0 ± 2.5[e]			7197 ± 10[c]
^{187}W	5470.3 ± 3.0[f]	5466.5 ± 1.5	5465.0 ± 4.0	5465 ± 10[c]
		5461 ± 5		

[a]Wapstra and Gove (1971).
[b]Groshev *et al.* (1969).
[c]Casten *et al.* (1972).
[d]Greenwood and Reich (1974).
[e]Calculated with Q_β = 432.6 ± 1.0 keV for $^{185}W(\beta^-)^{185}Re$ (Willett and Spejewski 1967).
[f]Calculated with Q_β = 1312 ± 2 keV for $^{187}W(\beta^-)^{187}Re$ (Wapstra and Gove 1971).

with the precise (n,γ) Q value

[10] $^{186}Re - {}^{185}Re = n - 6179.0 \pm 1.5$ keV

used in the input to the mass table (Wapstra and Gove 1971) to derive the difference

[11] $^{186}Re - {}^{186}W = 578.5 \pm 2.6$ keV

cf. 593.9 ± 3.8 keV (1971 mass table).

The values calculated for S_{2n} for even-N nuclides from this work are plotted as a function of N in Fig. 2. Also shown in the figure are values derived from a least squares adjustment including our data for the region $68 \leq Z \leq 72$ (Barber *et al.* 1974; Sharma *et al.* 1977) for Lu and Hf. The values shown for Ta and Os were taken from Wapstra and Gove (1971).

As noted in previous work (Duckworth *et al.* 1969; Meredith and Barber 1972; Barber *et al.* 1973) these curves in general exhibit a remarkably systematic behaviour in that, when viewed

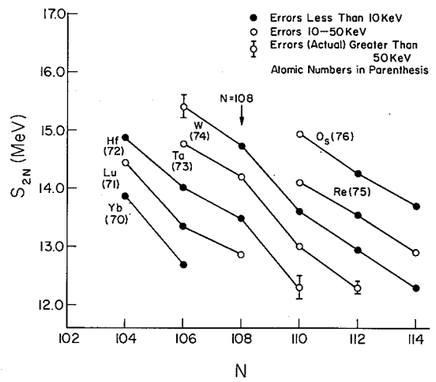

FIG. 2. Double neutron separation energies (S_{2n}) vs. neutron number (N).

over a range of two neutrons, the segments of adjacent curves are almost parallel. In this way, irregularities in the curve for one element are reproduced at the same neutron number in adjacent elements. On the basis of the present results, the Hf curve for $N = 104$ to 106 deviates somewhat from this systematic behaviour.

Previously we have drawn attention to the well-defined downward break in these curves for S_{2n} at $N = 108$ and have noted that it is reminiscent on a smaller scale of the changes following major shell closures (Barber *et al.* 1973). That is, the energy difference between the ground states, $E(N = 110) - E(N = 108)$, is greater than between their even-N neighbours. The nuclei in this region are known to be deformed so that one may interpret the shape of the S_{2n} curves in terms of Nilsson single-particle levels (Ogle *et al.* 1972). Thus, one would interpret these results to indicate a relatively large energy gap above the $9/2^+$ [624] level ($N = 108$). When a small tetroidal deformation ($\varepsilon_4 \sim 0.02$) is introduced along with the experimental values for the spheroidal deformation ($\varepsilon_2 \sim 0.25$) the levels appear in the correct order and with a larger gap than usual above $N \doteq 108$.

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