ATOMIC MASS DETERMINATIONS
FOR SOME ISOTOPES OF Ti , W AND Hg

by

Kenneth Stephen Kozier, B.Sc.

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

DOCTOR OF PHILOSOPHY

DEPARTMENT OF PHYSICS
UNIVERSITY OF MANITOBA
WINNIPEG, MANITOBA
AUGUST 1977

ATOMIC MASS DETERMINATIONS
FOR SOME ISOTOPES OF Ti, W AND Hg

BY

KENNETH STEPHEN KOZIER

A dissertation submitted to the Faculty of Graduate Studies of the University of Manitoba in partial fulfillment of the requirements of the degree of

DOCTOR OF PHILOSOPHY

DOCTOR OF PHILOSOPHY (1977)
Physics

UNIVERSITY OF MANITOBA
Winnipeg, Manitoba

TITLE: Atomic Mass Determinations for Some Isotopes of Ti, W and Hg

AUTHOR: Kenneth Stephen Kozier, B.Sc. (Hon.), University of Manitoba

SUPERVISOR: Professor R. C. Barber

PAGES: ix , 153

SCOPE AND CONTENTS:

A total of 16 new mass spectroscopic doublet determinations are reported. Nine of these involve the determination of absolute atomic masses for some of the isotopes of Ti, W and Hg. The remaining 7 doublets involve the determination of differences in atomic mass between the Hg isotopes. Precise atomic masses are established for all the naturally occurring isotopes of Ti, W , Re and Hg by combining the new determinations with other mass differences previously determined in this laboratory.

A new method of computer - assisted peak matching is reported and is compared in detail with the method previously used in this laboratory. The influence of peak limits and counting losses on the determined separation between two peaks is discussed.

ACKNOWLEDGEMENTS

This research has been supported by the National Research Council. Financial assistance from the National Research Council and the University of Manitoba is gratefully acknowledged.

I wish to thank my supervisor, Dr. R.C. Barber for his encouragement and guidance during the course of this research, and Dr. H.E. Duckworth who initiated this research group and remains a guiding influence. I also wish to thank the other members of my supervisory committee, Dr. N.E. Davison and Dr. G.S. Clark , for the interest they have shown in this work.

I am grateful for the timely reappearance of Dr. J.O. Meredith who assisted greatly in the statistical analysis and voluminous computations. Also, the electronic wizardry of Mr. K.S. Sharma has been relied upon extensively. In addition I wish to thank Mr. R.J. Ellis, Mr. V.P. Derenchuk, Dr. J.W. Barnard, Dr. S.S. Haque and many others who have contributed to a stimulating and pleasant environment for research.

I am indebted to Mr. S. Howes who prepared the figures and to Mr. G. Kozier who assisted in the photography. Especially, I wish to thank Miss Krys Polakowski who typed the manuscript in great haste and in good humour.

Finally I wish to thank my dear wife, Shirley, for her patience, support and understanding. She found the time to type the tables and references while caring for our children, Karen and Lisa, (who were also produced during the course of this work).

CONTENTS

Page

List of Tables vi

List of Figures vii

CHAPTER 1 INTRODUCTION 1

1-1 The Concept of Mass 1
1-2 Standards of Mass and Energy 4
1-3 The Importance of Atomic Mass Determinations 6
1-4 Methods of Atomic Mass Determination 9

A Alpha Decay 9
B Beta Decay 10
C Nuclear Reactions 11
D Mass Spectroscopy 12

1-5 Tables of Atomic Masses 14

CHAPTER 2 POSITIVE ION OPTICS AND MASS SPECTROSCOPIC ATOMIC MASS DETERMINATIONS 17

2-1 Historical Development 17
2-2 Positive Ion Optics (First Order Theory) 19

A Uniform Magnetic Field 20
B Radial Electric Field 23
C Double Focusing 25
D Second Order Double Focusing and Image Aberrations 26

2-3 Mass Spectroscopic Atomic Mass Determinations 27

A Bleakney's Theorem 29
B Peak Matching 31
C The Proportional Error and Problems Related to Peak Matching 32
D The Status of Atomic Masses 35

CHAPTER 3 THE MANITOBA II MASS SPECTROMETER 38

3-1 Instrument Geometry 38
3-2 Ion Source Region 40
3-3 Electrostatic Analyser Region 46
3-4 Magnetic Analyser Region 48
3-5 Ion Collection Region 50
3-6 Mechanical Support and Vacuum System 52
3-7 Focusing 52
3-8 Peak Matching Control Circuitry 54
3-9 Data Collection System 56

CHAPTER 4 PROCEDURES USED IN PEAK MATCHING Page 59

4-1 Visual Null Peak Matching 59
4-2 ΔM Calculations 62
4-3 Computer Assisted Peak Matching 63
4-4 The Advantages and Objectives of Computer Matching 67
4-5 Methods of Determining the Separation Between Two Peaks 70
4-6 The Centroid Method 72
4-7 The Least Squares Method 74
4-8 Counting Loss Corrections 84
4-9 A Comparison of the Centroid and Least Squares Methods 86

A Simulated Peaks 86
B Real Mass Spectral Peaks 94

4-10 Summary 103

CHAPTER 5 NEW ATOMIC MASS DETERMINATIONS 105

5-1 New Mass Spectroscopic Doublet Separations 105
5-2 Experimental Results 107

A Titanium Absolute Atomic Mass Determinations 107
B Tungsten Absolute Atomic Mass Determinations 109
C Mercury Absolute Atomic Mass Determinations 110
D Mercury Mass Difference Determinations 112

5-3 Least Squares Adjustment of Atomic Masses 118

A Titanium 118
B Tungsten and Rhenium 125
C Mercury 130

5-4 Discussion of the Results 139

A Absolute Atomic Mass Determinations 139
B S_{2n} Values for Hg 142

References 146

LIST OF TABLES

PAGE

1-1 Mass Conversion Factors and Related Fundamental Constants 15

1-2 Some Secondary Standards of Atomic Mass and Important Mass Differences 16

4-1 The Forward - Reverse Bias 68

4-2 Asymmetry Bias for Least Squares Matching 83

4-3 The Counting Loss Correction 87

4-4 Comparison of Centroid and Least Squares Methods for Simulated Peaks 90

4-5 Comparison of Centroid and Least Squares ΔM Values 95

4-6 Comparison of Intensity Ratios 100

4-7 Comparison of Closed Loops 102

5-1 New Doublet Determinations 106

5-2 Comparison with McMaster Doublet Separations 117

5-3 Additional Doublets Used for Ti Adjustment 119

5-4 Least Squares Adjustment for Ti 121

5-5 Comparison of Atomic Masses for Ti 122

5-6 S_n and S_{2n} Values for Ti 124

5-7 Additional Doublets Used for W and Re Adjustment 126

5-8 Least Squares Adjustment for W and Re 127

5-9 Comparison of Atomic Masses for W and Re 129

5-10 S_{2n} Values for W and Re 131

5-11 S_n Values for W 132

5-12 Least Squares Adjustment for Hg (Mass Spectroscopic data only) 134

5-13 Least Squares Adjustment for Hg (Including (n,γ) reaction values) 137

5-14 Comparison of Atomic Masses for Hg 138

5-15 Neutron Separation Energies for Hg 140

LIST OF FIGURES

PAGE

Frontispiece ix

2-1 Uniform Sector Magnetic Field 21

2-2 Radial Electric Field 21

2-3 Status of Atomic Masses for $40 \leq A \leq 210$ 37

3-1 Geometry of Manitoba II 39

3-2 Manitoba II (side view) 41

3-3 Manitoba II (front view) 42

3-4 Ion Source 43

3-5 Block Diagram of V and ΔV Circuitry 47

3-6 Peak Matching Control Circuitry 55

3-7 Data Collection System 58

4-1 Error Signal for Visual Matching 61

4-2 Quadrant System for Computer Matching 61

4-3 Comparison of Centroid and Least Squares Methods for Simulated Peaks 91

4-4 Comparison of Centroid and Least Squares ΔM Values:
  a. Doublets L, M, N, K and P 96
  b. Doublets O and J 97

5-1 The Mass Spectrum for Doublet J 114

5-2 High Resolution 115

5-3 Atomic Masses and Mass Differences for Ti Least Squares Adjustment 119

5-4 Atomic Masses and Mass Differences for W and Re Least Squares Adjustment 126

5-5 Atomic Masses and Mass Differences for Hg Least Squares Adjustment 133

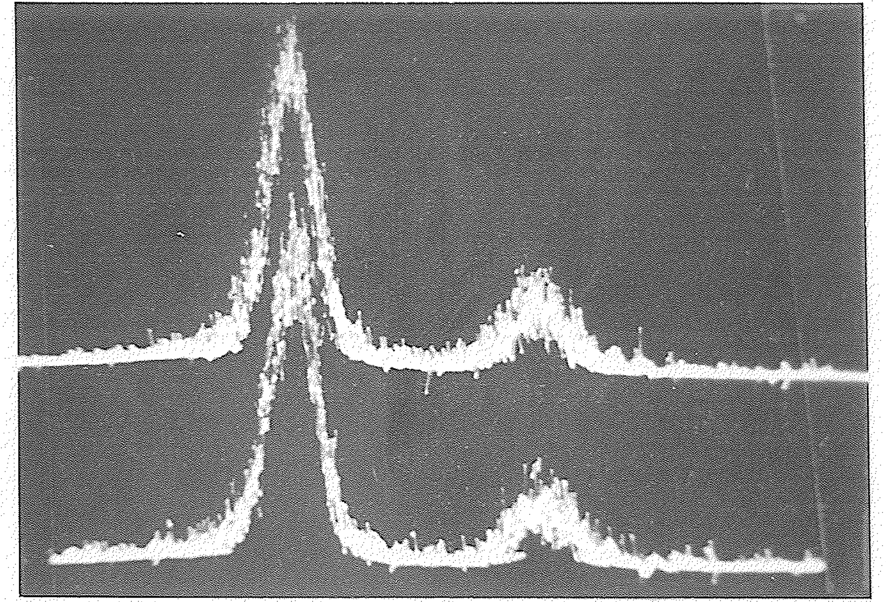
5-6 S_{2n} Values for Even -N Even -Z Nuclides for $106 \leq N \leq 126$ 143

One comes to regard the machine as having a personality - I had almost said a feminine personality - requiring humoring, coaxing, cajoling - even threatening! But finally one realizes that the personality is that of an alert and skillful player in an intricate but fascinating game - who will take immediate advantage of the mistakes of his opponent, who "springs" the most disconcerting surprises, who never leaves any result to chance - but who nevertheless plays fair - in strict accordance with the rules of the game. These rules he knows and makes no allowance if you do not. When *you* learn them and play accordingly, the game progresses as it should.

- Albert Abraham Michelson (1911)

Frontispiece

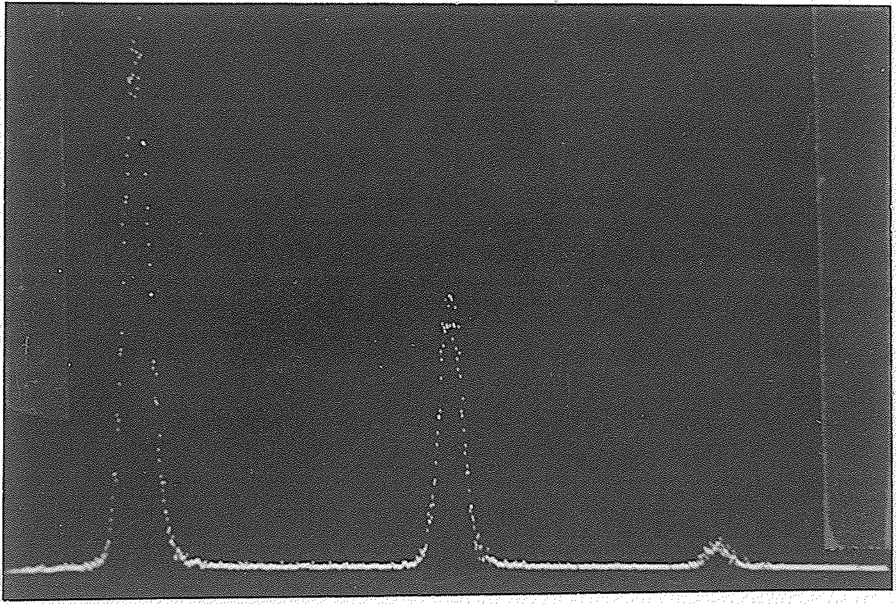
Manitoba I 1964
(at McMaster University (Barber *et al*, 1964))



$^{202}Hg^{35}Cl$ - $^{200}Hg^{37}Cl$

(1/44,900)

Manitoba II ("Betsy") 1977



$^{202}Hg^{35}Cl_2$ - $^{200}Hg^{35}Cl^{37}Cl$ - $^{198}Hg^{37}Cl_2$

(1/51,600) (1/60,100)

CHAPTER 1

INTRODUCTION

1-1. THE CONCEPT OF MASS

The word "mass" is derived from the Latin word "massa " which originally meant a lump of dough or paste (Jammer, 1961). The modern meaning of "mass" in physics is much harder to define, in part because it is of a fundamental - almost axiomatic - nature and in part because it performs several seemingly different functions.

Originally mass was regarded as an inherent property of an object which somehow described the quantity of matter contained in it and which was conserved when matter changed its form. The role of inertial mass in mechanics developed from ideas conceived by Johannes Kepler and brought to their succint expression by Isaac Newton in his second law of motion F=ma. In addition, Newton showed that gravitational mass could be expressed in terms of the attraction experienced as a result of the presence of another object according to the universal law of gravitation. Ernst Mach later disputed Newton's notion of absolute motion (in particular with regards to absolute rotational motion) and advanced the idea (later termed Mach's Principle by Einstein) that inertial mass, rather than being an inherent property, depends upon some interaction with the remaining mass in the universe (Clotfelter, 1970).

Albert Einstein's attempts to generalize the laws of physics with respect to any reference frame (his special and general theories of relativity) revealed unsuspected properties of mass. The special theory showed first, that inertial mass varies with velocity according to

$$m = m_o / (1 - v^2 / c^2)^{\frac{1}{2}} \qquad (1\text{-}1)$$

and second, that mass and energy are equivalent and are related by

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

This equivalence has been verified to within 64 ppm (Wapstra, 1967). The conservation of mass and energy can be shown to result from the lack of a preferred origin for time in the laws of physics (Messiah, 1958). This is also described by the terms "time independence" or "time homogeneity".

The general theory of relativity was a direct attempt to incorporate Mach's principle into the laws of physics. In the principle of equivalence, Einstein pointed out the impossibility of distinguishing between an acceleration and a uniform gravitational field. This resolved the previously coincidental equality between inertial and gravitational mass which has been confirmed to within 1 part in 10^{11} (Roll et al, 1964). Brans and Dicke (1961) have developed an alternative relativistic theory which allows for the variation of the universal constant of gravitation G in time.

At present all experiments confirm the general relativistic theories but are not sufficiently precise to distinguish between them. In particular Mach's principle has neither been proved nor disproved. In the course of such investigations it has been found that G is constant in time to within 1 part in 10^{11} per year (Reasonberg and Shapiro, 1976) and that any anisotropy in inertial mass is less than 1 part in 10^{23} (Drever, 1961).

1-2. STANDARDS OF MASS AND ENERGY

Inasmuch as the concept of mass spans the whole range of physical experience, several mass standards and scales have been found to be convenient. On the astronomic level, for example, the solar mass ($M_\odot = 1.989 \pm 2 \times 10^{30}$ kg, Mohler (1966)), although clearly changing with time, is often the unit used in comparisons. On the scale of everyday experience, and on the atomic scale, more precise standards have been adopted.

In the everyday world the mass standard is the kilogram (kg) which was originally defined as the mass of a cubic decimeter of water under certain conditions. The present standard kilogram was constructed in 1889 from a platinum - iridium alloy (90/10) and is in the form of a solid cylinder with height equal to its diameter. The primary standard kilogram is kept at the Bureau International des Poids et Mesures at Sèvres, France. Secondary standard copies may be compared to the original to a consistency of within 2 parts in 10^8. This mass standard although of a convenient size for commercial and everyday purposes has drawbacks for scientific purposes in that it is an arbitrary and unique standard which is not easily accessible, not indestructible and not amenable to precise duplication.

Prior to 1960 two standards of atomic mass were in common use. Chemists utilized a scale in which the gram atomic weight of oxygen (of natural isotopic composition) was defined to be equal to 16 grams while physicists chose to use a scale in which a single atom of ^{16}O had a mass of precisely 16 amu (atomic mass units). In 1960 a single new standard was chosen so that one isolated atom of ^{12}C at rest and in its nuclear and atomic ground state has a mass of exactly 12 u (mass units) (Wichers, 1962). Atomic masses of other nuclides may be compared to ^{12}C with precisions occasionally as high as 1 part in 10^9 (Smith and Wapstra, 1974). The connection between mass units and the kilogram mass scale is established by Avogadro's number N_A (see Table 1-1)

$$1 \text{ u} = \left(\frac{1}{N_A} \right) \text{kg} \qquad (1\text{-}3)$$

The electron volt (eV) (and multiples thereof) is also used as a unit of mass and energy in the atomic, nuclear and elementary particle domains. This unit is defined as the kinetic energy gained when an electron passes through a potential difference of 1 volt. The relationship between mass units and electron volts (the mass to energy conversion factor) is obtained from the fundamental constants N_A , e and c. Thus

$$1 \text{ u} = \left(\frac{c^2}{N_A e} \right) \text{eV} \qquad (1\text{-}4)$$

The numerical relationships between kilograms, mass units and electron volts as well as the values of the pertinent fundamental constants are summarized in Table 1-1.

1-3. THE IMPORTANCE OF ATOMIC MASS DETERMINATIONS

On the ^{12}C atomic mass scale all naturally occurring atoms have masses whose values lie within .1 u from a whole number. This remarkable fact, together with the discovery of the neutron and of isotopes, provides irrefutable evidence that the nucleus is a composite structure. Thus all of the various types of atoms can be considered as different numbers and configurations of neutrons, protons and electrons. The small differences from the whole number rule have proved to be most interesting and useful in elucidating the structure of the nucleus.

Precise atomic mass determinations showed that each type of atom has a unique mass which provides a means of identification and isolation. In addition it was found that the mass of an atom is less than the sum of the masses of its individual constituents by an amount equal to the total binding energy of the atom. The total atomic binding energy includes both the binding energy of the nuclear particles and of the orbital atomic electrons. However, because the relative sizes of the nuclear and electronic binding energies differ so greatly, the total binding energy of the atom almost entirely reflects the binding energy associated with the nuclear particles. Thus for ^{200}Hg , for example, the total binding energy amounts to 1581.2 MeV (Wapstra and Gove, 1971) of which the total electronic binding energy contribution is only .534 MeV (Huang et al, 1976). The total binding energy is largely a result of the strong attractive force between nucleons and gives a measure of the stability of the nucleus with respect to the various modes of decay.

Systematic variations of the total binding energy as a function of N and Z reveal the general nature of the nuclear force. Increased precision in the mass determinations shows finer variations attributed to collective nucleon behavior and nuclear shell structure. Williams and Duckworth (1972) have noted that in the past each major increase in the precision of mass determinations has elucidated stability effects previously obscured by the errors in measurement.

At present the accuracy of theoretical predictions of atomic mass generally lags behind that achieved in the experimental determinations. Experimentalists however still have much work to do. In particular the atomic masses of unstable species are not well known in comparison with the naturally occurring nuclides. Moreover the atomic masses of heavier atoms are generally less well known than those closer to the primary standard of ^{12}C.

Finally, the determination of atomic mass <u>differences</u> gives an unequivocal measure of the available energy between the ground states of two different nuclides. Accordingly, such measurements provide important information complementary to that obtained from the studies of nuclear reactions as described in the following section.

1-4. METHODS OF ATOMIC MASS DETERMINATION

A. ALPHA DECAY:

The alpha decay of a nucleus (${}^{A}_{Z}X$) may be represented by:

$$ {}^{A}_{Z}X \rightarrow {}^{A-4}_{Z-2}Y + \alpha + Q \qquad (1\text{-}5) $$

where Q accounts for all of the energy released. Thus the mass difference between parent and daughter nucleus may be determined by measuring the kinetic energy of the alpha particle and accounting for the recoil energy of the daughter nucleus. This technique has provided most of the mass information for nuclei heavier than Bi since these are all unstable to some extent with respect to alpha emission. Usually measurements of the highest precision are performed using a magnetic analyser which must first be calibrated by an alpha of known energy. Alpha energy standards have been determined with standard errors as low as .05 keV (Rytz et al, 1972) although most alpha energy measurements have uncertainties of the order of 20 keV. For atomic mass differences these measurements (and in principle any reaction or decay measurement in which Z changes) must be corrected for the total binding energies of the atomic electrons.

B. BETA DECAY:

The beta decay of a nucleus (${}^{A}_{Z}X$) may be described by:

$$\left.\begin{array}{l} {}^{A}_{Z}X \begin{array}{l} \nearrow {}^{A}_{Z+1}Y + e^- + \bar{\nu} + Q^- \\ \searrow {}^{A}_{Z-1}Y + e^+ + \nu + Q^+ \quad (Q^+ \geq 2m_oc^2) \end{array} \\ {}^{A}_{Z}X + e^- \longrightarrow {}^{A}_{Z-1}Y + \nu + Q^+ \qquad \text{(electron capture)} \end{array}\right\} (1-6)$$

Because the available energy is shared between the beta particles and the neutrino, beta particles are emitted with a continuum of energies up to a maximum or end point value which alone determines the mass difference. In the case of positron emission the Q value (expressed in terms of the difference in <u>atomic</u> masses between parent and daughter nuclides) must exceed $2m_oc^2$ since the total number of electrons in the final configuration is different from that prior to the decay. For Q^+ values in the range 0 to $2m_oc^2$ only electron capture will occur. Electron capture generally does not provide useful mass differences inasmuch as the neutrino energy cannot be measured directly.

Beta decay energies are usually measured in a magnetic analyser such as the large iron-free two dimensional focusing $\pi\sqrt{2}$ spectrometer at Chalk River. Although end point energies have been measured to better than .1 keV in specific instances (Bergkvist, 1972), typical uncertainties are on the order of 10 keV.

C. NUCLEAR REACTIONS:

Induced nuclear reactions may be expressed by:

$$a + X \rightarrow Y + b + Q \qquad (1-7)$$

where X and Y are the initial and final nuclei and a and b are the incoming and outgoing particles respectively. The particles a and b may be charged particles such as p, d, t, ^{3}He, α, ^{12}C , ^{16}O , etc. or neutrons or photons.

Charged particle reactions, in particular the (d,p) reaction, have provided many mass links. Despite the need to determine the energies of two particles the typical precision is about 10 keV. The development of heavy ion accelerators, notably the heavy ion cyclotron, should provide many new links involving larger mass differences and connections to exotic nuclei far off the line of stability.

The (n, γ) reaction initiated by thermal neutrons from a reactor is of particular importance for atomic mass determinations because it provides many precise mass differences between even -A and odd -A isotopes. Gamma ray energies below 1MeV may be determined with a curved crystal spectrometer while at higher energies Ge (Li) detectors are used. Precisions of .5 keV or better are not uncommon.

D. MASS SPECTROSCOPY:

Mass spectroscopic atomic mass determinations involve the direct comparison of charge to mass ratios for positive ions undergoing deflection and spatial separation in combinations of electric and magnetic fields. Absolute atomic masses may be determined in principle for any atom by using the doublet technique. In this method the mass separation between an unknown peak and a well known secondary standard, such as a hydrocarbon peak of nominally the same mass, is measured. In addition one may determine direct mass differences by using molecules such as chlorides which yield narrow and chemically identical doublets involving two mass unit differences for most of the elements. These differences are complemented by (n, γ) measurements since, with some exceptions (Barnard et al, 1977), it is somewhat difficult to form suitable chemically identical doublets for one mass unit differences. The precision of mass spectroscopic determinations can be as high as 1 part in 10^8 of the atomic mass M for absolute masses and 2 parts in 10^9 of M for mass differences. This translates into an uncertainty of about .5 keV, a value which competes quite favorably with those associated with nuclear reactions and decays.

Although most mass spectroscopic determinations have been made by means of magnetic deflection instruments the most precise measurements to date were obtained by the late L.G. Smith using the rf mass spectrometer at Princeton. These measurements have uncertainties as low as 5 eV and are of great importance inasmuch as they determine almost independently all of the important secondary atomic mass standards at low masses (Smith 1971, Smith and Wapstra 1974). The secondary atomic mass standards and mass differences used in this thesis are listed in Table 1-2.

Recently, mass spectroscopy has been applied to the direct mass determination of unstable nuclides (Thibault et al, 1976; Wollnik et al, 1976) and considerable work to this end is in progress in several laboratories.

1-5. TABLES OF ATOMIC MASSES

Mass spectroscopic atomic mass determinations are generally complementary to the nuclear reaction and decay data in that the former has involved the naturally occurring nuclides. By combining both groups of data atomic masses may be established for all the known nuclides. Since many of the masses and mass differences are in this case overdetermined the "best" values can be determined by performing a least squares adjustment of all the experimental data. Moreover erroneous and inconsistent data may be detected and removed in the adjustment procedure. Several such compilations of atomic masses have been made starting with Mattauch and coworkers in 1960 and continuing to the present day (Mattauch et al (1965), Wapstra et al (1967), Wapstra and Gove (1971), Wapstra and Bos (1976))with each new least squares adjustment producing more reliable values than the last.

TABLE 1 - 1

Mass Conversion Factors and Related Fundamental Constants

Fundamental Constant	Value	Ref.
Speed of light	$c = 299\ 792\ 458 \pm 1.2$ m/sec	a
Charge of the electron	$e = 1.602\ 189\ 2 \pm 46 \times 10^{-19}$ C	b
Avogadro's number	$N_A = 6.022\ 097\ 6 \pm 54 \times 10^{26}\ (\mathrm{kg\ mol})^{-1}$	c

a Cohen (1976)

b Cohen and Taylor (1973)

c Deslattes (1976)

Mass Conversion Factors

$$1\ \mathrm{u} = \left(\frac{1}{N_A}\right)\ \mathrm{kg} = 1.660\ 551\ 0 \pm 15 \times 10^{-27}\ \mathrm{kg}$$

$$1\ \mathrm{u} = \left(\frac{c^2}{N_A e}\right)\ \mathrm{eV} = 931.493\ 5 \pm 28 \times 10^{6}\ \mathrm{eV}$$

TABLE 1 - 2

Some Secondary Standards of Atomic Mass and Important Mass Differences

Atomic Mass	Value (u)	Ref.
n	1.008 665 02 ± 4	a
^{1}H	1.007 825 029 ± 5	b
^{13}C	13.003 354 831 ± 10	b
^{16}O	15.994 914 616 ± 22	b
^{35}Cl	34.968 852 76 ± 7	a
^{37}Cl	36.965 902 61 ± 12	a
$^{35}Cl - {}^{16}O_2$	2.979 023 79 ± 11	a
$^{37}Cl - {}^{35}Cl$	1.997 049 85 ± 13	a
	1.997 050 11 ± 30	c
	1.997 049 74 ± 10	d
	1.997 049 802 ± 76	weighted mean

a Wapstra and Gove (1971), including Smith (1971)

b Smith and Wapstra (1974)

c Katakuse and Ogata (1972)

d Barber _et_ _al_ (1976)

CHAPTER 2

POSITIVE ION OPTICS AND MASS SPECTROSCOPIC ATOMIC MASS DETERMINATIONS

2-1. HISTORICAL DEVELOPMENT

The discovery of positive ions in gas discharge tubes by Goldstein in 1886 initiated a new field of study and the development of new instruments. The first such instrument was a positive ray parabola apparatus constructed by J. J. Thomson in 1913 using crossed electric and magnetic fields (Thomson, 1907). With this he was able to separate ions for which $\Delta M/M \sim 1/10$.

Subsequently F. W. Aston in 1919 reported the first instrument constructed at the Cavendish Laboratory which became known as a mass spectrograph (Aston, 1919). This more closely resembled modern instruments in that electric and magnetic deflections of the ions were made to occur separately. A resolving power of 130 was achieved and velocity focusing was used for the first time. Simultaneously A. J. Dempster at the University of Chicago built an instrument using a 180° uniform magnetic field, thereby exploiting the advantages of direction focusing (Dempster, 1918).

Herzog in 1934 derived the general first order focusing equations for electric and magnetic fields in a form analogous to geometrical optics (Herzog, 1934). This understanding enabled the design of double focusing instrument geometries.

Double focusing mass spectrographs of superior resolving power were built by Dempster at Chicago (Dempster, 1938), Bainbridge and Jordan at Harvard (Bainbridge and Jordan, 1936) and Mattauch and Herzog at Vienna (Mattauch, 1936). Some of these instruments were in fact designed prior to Herzog's theory but required only minor modifications to achieve a double focus.

In the 1950's a number of very large instruments were constructed notably by Duckworth at McMaster University (Duckworth et al, 1957) and by Ogata in Japan (Ogata and Matsuda, 1957) and resolving powers in excess of 100,000 were achieved. Concurrently, instruments which attain at least partial second order double focusing were constructed by Hintenberger and Mattauch at Mainz (Everling et al, 1957), Nier at Minnesota (Nier et al, 1957), Bainbridge at Harvard (Collins and Bainbridge, 1957) and by Stevens at Argonne Stevens et al, 1960).

Hintenberger and König in 1957 extended Herzog's first order analysis to include second order image aberrations (Hintenberger and König, 1957) and in 1959 proposed a number of instrument designs which correct for some or all of these (Hintenberger and König, 1959). Instruments achieving complete second order double focusing have since been built notably by Matsuda at Osaka (Matsuda et al, 1966) and by Barber and Duckworth at Manitoba (Barber et al, 1967).

The Manitoba instrument (referred to as "Manitoba II") is the instrument used for all the new mass determinations reported in this thesis. A comprehensive history of mass spectroscopy and atomic mass determinations and comparisons of the various instruments may be found in Duckworth (1958) and Williams and Duckworth (1972).

Improvements in precision over the years were attained largely through higher resolution associated with increased size and better instrument design. In addition, advances were also made by the introduction of electrical detection, superior electrical and mechanical stability, efficient ion source design and the use of peak matching, signal averaging and computerized data analysis. The improvements in precision have progressed at a rate of approximately one order of magnitude per decade (Williams and Duckworth, 1972).

2-2. POSITIVE ION OPTICS (First Order Theory)

The trajectory of a particle of mass m charge q and velocity $\vec{v}$, moving under the influence of electromagnetic fields $\vec{E}$ and $\vec{B}$, may be calculated from the Lorentz force equation.

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

A. Uniform Magnetic Field

For the special case of an ion traversing at right angles a magnetic field $\vec{B}$ of constant magnitude and direction, the force constrains the ion to a circular path of radius a_m where

$$a_m = \left(\frac{mv}{q} \right) / B \tag{2-2}$$

Thus a uniform magnetic field acts like a prism in that it disperses ions according to their momentum to charge ratio. Simultaneously, such a magnetic field acts as a converging lens, focusing ions which initially diverge from a point source. The first general description of the focusing properties of uniform sector magnetic fields was given by Herzog (1934) in the form outlined below.

In Fig 2-1, let us consider a group of ions of mass m_o, velocity v_o and half angular spread α ($\alpha \ll 1$) which diverge from an object point 0 located a distance l_m' from the entrance boundary of the magnetic field. The ions following the optic axis or central path cross the field boundary at right angles, proceed along a circular path of radius a_m through an angle Φ_m and emerge normal to the exit boundary. The ion beam then converges to the image point I located a distance l_m'' from the exit boundary such that the

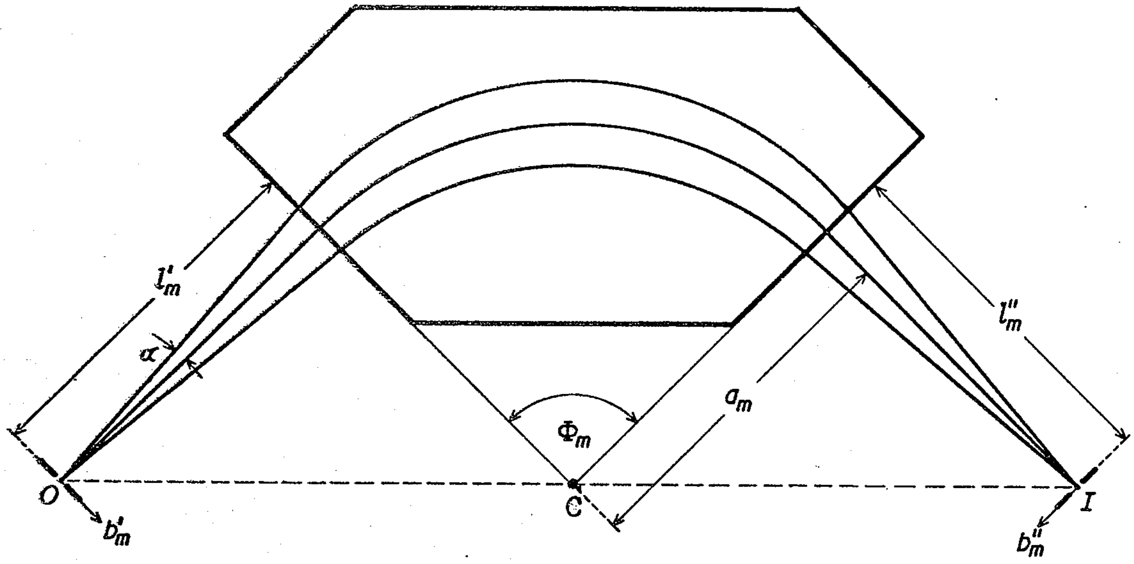


FIG. 2-1

Uniform Sector Magnetic Field

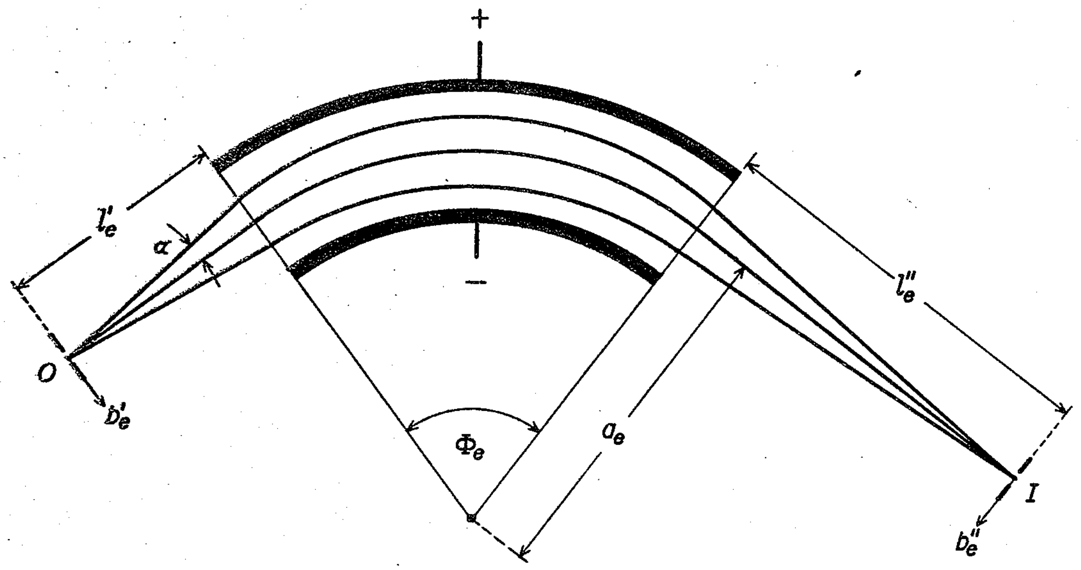


FIG. 2 -2

Radial Electric Field

image point I, the centre of curvature C and the object point O lie on the same straight line. Direction focusing occurs physically because the ions above the optic axis spend a longer time in the magnetic field, and thus receive an additional deflection back towards the optic axis. Similarly the ions below the axis return to the central path because they spend less time in the field and are deflected less.

Herzog calculated the ion trajectories for this arrangement, including only first order terms in α, and showed that the focal length is given by

$$f_m = a_m / \sin\Phi_m \tag{2-3}$$

Also the object and image distances are related by

$$(l'_m - g_m)(l''_m - g_m) = f_m{}^2 \tag{2-4}$$

where

$$g_m = f_m \cos\Phi_m \tag{2-5}$$

is the distance from the field boundary to the principal focus.

For ions having a mass $m = m_o(1+\gamma)$ and velocity $v = v_o(1+\beta)$ $(\gamma, \beta \ll 1)$, the trajectory at the image is displaced from the axis by an amount

$$b''_m = a_m(\beta+\gamma)\left[1 + \frac{f_m}{l'_m - g_m}\right] - b'_m \frac{f_m}{l'_m - g_m} \tag{2-6}$$

where b'_m is the displacement from the axis at the object position. Thus a velocity spread, $\Delta v = \beta v_o$, results in a first order image aberration which is proportional to the radius of curvature a_m in the magnetic field. Further, if we consider ions for which $\gamma = \beta = 0$, we see that the magnification is

$$b''_m / b'_m = f_m / (l'_m - g_m) \tag{2-7}$$

For the special case of an object slit of width $S_o = 2b'_m$ with a monoenergetic ion beam ($\gamma + 2\beta = 0$ to first order) and symmetrical object and image distances ($l'_m = l''_m$; magnification is unity) the mass resolution is given by

$$\Delta M / M = \gamma = S_o / a_m \tag{2-8}$$

When electrical detection is used an image slit of width S_i is placed at point I and the resolution is degraded to

$$\Delta M / M = \gamma = (S_o + S_i) / a_m \tag{2-9}$$

B. Radial Electric Field

The radial electric field is the electric analogue of the uniform magnetic field in the sense that it causes charged particles to travel in nearly circular orbits. This field may be established by applying a potential difference, V, between a pair of concentric cylindrical electrodes of radii $a_e - k$ and $a_e + k$ as indicated in Fig 2 -2 (the separation between the plates is 2k). When V is applied symmetrically (i.e. $V(r) = 0$ for $r = a_e$) the potential at any point between the plates is described by

$$V(r) = V \ln (r/a_e) / \ln \left(\frac{a_e + k}{a_e - k} \right) \qquad (2\text{-}10)$$

This produces an electric field of magnitude

$$E(r) = V / r \ln \left(\frac{a_e + k}{a_e - k} \right) \simeq V a_e / 2 rk \qquad (2\text{-}11)$$

(for $k \ll a_e$) and directed towards the center of curvature. For ions travelling along the optic axis ($r = a_e$) we then have

$$a_e \simeq (mv^2 / 2q) \, 4k/V \qquad (2\text{-}12)$$

Thus a radial electric field acts as a kinetic energy analyser, dispersing ions according to their energy to charge ratio.

The first order direction focusing equations are similar to the magnetic case:

$$f_e = a_e/\sqrt{2} \sin \sqrt{2} \, \Phi_e \qquad (2\text{-}13)$$

$$g_e = f_e \cos \sqrt{2} \, \Phi_e \qquad (2\text{-}14)$$

$$(l_e' - g_e) (l_e'' - g_e) = f_e^2 \qquad (2\text{-}15)$$

$$b_e'' = a_e (\beta + \gamma/2) \left[1 + \frac{f_e}{l_e' - g_e} \right] - b_e' \frac{f_e}{l_e' - g_e} \qquad (2\text{-}16)$$

For a monoenergetic ion beam ($\beta + \gamma/2 = 0$ to first order) ions of any mass are focused to the same point.

C. Double Focusing

Direction focusing may be preserved in a consecutive combination of electric and magnetic fields by using the image obtained from a radial electric field as the object for a uniform magnetic field. Combining equations 2-6 and 2-16 we see that in this case the final image displacement b_m'' is related to the initial object displacement b_e' by

$$b_m'' = a_m\,(\beta + \gamma)\left[1 + \frac{f_m}{l_m' - g_m}\right] - \frac{f_m}{l_m' - g_m}\left\{a_e\,(\beta + \gamma/2)\left[1 + \frac{f_e}{l_e' - g_e}\right] - b_e'\,\frac{f_e}{l_e' - g_e}\right\} \qquad (2\text{-}17)$$

Velocity focusing may be achieved by making the coefficient of β vanish in equation 2-17. This occurs when

$$a_m\left[\frac{l_m' - g_m}{f_m} + 1\right] = a_e\left[1 + \frac{f_e}{l_e' - g_e}\right] \qquad (2\text{-}18)$$

Physically this means selecting electric and magnetic elements which have equal but opposite velocity dispersions. The coincidence of a direction focus and a velocity focus constitutes a double focus. In this case the resolution for symmetrical arrangements ($l_e' = l_e''$; $l_m' = l_m''$) with electrical detection can be shown to be

$$\Delta M/M = (S_o + S_i) / a_e \qquad (2\text{-}19)$$

A comprehensive treatment of first order positive ion optics may be found in Duckworth (1958, 1963) and Kerwin (1963).

D. Second Order Focusing and Image Aberrations:

The trajectory of an ion at the final image of a double focusing combination may be described to second order in α and β by

$$Y_B = a_m (B_1\alpha + B_2\beta + B_{11}\alpha^2 + B_{12}\alpha\beta + B_{22}\beta^2) \qquad (2\text{-}20)$$

where Y_B represents the distance from the optic axis. The 5 coefficients B_i and B_{ij} may be expressed in terms of 8 geometrical instrument parameters: Φ_m, ϵ_m', ϵ_m'', $\sqrt{2}\,\Phi_e$, a_e / a_m, l_e' / a_m, Δ / a_m and l_m'' / a_m (Δ is the distance between the electric and magnetic fields while ϵ_m' and ϵ_m'' represent the angles of inclination of the entrance and exit boundaries of the magnetic field with respect to a direction perpendicular to the optic axis). Hintenberger and König (1959) selected values for 3 of the parameters and obtained unique solutions for the remaining 5 by solving the 5 simultaneous equations

$$B_1 = B_2 = B_{11} = B_{12} = B_{22} = 0 \qquad (2\text{-}21)$$

which together characterize the condition of a complete second order double focus. In this manner they obtained sets of parameters from which second order double focusing instruments could be constructed.

Additional image aberrations can result from the effects of fringing fields. For the radial electric field effective boundaries may be established by the use of grounded diaphragms positioned according to the theory of Herzog (1935). The effects of the magnetic fringe field on the ion beam are: (i) vertical focusing (ii) lateral displacement of the image position and (iii) image broadening (Kerwin, 1963). Magnetic fringing fields necessitate the use of effective rather than physical boundaries in design calculations.

2-3 MASS SPECTROSCOPIC ATOMIC MASS DETERMINATIONS

Two peaks forming a narrow mass spectroscopic doublet will be fully resolved when their centres are separated by an amount equal to the width at the base of one of the peaks. Thus the width of a peak at mass M for an instrument with resolution R is RM. If the position of a peak can be located to some fraction f of its width the resulting uncertainty in its mass, δM, will be

$$\delta M = fRM \qquad (2\text{-}22)$$

This corresponds to a precision in mass determination of

$$\frac{\delta M}{M} = fR \qquad (2\text{-}23)$$

while the precision attainable in determining the mass difference of a doublet of width ΔM is then

$$\frac{\delta M}{\Delta M} = fR\,\frac{M}{\Delta M} \qquad (2\text{-}24)$$

This represents the theoretical precision possible for a particular instrument when we assume that the major part of the error results from the uncertainty in peak location.

For mass spectrographs, in which photographic detection is used, f is limited to about 1/50 of a line width, while the resolution is limited by the grain size of the photographic plate. In addition the dispersion of the apparatus must be known accurately in the mass region of the doublet. For mass spectrometers, in which electrical detection is used, the introduction of an image defining slit degrades the resolution by a factor of ~ 2 when the slit width equals the width of the image. In this case the resolution is frequently limited by slit quality at narrow widths. The factor f, however, may be reduced to 1/1000 or less when peak matching is used, so that a significant overall improvement in precision is achieved.

For mass spectrometers, the mass difference between an "unknown" peak and a "standard" is usually determined by a procedure called "peak matching" which is based on an important theorem given by Swann (1931) and later by Bleakney (1936) in the form described below.

A. Bleakney's Theorem:

Bleakney's theorem is a statement of the conditions under which ions of different mass may be made to follow identical paths in electromagnetic fields. The electromagnetic force equation (2-1) may be rewritten in the form

$$M\vec{v}\cdot\frac{d\vec{v}}{ds} = q\,(\vec{E} + \vec{v} \times \vec{B}) \qquad (2\text{-}25)$$

where s is the path length measured along the trajectory. This equation, plus two initial conditions (e.g. s = o and $\vec{v}$ = o at time t = o), completely determines the trajectory if the $\vec{E}$ and $\vec{B}$ fields are known at every point traversed.

If $\vec{E}$, $\vec{B}$, $\vec{v}$ and M are now multiplied by the scalar constants α , β , γ and δ respectively while the charge q remains unchanged, equation (2-25) becomes

$$\delta\gamma^2 M\vec{v}\cdot\frac{d\vec{v}}{ds} = q\,(\alpha\vec{E} + \gamma\beta\,\vec{v} \times \vec{B}) \qquad (2\text{-}26)$$

This will reduce to (2-25), ensuring identical trajectories, provided that

$$\delta\gamma^2 = \alpha = \gamma\beta \qquad (2\text{-}27)$$

If additionally the magnetic fields are kept constant (or vary in an identical manner in both cases), then $\beta = 1$. The relationship between δ and γ becomes, in this case,

$$\delta\gamma = 1 \qquad (2\text{-}28)$$

For $M' = \delta M$ and $\vec{v}' = \gamma\vec{v}$, we have the result

$$M'\vec{v}' = M\vec{v} \qquad (2\text{-}29)$$

In principle this relation must also hold for the initial velocities. This will always be true in the special case when the ions are initially at rest. Small departures from this condition should produce only second order displacements of the trajectory in instruments which are double focusing. The relationship between δ and α is similarly given by

$$\delta\alpha = 1 \qquad (2\text{-}30)$$

which, for electric fields derived from voltages applied to electrodes such that $V' = \alpha V$, becomes

$$M'V' = MV \qquad (2\text{-}31)$$

For $M = M' + \Delta M$ and $V' = V + \Delta V$ this relationship may be expressed alternatively as

$$\frac{\Delta M}{M'} = \frac{\Delta V}{V} \qquad (2\text{-}32)$$

C. Peak Matching:

A mass spectral peak may be generated by sweeping the ion beam periodically across the image slit with an auxiliary sawtooth electric or magnetic field. The detected ion current is then displayed as a function of time on an oscilloscope which is synchronized with the modulating field. If the voltage across the electrostatic analyser plates is changed by an amount ΔV the spectrum viewed on the oscilloscope will be displaced laterally by a proportionate amount. If ΔV is applied on alternate sweeps both the original and the displaced spectra may be observed simultaneously. Peak matching involves the adjustment of ΔV until one member of a doublet on the displaced spectrum coincides with the other member on the original spectrum. When coincidence is achieved ΔV is measured and ΔM may be calculated from equation (2-32).

The technique of peak matching originated with Smith (Smith and Damm, 1953, 1956) and was first applied to deflection instruments by Nier's group at Minnesota (Giese and Collins, 1954; Quisenberry _et al_, 1956). The following advantages are obtained with the peak matching method:

(1) Peak matching involves a single direct determination of the doublet separation rather than two separate determinations of peak locations.

(2) The mass difference is calculated in terms of a voltage which may be measured very precisely (accurate knowledge of M and V is not required because they are in general much larger than ΔM and ΔV).

(3) Information concerning the mass dispersion of the instrument is not required since both ion groups traverse the same path.

(4) A "live" display of the ion beam arriving at the collector is available. This enables one to test that the ion beams satisfy Bleakney's theorem (see section 3-7) and facilitates in the focusing of the instrument.

C. The Proportional Error and Problems Related to Peak Matching

Two ion beams of mass difference ΔM will be in perfect coincidence along their entire trajectories only if all voltages are switched according to equation (2-32). If a small unswitched voltage gives rise to an electric field transverse to the direction of the ion beam it will displace the trajectories of M and M' by amounts which differ in proportion to ΔM. Coincidence at the image slit will then be observed only if the switched voltage ΔV is altered from the "true" value by an amount proportional to ΔM. This results in a calculated ΔM which is in error by an amount proportional to the doublet width.

In practice an appreciable systematic error of this type has been observed (typically - 100 ppm for Manitoba II). Southon (1973, 1977) has investigated the nature of this error in detail for Manitoba II and isolated the electrostatic analyser as the region where the prime contribution arises. He detected currents arriving at the analyser plates which are believed to result from secondary electrons and ions produced in charge exchange and dissociative collisions between the primary ion beam and residual gas molecules. Petit-Clerc and Carette (1968, 1970) have demonstrated that surface potentials develop on relatively clean metal surfaces under electron or ion bombardment and may persist for hours. They conclude that charges become trapped in polymer films formed by organic contaminants.

A sufficiently precise value of the proportional error may be ascertained by the determination of the separation of a wide calibration doublet of well known width. A correction is then applied to the determined separation of the narrow doublet of interest. The magnitude of this correction remains fairly constant over a period of a few hours although it may vary substantially from day to day (Stevens and Moreland, 1967).

A proportional error will also result if the measured value of the voltage V used to calculate ΔM in equation (2-32) is different from that experienced by the ion beam. The proportional correction will also account for this type of error, provided that the value of V remains constant between the time of calibration and the time that the narrow doublet determinations are made.

Systematic errors may also occur if the two ion groups do not start their trajectories under identical initial conditions. Chemically dissimilar ions may be formed at slightly different locations in the ion source and thus acquire different distributions in energy and direction. Additionally these effects may depend strongly on the particular source conditions. In practice the separations determined for chemically dissimilar doublets exhibit larger fluctuations than do those for chemically identical doublets. Dempster and Shaw (1950) have demonstrated that positive ions may suffer significant energy loss in collisions with residual gas molecules without an appreciable change in direction. The extent of this energy retardation depends on the type of ion and thus the separation determined for a chemically dissimilar doublet may depend on residual gas pressure (Isenor _et al_, 1956).

D. The Status of Atomic Masses:

The uncertainty in the atomic mass (in μu) for the most accurately known nuclide at a given mass number A from A = 40 to A = 210 is illustrated in Fig. 2-3. These uncertainties represent the output errors in the 1971 Atomic Mass Evaluation (Wapstra and Gove, 1971). It is seen that the magnitude of the uncertainty is substantially larger for the heavier nuclides and is a maximum for ^{193}Ir and ^{194}Pt.

Generally, the mass differences between neighbouring nuclides which differ in A by one or two units are known more accurately than the masses themselves. The atomic masses have relatively larger uncertainties for the following reasons.

(1) In recent years the majority of mass spectroscopic determinations in the mass region shown have been determinations of mass differences, since the most interesting nuclear properties are reflected in such differences (Williams and Duckworth, 1972). In most cases these determinations involve doublets in which the members are chemically identical or similar. Such doublets are particularly amenable to study, inasmuch as the members acquire the same distributions in α and β and the conditions required by Bleakney's Theorem may be satisfied precisely.

Moreover, the accuracy of these mass differences is enhanced by the inclusion of precise nuclear reaction and decay data in the least squares adjustments (see section 1-5).

(2) In contrast, absolute atomic masses may be determined at present using only mass spectroscopic techniques. In the past there has not always been good agreement between the determinations made in separate laboratories (Wapstra, 1967). Chemically dissimilar doublets must always be used for absolute mass determinations. Such doublet determinations usually have larger statistical errors and in addition are more susceptible to systematic errors (see section 2-3C).

(3) Further, the doublets used for absolute mass determination generally involve much wider mass separations (in comparison with the chloride doublets for example). For wide doublets the proportional correction (see section 2-3C) contributes a significant change in the ΔM value.

The straight line at the bottom of Fig. 2-3 indicates a precision of 1 part in 10^8 of M, a value which previous experience in this research group suggests should be attainable.

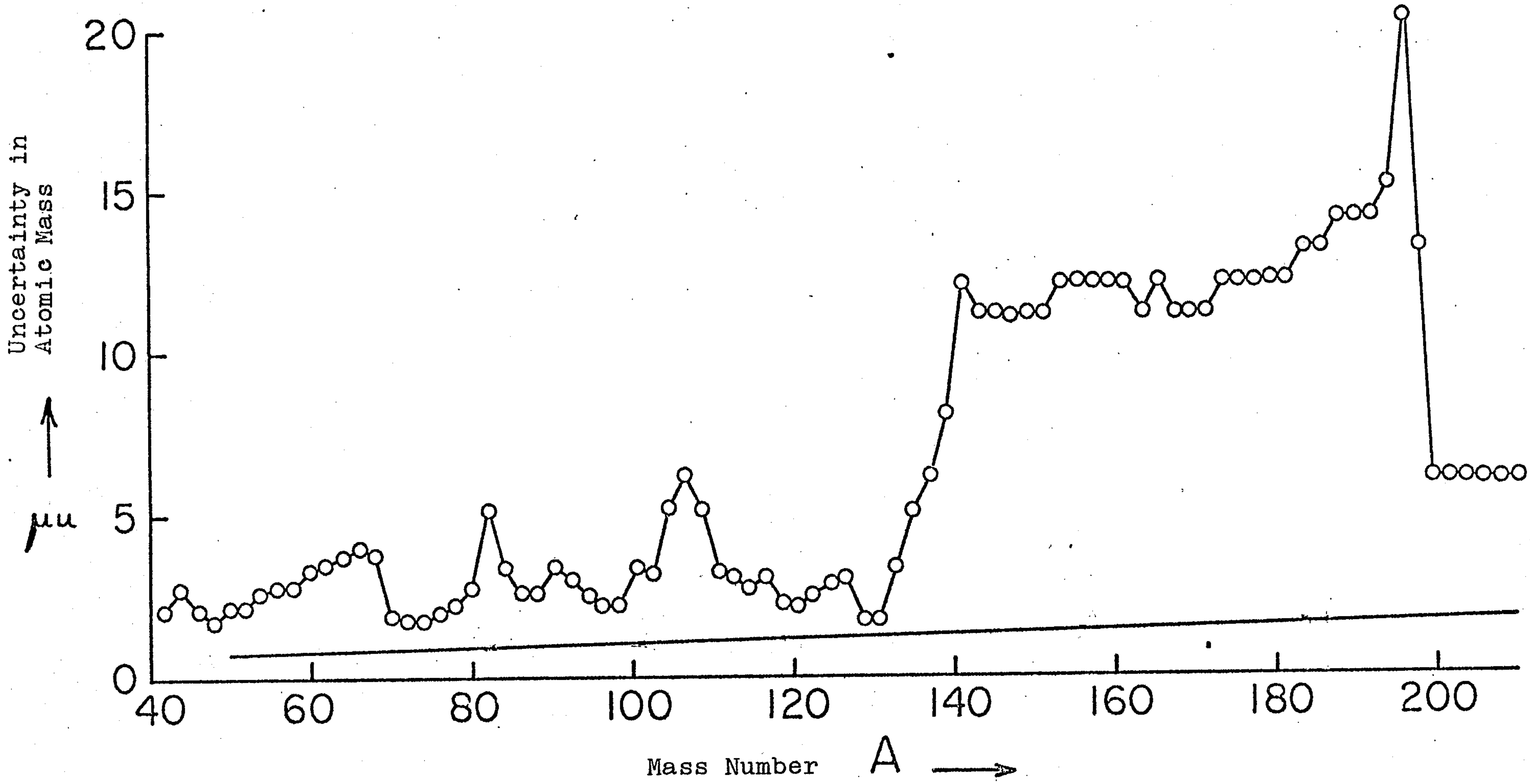


Fig 2-3

Status of Atomic Masses for 40 ≤ A ≤ 210

CHAPTER 3

THE MANITOBA II MASS SPECTROMETER

2-1. INSTRUMENT GEOMETRY

The Manitoba II mass spectrometer was constructed according to one of the complete second order double focusing instrument designs proposed by Hintenberger and König (1959). The particular geometry selected(depicted in Fig 3-1) has the following practical advantages:

(1.) An intermediate direction focus is obtained between the electrostatic and magnetic analysers. This permits the use of an energy defining slit (S_β) to control the range of ion energies transmitted and also aids in the focusing and operation of the instrument (see sec. 3-7).

(2.) The design is compact with ion deflection in the same sense in both the electric and magnetic fields and with relatively short lengths for l'_e, l''_e, l'_m and l''_m. This minimizes problems associated with mechanical vibrations and stray magnetic fields.

(3.) The ratio of the total ion path (4.59 m) to the mean radius of curvature in the electrostatic analyser ($a_e = 1$ m) is relatively small for this geometry. This both improves the transmission and reduces the vacuum requirements.

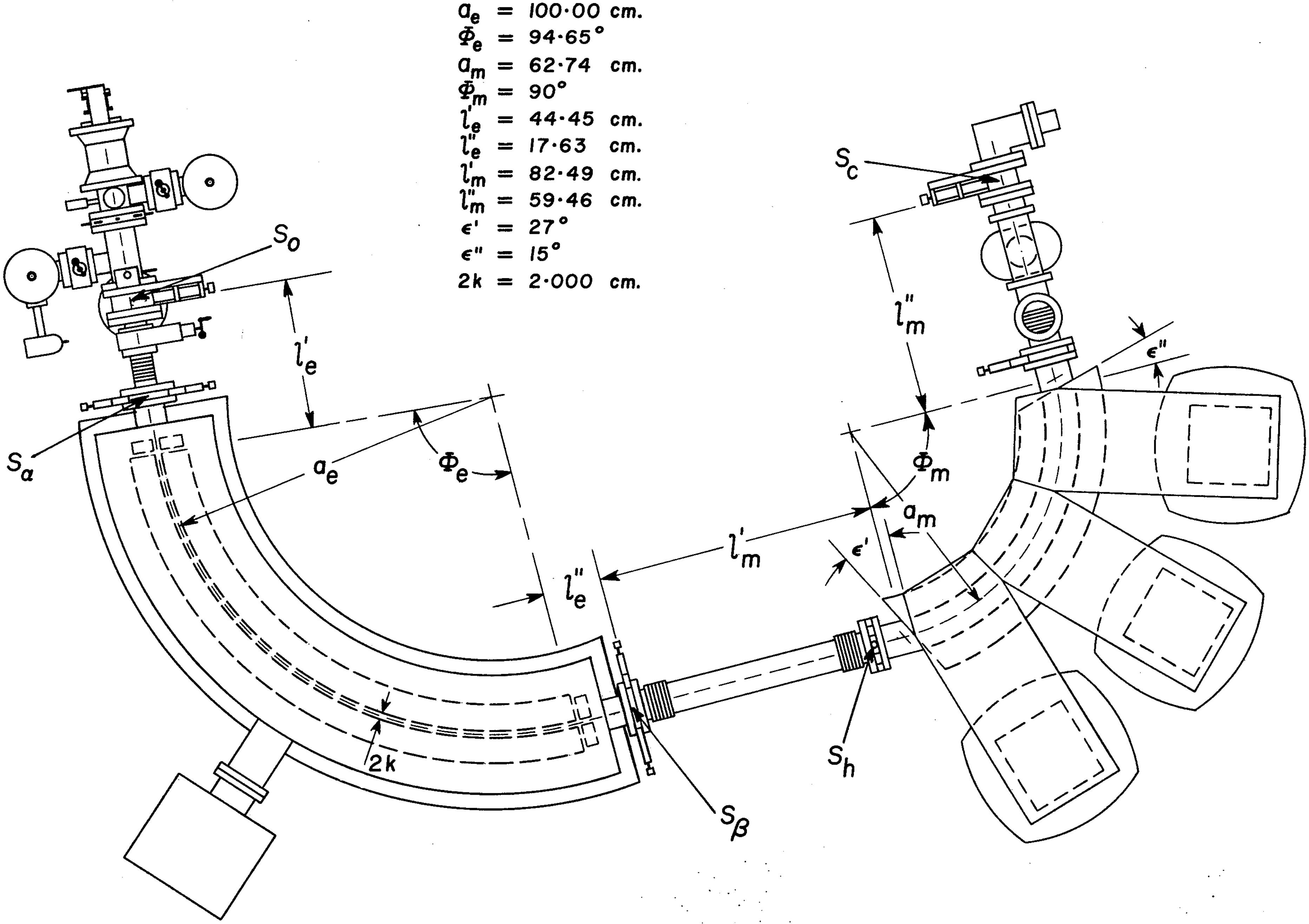


Fig 3-1 Geometry of Manitoba II

(4.) The overall magnification of the instrument is .50 and places less stringent requirements on the object slit quality. The slit (S_o) experiences more intense ion bombardment than the image slit (S_c) and consequently deteriorates more rapidly.

(5.) The magnetic field boundaries are straight and thus are easily constructed and aligned.

The overall size of the instrument was determined by selecting the mean radius of curvature of the electrostatic analyser a_e to be equal to 1 m. The mass dispersion of the instrument is 5.3 mm for a 1% mass difference. For a resolving power of 200,000 the calculated slit widths are $S_o = 2.7\mu$ and $S_c = 1.8\mu$. Two views of the complete instrument are presented in Fig 3-2 and 3-3. Detailed descriptions of the mass spectrometer have been previously published (Barber et al. 1967, 1971).

3-2. ION SOURCE REGION

The ion source is a modified version of the Finkelstein ion source (as described by Von Ardenne, 1962) and is shown in Fig 3-4. Ions are produced by electron bombardment in the vicinity of a small hole in the stainless steel oven containing the sample vapour. The ion acceleration potential V_a (about + 20kV) is applied directly to the oven and thus defines the energy of the ions produced. The rhenium filament

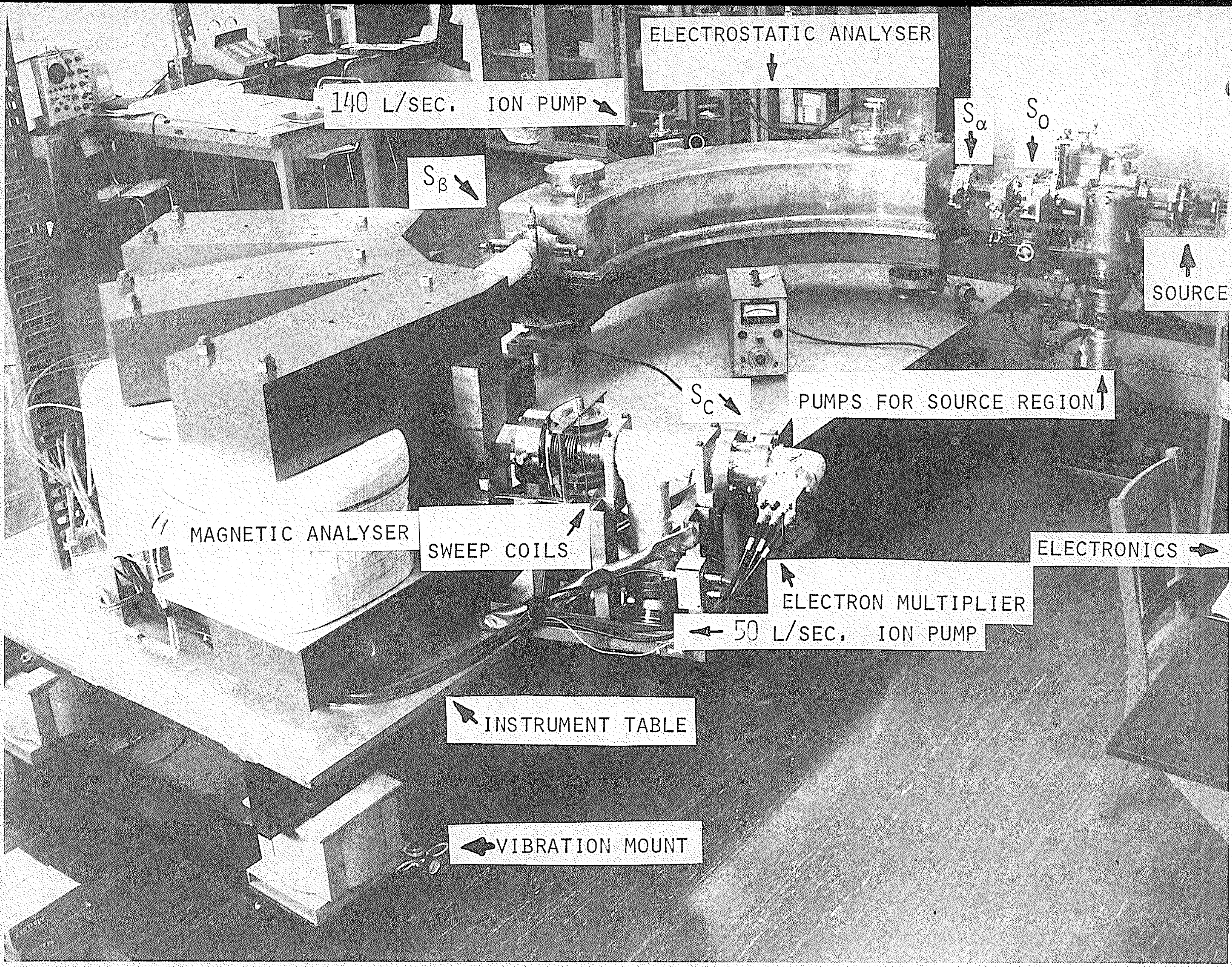


Fig 3-2 Manitoba II (side view)

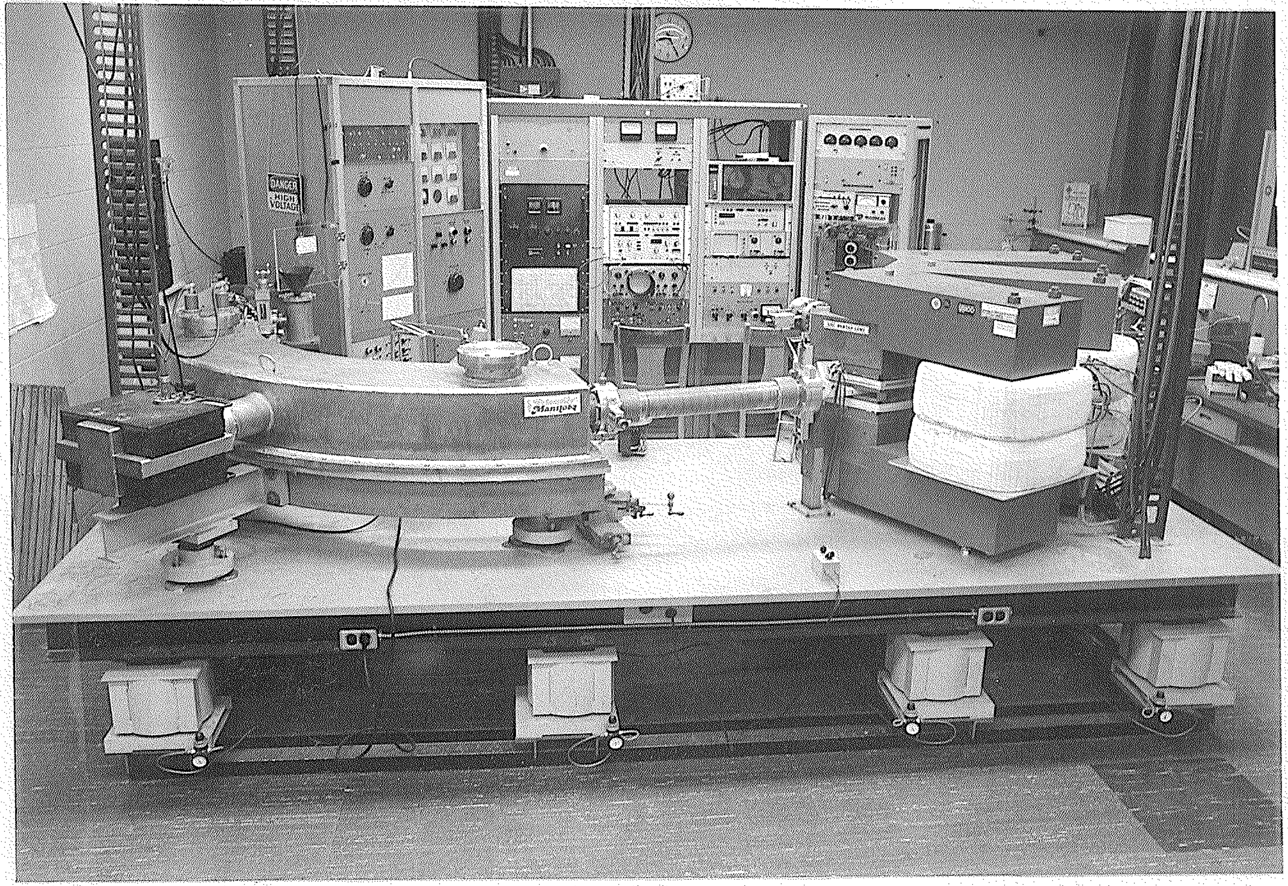
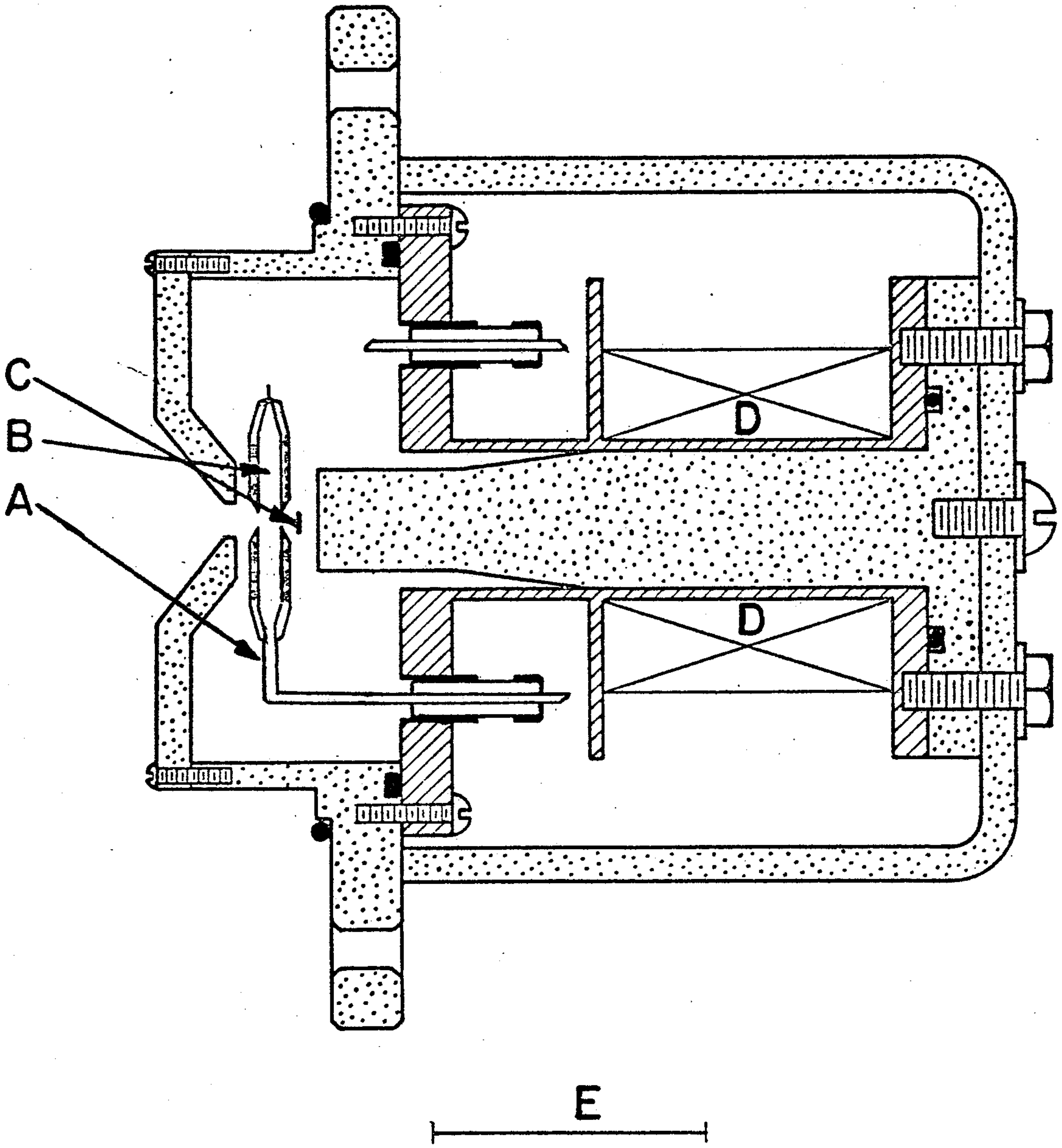


Fig 3-3 Manitoba II (front view)



▨ BRASS

░ IRON

A SAMPLE VAPOUR INLET
B OVEN
C Re FILAMENT

D Cu WINDINGS FOR ELECTROMAGNET
E 5 cm.

Fig 3-4 Ion Source

is held about 100 V negative with respect to the oven. The source case is held approximately 300 V negative with respect to the oven and thus acts as both an electron repeller and a positive ion extractor. The copper coil generates an axial magnetic field of about 1 kG across the pole gap in which the oven is located. Thus the emitted electrons oscillate back and forth along the source axis in tight helical trajectories and create a plasma of positive ions and electrons within the oven. Positive ion currents of the order of 10 μA with an energy spread of about 1 eV are extracted from the front hole of the oven. The sample is contained in a copper tube located outside the ion source body and may be heated by a current passing through a nichrome ribbon wrapped around the tube. The sample vapour enters the oven through a narrow gas inlet tube which is insulated electrically from the source body.

The ion accelerating potential V_a is provided by a commercial power supply (Universal Voltronics Corp., Model BRE 30-2, 30kV, 2mA) which has a short term stability of about .5V. The source voltage, V_a, may be switched according to equation (2-32) by adding to it a voltage ΔV_a derived from a separate power supply.

The ion beam emerging from the source is first steered by a pair of vertical and horizontal deflection plates and then focused on the principal or object slit by an electrostatic quadrupole lens pair. For wide doublets the voltages supplying these electrodes are also switched according to equation (2-32). The steering and focusing system is described in detail by Southon (1973).

The principal slit is variable in width and in orientation about the optic axis. The object height is limited to 2mm. The position of the object slit and the angle of entry of the ion beam may be adjusted relative to the electrostatic analyser by means of lathe slides located directly beneath the principal slit.

In the hope that the proportional correction might be minimized, modifications were made to the vacuum system to reduce the amount of oil vapour present in the instrument (see section 2-3C). The Minnesota group found that their proportional error reduced slowly to zero after an oil free vacuum pumping system was installed (Johnson, 1973). Accordingly one of the oil diffusion pumps in the source region was replaced by a 20 l/s ion pump. It was found necessary to retain one diffusion pump because the ion pump required long start up times and because the titanium ion pump elements had a relatively short lifetime when subjected to the heavy gas loads encountered in the source region. A cryogenic vacuum adsorption pump was also installed to evacuate the source region from atmospheric pressure to a few millitorr in an oil free manner. The remainder of the instrument may also be rough pumped in the same fashion. Despite these modifications a significant proportional correction has persisted.

3-3. ELECTROSTATIC ANALYSER REGION

The angular width of the ion beam (2α) accepted by the electrostatic analyser is limited to $\alpha \sim \pm 2 \times 10^{-3}$ radians by the variable slit S_α located at the analyser entrance. The energy range transmitted by the electrostatic analyser is controlled by the variable slit S_β located at the intermediate direction focus. This slit limits the velocity dispersion to $\beta \sim \pm 8 \times 10^{-4}$. Lathe slides located directly beneath the intermediate direction focus allow the position of the electrostatic analyser to be adjusted relative to the magnetic analyser. In addition the electrostatic analyser and the ion source arm may be rotated as a unit about the intermediate direction focus.

The electrostatic analyser has a mean radius of curvature a_e of 1m and a sector angle Φ_e of 94.65°. The cylindrical plates are made of gold plated Armco iron and are separated by a gap of 2 cm which is uniform to within 10μ. The electric field is terminated at the physical boundaries of the plates by grounded blocks positioned according to the theory of Herzog (1935).

A block diagram of the circuitry pertaining to the electrostatic analyser is presented in Fig. 3-5. The potential difference V across the plates is about 778 V and is derived from eight 97.2 V batteries. Each of these batteries consists of

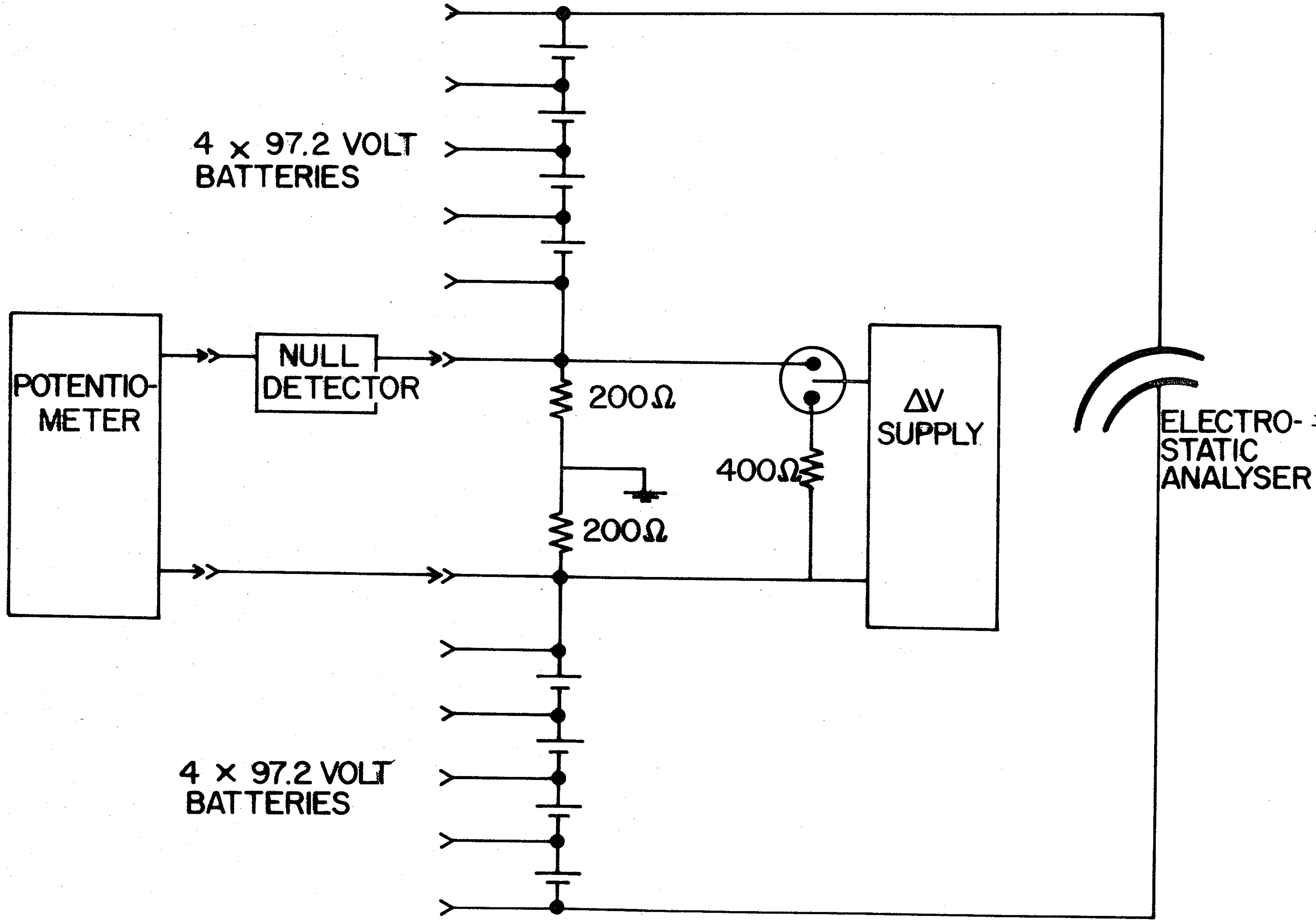


Fig 3-5 Block Diagram of V and ΔV Circuitry

twelve 8.1V mercury batteries (Mallory TR-136R) connected in series. The stability of V was improved by spot welding metal strips directly between the terminals of consecutive mercury batteries in order to minimize contact resistances. Two power supplies are available to supply the switched voltage ΔV, one of which is used for wide calibration doublets and the other for narrow doublets. Both ΔV supplies are described in detail by Southon (1973). The precision potentiometer was constructed by Bishop (Bishop, 1969; Bishop and Barber, 1970) and is used to measure separately both V and ΔV. The ratio $\Delta V/V$ (used to calculate ΔM in equation (2-32) can be determined to a precision of $.4/\Delta V$ ppm with this potentiometer (Bishop and Barber, 1970).

3-4. MAGNETIC ANALYSER REGION

The variable slit S_h located at the entrance to the magnetic analyser may be used to define the vertical position of the ion beam relative to the median plane. This slit limits the vertical extent of the ion beam to about 2 mm.

The magnetic analyser has a sector angle, Φ_m, of 90° with the optic axis describing a circle of radius $a_m = 62.74$ cm. The magnetic field is uniform to one part in 5000 over a region extending to within one gap width of the field boundary for values of the magnetic field from 3 to 8 kG. The magnetic field is generated by six coils arranged in pairs on three "C" shaped yokes. The coils are connected in parallel electrically and are water cooled for temperature stability.

The cooling system was modified after the copper tubing inside one of the coils developed a leak which seriously impaired the stability of the magnetic field. The leak appeared to be caused by small cracks in the copper tubing resulting from corrosive wear and was cured by flushing the cooling system with a radiator repair fluid. In order to prevent future leaks a closed loop cooling system was installed in which a mechanical pump circulates water containing the repair fluid through the magnet coils to a heat exchanger submerged in a reservoir of flowing tap water.

The power supply for the magnet provides up to 60A at 40V and has a stability of about 1 ppm over a period of a few minutes. A circuit diagram of this supply is given by Southon (1973). The short term stability of the magnetic field has been improved by the addition of an auxilliary regulating circuit. This circuit detects fluctuation in the magnetic field by means of two sensing coils, each consisting of 26 turns of fine wire wrapped around the pole pieces immediately above and below the gap. The detected signal is integrated and amplified and applied to a correction coil consisting of a single turn of wire wrapped around the upper pole piece. Details concerning this circuit will be given by Sharma (1978).

3-5. ION COLLECTION REGION

The collector or image slit S_c is variable in width and in orientation about the optic axis. The position of the collector slit in a plane perpendicular to the ion beam can be adjusted by screw drives. The height of the detected ion beam is limited by a fixed aperture located in front of the collector slit jaws. Increased intensity was obtained without loss of resolution by extending the height limits to take advantage of the net vertical focusing effect of the magnetic analyser fringe field.

The positive ions passing through the collector slit are detected by a high gain low noise channel electron multiplier which replaced the magnetic strip multiplier used previously. The noise level of the new detector corresponds to a spurious count rate of 1.0 counts / sec with the ion pump at the collector operating and is reduced to .043 counts / sec with this pump turned off. A new detector housing was fabricated to mount the detector as close as possible behind the collector slit. The detected signal is amplified and displayed on an oscilloscope.

The ion beam is swept across the collector slit by a sawtooth magnetic field generated by a pair of Helmholtz coils located between the slit and the exit boundary of the magnetic analyser. At times a systematic bias (see section 4-3) was observed between the ΔM determinations obtained with the ion beam being swept in the "forward" direction (see section 4-2) and those obtained with the sweep direction reversed. The power supply for the sweep coils was modified with the aim of minimizing this effect. A constant bias voltage was added to the sawtooth waveform from the oscilloscope to give a linear ramp voltage signal passing symmetrically through ground potential. A bipolar operational power supply (Kepco model BOP36-5(M)) is then used to drive a current through the sweep coils which follows this input signal. This produces a linear magnetic sweep field which has zero value at the center of the sweep. This circuit provides the following advantages:

(1) If the peak observed on the oscilloscope is positioned at the center of the sweep its position will be independent of the sweep amplitude.

(2) If the connections to the coils are reversed to sweep the beam in the opposite direction the observed peak will appear to be reflected about the center of the sweep. Thus the magnetic field of the magnetic analyser need not be altered to bring the peak back to the center of the oscilloscope screen when the sweep direction is reversed. In the previous arrangement such a change was required.

A detailed circuit diagram for this power supply will be given by Sharma (1978).

3-6. MECHANICAL SUPPORT AND VACUUM SYSTEM

The entire mass spectrometer rests on a 1 inch thick steel table 12 feet long and 5 feet wide. The table is supported by 8 pneumatic mounts which isolate the instrument from building vibrations. The main vacuum chamber is made of 304 stainless steel and may be isolated from the source region by a gate valve located at the entrance to the electrostatic analyser. Aluminum or copper gaskets are used throughout the main chamber except for the electrostatic analyser housing which is sealed by a gold wire. Vacuum pumping is provided by a 140 l/s ion pump on the electrostatic analyser housing and a 50 l/s ion pump located near the collector slit. The main chamber maintains a pressure in the 10^{-8} torr range under operating conditions although the pressure may be two to three orders of magnitude higher on the source side of the object slit.

3-7. FOCUSING

The focusing of the mass spectrometer usually begins by pivoting the electrostatic analyser about the intermediate direction focus until the peaks observed on the oscilloscope move to a position where the intensity and resolution are maximized.

This usually occurs near the "turn around" position at which small angular displacements in either direction cause the observed peak to move in the same direction.

The velocity focus is then checked by switching the ion accelerating potential V_a by about 10V on alternate sweeps of the oscilloscope. Lack of a velocity focus is characterized by a peak being displaced with respect to itself on alternate traces. A small lateral adjustment of the collector slit position is usually sufficient to achieve a velocity focus.

The direction focus is then moved to this position by adjusting l_e' while varying the angle α of the ion beam with the horizontal deflection plates. The position of direction focus is characterized by improved resolution and lack of peak movement with small changes in α.

When a first order double focus is achieved a second order focus will also be obtained as the second order coefficients (see section 2-2D) B_{11} and B_{22} are relatively insensitive to small changes in the instrument geometry. When the direction focus and the velocity focus coincide B_{12} is also zero.

In the peak matching procedure (see section 2-3B) the trajectories of the doublet members are made to coincide at the collector slit. One may also test for coincident trajectories at the intermediate direction focus by varying the accelerating voltage until the ion beams are cut off by one jaw of the energy defining slit S_β. Bleakney's Theorem will be adhered to if the corresponding peaks observed on the oscilloscope decrease together. Such a test is particularly important for chemically dissimilar doublets since in this case the two ion groups may be formed with slightly different distributions in α and β as discussed in section 2-3C.

3-8. PEAK MATCHING CONTROL CIRCUITRY

A block diagram of the control circuitry used in visual peak matching is presented in Fig. 3-6. A master trigger is derived from a mechanical chopper which also controls the switching of the voltage ΔV applied to the electrostatic analyser. The trigger signal starts the sweep of both the display oscilloscope and the signal average simultaneously. Since the Helmholtz coils are driven by a signal derived from the sawtooth of the oscilloscope the ion beam is swept in a synchronous manner with the oscilloscope and the averager. After the sweep is completed the flyback of the sawtooth triggers the flip flop. This activates relays which (i) route the signal from the detector through gain A or B (ii) vertically displace alternate traces of the display oscilloscope (iii) turn the neon on or off and thereby control the switching of the voltage ΔV_a added to the ion accelerating voltage and (iv) switch the voltages applied to the steering and quadrupole lens system (for wide doublets).

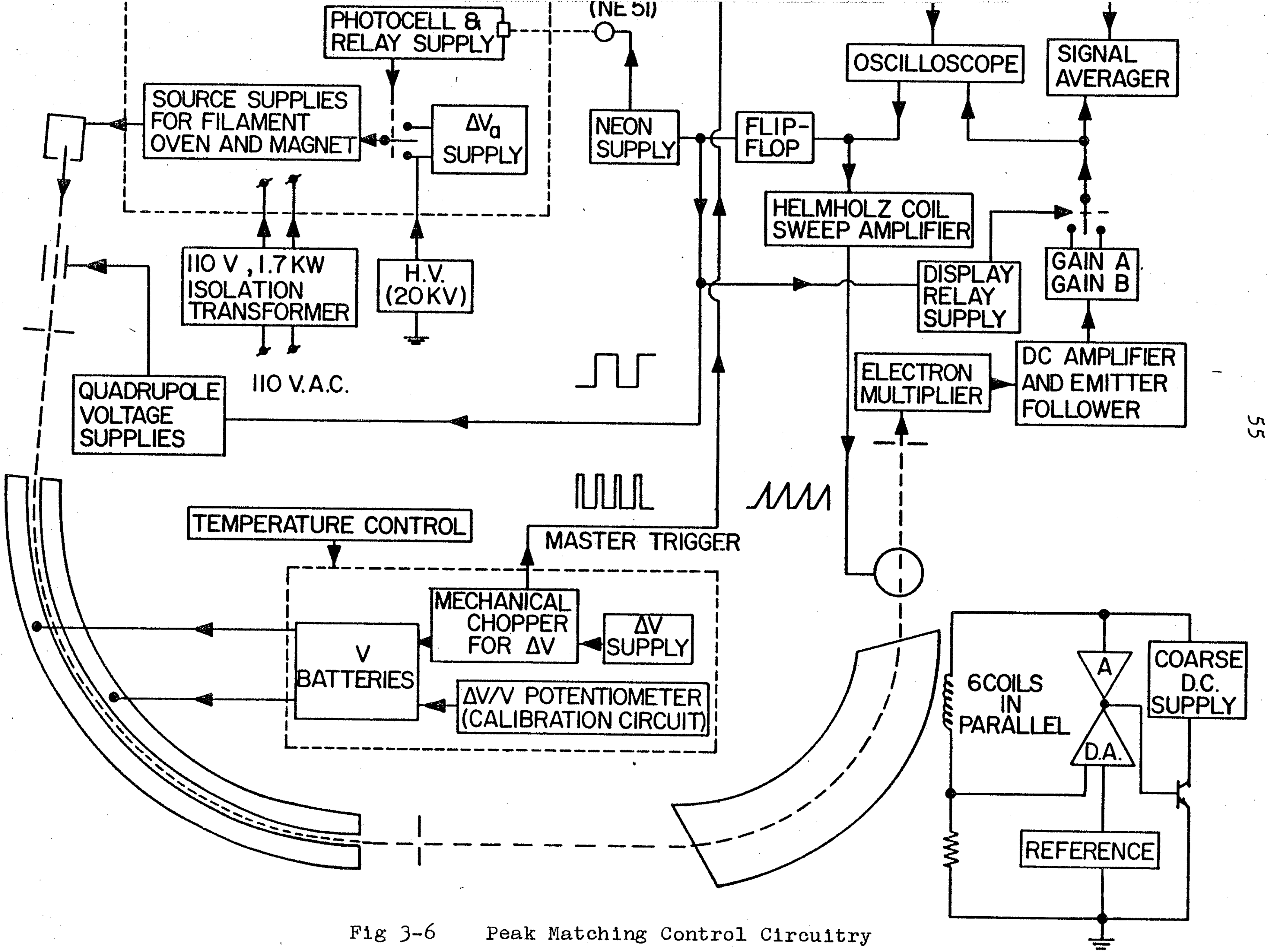


Fig 3-6 Peak Matching Control Circuitry

Detailed descriptions of this control system may be found in Meredith (1971) and Southon (1973) including the modifications necessary for computer - assisted peak matching.

3-9. DATA COLLECTION SYSTEM

Although the data are collected in the same basic manner as described by Meredith (1971) and Southon (1973) extensive hardware modifications have been made to improve the data handling capability of Manitoba II. The following changes were made:

(1) A new preamplifier was constructed which produces a fast voltage pulse for each pulse arriving from the electron multiplier. This permits the signal averager to be used in a pulse counting mode and results in improved sensitivity for weak peaks (Sharma et al, 1977a).

(2) The signal averager has been replaced by a more advanced unit (Nicolet Model NIC-1074) having 4096 memory channels and a dwell time which is adjustable to as short as 10 μsec per point.

(3) A new magnetic tape drive (Kennedy Model 9700) and interface (Nicolet Model NIC-283A) has been installed and is used to read and record data from

the signal averager memory onto magnetic tape or to write data from tape into the memory.

(4) A new master trigger unit has been constructed and will be described in detail by Sharma (1978).

The new data collection system together with most of the controls necessary for a mass determination is shown in Fig 3-7.

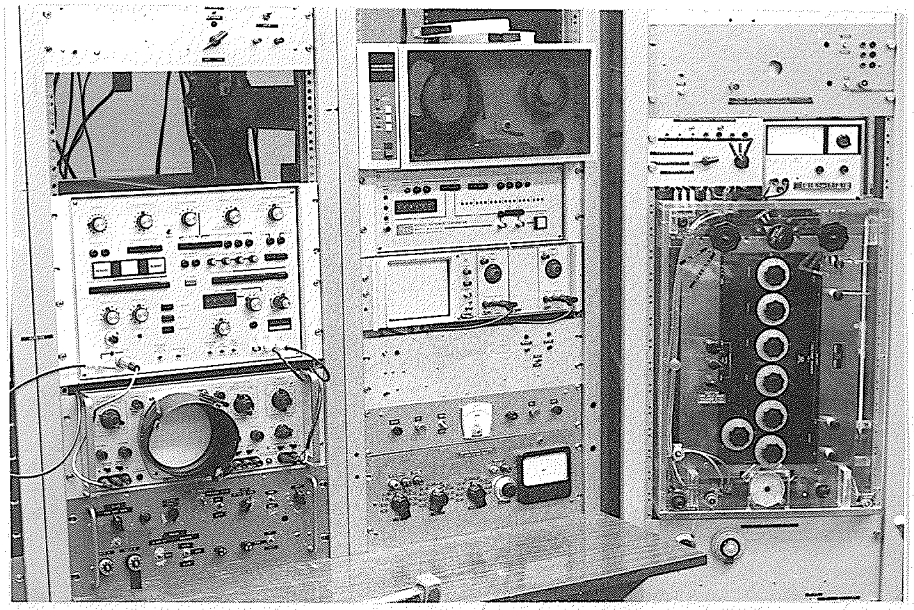


Fig 3-7 Data Collection System

CHAPTER 4

PROCEDURES USED IN PEAK MATCHING

4-1. VISUAL NULL PEAK MATCHING

Two ion peaks of different mass will appear to coincide on alternate traces of the oscilloscope when all the voltages are switched according to Bleakney's theorem as discussed in Chapter 2. The "visual null" technique is a simple and sensitive method for determining the condition of best coincidence. This technique was first introduced by Benson in 1965 (Benson, 1965; Benson and Johnson, 1966) and was quickly adopted by others (Macdougall *et al*, 1966; Stevens and Moreland, 1967; Barber *et al*, 1967).

For visual null peak matching, the signal corresponding to one member of a doublet is added to the contents of the signal averager memory on every second sweep. On alternate sweeps the signal corresponding to the other member of the doublet is subtracted from the memory. The two signals may be matched in amplitude by routing them through separate adjustable gain controls (gain A and B in Fig 3-6). The current contents of the signal averager memory, representing the accumulated difference signal, is continuously displayed on an oscilloscope.

If the two ion peaks do not coincide in position an asymmetrical "S" shaped error signal will grow with time out of the random noise as illustrated in Fig 4-1. The position of the switched peak is then adjusted by changing the switched voltage, ΔV, applied to the electrostatic analyser until the error signal disappears leaving only the random noise.

Visual peak matching is performed with the data collection system operating in the signal averaging mode. The analog voltage signal entering the signal averager is partitioned into 2048 short time intervals for each sweep. In each time interval the input signal is integrated and converted to a proportional digital value which is then added to or subtracted from the previous value stored in the corresponding memory channel. The primary advantage of signal averaging is that the signal -to-noise ratio improves as $\sqrt{N}$ where N is the number of sweeps accumulated. This permits weak peaks to be matched provided the overall stability is sufficient for a large number of sweeps to be recorded. If however the input wave form contains a spurious signal component (such as A.C. ripple which modulates the peak intensity) its effects will also be accumulated and may mask or alter the shape of the error signal for weak peaks.

Visual peak matching is performed "on-line", and thus the calculated ΔM determinations may be obtained with a minimum of delay. The operator observes the entire error signal develop

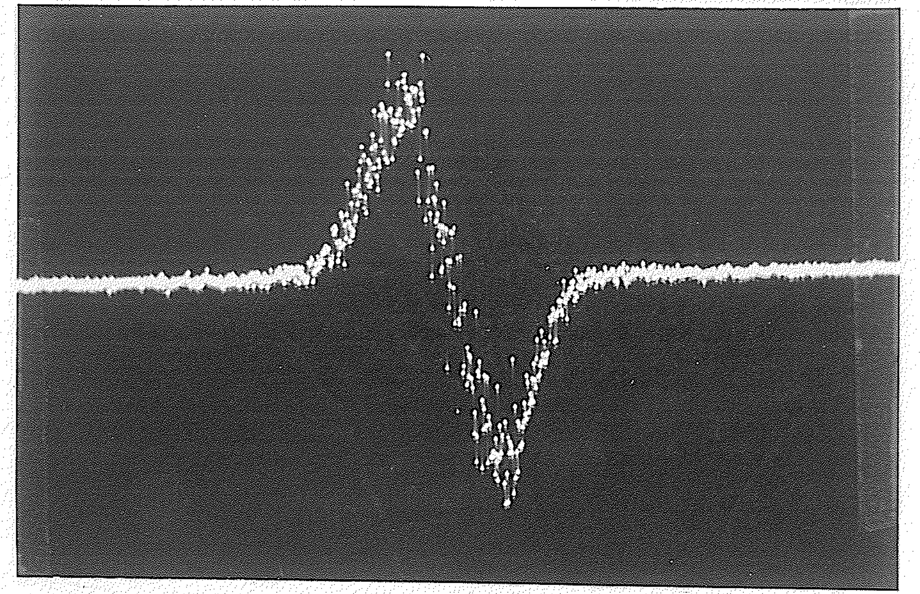


Fig 4-1 Error Signal for Visual Matching

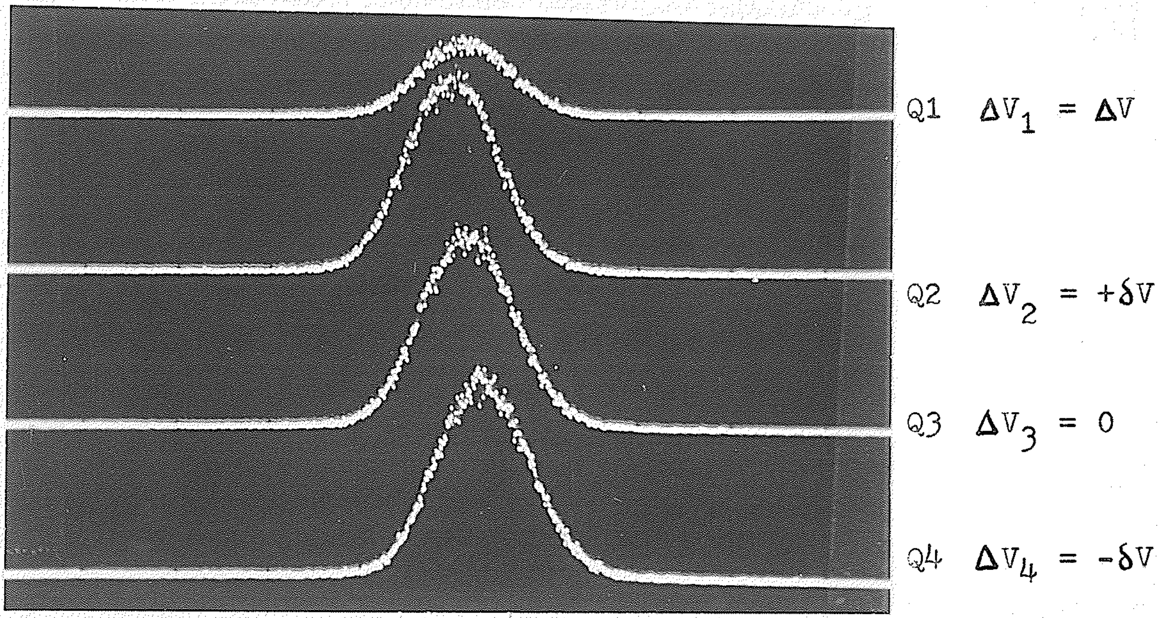


Fig 4-2 Quadrant System for Computer Matching

(normal, add, forward)

with time and may detect problems such as peak movement. However, the primary drawback of visual matching is that most of the collected information is discarded as the memory is erased each time ΔV is adjusted. Also no permanent record of the data, other than the value of ΔV, is kept for future reference.

4-2. <u>ΔM CALCULATIONS</u>

When peak coincidence is achieved ΔV is measured by the potentiometer. If V and M are known, ΔM may then be calculated from equation (2-32). When ΔV is <u>added</u> to the electrostatic analyser voltage V the peak corresponding to the lighter member of the doublet, M_l, will be switched in position to line up with the heavier member, M_h, on the unswitched or reference spectrum. In this case ΔM is calculated from

$$\Delta M = \frac{M_l \Delta V_+}{V} \qquad (4\text{-}1)$$

If ΔV is <u>subtracted</u> from V, the heavier member of the doublet is switched and ΔM is calculated from

$$\Delta M = \frac{M_h \Delta V_-}{V} \qquad (4\text{-}2)$$

In addition, the attenuated peak may be sent through either "gain A" or "gain B". Also the ion beam may be swept across the collector slit in either the "forward" or "reverse" direction (when a forward sweep is used the mass scale increases from right to left on the oscilloscope screen). Permutations of these three arrangements result in eight distinct matching configurations which constitute one "run". A straight average of the 8 separate ΔM determinations is then taken in order to cancel any systematic variations.

Usually at least 20 visual runs are taken spread over a period of several days. A straight average of this set is taken for the final doublet separation and the quoted error is given by the standard deviation of the mean.

$$\sigma_{\overline{\Delta M}} = \left[\frac{\sum_{i=1}^{N} (\Delta M_i - \overline{\Delta M})^2}{N(N-1)} \right]^{\frac{1}{2}} \qquad (4\text{-}3)$$

4-3. COMPUTER ASSISTED PEAK MATCHING

Computer matching was first applied to Manitoba II by Meredith (Meredith, 1971, Meredith et al, 1972). In computer assisted peak matching the memory of the signal averager is divided into 4 quadrants of 1024 channels each, with one sweep of the ion beam corresponding to each quadrant. The reference peak is stored in quadrant 3 ($\Delta V_3 = 0$). A small voltage δV

is added or subtracted in quadrants 2 and 4 to displace the reference peak by a small amount to either side of its position in quadrant 3 ($\Delta V_2 = + \delta V$; $\Delta V_4 = - \delta V$). The switched peak appears in quadrant 1 ($\Delta V_1 = \Delta V$) and ΔV is adjusted until its position coincides approximately with the reference peak in quadrant 3. The spectra are accumulated over many complete cycles with no attenuation of the larger member of the doublet. The relative positions of the 4 peaks collected may be observed on an oscilloscope which displays the 4 quadrants one above the other as illustrated in figure 4-2. After a sufficient number of sweeps have been accumulated, the data are stored on magnetic tape for later analysis and the switched voltages are measured for each quadrant.

As in visual matching, either the heavier or lighter member of the doublet may be used as the reference peak (corresponding to $\Delta V_+$and ΔV_-) and independently, the ion beam can be swept in either the forward or reverse directions. In addition the voltages δV may be applied to quadrants 2, 3, and 4 in a decreasing staircase ("normal") or an increasing staircase ("backward"). A complete set of all eight possible combinations constitutes one run. The voltages are usually adjusted only at the start of each run.

Until recently, computer assisted matching was performed with the data collection system operating in the "signal averaging" mode. In this configuration (which is still used for visual matching) low frequency variations can occur in the baseline which may modulate the position of weak peaks. In addition noise is intentionally added in the digitizer of the averager. These effects have been eliminated by using the signal averager in a pulse counting mode. In this mode the signal averager counts directly the number of ion pulses arriving in a short time interval and adds this value to the previous contents of the appropriate memory channel. The sensitivity for weak peaks has been greatly improved (Sharma et al, 1977a, see also figure 5-1).

Each of the eight matches in a computer run has an assigned statistical error which reflects primarily the number of ions collected. A weighted average may then be calculated for a run according to:

$$\overline{\Delta M} = \frac{\sum_{i=1}^{N} \frac{1}{\sigma_i^2} \Delta M_i}{\sum_{i=1}^{N} 1/\sigma_i^2} \qquad (4\text{-}4)$$

Two different errors may be calculated for the mean (Birge, 1932). The internal error, σ_{int}, gives the estimated error in the mean due to the magnitude of the individual assigned errors:

$$\sigma_{\text{int}} = \frac{1}{\left(\sum_{i=1}^{N} 1/\sigma_i^2 \right)^{\frac{1}{2}}} \qquad (4\text{-}5)$$

The external error, σ_{ext}, reflects primarily the size of the scatter of the individual measurements about the mean:

$$\sigma_{\text{ext}} = \left(\frac{\sum_{i=1}^{N} \frac{1}{\sigma_i^2} \left[\Delta M_i - \overline{\Delta M} \right]^2}{(N-1) \sum_{i=1}^{N} 1/\sigma_i^2} \right)^{\frac{1}{2}} \qquad (4\text{-}6)$$

If the scatter in the data agrees with the variability expected from the assigned errors, the Birge ratio, defined as:

$$R = \sigma_{\text{ext}} / \sigma_{\text{int}} \qquad (4\text{-}7)$$

will have a value close to unity. In practice the Birge ratio for a single computer run is usually greater than 2 (Meredith _et_ _al_, 1972).

In the light of the large Birge ratio, the value for one run is taken to be the unweighted average of the ΔM values for the 8 configurations, with the standard deviation of the mean as the quoted error. The final ΔM value for the doublet is taken to be the weighted average of about 6 computer runs and has an assigned error which is the larger of σ_{int} and σ_{ext} for this set.

Large values of the Birge ratio appear to reflect the systematic discrepancy, which is often present, between the ΔM values obtained for the forward and reverse matching configurations. This "forward - reverse bias" is illustrated in Table 4-1. Each of the values given represent the averages of 26 computer determinations for either forward or reverse sweep directions. The more recent determinations were performed after the modifications to the magnetic sweep circuit discussed in section 3-5 and indicate that the bias is still present although of reduced magnitude and reversed in sign. This bias does disappear on occasion, resulting in a reduction in the standard deviation of the mean for a single run by at least a factor of two.

4-4. THE ADVANTAGES AND OBJECTIVES OF COMPUTER MATCHING

The use of off-line computer assisted peak matching has provided improved precision in a given operating time over that attained with visual matching (Meredith *et al*, 1972). This is partly the result of the removal of human judgment in determining the matched condition, but is primarily the result of more efficient use of the collected data. As described earlier, in visual matching the majority of the collected data is discarded in arriving at the matched condition and does not influence directly the final judgment of best coincidence. For computer matching the peaks are accumulated separately for a period of

TABLE 4-1

THE FORWARD - REVERSE BIAS[a]

ΔM Value (μu)

DATE	FORWARD	REVERSE	FORWARD - REVERSE
June 1976	5 274.08 ± 2.09	5 262.29 ± 1.08	11.79 ± 2.35
Feb. 1977	5 263.99 ± 0.57	5 268.24 ± 0.73	-4.25 ± 0.93

[a] for doublet L in Table 5-1

several hundred sweeps. Virtually all of the data collected are used subsequently to determine the matched condition. Efficient use of the data is important, since the theoretical limit to the precision of a match is determined by the total number of ions detected (Campbell and Halliday 1965, Kayser et al, 1972, Meredith et al, 1972). Additionally, in computer matching a permanent record of the data is kept for future comparison.

The two members of the doublet (quadrants 1 and 3 in Fig 4-2) coincide only approximately in position in computer matching. Thus any method of computer analysis must determine the relative separation between the two members of the doublet and then derive the correct voltage ΔV that would have resulted in perfect coincidence. The mass difference ΔM may then be calculated from equation (2-32) as in visual matching.

The peaks collected in quadrants 2, 3 and 4 in Fig 4-2 provide three different, but nearly - matched conditions, which bracket the matched configuration when their positions are compared to the switched peak in quadrant 1. Three separations may thus be obtained at known switched voltages measured relative to quadrant 3 ($\Delta V_2 = + \delta V$, $\Delta V_3 = 0$, $\Delta V_4 = - \delta V$ for the "normal, add, forward" configuration). Over this range the change in position has been shown to be linearly dependent on the switched voltage applied (Meredith, 1971; Meredith et al, 1972). Thus the three pairs of separations relative to quadrant 1 and switched voltages relative to quadrant 3 for quadrants 2, 3 and 4 may be fitted to a straight line. The intercept of this line (i.e. the voltage required to produce zero separation) then gives the correction to be applied to the switched voltage in quadrant 1 to derive the desired ΔV. All computer matching techniques rely on a linear calibration procedure similar to the above method and differ only in the details of how relative peak separations are determined.

4-5. METHODS OF DETERMINING THE SEPARATION BETWEEN TWO PEAKS

The various techniques used to determine peak separations may be grouped into two broad categories:

(1) Peak Location Methods:

These methods require some absolute measure of the position of the center of a peak such as its centroid (Stevens and Moreland, 1967; Meredith et al, 1972). The two peak positions are calculated separately and their difference is used as the separation. Various definitions of peak position may be used (Katakuse and Ogata, 1972) all of which are strictly applicable only to fully resolved peaks.

(2) "Error Signal" Methods:

For these methods one peak is scaled in height and shifted in position until it coincides point by point with the other peak as in visual matching. The displacement required to minimize the degree of mismatch gives a direct measure of the separation. Two numerical criteria have been used to determine the matched condition. These correspond to adjusting the height and displacement of one peak until either:

(i) the magnitude of the sum of the differences between the two peaks is a minimum (Stevens and Moreland, 1967; Southon, 1973). This method is almost a numerical equivalent of the visual null method.

or (ii) the sum of the squares of the differences is a minimum (Kayser, 1975; Kayser et al, 1972, 1975, 1976; Katakuse and Ogata, 1972).

These criteria may be statistically weighted to allow for expected random differences and can be generalized for use with partially resolved peaks (Kayser 1975; Kayser et al, 1972, 1976).

The remainder of this chapter largely consists of a detailed comparison of two numerical methods of determining peak separations which are believed to be representative of the two categories outlined above. It must be emphasized that for the separation between two peaks to be of general significance the two peaks must be of the same shape (apart from random noise). Otherwise the separation obtained will depend on the particular definition used.

4-6. THE CENTROID METHOD

The centroid method of determining peak separation was developed for Manitoba II by Meredith (Meredith, 1971; Meredith et al, 1972) and has been successfully applied for several years. The main feature of this peak location method is its conceptual and computational simplicity.

Each peak stored in the memory of the signal averager can be interpreted as a discrete distribution of values x_i (channel number) occurring with frequency f_i (number of counts) for $i = 1, 2, \ldots, N$. The centroid or mean of such a distribution is defined by:

$$x_c = \frac{\sum_{i=1}^{N} f_i \; x_i}{\sum_{i=1}^{N} f_i} \qquad (4\text{-}8)$$

The fraction $f_i \,/ \sum_{i=1}^{N} f_i$ gives the probability of occurrence of the value x_i. The uncertainty in the centroid is taken as the standard deviation of the mean:

$$\sigma_c = \left\{ \frac{\sum_{i=1}^{N} f_i \,(x_i - x_c)^2}{\sum_{i=1}^{N} f_i \,(\sum_{i=1}^{N} f_i - 1)} \right\}^{\frac{1}{2}} \qquad (4\text{-}9)$$

The separation between two peaks is then given by

$$S_{21} = x_{c2} - x_{c1} \qquad (4\text{-}10)$$

with uncertainty

$$\sigma_{21} = \left[\sigma_{c2}^{\ 2} + \sigma_{c1}^{\ 2} \right]^{\frac{1}{2}} \qquad (4\text{-}11)$$

Prior to the centroid calculation a constant baseline is determined by averaging the counts obtained in channels far removed from the center of the peak. The baseline is then subtracted from the peak. In practice the magnitude of this baseline represents only a small fraction of the total peak height and, for resolved peaks, is caused by scattered ions and by noise generated in the detector. For partially resolved peaks the use of a constant baseline is not justified.

The centroid is calculated over a range of channels between peak limits defined in terms of a fraction of the peak height. In previous work peak limits have been chosen at 15% of the peak maximum in order to minimize contributions to the centroid from the overlapping tails of partially resolved peaks. Meredith (1971) has shown that for partially resolved doublets, the determined separation is reduced when lower limits are set. Uncertainty in the correct location of the peak limits caused by random statistical noise can introduce a variation in the calculated centroid. This variation is aggravated by the uncertainty in the true peak height arising from the large statistical fluctuations which occur at the peak maximum. In practise the peak height is obtained by fitting a smooth parabola to the top of the peak. Moreover the problem of defining correctly the peak limits occurs independently for each member of the doublet and thus the variation in the value derived for the separation reflects this effect for both peaks. Evidence will be presented in section 4-9A which suggests that, for resolved peaks, the variation in the calculated separation is substantially reduced when peak limits corresponding to less than 15% of the peak height are used.

THE LEAST SQUARES METHOD

A least squares method of determining the separation between two peaks has been developed recently for Manitoba II and will be described in detail. This "error signal" method minimizes the sum of the squares of the differences between two peaks and follows in some respects the peak unfolding technique introduced by Kayser at Minnesota (Kayser, 1975; Kayser et al, 1972, 1975, 1976).

The mass spectrum $F(x_i)$ for a doublet can be considered as a superposition of two different peaks $A(x_i)$ and $B(x_i)$, both of which are assumed to be representations of the same idealized peak shape function $f(x)$. Thus, apart from random noise, the spectrum for a doublet can be described by

$$F(x_i) = A(x_i) + B(x_i) = f(x_i) + rf(x_i - S) \quad (i=1, 2, \ldots, N) \qquad (4\text{-}12)$$

where r is the intensity ratio of the two peaks, s is their separation and x_i denotes the position corresponding to channel i. In practise the peaks are approximately triangular in shape although the precise shape is arbitrary and depends on such factors as slit quality and alignment, image aberrations and small angle scattering.

Two mathematical operations which preserve the ratio and separation may be performed on the spectrum:

(1) the spectrum may be multiplied by a constant r'

$$r'F(x_i) = r'f(x_i) + r'rf(x_i - s) \qquad (4\text{-}13)$$

(2) the spectrum may be displaced by an amount s'

$$F (x_i + s') = f (x_i + s') + r f (x_i - s + s') \qquad (4\text{-}14)$$

Subtraction of (4-14) from (4-13) then gives

$$r'F(x_i) - F(x_i+s') = r'rf(x_i-s) - f(x_i+s') + \left\{ r'f(x_i) - rf(x_i-s+s') \right\} \qquad (4\text{-}15)$$

The term in brackets in (4-15) gives the error signal E (x_i) at the point x_i:

$$E (x_i) = r' A (x_i) - B (x_i+s') = r'f (x_i) - rf (x_i - s+s') \qquad (4\text{-}16)$$

A null signal (E (x_i) = 0 for all x_i) will be obtained when $r' = r$ and $s' = s$. The achievement of a null error signal corresponds to the fitting of one peak to match the height and position of the other. For a fully resolved doublet the error signal can be evaluated over a range of channel numbers x_i, for which the first two terms on the right hand side of equation (4-15) make no contribution.

The "goodness of fit" may be determined by evaluating the weighted sum of the squares of the residuals of the error signal defined by

$$\chi^2 = \sum_{i=n_1}^{n_2} \frac{1}{\sigma_i^2} \left[r A (x_i) - B (x_i + s) \right]^2 \qquad (4\text{-}17)$$

The condition of best match will be determined in a least squares sense when χ^2 is minimized with respect to the fitted parameters r and s. It should be noted that the weights $1/\sigma_i^2$ also depend on the values of the parameters fitted. When Poisson statistical weights are used, the expected variance of the error signal is given by

$$\sigma_i^2 = r^2 A(x_i) + B(x_i+s) \tag{4-18}$$

The sum in equation (4-17) is carried out from channels n_1 to n_2 which act as peak limits for the fixed peak A (x). These limits define a "matching window" which moves across peak B (x) as s is varied. Only one set of peak limits is required.

Since χ^2 depends nonlinearly on the parameters r and s there is no guarantee that a unique minimum will be found. In practise, a minimum χ_o^2 (s_o, r_o) does exist about which χ^2 may be expanded in a Taylor series which is linear in the parameter increments $\delta s = s-s_o$ and $\delta r = r - r_o$:

$$\chi^2 = \chi_o^2 + \frac{\partial \chi_o^2}{\partial s}\,\delta s + \frac{\partial \chi_o^2}{\partial r}\,\delta r + \text{higher order terms} \tag{4-19}$$

The conditions for a minimum in χ^2 are obtained by setting the partial derivatives of χ^2 with respect to s and r equal to zero. This may be expressed as a matrix equation of the form

$$\overleftrightarrow{A}\,\vec{x} = \vec{b} \tag{4-20}$$

$$\text{where} \quad \overleftrightarrow{A} = \tfrac{1}{2} \begin{bmatrix} \dfrac{\partial^2 \chi_o{}^2}{\partial s^2} & \dfrac{\partial^2 \chi_o{}^2}{\partial s\, \partial r} \\[2ex] \dfrac{{}^2 \chi_o{}^2}{\partial r\, \partial s} & \dfrac{\partial^2 \chi_o{}^2}{\partial r^{\,2}} \end{bmatrix} \tag{4-21}$$

$$\vec{x} = \begin{bmatrix} \delta s \\[2ex] \delta r \end{bmatrix} \qquad \vec{b} = -\tfrac{1}{2} \begin{bmatrix} \dfrac{\partial \chi_o{}^2}{\partial s} \\[2ex] \dfrac{\partial \chi_o{}^2}{\partial r} \end{bmatrix}$$

The solution of equation (4-20)is equivalent to approximating the χ^2 hypersurface by a paraboloid in the region of the minimum (Bevington, 1969). The factor of ½ is included in $\overleftrightarrow{A}$ and $\vec{b}$ so that the symmetric matrix $\overleftrightarrow{A}$ may be interpreted as representing the curvature of the χ^2 hypersurface.

The values of the parameters s_o and r_o at the minimum $\chi_o^{\,2}$ are obtained using an iterative algorithm as follows.

(1) Initial guesses s_i and r_i are obtained from the difference in centroids and ratio of areas for the two peaks.

(2) The initial values are used to evaluate $\chi_i{}^2$ and the partial derivatives necessary to determine $\overleftrightarrow{A}$ and $\vec{b}$.

(3) The matrix equation (4-14) is solved to determine the parameter increments δs and δr.

(4) The parameter increments are used to update the values of s_i and r_i.

(5) The procedure from step 2 is repeated until s_i, r_i, and $\chi_i{}^2$ converge to s_o, r_o and $\chi_o{}^2$.

Error estimates for the final values of the parameters s_o and r_o are obtained from the inverse matrix of $\overleftrightarrow{A}$ (Bevington, 1969).

$$\sigma_i = \sqrt{A_{ii}^{-1}} \qquad (4\text{-}22)$$

Since r is a continuous variable, the partial derivatives of χ^2 with respect to r can be calculated analytically for a given s value and then summed from n_1 to n_2. The r dependence of the weights is ignored in this calculation to simplify the computations. The weights are however updated with the current value for r after each iteration. The quantity χ^2 and its derivatives with respect to s can be evaluated only at discrete integer values of s corresponding to increments of one channel. Interpolation between channels is achieved by fitting a parabola to the values of χ^2 obtained at values of s which bracket the true minimum. The weights are allowed to change with s in this calculation. For the first few iterations a coarse grid is used, with 3 values of s each separated by

4 channels. The final value for s_o is obtained by fitting a parabola to 11 points (with increments of 1 channel for s) which symmetrically bracket the minimum. In practise, the value obtained for s_o is independent to within about .001 channels of the value of r_o at the two dimensional minimum χ_o^2 (s_o, r_o).

For a two parameter fit, the number of degrees of freedom is given by

$$\nu = n_2 - n_1 - 1 \qquad (4\text{-}23)$$

The "reduced χ^2", χ_ν^2, is then defined as

$$\chi_\nu^2 = \chi^2/\nu \qquad (4\text{-}24)$$

If the two peaks differ in shape as a result of the random statistical noise only the value of χ_ν^2 should be close to unity. Thus the magnitude of χ_ν^2 gives a measure of the "goodness of fit". Values of χ_ν^2 systematically greater than one indicate that the differences between the two peaks are on the average greater than that anticipated by the assigned variances σ_i^2 (see equations (4-17) and (4-18)).

A fundamental objection to the least squares method has been raised (Davison, 1977) regarding the use of a least squares fitting procedure for data which are randomly distributed according to counting statistics. Least squares techniques are rigorously valid only for data which have a normal or Gaussian probability distribution. The observed counts however are distributed according to a Poisson probability distribution function given by

$$P\ (m;\lambda) = \lambda^{m} e^{-\lambda} / m! \qquad (4\text{-}25)$$

where λ is the expected number of counts and m is the number actually observed. The correct fitting procedure in this case involves the use of maximum likelihood techniques. In the present circumstances the application of this method appears to be impractical, in that the probability distribution function for the <u>difference</u> of two Poisson random variables does not yield a simple mathematical form analogous to equation (4-25).

The distribution function for the error signal $P(rm_1 - m_2;\ r\lambda_1 - \lambda_2 = o\ )$ has been investigated empirically using a Poisson random number generating routine. For equal expected values ($\lambda_1 = \lambda_2;\ r = 1$) this distribution is symmetric about zero and narrower than a Gaussian at low values of λ. When $\lambda_1 \neq \lambda_2$ the distribution is slightly asymmetric at low values of λ with a mean of zero. At larger values of λ the distribution becomes a Gaussian symmetric about zero and in all cases the standard deviation of the mean agrees with equation (4-18). It appears that the probability distribution for the difference of two Poisson random variables is a better approximation to a Gaussian distribution than is (4-25) for all values of λ and thus the need to use maximum likelihood methods is reduced. Further evidence will be presented in section 4-9A which suggests that no bias is introduced in the ΔM determination due to the use of a least squares fitting procedure.

When the peaks are asymmetric a small systematic bias in the calculated separation may occur if the peak limits are set at too high a level. In this case χ^2 (which is evaluated between the fixed peak limits) will change by different amounts depending on whether the moveable peak is shifted to the right or to the left of the minimum. In order to determine the magnitude of this effect, tests were performed on 96 recorded peaks (from doublets K and M in Table 5-1) with peak limits set at 1%, 5% and 15% of the peak height. Each peak was matched to itself by displacing the peak with respect to itself and evaluating χ^2 (with r=1) at 10 positions about s=o. The value s=o where perfect coincidence occurs was excluded. A parabola was fitted to the 10 points and both the location of the minimum and the corresponding value of χ^2 were determined. If a bias due to asymmetry were present it would change its sign when the sweep direction is reversed (this is not to be confused with the forward - reverse bias discussed in section 4-3). The averages for forward and reverse for each of the three levels are presented in Table 4-2. At the 15% level a small

TABLE 4-2

ASYMMETRY BIAS FOR LEAST SQUARES MATCHING[a]

PEAK LIMITS:	1%	5%	15%
FORWARD (channels)	-.010 ± .006	+.004 ± .006	+.037 ± .008
REVERSE (channels)	-.007 ± .007	-.014 ± .006	-.023 ± .011
χ_ν^2	2.05 ± .02	2.06 ± .02	2.07 ± .02

[a] for doublets K and M in Table 5-1

bias does occur and at lower levels its magnitude is diminished. Although the size of this bias is too small to be of any significance in the ΔM determinations, it does indicate that lower peak limit levels should be used in the least squares method.

The most curious feature of Table 4-2 is the fact that χ_{ν}^{2} has an average value of 2.0. Since each peak is being artificially matched to itself there is no difference in peak shape. It would appear then that the noise in the data is larger than the $\sqrt{N}$ noise assumed from Poisson counting statistics.

4-8. COUNTING LOSS CORRECTIONS

At high count rates some of the ions arriving at the detector may not be registered as corresponding counts in the memory of the signal averager as a result of the finite resolving time of the detector and its associated electronics. With the present detection apparatus for Manitoba II these counting losses appear to occur primarily in the preamplifier. The preamplifier is in effect " dead " for a small fixed time ρ following the arrival of a pulse. If N_o counts are observed in time t the total dead time is $N_o\rho$ and the live time is then $(t - N_o\rho)$. The fraction of the true number of events N_c which are observed is the same as the ratio of the live time to the total observation time.

$$N_o / N_c = (t - N_o \rho) / t \qquad (4\text{-}26)$$

Thus the true number of events is given by

$$N_c = N_o / (1 - N_o \rho / t) \qquad (4\text{-}27)$$

The variance of the true number of events can be shown to be

$$\sigma^2_{N_c} \simeq N_c (1 + N_c \rho / t) \qquad (4\text{-}28)$$

for long observation times ($\rho \ll t$) (Campbell, 1956).

In the present case, the total observation time per channel is given by the product of the number of sweeps recorded and the dwell time per point of the signal averager. The resolving time ρ of the preamplifier has been determined with a pulse generator to be $200 \pm 10 \times 10^{-9}$ sec (Sharma, 1978). Thus the peaks recorded can be corrected point by point according to equation (4-27) to give a better representation of the true peak shape. However this correction must be viewed as an approximation since the peak may move slightly causing the count rate in a given channel to change during the data collection period. The count rate will also fluctuate as a result of changing conditions in the ion source. In practice the correction applied at the peak maximum amounts to about

5% and corresponds to a count rate of 250 kHz.

Counting losses produce a differential peak shape distortion inasmuch as the more intense member of a doublet will appear to be flatter near the maximum as compared to the weak peak. If the peaks are symmetric this should not alter the determined separation. For asymmetric peaks, however, the counting losses will introduce a small systematic bias which depends on the particular doublet studied. The peaks recorded on Manitoba II are frequently slightly skewed to the lighter mass side of the peak. In this case the determined separation will be too small when the heavier member of the doublet is the more intense peak and too large when the lighter member is more intense.

A comparison of the ΔM determinations obtained using the centroid method with and without counting loss corrections is presented in Table 4-3 (these values differ slightly from those reported later since program modifications were subsequently made.) Doublet N is the only one for which the lighter member is more intense. In every case the difference in the ΔM values is within the assigned error although for doublets N and O the change is significant at the current level of precision.

4-9. A COMPARISON OF THE CENTROID METHOD AND THE LEAST SQUARES METHOD

A. Simulated Peaks:

Synthetic peaks were constructed to test the two

TABLE 4-3

THE COUNTING LOSS CORRECTION

ΔM Values[b] (μu)

DOUBLET[a]	WITHOUT CORRECTION	WITH CORRECTION	DIFFERENCE
L	4972.14 ± 0.57	4972.16 ± 0.48	.02
M	5266.37 ± 0.57	5266.16 ± 0.48	.13
N	5800.70 ± 0.56	5800.17 ± 0.59	-.53
K	4508.42 ± 0.62	4508.31 ± 0.59	-.11
P	11066.20 ± 0.42	11066.36 ± 0.44	.16
O	9755.13 ± 0.95	9775.42 ± 0.80	.29

[a] See Table 5-1

[b] Centroid Values with 15% Peak Limits

methods of analysis for inherent systematic biases, apart from instrumental considerations, and to judge their relative merits. Four identical peaks, whose separations are known exactly, were constructed to represent the data collected for a given matching configuration. In order to approximate typical real peaks, each peak was chosen to be an isosceles triangle with a height of 400 counts and a width at the base of 200 channels. A Poisson random number generating routine was then used to add statistical noise to each of the peaks and to superimpose a baseline noise corresponding to an expected value of one count. This process was repeated 96 times to generate the equivalent of 12 complete runs. The 96 records thus differ slightly but only in a random manner as a result of the statistical noise applied.

It should be noted that although the addition of random noise alters only the number of counts in each channel, this can cause an apparent shift in the peak position from its idealized value. Consequently a large number of synthetic peaks must be generated to distinguish systematic effects from the random variations introduced by the noise.

The least squares and the centroid methods were merged into a composite computer program to insure that the baseline subtracted and the peak limits selected are identical for both methods of analysis. For the least squares method any negative value obtained after the subtraction of the baseline is truncated to zero to avoid the erroneous scaling of it by the intensity ratio r. This procedure is questionable in that it halves the noise level on the tails of the peaks, although these regions are not used in the separation determination (except perhaps at the lowest peak limit levels). The statistical weights used in the least squares method are obtained from the number of counts in each channel prior to the subtraction of the baseline. A minimum value of one count in each channel is assumed in the calculation of the weights.

Both the least squares method and the centroid method were tested with the simulated data using peak limits set at 1%, 5%, 10%, 15%, 20% and 25% of the peak height. The deviation of the average ΔM from the "true" value and the standard deviation from the mean are tabulated for both methods at each of the 6 cut off levels in Table 4-4 along with the average value of χ_ν^2 for the least squares method. The results are also presented in Fig 4-3. The theoretical precision is also indicated in the diagram and is obtained from the total number of counts N and the peak width at the base of the triangle, W, using (Meredith <u>et</u> <u>al</u>, 1972)

$$\sigma_{th} = W / \sqrt{24 N} \qquad (4\text{-}29)$$

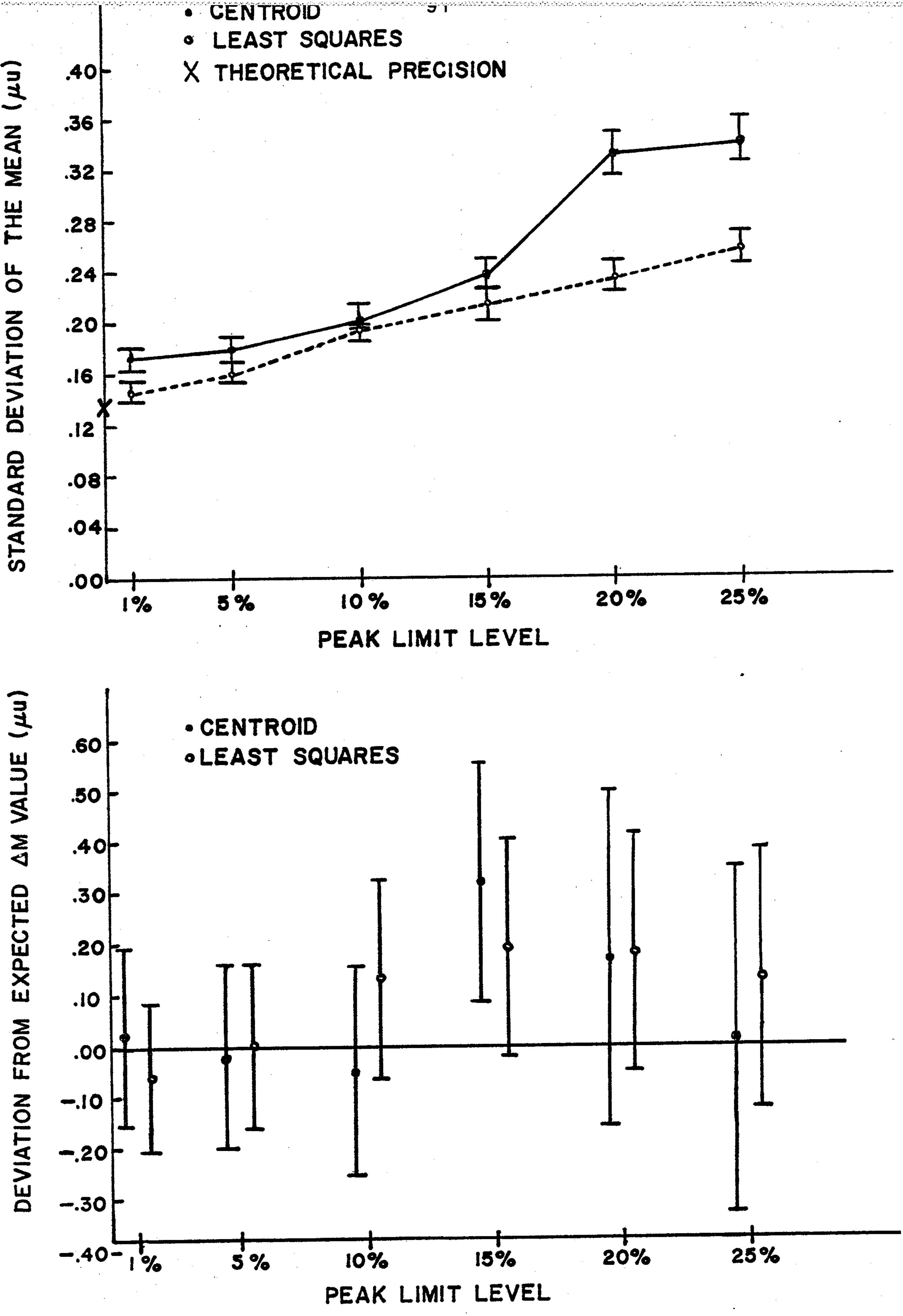
TABLE 4-4

COMPARISON OF CENTROID AND LEAST SQUARES METHODS FOR SIMULATED PEAKS

Deviation from expected value (μu)

PEAK LIMIT LEVEL

	1%	5%	10%	15%	20%	25%
CENTROID METHOD	.02 ± .17	-.02 ± .18	-.05 ± .21	.32 ± .24	.17 ± .33	.01 ± .34
LEAST SQUARES METHOD	-.06 ± .15	0.00 ± .16	.13 ± .20	.19 ± .21	.18 ± .23	.13 ± .26
χ^2_ν	(1.03)	(.99)	(1.00)	(1.00)	(1.00)	(1.00)



4-3 Comparison of Centroid and Least Squares Methods for simulated peaks.

Fifty percent confidence limits on the values indicated for the standard deviation of the mean are also shown (Snedecor and Cochran, (1967)).

The following observations may be made concerning these results:

(1) Both methods yield average ΔM values which generally agree with the expected value and with each other to within their assigned errors at all values of the peak limits.

(2) The deviations from the expected value and the standard deviations of the mean are substantially reduced for both methods when lower peak limits are used.

(3) The least squares method has a slightly smaller standard deviation of the mean than the centroid method in all cases. Moreover precision deteriorates less rapidly for the least squares method as higher cut off levels are used. This likely reflects the fact that the least squares method requires only one set of peak limits.

(4) The average χ^2_ν is 1.0 for the least squares method at all peak limit levels, as expected.

Similar tests of the two methods, although not as extensive, have been performed on simulated peaks using (i) a peak height of 100 counts (ii) various baseline noise levels (iii) various intensity ratios different from unity, and (iv) Gaussian rather than triangular peak shapes. The results obtained are similar in all cases.

Separate tests involving only the centroid method indicate that the magnitude of the variations introduced by the need to define peak limits depends on the precise manner in which they are determined for a given percentage level. At present the peak limits are defined as follows:

(1) The entire peak is first "smoothed" using a 9 point parabolic smoothing routine (the smoothed values are used <u>only</u> for defining peak limits).

(2) A parabola is fitted to 7 points surrounding the maximum value and is used to determine the peak height.

(3) Starting at the tails, points are searched for whose values exceed the desired fraction of the peak height.

(4) When 8 consecutive points are found in this manner, the first of these is taken as the location of the peak limit corresponding to the percentage of the peak height used.

The magnitude of the variation introduced by the definition of peak limits is somewhat surprising when one considers that very little of the information contained in the peak is excluded at the cut off levels considered.

B. Real Mass Spectral Peaks:

A similar test of the two methods was performed using real data obtained at high resolution with the Manitoba II mass spectrometer (doublets J to P in Table 5-1). For these data a counting loss correction was applied as discussed in section 4-8. The average ΔM values obtained for each method at peak limit levels of 5%, 10%, 15% and 20% of the peak height are presented in Table 4-5. The errors tabulated represent the larger of σ_{int} or σ_{ext} as discussed in section 4-3. The doublets are listed in order of increasing "difficulty" as determined by the intensity ratio and the width of the doublet. The experimentally determined intensity ratios (taken from the centroid method at 5% peak limits; see below) are tabulated along with the ratio expected from the known natural abundances (Holden and Walker, 1972), which are shown enclosed in brackets. Doublets O and P are actually mass triplets in which the separation between the outside members was determined. For these doublets the expected intensity ratio for the middle peak with respect to the weakest peak

TABLE 4 -5 COMPARISON OF CENTROID AND LEAST SQUARES ΔM VALUES (μu)

DOUBLET[a]	RATIO[b]		5%	10%	15%	20%
L	1.22	C:	* 4 972.65 ± 0.37	4 972.39 ± 0.48	4 972.41 ± 0.38	4 973.37 ± 0.51
	(1.22)	L:	2.74 ± 0.46	2.70 ± 0.47	2.37 ± 0.45	2.81 ± 0.42
		X:	(2.12)	(2.12)	(2.12)	(2.11)
M	1.99	C:	* 5 266.76 ± 0.43	5 266.99 ± 0.50	5 266.49 ± 0.54	5 267.20 ± 0.54
	(2.01)	L:	7.30 ± 0.42	7.25 ± 0.40	7.38 ± 0.41	7.36 ± 0.42
		X:	(2.16)	(2.14)	(2.13)	(2.12)
N	2.75	C:	* 5 800.67 ± 0.53	5 800.93 ± 0.51	5 800.94 ± 0.58	5 800.91 ± 0.64
	(2.80)	L:	0.61 ± 0.41	0.58 ± 0.39	0.53 ± 0.41	0.37 ± 0.39
		X:	(2.26)	(2.22)	(2.18)	(2.21)
K	3.54	C:	* 4 508.80 ± 0.48	4 509.21 ± 0.55	4 509.20 ± 0.63	4 508.75 ± 0.61
	(3.57)	L:	9.38 ± 0.48	9.44 ± 0.52	9.66 ± 0.51	9.48 ± 0.51
		X:	(2.16)	(2.13)	(2.10)	(2.08)
P	2.86	C:	11 066.52 ± 0.30	11 066.67 ± 0.39	*11 066.85 ± 0.55	11 066.88 ± 0.42
	(2.87)	L:	6.76 ± 0.32	6.93 ± 0.34	6.85 ± 0.41	6.79 ± 0.42
	(8.02)	X:	(2.40)	(2.36)	(2.33)	(2.31)
O	26.9	C:	9 773.66 ± 0.82	9 774.10 ± 1.01	* 9 774.87 ± 1.06	9 773.42 ± 1.25
	(28.8)	L:	5.55 ± 0.81	5.71 ± 0.77	7.05 ± 0.56	5.36 ± 0.74
	(14.3)	X:	(3.35)	(3.18)	(3.05)	(2.96)
J	87.1	C:	3 883.86 ± 1.20	3 884.67 ± 1.45	3 884.68 ± 1.16	* 3 885.91 ± 1.66
	(105.)	L:	7.97 ± 1.50	8.62 ± 1.44	7.70 ± 1.41	7.94 ± 1.63
		X:	(3.43)	(3.55)	(3.54)	(3.51)

a see Table 5-1
* adopted value
b see text

C: Centroid Method
L: Least Squares Method
X: χ^2_ν

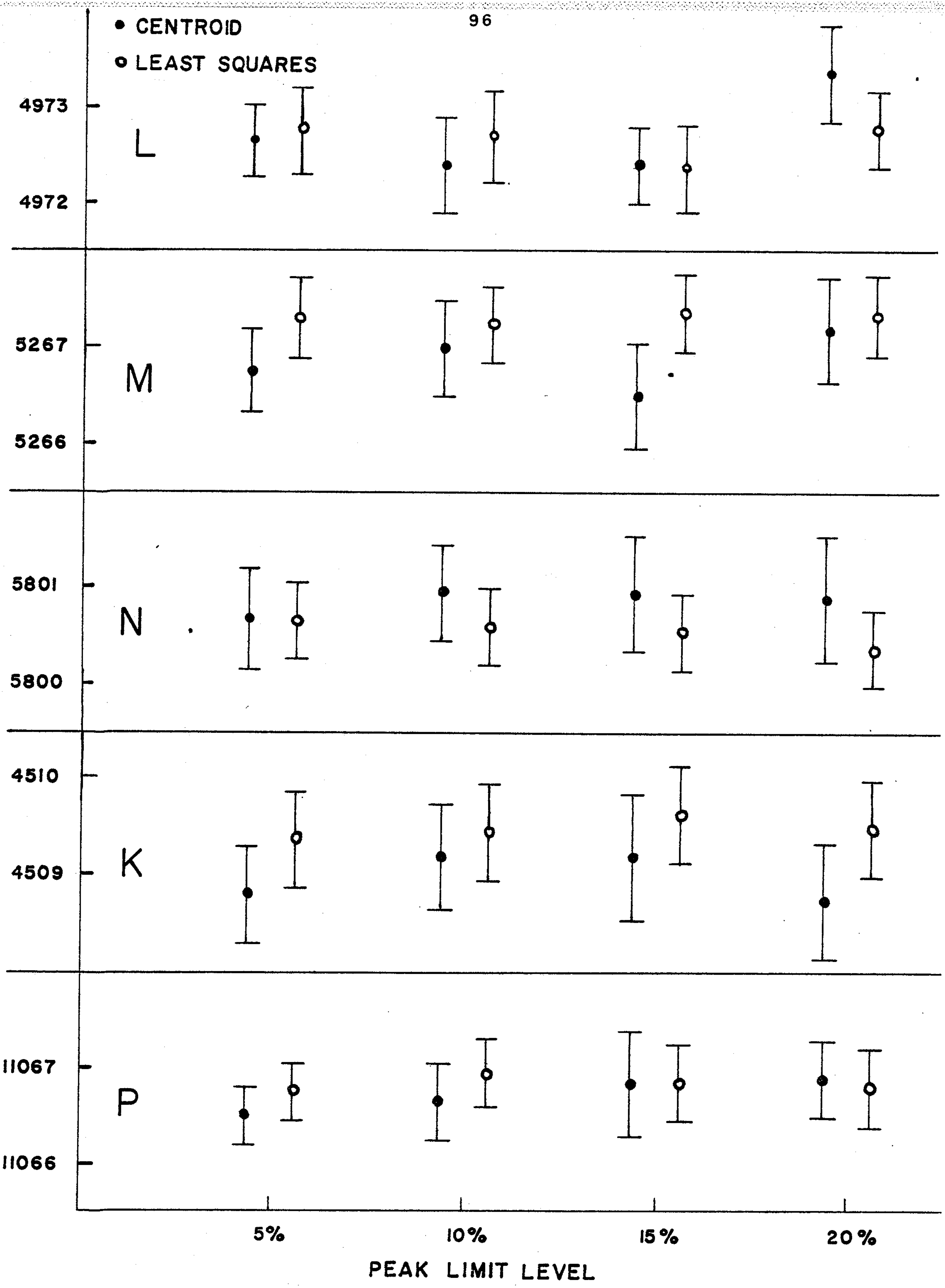


Fig 4-4a Comparison of Centroid and Least Squares ΔM Values
Doublets L,M,N,K and P

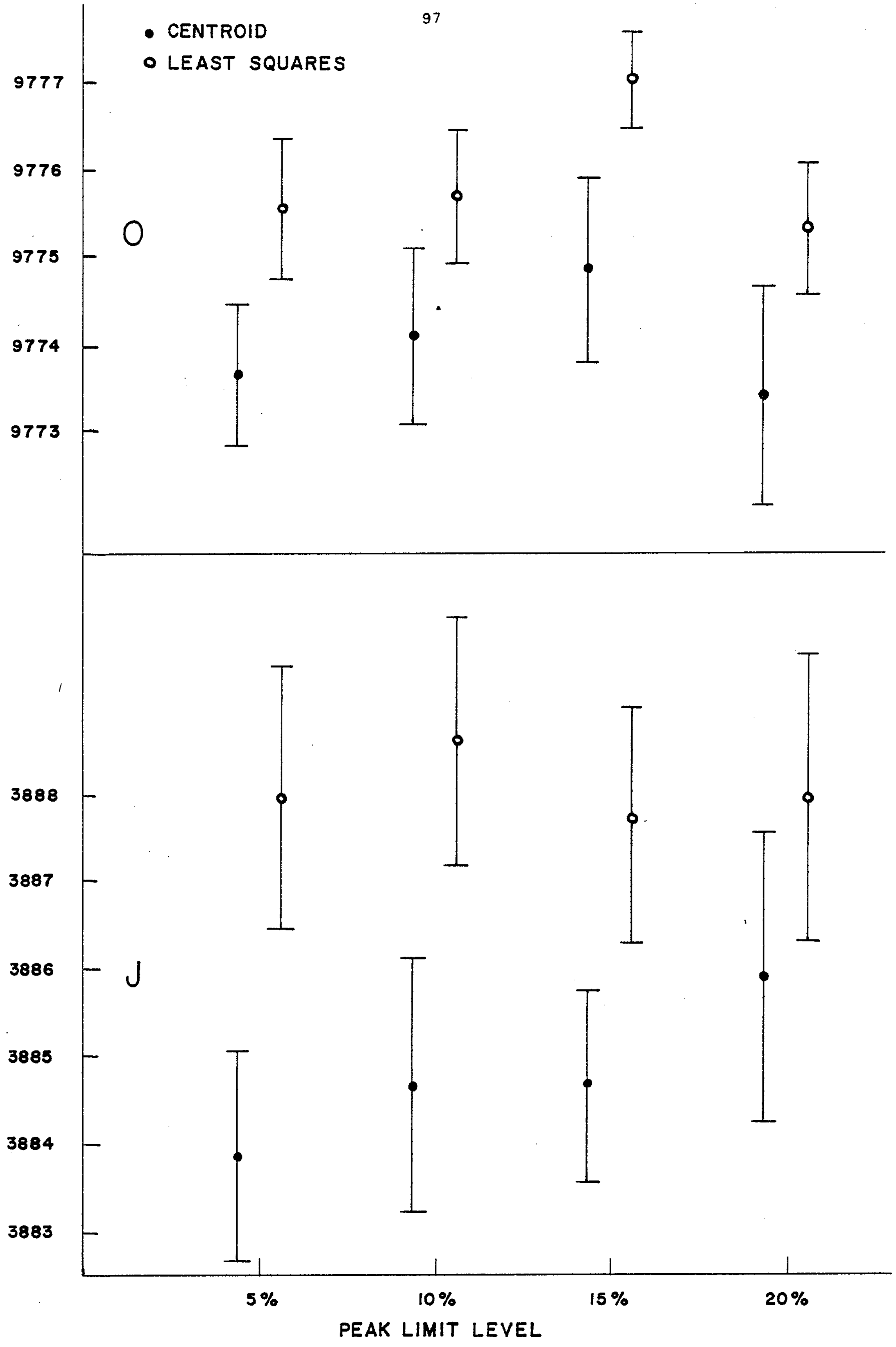


Fig 4-4b Comparison of Centroid and Least Squares ΔM Values
Doublets O and J

being measured is also shown. Doublet N is the only one for which the lighter mass member is the more intense peak. The results are also shown in Figs. 4-4a and 4b.

The following observations may be made:

(1) The ΔM values for the least squares method are in general slightly higher than the centroid values; the only exception is doublet N. This behavior is similar to that discussed in connection with the counting losses (section 4-8) and may indicate the presence of small systematic differences in peak shape.

(2) The ΔM values for both methods show greater variations at the higher levels for the peak limits. The errors for the centroid method tend to increase regularly, while the errors for the least squares method remain relatively constant at the various cut off levels. This behavior is in agreement with that obtained for the artificial data.

(3) For the last three doublets (P, O and J) the ΔM value for the centroid method increases as higher peak limit levels are used. (The 20% level for doublet O is an exception and may reflect the greater variability at the higher cut off levels).

(4) The value of χ^2 for the least squares method is, in every case, greater than 2.0 and generally increases with the "difficulty" of the doublet while decreasing slightly at the higher peak limit levels. This suggests systematic differences in the peak shape for the two doublet members. Such differences could arise from either (i) overlapping peak tails or (ii) an insufficient counting loss correction at the larger intensity ratios.

The intensity ratios obtained by the two methods are presented in Table 4-6 and are compared with the ratios derived from the relative natural abundances of the Hg and Cl isotopes. For the centroid method the ratio is calculated from the peak areas between the peak limits and above the baseline, while for the least squares method the ratio is obtained as one of the fitted parameters.

The following observations may be made:

(1) For both methods the ratios agree with the expected values at smaller ratios and disagree systematically at higher values. The fact that the ratios obtained in this work are invariably smaller than the expected values undoubtedly reflects an insufficient counting loss correction.

TABLE 4-6

COMPARISON OF INTENSITY RATIOS

Doublet	Natural Abundance Ratios		EXPERIMENTALLY DETERMINED RATIOS 5%	10%	15%	20%
L	1.22	a	C: 1.215 ± .002	1.214 ± .002	1.215 ± .002	1.215 ± .002
	1.221 ±.009	b	L: 1.215 ± .002	1.215 ± .002	1.215 ± .002	1.216 ± .002
M	2.01	a	C: 1.988 ± .008	1.989 ± .008	1.990 ± .008	1.988 ± .008
	2.009 ±.015	b	L: 1.989 ± .008	1.988 ± .008	1.987 ± .008	1.986 ± .008
N	2.80	a	C: 2.75 ± .02	2.75 ± .03	2.75 ± .02	2.75 ± .02
	2.79 ±.03	b	L: 2.75 ± .03	2.75 ± .03	2.74 ± .02	2.74 ± .02
K	3.57	a	C: 3.537 ± .008	3.535 ± .007	3.535 ± .027	3.545 ± .007
	3.56 ± .04	b	L: 3.535 ± .007	3.531 ± .007	3.529 ± .006	3.528 ± .006
P	2.87	a	C: 2.86 ± .02	2.86 ± .02	2.86 ± .03	2.86 ± .03
	2.88 ±.03	b	L: 2.87 ± .03	2.86 ± .03	2.86 ± .03	2.86 ± .03
O	28.8	a	C: 26.8 ± .5	26.8 ± .5	26.9 ± .5	27.0 ± .5
	28.6 ±.3	b	L: 27.5 ± .6	27.2 ± .6	26.9 ± .5	26.7 ± .5
J	105.	a	C: 87.1 ±1.2	89.4 ±2.2	90.0 ±2.1	90.7 ±2.1
	101.4 ± 6.6	b	L: 95.9 ±2.5	95.4 ±2.5	94.6 ±2.5	93.6 ±2.4

a Calculated from the Chart of the Nuclides (Holden and Walker, 1972)

b Calculated using Hg Abundances
from Dibeler (1955) and Cl Abundances
from IUPAC (1975)

C: Centroid Method
L: Least Squares Method

(2) The ratios obtained with the least squares method generally agree with the centroid values. The least squares values tend to decrease slightly with increasing peak limit levels, whereas the centroid values show a slight increase.

Some of the doublets listed in Table 4-5 form "closed loops" which provide an additional test of the two methods of analysis. For example, the value determined for doublet M plus the value for doublet K should equal the value determined for doublet O to within the combined errors (see Table 5-1). Doublets N, M and P form a similar closed loop.

The degree to which these loops close for both methods, with the ΔM values obtained with 15% peak limits, is shown in Table 4-7. It is seen that both loops close for the centroid method, whereas only one loop closes for the least squares method. Moreover, the closed loop for the least squares method appears to result from a value for doublet O which is abnormally high (see Table 4-5 and Fig 4-4b). When the values obtained with limits at 20% of the peak height are used, neither method yields closed loops. This likely reflects the larger variations introduced at the higher cut off levels. The loops also fail to close at the lower peak limit levels, however this appears to be the result of overlapping tails for doublets O and P.

TABLE 4-7

COMPARISON OF CLOSED LOOPS

ΔM VALUES at 15% (μu)

DOUBLET	CENTROID METHOD	LEAST SQUARES METHOD
M	5 266.49 ± 0.54	5 267.38 ± 0.41
K	4 509.20 ± 0.63	4 509.66 ± 0.51
	9 775.69 ± 0.83	9 777.04 ± 0.65
O	-9 774.87 ± 1.06	-9 777.05 ± 0.56
	0.82 ± 1.35	-.01 ± 0.86
N	5 800.94 ± 0.58	5 800.53 ± 0.41
M	5 266.49 ± 0.54	5 267.38 ± 0.41
	11 067.43 ± 0.79	11 067.91 ± 0.58
P	-11 066.85 ± 0.55	-11 066.85 ± 0.41
	0.58 ± 0.96	1.06 ± 0.71

The fact that the loops generally fail to close for the least squares method appears to indicate a small systematic bias for this method of analysis. This bias must result from the inherent nature of the real mass spectral data since no discrepancy is observed with the simulated peaks. The discrepancy between the two methods likely reflects small systematic differences in the shape of the peaks for the two doublet members. The least squares method may be more sensitive to differences in peak shape, since for this method, a point by point comparison is made between the two peaks. For this reason the centroid method, although slightly less precise, is recommended for general use at present and is adopted for the experimental results reported in Chapter 5.

4-10. SUMMARY

The following conclusions may be drawn from this investigation of computer peak matching techniques:

(1) The definition of peak limits introduces variations in the ΔM value and reduces the precision of the ΔM determination. These effects are minimized when the peak limits are set at 5% (or less) of the peak height.

(2) The real mass spectral data have a noise level which is greater than anticipated from Poisson counting statistics.

(3) The counting losses are important at the current level of precision and appear to be insufficiently accounted for at present.

(4) The least squares technique promises improved precision which results primarily from the need to define only one set of peak limits. At present, a small systematic bias prevents the general use of this method for real peaks.

(5) The centroid method, although less precise, appears to be unbiased. However precautions must be taken in the case of overlapping peak tails.

From these considerations the centroid values for the doublets listed in Table 4-5 have been adopted for use in Chapter 5. For doublets L, M, N and K the centroid values at 5% have been selected in order to minimize the variations introduced by the peak limits. For doublets O and P, which show a moderate influence of the peak tails, the values at 15% have been selected. For the most difficult doublet, J, the value at 20% was chosen since the centroid ΔM value is still increasing at this peak limit level.

CHAPTER 5

NEW ATOMIC MASS DETERMINATIONS

5-1. NEW MASS SPECTROSCOPIC DOUBLET SEPARATIONS

A total of 16 new doublet separations have been determined with the Manitoba II mass spectrometer. The doublets studied and the ΔM values obtained are presented in Table 5-1.

In the first 9 doublets (A-I), one member of the doublet is composed entirely of carbon and chlorine atoms. Such doublet members act as secondary standards of atomic mass, since the atomic masses of ^{13}C, ^{35}Cl and ^{37}Cl are accurately known relative to ^{12}C (see Table 1-2), and the molecular binding energy of such a fragment is negligible compared to the error associated with the doublet determination. The absolute atomic mass of the other member of the doublet may then be calculated from the doublet separation ΔM. In this manner, direct absolute atomic masses are determined from the first 9 doublets for some of the naturally occurring isotopes of T_i, W and H_g .

The last 7 doublets are mercury chloride doublets of the form

$$^{A+2}H_g\ ^{35}Cl_2 - {}^{A}H_g\ ^{35}Cl\ ^{37}Cl \qquad (5\text{-}1)$$

or

$$^{A+4}H_g\ ^{35}Cl_2 - {}^{A}H_g\ ^{37}Cl_2 \qquad (5\text{-}2)$$

TABLE 5-1

NEW DOUBLET DETERMINATIONS:

	DOUBLET	ΔM (μu)
A	$^{12}\mathrm{C}^{35}\mathrm{Cl}_2 - {}^{47}\mathrm{Ti}^{35}\mathrm{Cl}$	17 085.94 ± 0.82
B	$^{13}\mathrm{C}^{35}\mathrm{Cl}_2 - {}^{48}\mathrm{Ti}^{35}\mathrm{Cl}$	24 261.73 ± 0.75
C	$^{183}\mathrm{W}^{16}\mathrm{O} - {}^{12}\mathrm{C}_2{}^{35}\mathrm{Cl}_5$	100 856.60 ± 2.94
D	$^{186}\mathrm{W}^{16}\mathrm{O} - {}^{13}\mathrm{C}^{12}\mathrm{C}^{35}\mathrm{Cl}_4{}^{37}\mathrm{Cl}$	104 591.41 ± 6.65
E	$^{199}\mathrm{Hg} - {}^{12}\mathrm{C}_2{}^{35}\mathrm{Cl}_5$	124 023.43 ± 0.53
F	$^{200}\mathrm{Hg} - {}^{13}\mathrm{C}^{12}\mathrm{C}^{35}\mathrm{Cl}_5$	120 707.97 ± 1.22
G	$^{201}\mathrm{Hg} - {}^{12}\mathrm{C}_2{}^{35}\mathrm{Cl}_4{}^{37}\mathrm{Cl}$	128 995.43 ± 0.61
H	$^{202}\mathrm{Hg} - {}^{13}\mathrm{C}^{12}\mathrm{C}^{35}\mathrm{Cl}_4{}^{37}\mathrm{Cl}$	125 976.01 ± 1.32
I	$^{204}\mathrm{Hg} - {}^{13}\mathrm{C}^{12}\mathrm{C}^{35}\mathrm{Cl}_3{}^{37}\mathrm{Cl}_2$	131 776.05 ± 1.25
J	$^{198}\mathrm{Hg}^{35}\mathrm{Cl}_2 - {}^{196}\mathrm{Hg}^{35}\mathrm{Cl}^{37}\mathrm{Cl}$	3 885.91 ± 1.66
K	$^{200}\mathrm{Hg}^{35}\mathrm{Cl}_2 - {}^{198}\mathrm{Hg}^{35}\mathrm{Cl}^{37}\mathrm{Cl}$	4 508.80 ± 0.48
L	$^{201}\mathrm{Hg}^{35}\mathrm{Cl}_2 - {}^{199}\mathrm{Hg}^{35}\mathrm{Cl}^{37}\mathrm{Cl}$	4 972.65 ± 0.37
M	$^{202}\mathrm{Hg}^{35}\mathrm{Cl}_2 - {}^{200}\mathrm{Hg}^{35}\mathrm{Cl}^{37}\mathrm{Cl}$	5 266.76 ± 0.43
N	$^{204}\mathrm{Hg}^{35}\mathrm{Cl}_2 - {}^{202}\mathrm{Hg}^{35}\mathrm{Cl}^{37}\mathrm{Cl}$	5 800.67 ± 0.53
O	$^{202}\mathrm{Hg}^{35}\mathrm{Cl}_2 - {}^{198}\mathrm{Hg}^{37}\mathrm{Cl}_2$	9 774.87 ± 1.06
P	$^{204}\mathrm{Hg}^{35}\mathrm{Cl}_2 - {}^{200}\mathrm{Hg}^{37}\mathrm{Cl}_2$	11 066.85 ± 0.55

Five of these doublets (J-N) are of the type (5-1). For these, the doublet separations, ΔM, when combined with the accurately known chlorine mass difference ^{37}Cl - ^{35}Cl, yield two mass unit differences between all the naturally occurring isotopes of Hg. The last two doublets (O and P) are of the type (5-2), involving four mass unit differences between the Hg isotopes and can be used to check the internal consistency of the ΔM values for doublets K to N.

5-2. EXPERIMENTAL RESULTS

A. Titanium Absolute Atomic Mass Determinations

The titanium doublets (A and B in Table 5-1) determined in this work involved the double chloride fragment formed by the dissociation of titanium tetrachloride ($TiCl_4$). The liquid $TiCl_4$ sample was contained in a separate flask which was connected to the ion source by a long plastic tube. The leak rate of the sample vapour was controlled by a needle valve.

Initially the CCl_2^+ reference peaks were obtained as fragments from a hexachloroethane (C_2Cl_6) sample. This substance is a crystalline solid with a relatively high vapour pressure (1 torr at 32.7°C). Hexachloroethane provides convenient reference peaks over a wide mass range which may be easily identified by the ^{35}Cl to ^{37}Cl and ^{12}C to ^{13}C relative abundances. About half the runs for each doublet were obtained using the hexachloroethane sample. The identical reference peaks for the remaining runs were obtained as fragments of carbon tetrachloride ($C\,Cl_4$). The leak rate for this sample was controlled by a second needle valve which facilitated the matching of the intensity ratios for the two peaks of interest.

It should be noted that with the $C_2\,Cl_6$ reference sample some doubly charged ion peaks were observed in the spectrum. For the doublet under study there would then be one component of the reference peaks which was $C\,Cl_2^+$ and a second one which was $C_2\,Cl_4^{++}$. The latter would not necessarily be formed at the same location in the ion source as the former and accordingly the conditions required by Bleakney's Theorem might not be fulfilled. This problem is eliminated by the use of $C\,Cl_4$ as the source material.

The ΔM values for doublets A and B represent the straight averages obtained from 21 and 25 (predominantly computer) runs respectively, taken over a period of a few months. Straight (unweighted) averages have been adopted for the absolute atomic mass determinations since, for these chemically dissimilar doublets, relatively large fluctuations are observed in the ΔM values obtained for different runs. The eight ΔM determinations within a run however, vary by smaller amounts inasmuch as the source conditions and the focusing adjustments are not usually altered during the course of a run. In this case, the standard deviation of the mean for a single run does not accurately represent the uncertainty in the determined ΔM value. Consequently, the use of a weighted average of all the runs is inappropriate.

When the ΔM values are combined with atomic masses for ^{13}C, ^{35}Cl and ^{37}Cl from Table 1-2, the following values are obtained for the atomic masses of ^{47}Ti and ^{48}Ti

$$^{47}Ti = 46.951\ 766\ 82 \pm 82\ u$$

$$^{48}Ti = 47.947\ 945\ 86 \pm 75\ u$$

These atomic mass values are thus based only on the doublets reported in Table 5-1 and do not take into account other precise mass spectroscopic data from this laboratory (Barnard *et al*, 1977). A discussion of this point is deferred to section 5-3A.

B. Tungsten Absolute Atomic Mass Determinations:

For doublets C and D in Table 5-1 the WO peaks were obtained from a W Cl_6 sample which was allowed to oxidize to an oxychloride in air. The $C_2Cl_5^+$ reference peaks were obtained as fragments from a C_2Cl_6 sample. Nine visual runs were used to determine the ΔM value for each doublet. When combined with the atomic masses for ^{13}C, ^{16}O, ^{35}Cl and ^{37}Cl from Table 1-2, the following values are obtained for the atomic masses of ^{183}W and ^{186}W

$$^{183}W = 182.950\ 205\ 78 \pm 2\ 96\ u$$

$$^{186}W = 185.954\ 345\ 28 \pm 6\ 66\ u$$

As in the case of Ti, a discussion of the effects of other precise mass spectroscopic data from this laboratory on these values is deferred to section 5-3B.

C. <u>Mercury Absolute Atomic Mass Determinations</u>:

The mass separations for doublets E to I in Table 5-1 enable the direct determination of absolute atomic masses for ^{199}Hg, ^{200}Hg, ^{201}Hg, ^{202}Hg and ^{204}Hg. These doublets have $\Delta M/M$ values in the range $1/1548 \leq \Delta M/M \leq 1/1656$ and are the widest doublets determined to date with the Manitoba II mass spectrometer.

The reference peaks for these doublets are the same as those used for the tungsten doublets and were again obtained from a hexachloroethane sample. This sample was contained in a glass vial which was connected to the source by a plastic tube. The tube was clamped to control the leak rate of the sample vapour. The mercury sample was contained in a separate copper tube and was heated to equalize the intensities of the Hg^+ and $C_2Cl_5^+$ peaks.

The even-A absolute mass doublets were determined first and proved to be the most difficult to study. Since the reference peaks for the even-A doublets involve the relatively rare ^{13}C isotope (1.11% natural abundance) higher pressures were required in the source region (approximately 1 x 10^{-5} torr). Moreover large total ion currents were present since the reference peaks with ^{12}C at one mass number removed are about 50 times more intense. Consequently the proportional correction (see section 2-3C) applied to the ΔM value for each run had an average value of 115 ± 4 ppm. The ΔM values for these doublets were determined by the visual null method predominantly, with the runs spread over a period of about one month and with each of the three doublets being measured every other day. Relatively large fluctuations were observed in the ΔM values for different runs. The final ΔM values quoted for doublets F, H and I represent the straight averages of 37, 68 and 35 runs respectively. When these values are combined with the atomic masses for ^{13}C, ^{35}Cl and ^{37}Cl from Table 1-2 the following atomic masses are obtained

$$^{200}\mathrm{Hg} = 199.968\ 326\ 60 \pm 1\ 27\ \mathrm{u}$$

$$^{202}\mathrm{Hg} = 201.970\ 644\ 49 \pm 1\ 35\ \mathrm{u}$$

$$^{204}\mathrm{Hg} = 203.973\ 494\ 38 \pm 1\ 29\ \mathrm{u}$$

In contrast, the odd-A doublets E and G proved to be less troublesome. For these doublets the more intense reference peaks with ^{12}C were used enabling the operation of the instrument with the C_2Cl_6 sample almost entirely closed off. The pressure in the source region was reduced to approximately 2×10^{-6} torr and the average proportional correction was also reduced to 70 ± 4 ppm. The fluctuations in the ΔM values for different runs were reduced substantially and a higher precision was achieved with fewer runs. The doublet separations E and G in Table 5-1 represent the straight averages of 30 visual runs each and, when combined with the atomic masses for ^{35}Cl and ^{37}Cl, yield the following atomic masses for ^{199}Hg and ^{201}Hg

$$^{199}Hg = 198.968\ 287\ 23 \pm 64 \text{ u}$$

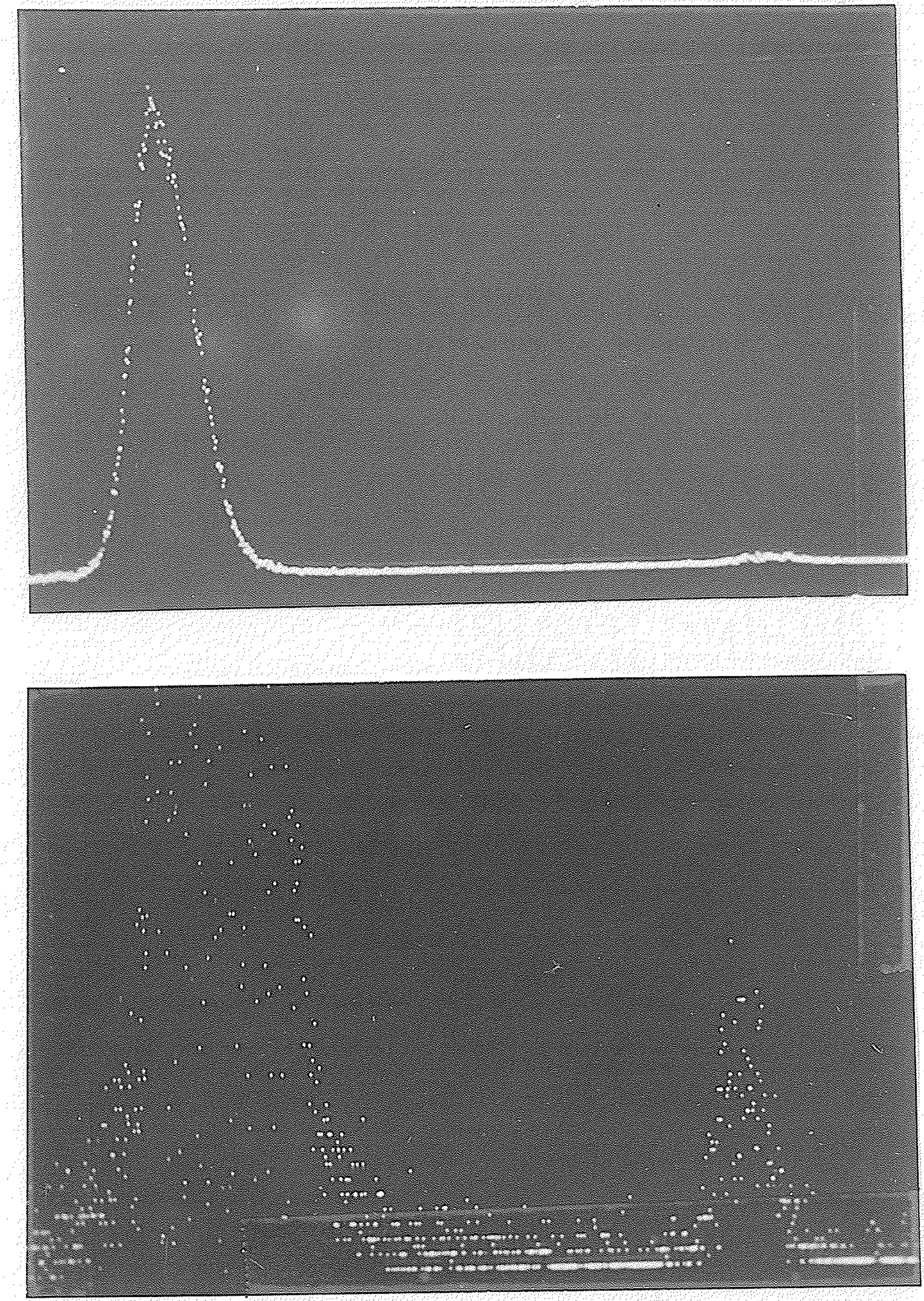
$$^{201}Hg = 200.970\ 309\ 08 \pm 68 \text{ u}$$

The precision achieved for the odd-A absolute atomic mass determinations is about 3.4 parts in 10^9 of the atomic mass.

D. Mercury Mass Difference Determinations:

The mercury chloride doublets J to N in Table 5-1 enable the determination of two mass unit differences between all the naturally occurring isotopes of Hg. The sample used was in the form of Hg Cl_2 and all determinations were performed with the parent ion peaks. This enabled the determination of doublets O and P involving four mass unit differences and also provided more favorable intensity ratios than would be obtained with the fragment ions Hg Cl^+. For example doublet J, which involves the rare ^{196}Hg isotope (.15% natural abundance), could also have been measured using the corresponding Hg Cl doublet. In this case the intensity ratio of the two doublet members is 210 to 1. By using the Hg Cl_2 doublet this ratio is halved to 105 to 1 since there are two ways of selecting the ^{35}Cl and ^{37}Cl atoms for ^{196}Hg ^{35}Cl ^{37}Cl whereas there is only one way in which to form ^{198}Hg $^{35}Cl_2$. This doublet, which has not been previously determined, is illustrated in Fig 5-1 and demonstrates the sensitivity of the mass spectrometer in the pulse counting mode. The small peak typically contained about 3000 ions and corresponds to a detected ion current of approximately 5.3×10^{-17} amperes.

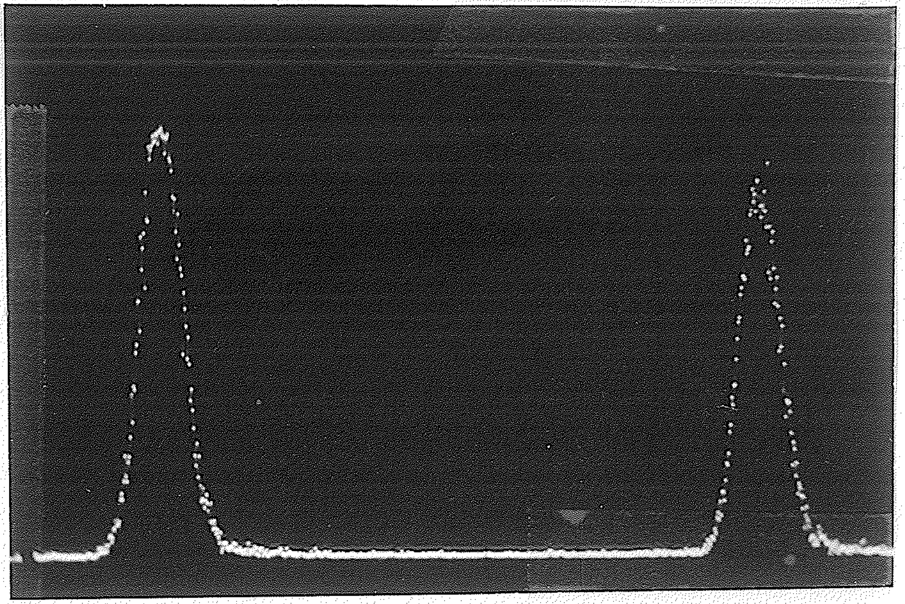
The resolution obtained for the mercury chloride doublets is the highest attained to date with the Manitoba II mass spectrometer. For a single record a resolution of 1 part in 564,000 (measured at 15% of the peak height) was obtained (for doublet O) while a resolution of well over 1 part in 400,000 was obtained for a complete run. The overall average resolution for these doublets would be in the range of 1 part in 250 - 300,000. This high resolution is illustrated in Fig 5-2 which shows spectra for doublets L and P. The frontispiece provides



$^{198}\mathrm{Hg}^{35}\mathrm{Cl}_2$ - $^{196}\mathrm{Hg}^{35}\mathrm{Cl}^{37}\mathrm{Cl}$

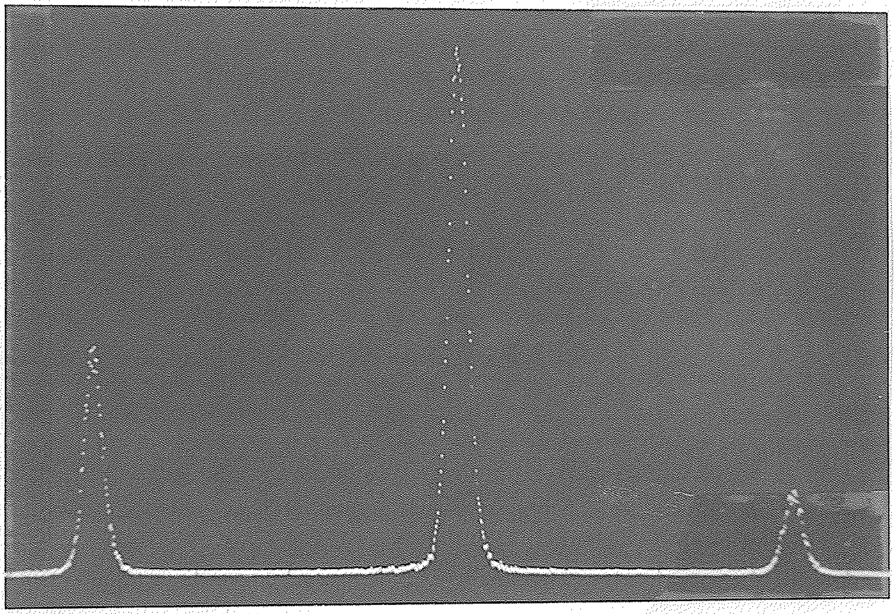
(1/68,900)

Fig 5-1 The Mass Spectrum for Doublet J



$^{201}Hg^{35}Cl_2$ - $^{199}Hg^{35}Cl^{37}Cl$ Doublet L

(1/54,500)



$^{204}Hg^{35}Cl_2$ - $^{202}Hg^{35}Cl^{37}Cl$ - $^{200}Hg^{37}Cl_2$ Doublet P

(1/47,200) (1/52,000)

Fig 5-2 High Resolution

a comparison of the triplet $^{202}\text{Hg}\ ^{35}\text{Cl}_2 - ^{200}\text{Hg}\ ^{35}\text{Cl}^{37}\text{Cl} - ^{198}\text{Hg}^{37}\text{Cl}_2$ obtained with Manitoba II with the slightly wider doublet $^{202}\text{Hg}\ ^{35}\text{Cl} - ^{200}\text{Hg}\ ^{37}\text{Cl}$ obtained in 1964 at McMaster University (Barber et al, 1964) using the 9 ft. radius mass spectrometer now known as Manitoba I.

The ΔM values for doublets J, K, L, M, N, O and P represent the weighted averages of 10, 6, 8, 6, 4, 8 and 10 computer runs respectively with the quoted error being the larger of the internal or external errors as discussed in section 4-3. These doublet separations are compared directly with the corresponding McMaster values (McLatchie et al, 1964) determined with single chloride doublets in Table 5-2. The McMaster values are seen to be systematically higher than the new determinations with deviations which exceed the combined errors. Moreover the present values are more precise by a factor of 4, which appears to correspond to the increase in resolution.

When combined with the accurately known chlorine mass difference from Table 1-2 ($^{37}\text{Cl} - ^{35}\text{Cl} = 1.997\ 049\ 802 \pm 76\text{u}$) the doublets I to P yield the following mass differences between the Hg isotopes.

$$^{198}\text{Hg} - ^{196}\text{Hg} = 2.000\ 935\ 71 \pm 1\ 66\ \text{u}$$

$$^{200}\text{Hg} - ^{198}\text{Hg} = 2.001\ 558\ 60 \pm 49\ \text{u}$$

$$^{201}\text{Hg} - ^{199}\text{Hg} = 2.022\ 022\ 45 \pm 38\ \text{u}$$

$$^{202}\text{Hg} - ^{200}\text{Hg} = 2.002\ 316\ 56 \pm 44\ \text{u}$$

TABLE 5-2

COMPARISON WITH McMASTER DOUBLET SEPARATIONS (μu)

MASS DIFFERENCE	McMASTER[a]	THIS WORK	McMASTER - THIS WORK
$^{200}Hg^{35}Cl - ^{198}Hg^{37}Cl$	4 525 ± 2	4 508.80 ± 0.48	16.2 ± 2.1
$^{201}Hg^{35}Cl - ^{199}Hg^{37}Cl$	4 981 ± 2	4 972.65 ± 0.37	8.4 ± 2.0
$^{202}Hg^{35}Cl - ^{200}Hg^{37}Cl$	5 271 ± 3	5 266.76 ± 0.43	4.2 ± 3.0
$^{204}Hg^{35}Cl - ^{202}Hg^{37}Cl$	5 807 ± 2	5 800.67 ± 0.53	6.3 ± 2.1

[a] McLatchie *et al* (1964)

$$^{204}\mathrm{Hg} - {}^{202}\mathrm{Hg} = 2.002\ 850\ 47 \pm \quad 54\ \mathrm{u}$$

$$^{202}\mathrm{Hg} - {}^{198}\mathrm{Hg} = 4.003\ 874\ 47 \pm 1\ 07\ \mathrm{u}$$

$$^{204}\mathrm{Hg} - {}^{200}\mathrm{Hg} = 4.005\ 166\ 45 \pm \quad 57\ \mathrm{u}$$

5-3. LEAST SQUARES ADJUSMENT OF ATOMIC MASSES

A. Titanium

Absolute atomic masses for all the naturally occurring isotopes of Ti may be established by combining the present determinations for ^{47}Ti and ^{48}Ti with mass differences for Ti previously determined with the Manitoba I and Manitoba II mass spectrometers. The additional doublet separations required have been reported elsewhere (Barnard et al, 1977) and are tabulated in Table 5-3.

A self consistent set of atomic masses and mass differences is obtained from a least squares adjustment of the data shown schematically in Fig 5-3. Inasmuch as the ^{50}Ti - ^{49}Ti mass difference is not overdetermined, the adjustment involves the solution of 6 linear equations in 4 unknowns (the atomic masses of ^{46}Ti, ^{47}Ti, ^{48}Ti and ^{49}Ti). The least squares adjustment follows the procedure applied to this problem originally by Mattauch and his coworkers (Mattauch, 1960) and more recently on a smaller scale by Meredith and Barber (1972) and by Sharma et al (1977b).

TABLE 5-3

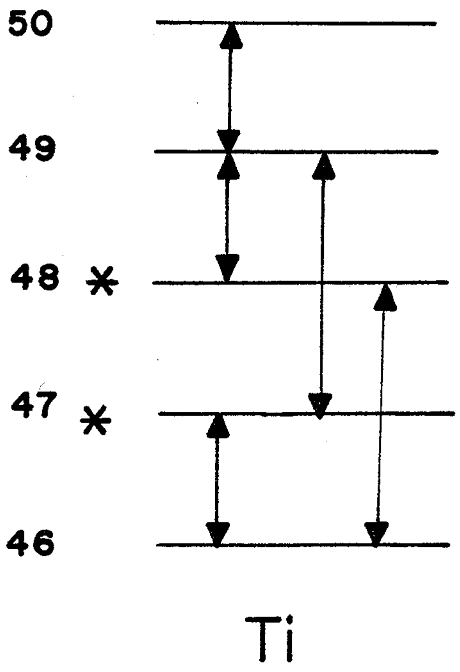
ADDITIONAL DOUBLETS USED FOR Ti ADJUSTMENT [a]

DOUBLET	ΔM (μu)
${}^{46}\mathrm{Ti}{}^{13}\mathrm{C}{}^{12}\mathrm{C}_4\mathrm{H}_5{}^{35}\mathrm{Cl} - {}^{47}\mathrm{Ti}{}^{12}\mathrm{C}_5\mathrm{H}_5{}^{35}\mathrm{Cl}$	4 218.03 ± 0.94
${}^{48}\mathrm{Ti}{}^{13}\mathrm{C}{}^{12}\mathrm{C}_4\mathrm{H}_5 - {}^{49}\mathrm{TiC}_5\mathrm{H}_5$	3 432.64 ± 0.80
${}^{49}\mathrm{Ti}{}^{13}\mathrm{C}{}^{12}\mathrm{C}_4\mathrm{H}_5{}^{37}\mathrm{Cl} - {}^{50}\mathrm{Ti}{}^{12}\mathrm{C}_5\mathrm{H}_5{}^{37}\mathrm{Cl}$	6 440.47 ± 0.88
${}^{46}\mathrm{Ti}{}^{37}\mathrm{Cl}{}^{35}\mathrm{Cl} - {}^{48}\mathrm{Ti}{}^{35}\mathrm{Cl}_2$	1 730.29 ± 0.87
${}^{47}\mathrm{Ti}{}^{35}\mathrm{Cl}{}^{37}\mathrm{Cl} - {}^{49}\mathrm{Ti}{}^{35}\mathrm{Cl}_2$	944.46 ± 0.35

[a] Barnard _et_ _al_ , 1977

Fig 5-3

ATOMIC MASSES AND MASS DIFFERENCES FOR Ti LEAST SQUARES ADJUSTMENT



* denotes an absolute mass determination

A comparison of the input and output values for the adjustment is presented in Table 5-4. The residuals (r_i = output value - input value) and the ratio r_i / σ_i (residual / input error) are also tabulated. The χ^2 for the adjustment is obtained by summing the values of $(r_i/\sigma_i)^2$. The quantity $\sqrt{\chi^2/f}$ (f is the number of degrees of freedom; in this case f = 2) is also calculated and compared with the expected value of $1 \pm 1/\sqrt{2f}$ (Meredith and Barber, 1972).

It is seen that the value of $\sqrt{\chi^2/f}$ is somewhat larger than anticipated, with the greatest contribution to χ^2 arising from the two absolute mass determinations and the ^{49}Ti - ^{48}Ti mass difference. This indicates either that the assigned errors for these determinations may be overly optimistic or that a small systematic error may be present. This apparent discrepancy between the absolute mass determinations and the mass differences will be discussed later in connection with a similar problem with the Hg absolute masses.

The least squares adjusted atomic masses for the Ti isotopes are presented in Table 5-5 and compared with other values. The atomic masses obtained in the present work are seen to be in excellent agreement with the 1975 Midstream Atomic Mass Evaluation values (Wapstra and Bos, 1976) with the possible exception of ^{46}Ti. The agreement is only slightly poorer when the present values are compared with the 1971 Atomic Mass Evaluation values

TABLE 5-4

LEAST SQUARES ADJUSTMENT FOR Ti
(atomic masses and mass differences in u; errors in μu)

Atomic Mass or Mass Difference	Input Value	Output Value	Residual r_i	r_i/σ_i
^{47}Ti	46.951 766 82 ± 0.82	46.951 765 30 ± 0.64	-1.52	-1.85
^{48}Ti	47.947 945 86 ± 0.75	47.947 947 13 ± 0.62	1.27	1.69
^{47}Ti - ^{46}Ti	.999 136 80 ± 0.94	.999 137 28 ± 0.72	.48	.51
^{49}Ti-^{48}Ti	.999 922 19 ± 0.80	.999 923 29 ± 0.60	1.10	1.38
^{48}Ti-^{46}Ti	1.995 319 51 ± 0.87	1.995 319 10 ± 0.70	- .41	- .47
^{49}Ti-^{47}Ti	1.996 105 34 ± 0.36	1.996 105 12 ± 0.34	- .22	- .61
^{50}Ti-^{49}Ti	.996 914 36 ± 0.88	—	—	—

$\chi^2 = 9.04$ $\sqrt{\frac{\chi^2}{f}} = 2.13$ expected value $.50 \le \sqrt{\frac{\chi^2}{f}} \le 1.50$

TABLE 5-5

COMPARISON OF ATOMIC MASSES FOR Ti

Mass (u) (errors in μu)

Nuclide	This Work	Mass Table Values	Minnesota Values	Russian Values[e]
^{46}Ti	45.952 628 03 ± .84	45.952 629 6 ± 1.8[a]	45.952 632 ± 2[c]	45.952 602 ± 8
		631 ± 2[b]	335 ± 40[d]	
^{47}Ti	46.951 765 03 ± .64	46.951 767 0 ± 1.7[a]	46.951 759 ± 3[c]	46.951 691 ± 8
		765 ± 2[b]	733 ± 90[d]	
^{48}Ti	47.947 947 13 ± .62	47.947 949 1 ± 1.5[a]	47.947 947 ± 1[c]	47.947 900 ± 8
		947 ± 1[b]	817 ± 60[d]	
^{49}Ti	48.947 870 42 ± .68	48.947 872 1 ± 1.5[a]	48.947 866 ± 2[c]	48.947 864 ± 8
		871 ± 2[b]	914 ± 50[d]	
^{50}Ti	49.944 784 8 ± 1.1	49.944 784 3 ± 2.7[a]	49.944 789 ± 2[c]	49.944 787 ± 8
		785 ± 3[b]	781 ± 30[d]	

a. 1971 mass table (Wapstra and Gove, 1971)
b. 1975 midstream atomic mass evaluation (Wapstra and Bos, 1976)
c. Giese and Benson, 1958
d. Collins et al, 1952
e. Demirkhanov et al, 1972

(Wapstra and Gove, 1971) and with the more recent Minnesota values (Giese and Benson, 1958). The fairly recent Russian values (Demirkhanov et al, 1972) are seen to be erratic.

Single and two neutron separation energies may be calculated from the atomic masses according to the definitions

$$S_n(Z,N) = n - \left[M(Z,N) - M(Z,N-1) \right] \qquad (5\text{-}3)$$

$$S_{2n}(Z,N) = 2n - \left[M(Z,N) - M(Z,N-2) \right] \qquad (5\text{-}4)$$

These neutron separation energies are derived from the least squares adjusted Ti atomic mass differences using, the mass of the neutron ($n = 1.008\ 665\ 02 \pm 4$ u from Table 1-2), and the mass to energy conversion factor ($1\ u = 931.4935 \pm 28$ MeV from Table 1-1) and are presented in Table 5-6 along with comparison values. The quoted errors for the present work include the covariances obtained from the inverse matrix of the least squares adjustment. In all cases the values obtained from the present work agree either with the 1971 or 1975 Mass Table values.

The 1975 Mass Table values for S_n and S_{2n} are calculated from the mass excesses published by Wapstra and Bos (1976) which are tabulated only to the nearest keV. It is not possible to calculate the errors in the S_n and S_{2n} values thus derived since this requires knowledge of the covariance matrix. These errors however should be generally less than , or equal to , the output errors obtained in the 1971 Mass Evaluation.

TABLE 5-6

S_n And S_{2n} Values For Ti

Isotope	S_n (keV)		S_{2n} (keV)	
	This Work	Comparison Values	This Work	Comparison Values
^{47}Ti	8 875.03 ± 0.67	8 875.1 ± 1.5[a]	----------	----------
		8 878 [b]		
		8 879.0 ± 1.7[c]		
		8 884 ± 7[d]		
^{48}Ti	11 628.01 ± 0.56	11 628.1 ± 1.0[a]	20 503.05 ± 0.65	20 503.2 ± 1.3[a]
		11 627 [b]		20 506 [b]
		11 627.6 ± 1.3[d]		
^{49}Ti	8 142.86 ± 0.56	8 143.4 ± 0.8[a]	19 770.87 ± 0.32	19 771.5 ± 1.0[a]
		8 142 [b]		19 770 [b]
		8 143.0 ± 1.7[c]		
		8 142.3 ± 1.0[d]		
^{50}Ti	10 945.66 ± 0.82	10 948.0 ± 2.0[a]	19 088.53 ± 1.18	19 091.14 ± 2.5[a]
		10 945 [b]		19 088 [b]
		10 949 ± 2 [e]		

a. 1971 Mass Table Output Values (Wapstra and Gove, 1971)
b. Derived from 1975 Midstream Atomic Mass Evaluation (Wapstra and Bos, 1976)
c. (d,p) Jolivette *et al*, (1975)
d. (n,γ) Input Values to 1971 Mass Table
e. (n,γ) Tripathi *et al*, (1969)

B. Tungsten and Rhenium:

A similar least squares adjustment has been performed for W and Re (Sharma et al, 1977a) where the two absolute mass determinations for ^{183}W and ^{186}W are combined with previously determined mass differences linking all the naturally occurring isotopes of W and Re. In this manner new atomic mass values are obtained for all of these nuclides.

The additional doublets required are given in Table 5-7 and the least squares adjustment is shown schematically in Fig 5-4. Inasmuch as the $^{183}W - ^{180}W$ difference is not overdetermined the least squares adjustment involves the solution of 10 linear equations in 6 unknowns (the atomic masses for ^{182}W, ^{183}W, ^{184}W, ^{186}W, ^{185}Re and ^{187}Re).

The input and output values for this adjustment are presented in Table 5-8. The values shown here differ somewhat from those used in Sharma et al (1977a) in that straight averages have been used for the absolute mass determinations (see section 5-2A). Additionally, the atomic masses for ^{13}C and ^{16}O have been obtained from Smith and Wapstra (1974). These modifications alter the values and precision of the adjusted atomic masses to some extent; however the derived quantities (S_n and S_{2n}) are largely unaffected.

TABLE 5-7

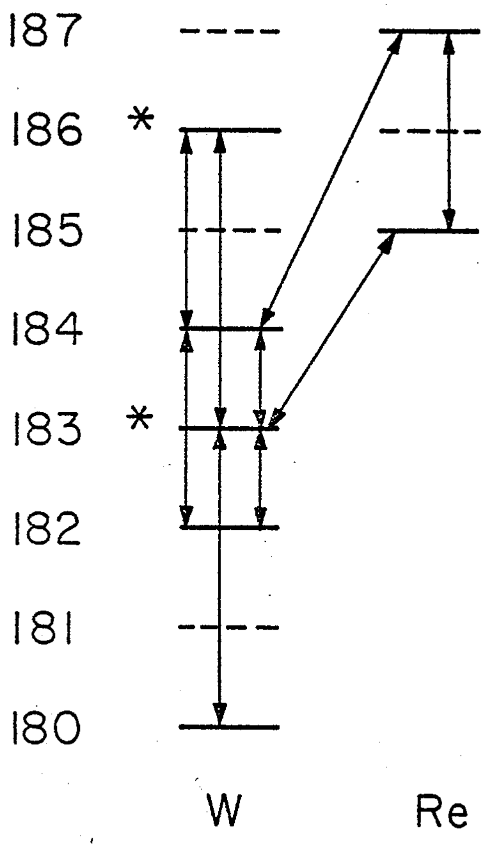
ADDITIONAL DOUBLETS USED FOR W AND Re ADJUSTMENT [a]

DOUBLET	ΔM (μu)
$^{183}W^{16}O_2$ - $^{180}W^{35}Cl$	24 509 ± 6
$^{186}W^{35}Cl$ - $^{184}W^{37}Cl$	6 382.0 ± 1.6
$^{184}W^{35}Cl$ - $^{182}W^{37}Cl$	5 676.3 ± 2.2
$^{184}W^{16}O_2{}^{37}Cl$ - $^{183}W^{35}Cl_2$	18 734.7 ± 3.0
$^{183}W^{16}O_2{}^{37}Cl$ - $^{182}W^{35}Cl_2$	20 045.6 ± 1.8
$^{186}W^{16}O_2$ - $^{183}W^{35}Cl_2$	25 122 ± 5
$^{187}ReO^{35}Cl$ - $^{185}Re^{37}Cl$	5 744.2 ± 1.2
$^{187}ReO_2$ - $^{184}W^{35}Cl$	25 797.4 ± 3.5
$^{185}Re^{35}Cl$ - $^{183}W^{37}Cl$	5 678.7 ± 1.0

[a] Sharma _et al_, 1977a

Fig 5-4

ATOMIC MASSES AND MASS DIFFERENCES FOR W and Re LEAST SQUARES ADJUSTMENT



* denotes an absolute mass determination

TABLE 5-8

LEAST SQUARES ADJUSTMENT FOR W AND Re
Mass u (errors in μu)

Atomic Mass or Mass Difference	Input Value	Output Value	Residual r_i	r_i/σ_i
$^{183}\mathrm{W}$	182.950 205 78 ± 2.96	182.950 205 79 ± 2.73	.01	.00
$^{186}\mathrm{W}$	185.954 345 28 ± 6.66	185.954 345 25 ± 3.22	-.03	.00
$^{183}\mathrm{W}-{}^{182}\mathrm{W}$	1.002 019 59 ± 1.80	1.002 019 40 ± 1.55	-.19	-.11
$^{184}\mathrm{W}-{}^{183}\mathrm{W}$	1.000 708 69 ± 1.68	1.000 706 98 ± 1.68	-1.71	-.57
$^{184}\mathrm{W}-{}^{182}\mathrm{W}$	2.002 726 10 ± 2.19	2.002 726 38 ± 1.71	.28	.13
$^{186}\mathrm{W}-{}^{184}\mathrm{W}$	2.003 431 81 ± 1.63	2.003 432 48 ± 1.53	.67	.41
$^{186}\mathrm{W}-{}^{183}\mathrm{W}$	3.004 145 79 ± 5.00	3.004 139 46 ± 2.10	-6.33	-1.27
$^{185}\mathrm{Re}-{}^{183}\mathrm{W}$	2.002 728 54 ± 1.00	2.002 728 93 ± 0.97	.39	.39
$^{187}\mathrm{Re}-{}^{184}\mathrm{W}$	3.004 821 18 ± 3.52	3.004 816 41 ± 1.99	-4.77	-1.36
$^{187}\mathrm{Re}-{}^{185}\mathrm{Re}$	2.002 793 95 ± 1.15	2.002 794 46 ± 1.11	.51	.44
$^{183}\mathrm{W}-{}^{180}\mathrm{W}$	3.003 532 97 ± 5.83	—	—	—

$\chi^2 = 4.33$ $\sqrt{\frac{\chi^2}{f}} = 1.04$ expected value $.65 \le \sqrt{\frac{\chi^2}{f}} \le 1.35$

In Table 5-8 it is seen that the absolute atomic mass determinations for ^{183}W and ^{186}W remain essentially unchanged by the adjustment, although the determination of the difference $^{186}W - {}^{183}W$ changes by 6.33 μu. The χ^2 for this adjustment agrees with the expected value.

The least squares adjusted atomic masses obtained for W and Re are presented in Table 5-9 and are compared with other values. It is evident that the new atomic mass values differ systematically by ~60 μu from the 1971 Mass Table values and by ~35 μu from the 1975 Midstream Atomic Mass Evaluation. Inasmuch as the previous absolute mass determinations for these nuclides are relatively imprecise (columns 3 and 4 in Table 5-9), this discrepancy likely reflects an accumulation of small systematic errors in a chain of mass differences linking W and Re to other nuclides whose atomic masses are more accurately known.

Recent absolute mass determinations for Er, Hf and Os performed at Minnesota (Halverson, 1977) indicate similar deviations of 44, 28 and 50 μ u respectively from the 1971 mass table values and deviations of 24, 13 and 18 μu respectively from the 1975 mass evaluation. One of these absolute mass determinations, $^{189}Os = 188.958\ 1383 \pm 52$ u (Halverson, 1977), may be compared with the mass of ^{187}Re from Table 5-9 by means of the McMaster chloride doublet $^{189}Os\ ^{35}Cl - {}^{187}Re\ ^{37}Cl = 5341 \pm 3\ \mu$u (McLatchie _et_ _al_, 1970). When the calculation is performed this loop fails

TABLE 5-9

COMPARISON OF ATOMIC MASSES FOR W AND Re

Mass (u) (errors in μu)

Nuclide	This Work	Mass Table Values	Minnesota Values[c]	Russian Values[d]
$^{180}\mathrm{W}$	179.946 672 8 ± 6.4	179.946 700 ± 210[a] 724 ± 12[b]	----------	179.946 450 ± 130
$^{182}\mathrm{W}$	181.948 186 4 ± 3.1	181.948 248 ± 13[a] 223 ± 11[b]	181.948 152 ± 40	181.948 385 ± 250
$^{183}\mathrm{W}$	182.950 205 8 ± 2.7	182.950 266 ± 13[a] 241 ± 9[b]	182.950 108 ± 40	182.950 248 ± 70
$^{184}\mathrm{W}$	183.950 912 8 ± 3.1	183.950 975 ± 13[a] 950 ± 9[b]	----------	183.950 735 ± 100
$^{186}\mathrm{W}$	185.954 345 3 ± 3.2	185.954 402 ± 14[a] 372 ± 9[b]	185.954 299 ±130	185.954 619 ± 70
$^{185}\mathrm{Re}$	184.952 934 7 ± 2.9	184.953 007 ± 14[a] 952 973 ± 9[b]	184.952 603 ± 80	184.953 262 ± 90
$^{187}\mathrm{Re}$	186.955 729 2 ± 3.1	186.955 791 ± 14[a] 759 ± 9[b]	----------	186.955 907 ± 30

a. 1971 Mass Table (Wapstra and Gove, 1971)
b. 1975 Midstream Atomic Mass Evaluation (Wapstra and Bos, 1976)
c. Bhanot et al, 1960
d. Demirkhanov et al, 1961

to close by 18 $\pm$ 7 μu; however this discrepancy is about one half of that between the 1975 mass evaluation values and those obtained in the present work.

The S_n and S_{2n} values calculated from the least squares adjusted atomic masses for W and Re are presented in Tables 5-10 and 5-11. The S_n values for ^{185}W, ^{186}W and ^{187}W were derived by combining the mass spectroscopic differences with Q_β values for ^{185}W and ^{187}W as indicated. In contrast with the absolute masses, the S_n and S_{2n} values are seen to be in good agreement with the mass table values and with other recent measurements.

C. Mercury:

The input data for the least squares adjustment for mercury are illustrated schematically in Fig 5-5. Initially only the mass spectroscopic data shown were adjusted. In this case the adjustment is divided into two separate least squares adjustments, inasmuch as no direct mass difference determination between the even -A and odd -A isotopes was made in the present work. For the even -A adjustment the ^{198}Hg - ^{196}Hg mass difference is not overdetermined, so that the adjustment involves the solution of 8 linear equations in 4 unknowns (viz the atomic masses of ^{198}Hg, ^{200}Hg, ^{202}Hg and ^{204}Hg). The odd -A adjustment involves the solution of 3 equations in 2 unknowns (the atomic masses for ^{199}Hg and ^{201}Hg). The results of these adjustments are presented in Table 5-12. The absolute mass determinations are seen to be in excellent agreement with the mass spectroscopic mass difference determinations.

TABLE 5-10

S_{2n} FOR W AND Re (keV)

Nuclide	This Work	Mass Tables		Other
^{182}W	14 732.9 ± 5.6	14 700 ± 200	a	14 755 ± 7 c
		14 747	b	14 743 ±10 d
^{184}W	13 603.2 ± 1.6	13 602.5 ± 1.9	a	13 609 ± 7 c
		13 603	b	13 606 ± 5 d
^{186}W	12 945.5 ± 1.4	12 951.8 ± 3.4	a	12 956 ± 5 d
		12 955	b	
^{187}Re	13 539.8 ± 1.0	13 550.4 ± 3.4	a	
		13 548	b	

a. 1971 Mass Table Output Values (Wapstra and Gove, 1971)
b. Derived from 1975 Midstream Atomic Mass Evaluation (Wapstra and Bos, 1976)
c. Casten *et al*, (1976)
d. Oothoudt and Hintz (1973)

TABLE 5-11

S_n FOR W (keV)

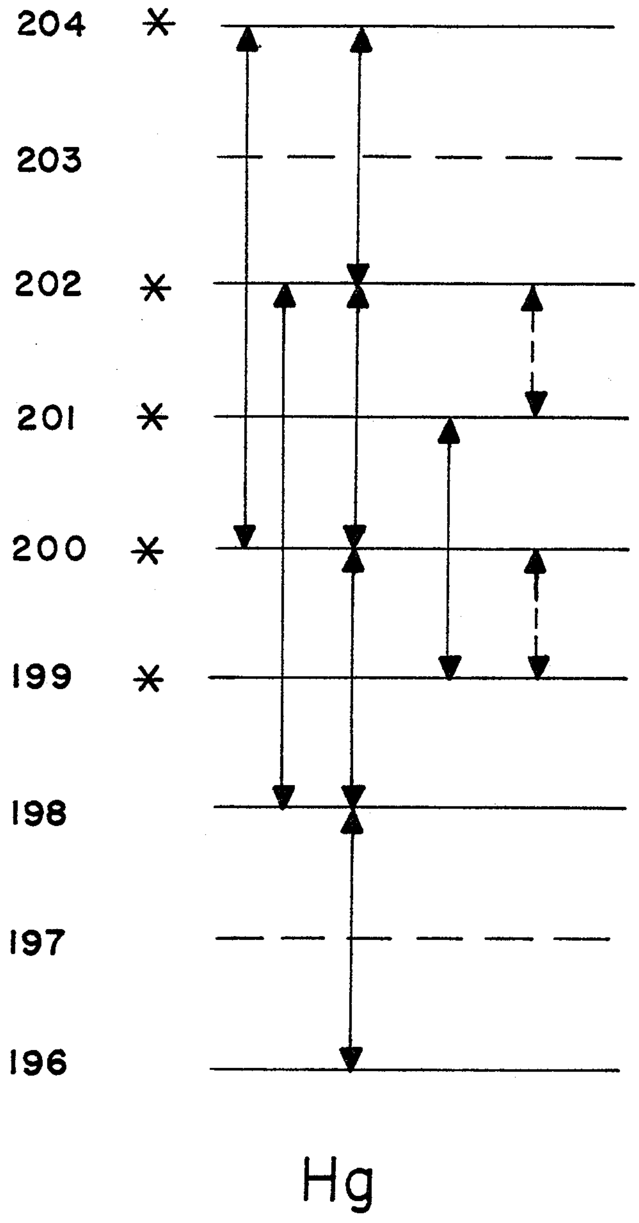
Nuclide	This Work		Tabulated Values		Other	
^{183}W	6190.4 ± 1.4		6191.4 ± 1.4	a	6201 ± 15	d
			6191	b	6204 ± 10	d
			6191.0 ± 2.5	c		
^{184}W	7412.9 ± 1.6		7411.1 ± 1.4	a	7411.1 ± 0.6	e
			7411	b	7412 ± 8	d
			7413.0 ± 3.5	c		
^{185}W	5755.4 ± 2.0	f	5749.7 ± 3.1	a	5758 ± 10	d
			5753	b		
^{186}W	7190.1 ± 2.3	f	7202.0 ± 3.8	a	7197 ± 10	d
			7201	b		
^{187}W	5470.3 ± 3.0	g	5466.1 ± 1.4	a	5465 ± 10	d
			5466	b		
			5465 ± 4.0	c		

---

a. 1971 Mass Table Output Values (Wapstra and Gove, 1971)
b. Derived from 1975 Midstream Atomic Mass Evaluation (Wapstra and Bos, 1976)
c. Nuclear Data Tables (Groshev *et al*, 1969)
d. Casten *et al*, (1972)
e. Greenwood and Reich (1974)
f. Calculated with Q_β = 432.6 ± 1.0 keV for $^{185}\mathrm{W}(\beta^-)^{185}\mathrm{Re}$ (Willet and Spejewski, 1967)
g. Calculated with Q_β = 1312 ± 2 keV for $^{187}\mathrm{W}(\beta^-)^{187}\mathrm{Re}$ (Wapstra and Gove, 1971)

Fig 5-5

ATOMIC MASSES AND MASS DIFFERENCES
FOR Hg LEAST SQUARES ADJUSTMENT



* denotes an absolute mass determination

-- denotes (n,γ) reaction values

TABLE 5-12

LEAST SQUARES ADJUSTMENT FOR Hg

(atomic masses and mass differences in u; errors in μu)

Atomic Mass or Mass Difference	Input Value	Output Value	Residual r_i	r_i/σ_i
^{200}Hg	199.968 326 60 ± 1.27	199.968 327 42 ± 0.78	.82	.65
^{202}Hg	201.970 644 49 ± 1.35	201.970 643 84 ± 0.78	-.65	-.48
^{204}Hg	203.973 494 38 ± 1.29	203.973 494 13 ± 0.79	-.25	-.19
^{200}Hg-^{198}Hg	2.001 558 60 ± 0.49	2.001 558 50 ± 0.45	-.10	-.20
^{202}Hg-^{200}Hg	2.002 316 56 ± 0.44	2.002 316 43 ± 0.36	-.13	-.30
^{204}Hg-^{202}Hg	2.002 850 47 ± 0.54	2.002 850 28 ± 0.42	-.19	-.35
^{202}Hg-^{198}Hg	4.003 874 47 ± 1.07	4.003 874 93 ± 0.53	.46	.43
^{204}Hg-^{200}Hg	4.005 166 45 ± 0.57	4.005 166 71 ± 0.42	.26	.46
^{198}Hg-^{196}Hg	2.000 935 71 ± 1.66			

$\chi^2 = 1.34$ $\sqrt{\frac{\chi^2}{f}} = 0.58$ expected value $.65 \leq \sqrt{\frac{\chi^2}{f}} \leq 1.35$

Atomic Mass or Mass Difference	Input Value	Output Value	Residual r_i	r_i/σ_i
^{199}Hg	198.968 287 23 ± 0.64	198.968 286 99 ± 0.49	-.24	-.38
^{201}Hg	200.970 309 08 ± 0.68	200.970 309 35 ± 0.50	.27	.40
^{201}Hg-^{199}Hg	2.002 022 45 ± 0.38	2.002 022 36 ± 0.35	-.09	-.24

$\chi^2 = 0.36$ $\sqrt{\frac{\chi^2}{f}} = .60$ expected value $.29 \leq \sqrt{\frac{\chi^2}{f}} \leq 1.71$

The results of this adjustment may be directly compared with two precise S_n values obtained from (n,γ) reaction measurements:

(1) S_n (^{200}Hg) = 8 028.8 ± 0.5 keV (Schult et al, 1967; Bartholomew et al, 1967).

(2) S_n (^{202}Hg) = 7 754.1 ± 0.3 keV (Breitig et al, 1975); a correction of .2 keV has been applied to the ground state transition γ ray energy reported, in order to account for the recoil energy of the atom).

The corresponding S_n values calculated from the adjusted atomic masses of Table 5-12 are 8033.7 ± .9 keV and 7759.8 ± .9 keV. The differences between the mass spectroscopic values and the (n,γ) reaction values are then 4.9 ± 1.0 keV and 5.7 ± 0.9 keV respectively. Since the (n,γ) values appear to be reliable, this discrepancy undoubtedly reflects a systematic bias of about 5.3 keV (5.7 μu) between the even -A and odd -A absolute atomic mass determinations. A discussion of this systematic discrepancy is deferred to section 5-4.

In view of the discrepancy, the (n,γ) reaction values were included in a second adjustment of the mercury data in order to insure that the mass differences between the even -A and odd -A isotopes do not include a systematic error. A consistency factor (Wapstra and Gove, 1971) of 2.59 was determined for the absolute mass determinations from the average value of r_i / σ_i for this group of data. A final adjustment of the data was then performed with the input errors for the absolute mass determinations enlarged by the consistency factor. This procedure insures that the absolute mass determinations do not substantially influence the mass differences, yet still enables the establishment of atomic masses for the Hg isotopes. However, it must be emphasized that the atomic masses so obtained will likely contain a systematic bias of 2.8μu, inasmuch as the average mass obtained from the absolute mass determinations is unaltered by the adjustment. This procedure has been followed since, at present, there is no firm evidence to support the selective rejection of either the even -A or odd -A absolute mass determinations.

The results of this adjustment are presented in Table 5-13. It is seen that the absolute mass determinations are altered substantially in order to accommodate the (n,γ) reaction values. The even -A values increase while the odd -A values decrease by amounts which are related to their assigned errors. In contrast, the mass spectroscopic mass differences and the (n,γ) values are modified only slightly.

The least squares adjusted atomic masses are compared with other values in Table 5-14. The values from the present work are seen to be, on the average, 10μu higher than the 1971

TABLE 5-13

LEAST SQUARES ADJUSTMENT FOR Hg

(atomic masses and mass differences in u; errors in μu)

Atomic Mass or Mass Difference	Input Value	Output Value	Residual r_i	r_i/σ_i
^{199}Hg	198.968 287 23 ± 1.66*	198.968 285 47 ± 1.04	-1.76	-1.06
^{200}Hg	199.968 326 60 ± 3.29*	199.968 331 51 ± 1.07	4.91	1.49
^{201}Hg	200.970 309 08 ± 1.76*	200.970 307 67 ± 1.04	-1.41	- .80
^{202}Hg	201.970 644 49 ± 3.50*	201.970 648 10 ± 1.06	3.61	1.03
^{204}Hg	203.973 494 38 ± 3.34*	203.973 498 23 ± 1.10	3.85	1.15
^{200}Hg-^{198}Hg	2.001 558 60 ± 0.49	2.001 558 48 ± 0.45	- .12	- .24
^{201}Hg-^{199}Hg	2.002 022 45 ± 0.38	2.002 022 21 ± 0.33	- .24	- .63
^{202}Hg-^{200}Hg	2.002 316 56 ± 0.44	2.002 316 59 ± 0.33	.03	.07
^{204}Hg-^{202}Hg	2.002 850 47 ± 0.54	2.002 850 13 ± 0.42	- .34	- .63
^{202}Hg-^{198}Hg	4.003 874 47 ± 1.07	4.003 875 07 ± 0.52	.60	.56
^{204}Hg-^{200}Hg	4.005 166 45 ± 0.57	4.005 166 72 ± 0.43	.27	.47
^{200}Hg-^{199}Hg	1.000 045 74 ± 0.54	1.000 046 05 ± 0.40	.31	.57
^{202}Hg-^{201}Hg	1.000 340 65 ± 0.32	1.000 340 43 ± 0.29	- .22	- .69
^{198}Hg-^{196}Hg	2.000 935 71 ± 1.66			

$\chi^2 = 8.56$ $\sqrt{\frac{\chi^2}{f}} = 1.11$ expected value $.73 \le \sqrt{\frac{\chi^2}{f}} \le 1.27$

* including consistency factor of 2.59

TABLE 5-14

COMPARISON OF ATOMIC MASSES FOR Hg

Mass (u) (errors in μu)

Nuclide	This Work	Mass Table Values	Minnesota Values[c]	Russian Values[d]
^{196}Hg	195.965 837 3 ± 2.0	195.965 822 ± 13[a]	195.965 836 ± 8	
		823 ± 12[b]		
^{198}Hg	197.966 773 0 ± 1.2	197.966 748 ± 6[a]	197.966 756 ± 7	
		759 ± 6[b]		
^{199}Hg	198.968 285 5 ± 1.0	198.968 275 ± 6[a]	198.968 234 ± 10	
		269 ± 6[b]		
^{200}Hg	199.968 331 5 ± 1.1	199.968 321 ± 6[a]	199.968 341 ± 5	
		315 ± 6[b]		
^{201}Hg	200.970 307 7 ± 1.0	200.970 304 ± 6[a]	200.970 302 ± 9	
		293 ± 6[b]		
^{202}Hg	201.970 648 1 ± 1.1	201.970 643 ± 6[a]	201.970 628 ± 8	201.970 617 ± 40
		632 ± 6[b]		201.970 678 ± 60
^{204}Hg	203.973 498 2 ± 1.1	203.973 498 ± 6[a]	203.973 476 ± 8	
		481 ± 8[b]		

a. 1971 Mass Table Output Values (Wapstra and Gove, 1971)
b. 1975 Midstream Atomic Mass Evaluation (Wapstra and Bos, 1976)
c. Benson et al, (1959)
d. Demirkhanov and Dorokhov (1969)

Mass Table values and 16μu higher than the 1975 Midstream Atomic Mass Evaluation values. As discussed in section 5-3B above, similar discrepancies have been found by this group for W and Re and by Halverson (1977) for Er, Hf and Os. These discrepancies reflect the scarcity of precise absolute mass determinations for the heavier nuclides.

The S_n and S_{2n} values derived from the least squares adjusted values are presented in Table 5-15. The S_n values are seen to be in excellent agreement with the 1975 Midstream Atomic Mass Evaluation values, although for ^{200}Hg and ^{202}Hg this reflects primarily the inclusion of the (n,γ) values in the present least squares adjustment. The derived S_{2n} values, which reflect primarily the mass spectroscopic mass difference determinations, are also seen to be in excellent agreement with the 1975 Midstream Atomic Mass Evaluation values.

5-4. DISCUSSION OF THE RESULTS

A. Absolute Atomic Mass Determinations:

The absolute atomic masses determined for Ti in the present work are in excellent agreement with the values obtained from the 1975 Midstream Atomic Mass Evaluation. In contrast, the absolute mass determinations for W and Hg indicate that the 1975 values for these heavier nuclides are in error by amounts which exceed the already large output errors. This reflects the

TABLE 5-15

NEUTRON SEPARATION ENERGIES FOR Hg

S_n (keV)

NUCLIDE	THIS WORK	COMPARISON VALUES	
^{199}Hg	6 662.59 ± 0.59	6 648.8 ± 2.8	a
		6 664	b
^{200}Hg	8 028.51 ± 0.37	8 028.7 ± 0.5	a
		8 028	b
^{201}Hg	6 230.63 ± 0.36	6 225.4 ± 2.3	a
		6 229	b
^{202}Hg	7 754.30 ± 0.27	7 755.6 ± 1.4	a
		7 755	b

S_{2n} (keV)

NUCLIDE	THIS WORK	COMPARISON VALUES	
^{198}Hg	15 271.2 ± 1.5	15 281 ± 12	a
		15 271	b
^{200}Hg	14 691.10 ± 0.42	14 677.6 ± 2.8	a
		14 693	b
^{201}Hg	14 259.14 ± 0.31	14 254.1 ± 2.3	a
		14 258	b
^{202}Hg	13 984.93 ± 0.31	13 980.9 ± 2.5	a
		13 985	b
^{204}Hg	13 487.94 ± 0.39	13 483.5 ± 2.6	a
		13 489	b

---

a 1971 Atomic Mass Evaluation output values (Wapstra and Gove, 1971)

b Derived from 1975 Midstream Atomic Mass Evaluation (Wapstra and Bos, 1976) imprecise nature of previous absolute mass determinations in this mass region, as illustrated by the uncertainties shown in Fig 2-3. The values obtained in the present work, which are currently the most precise absolute mass determinations above A = 40, will improve this situation significantly. In particular, the determinations for W and Hg strategically bracket the region of highest uncertainty (A = 193 - 194).

The present work indicates that the 1975 Midstream Atomic Evaluation values for W are too high whereas the values for Hg are too low. Thus the discrepancy is enlarged when one compares, for example, the mass difference between $^{200}\mathrm{Hg}$ and $^{184}\mathrm{W}$ as shown below

$$
\begin{array}{rll}
{}^{200}\mathrm{Hg} - {}^{184}\mathrm{W} = & 16.017\ 419 \pm 3 & \text{u (this work)} \\
- & 16.017\ \underline{365} \pm 11 & \text{u (Wapstra and Bos, 1976)} \\
 & \qquad\quad\ 54 \pm 11\,\mu\text{u} &
\end{array}
$$

This difference could be confirmed by future doublet determinations of mixed doublets such as $^{184}\mathrm{W}^{16}\mathrm{O} - {}^{200}\mathrm{Hg}$ or $^{184}\mathrm{W}^{16}\mathrm{O}^{35}\mathrm{Cl} - {}^{200}\mathrm{Hg}^{35}\mathrm{Cl}$. Such doublets would test the reliability of the absolute mass determinations reported in this work and in addition would establish a connection between mass regions which at present are not firmly linked by precise mass spectroscopic determinations.

The high precision of the absolute mass determinations reported in this work has enabled the detection of a small systematic bias between the even -A and odd -A determinations for Hg. A similar, but less significant, discrepancy may also be present in the Ti absolute mass determinations since these values change somewhat in the least squares adjustment of the Ti data. In the case of W, the errors on both the absolute mass determinations and the mass difference determinations are too large to detect such a discrepancy.

This discrepancy likely reflects the fact that the even -A absolute mass determinations were obtained with reference peaks which involve the rare ^{13}C isotope. In this case higher pressures in the source region are required which may lead to a differential retardation of chemically dissimilar ions as discussed in section 2-3C. Chemically dissimilar ions may thus appear to lie on separate mass scales which are displaced by an amount proportional to the residual gas pressure. This effect could be investigated by redetermining one of the even -A absolute masses for Hg using a reference sample which is enriched in ^{13}C.

B. S_{2n} Values for Hg:

The S_{2n} values derived from the even -A Hg mass differences from the present work are plotted in Fig 5-6 along with the S_{2n} values for other even -N even -Z nuclides for $106 \leq N \leq 126$.

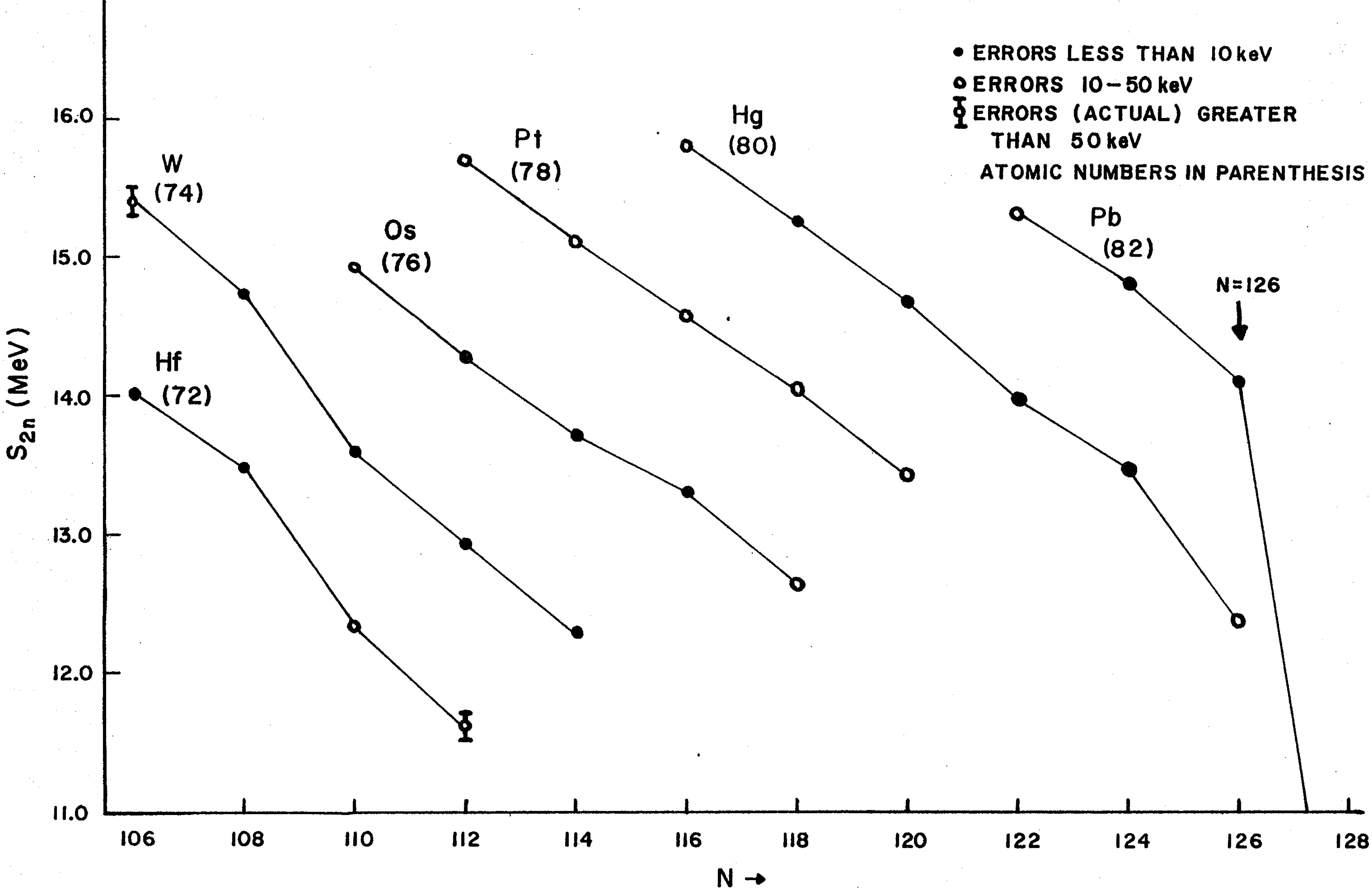


Fig 5-6 S_{2n} Values for Even-N Even-Z Nuclides for $106 \leq N \leq 126$

The S_{2n} values derived from the 1975 Midstream Atomic Mass Evaluation mass excesses have been used to supplement the values obtained in the present work, in light of the excellent agreement shown for Hg. The errors for the supplementary values have been taken as the smaller of the errors calculated from the 1975 mass excesses or the 1971 Mass Evaluation output errors (see section 5-3A). The lower mass region containing the S_{2n} curve for W has been discussed recently in Sharma et al (1977a).

In the region above the Hg curve, it is seen that the curve for Pb shows a pronounced downward break characteristic of the well known closed neutron shell at N = 126. On the low mass side, the curve for Pt is remarkably free of such discontinuities (A comparison with previous representations (Duckworth et al, 1969; Bhanot et al, 1960) shows that gradually the curve for Pt has been straightened out). The curve for Hg is intermediate between these two extremes and shows some interesting features.

In recent years a great deal of theoretical and experimental interest has been focused on the Hg isotopes, following the prediction that the low-lying excited states, perhaps even the ground states, of ^{184}Hg and ^{200}Hg may be "bubble nuclei" (ie. nuclei with a reduced central core density) (Wong, 1972, 1973). Single particle shell model calculations show that the "magic numbers" are altered in the bubble configuration, such that the neutrons form closed shells at N = 104 and 120, while the proton shell is closed at Z = 80. This results in doubly magic configurations for ^{184}Hg and ^{200}Hg. In the case of ^{184}Hg, the large values observed for the nuclear radius in this region (Bonn et al, 1972) have been explained alternatively in terms of a change in the distortion of the nucleus (Nilsson et al, 1973). For ^{200}Hg a small oblate deformation of the nucleus has been indicated for the ground state, although the bubble configuration has not yet been ruled out for one of the low lying excited states (Kolb and Wong, 1975; Breitig et al, 1974). The mass region surrounding ^{200}Hg appears to be of a transitional character (Breitig et al, 1974, 1975) in that it lies between the oblate ^{199}Tl (Nakai, 1971) and the spherical ^{208}Pb nuclei.

The subtleties observed in the S_{2n} curve for Hg appear to be explained in terms of the usual single particle level schemes. Thus the downward break at ^{204}Hg (N = 124), pointed out previously in McLatchie et al (1964), reflects the filling of the $P_{\frac{1}{2}}$ state for this nucleus. A similar effect is observed for Pb at N = 124. Similarly the smaller downward break at ^{200}Hg (N = 120) is interpreted to reflect the filling of the $p_{3/2}$ level which lies above the $f_{5/2}$ level. The $p_{3/2}$ and $f_{5/2}$ states, which lie close together in ^{208}Pb, are separated by a significant amount even for a spherical ^{200}Hg nucleus (Kolb and Wong, 1975).

REFERENCES

Aston, F.W. (1919). Phil. Mag. 38, 707.

Bainbridge, K.T. and Jordan, E.B. (1936). Phys. Rev. 50, 282.

Barber, R.C., Bishop, R.L. Cambey, L.A., Duckworth, H.E., Macdougall, J.D., McLatchie, W., Ormrod, J.H. and Van Rookhuyzen, P. (1964). Nuclidic Masses, ed. by W.H. Johnson, Jr. (Springer-Verlag, Wien), p. 393.

Barber, R.C., Meredith, J.O., Bishop, R.L., Duckworth, H.E., Kettner, M.E. and Van Rookhuyzen, P. (1967). Pro. of the Third Int. Conf. on Atomic Masses, ed. by R.C. Barber (Univ. of Manitoba, Winnipeg), p. 717.

Barber, R.C., Bishop, R.L., Duckworth, K.E., Meredith, J.O., Southon, R.C.G., Van Rookhuyzen, P. and Williams, P. (1971). Rev. Sci. Instr. 42, 1.

Barber, R.C., Barnard, J.W., Haque, S.S., Kozier, K.S., Meredith, J.O., Sharma, K.S., Southon, F.C.G., Williams, P. and Duckworth, H.E. (1976). Atomic Masses and Fundamental Constants, Vol 5, ed. by J.H. Sanders and A.H. Wapstra (Plenum Publishing Corp., London), p.1

Barnard, J.W., Williams, P., Barber, R.C., Haque, S.S., Kozier, K.S., Sharma, K.S. and Duckworth, H.S. (1977). Can. J. Phys. 55, 200.

Bartholomew, G.A., Naqvi, S.I.H., Gunye, M.R. and Earle, E.D. (1967). Can. J. Phys. 45, 1517.

Benson, J.L., Damerov, R.A. and Ries, R.R. (1959). Phys. Rev., A113, 1105.

Benson, J.L. (1965). PhD. Thesis, U. of Minnesota.

Benson, J.L. and Johnson, W.H. (1966). Phys. Rev. 141, 1112.

Berghvist, K.E. (1972). Atomic Masses and Fundamental Constants, Vol 4, ed. by J.H. Sanders and A.H. Wapstra (Plenum Publishing Corp., London), p.77.

Bevington, P.R. (1969). Data Reduction and Error Analysis for the Physical Sciences (McGraw-Hill Book Co.,New York),p.204.

Bhanot, V.B., Johnson, W.H. Jr. and Nier, A.O. (1960). Phys. Rev. 120, 325.

Birge, R.T. (1932). Phys. Rev. 40, 207.

Bishop, R.L. (1969). PhD. Thesis, U. of Manitoba.

Bishop, R.L. and Barber, R.C. (1970). Rev. Sci. Instr. 42, 327.

Bleakney, W. (1936). Am. Phys. Teacher 4, 12.

Bonn, J., Huber, G., Kluge, H.J., Kopf, U., Kugler, L. and Otten, E.W. (1972). Phys. Lett. 38 B, 308.

Brans, C.H. and Dicke, R.H. (1961) Phys. Rev. 124 P. 925

Breitig, D., Casten R.F. and Cole, G.W. (1974). Phys. Rev. C 9, 366.

Breitig, D., Casten, R.F., Kane, W.R., Cole, G.W. and Cizewski, J.A. (1975). Phys. Rev. C 11, 546.

Campbell, L.L. (1956). Can. J. Phys. 34, 929

Campbell, A. . and Halliday, J.S. (1965). 13 th Ann. Conf. Mass Spectrom. and Allied Topics, St. Louis.

Casten, R.F., Kleihneinz, P., Daly, P.J. and Elbek, B. (1972). K. Dan. Vidensk. Selsk. Mat. - Fys. Medd. 38, No. 13.

Casten, R.F., Burke, D. and Hansen, O. (1976). Nucl. Phys. A, 261, 445.

Clotfelter, B.E. (1970). Reference Systems and Inertia, (Iowa State Univ. Press,Ames), p.60.

Cohen, E.R. (1976). Atomic Masses and Fundamental Constants, Vol. 5, ed. by J.H. Sanders and A.H. Wapstra (Plenum Publishing Corp., London), p. 676.

Cohen, E.R. and Taylor, B.N.(1973). J. Phys. Chem. Ref. Data, 2, 663.

Collins, T.L., Nier, A.O. and Johnson, W.H. (1952). Phys. Rev. 86, 408.

Collins, T.L. and Bainbridge, K.T. (1957). Nuclear Masses and their Determinations, ed. by H.Hintenberger, (Pergamon Press, London), p. 213.

Davison, N.E. (1977). Private communication to K.S. Kozier.

Demirkhanov, R.A., Gutkin, T.I. and Dorokhov, V.V. (1961). Izvestiya Akademii Nauk SSR, Seriya Fizicheskaya, A25, 124.

Demirkhanov, R.A. and Dorokhov, V.V. (1969). Yadernaya Fizika, A10, 247.

Demirkhanov, R.A., Dorokhov, V.V. and Dzkuya, M.R. (1972). Atomic Masses and Fundamental Constants, Vol 4, ed. by J.H. Sanders and A.H. Wapstra (Plenum Publishing Corp., London). p. 210

Dempster, A.J. (1918). Phys. Rev. II, 316.

Dempster, A.J. (1938). Phys. Rev. 53, 64, 869.

Dempster, A.J. and Shaw, A.E. (1950). Phys. Rev. 77, 746.

Deslattes, R.D. (1976). Atomic Masses and Fundamental Constants, Vol 5, ed. by J.H. Sanders and A.H. Wapstra (Plenum Publishing Corp., London), p. 557.

Dibeler, V.H. (1955) Anal. Chem. 27, 1958.

Drever, R.W.P. (1961).Phil. Mag. 6, 683.

Duckworth, H.E. (1958). Mass Spectroscopy (Cambridge Univ. Press, Cambridge).

Duckworth, H.E., Kerr, J.T. and Bainbridge, G.R. (1957). Nuclear Masses and their Determinations, ed. by H. Hintenberger (Pergamon Press, London), p. 218.

Duckworth, H.E. and Goshal, S.N. (1963). Mass Spectrometry, ed. by C.A. McDowell (McGraw-Hill Book Co., New York), p. 201.

Duckworth, H.E., Barber, R.C., Van Rookhuyzen, P., Macdougall, J.D., McLatchie, W., Whimeray, S., Bishop, R.L., Merdith, J.O., Williams, P., Southon, G., Wong, W., Hogg, B.G. and Kettner, M.E. (1969). Phys. Rev. Lett. 23, 592.

Everling, F., Hintenberger, H., Konig, L.A., Mattauch, J., Muller-Warmuth, W. and Wende, H. (1957). Nuclear Masses and the Determinations, ed. by H. Hintenberger, (Pergamon Press, London), p. 221.

Giese, C.F. and Benson, J.L. (1958). Phys. Rev 110, 712.

Giese, C.F. and Collins, T.L. (1954). Phys. Rev. 96, 823.

Greenwood, R.C. and Reich, C.W. (1974). Nucl. Phys. A, 223, 66.

Groshev, L.V., Demidov, A.M., Pelekhov, V.I., Sokolevskii, L., Kurchatov, I.V., Bartholomew, G.A., Doveika, A., Eastwood, K.M. and Monaro, S. (1969). Nucl. Data Tables, A5, 243.

Halverson, J. (1977). private communication to R.C. Barber.

Herzog, R. (1934). Z. fur Physik 89, 447.

Herzog, R. (1935). Z. fur Physik 87, 596.

Hintenberger, H. and König, L.A. (1957). Z. Naturforschg 12 a, 773.

Hintenberger, H. and König, L.A. (1959). Adv. in Mass Spectrometry, ed. by J.D. Waldron (Pergamon Press, London), p. 16.

Holden, N.E. and Walker, F.W. (1972) Chart of the Nuclides, 11 th edition, General Electric Co.

Huang, K.-N., Aoyagi, M., Chen, M.H., Craseman, B. and Mark, H. (1976). Atomic Data and Nucl. Data Tables, 18, 243.

Isenor, N.R., Bainbridge, G.R., Eastman, P.C. and Duckworth, H.E. (1956). Can J. Phys. 34, 993.

IUPAC (1975). Atomic Weights of the Elements 1975, Int. Union Pure & Appl. Chem., Inorganic Chem. Div., Comm. on Atomic Weights (E. Roth, Chairman), Pure & Appl. Chem., 47, 75.

Jammer, M. (1961). Concepts of Mass, Harvard University Press, Cambridge Massachusetts, p. 7.

Johnson, W.H. Jr. (1973). private communication to R.C. Barber.

Jolivette, P.L., Goss, J.D., Marolt, G.L., Rollefsun, A.A. and Browne, C.P. (1975). Atomic Masses and Fundamental Constants, Vol 5, ed. by J.H.Sanders and A.H. Wapstra (Plenum Publishing Corp., London), p. 133.

Katakuse, I. and Ogata, K. (1972). Atomic Masses and Fundamental Constants, Vol 4, ed. by J.H. Sanders and A.H. Wapstra (Plenum Publishing Corp., London). p. 153.

Kayser, D.C. (1975). PhD. Thesis, Univ. of Minnesota.

Kayser, D.C., Britten, R.A. and Johnson, W.H., Jr. (1972). Atomic Masses and Fundamental Constants, Vol 4, ed. by J.H.Sanders and A.H. Wapstra (Plenum Publishing Corp., London). p. 172.

Kayser, D.C. and Johnson, W.H. Jr. (1975). Phys. Rev. C 12. 1054.

Kayser, D.C., Halverson, J. and Johnson, W.H. Jr. (1976). Atomic Masses and Fundamental Constants Vol 5, ed. by J.H. Sanders and A.H. Wapstra (Plenum Publishing Corp., London), p. 178.

Kerwin,L. (1963). Mass Spectrometry , ed. by C.A. McDowell (McGraw-Hill Book Co., New York), p. 104.

Kolb, D. and Wong, C.Y. (1975). Nucl. Phys. A,245, 205.

Macdougall, J.D., McLatchie, W., Whineray, S. and Duckworth, H.E. (1966). Z. Naturforshg. 21A, 63.

Mattauch, J. (1960). Proc. Int. Conf. Nuclidic Masses, ed. by H.E. Duckworth (Univ. of Toronto Press, Toronto),p.3.

Mattauch, J., Thiele, W. and Wapstra, A.H. (1967). Nucl. Phys. 67, 1.

Matsuda, H., Fukumoto, S. and Kuroda, Y. (1966). Z. Naturforschg 21A, 25.

McLatchie, W., Barber, R.C., Bishop, R.L., Duckworth, H.E., Hogg, B.G., Macdougall, J.D. and Van Rookhuyzen, P. (1964). Can. J. Phys. 42, 926.

McLatchie, W., Whinery, S., Macdougall, J.D. and Duckworth, H.E. (1970). Nucl. Phys. A,145, 244.

Meredith, J.O. (1971). PhD Thesis, U. of Manitoba.
Meredith, J.O. and Barber, R.C. (1972). Can. J. Phys. 50, 1195.
Meredith, J.O., Southon, F.C.G., Barber, R.C., Williams, P. and Duckworth, H.E. (1972). Int. J. Mass Spectrom. Ion Phys. 10, 359.

Messiah, A. (1958). Quantum Mechanics, Vol 2, (John Wiley and Sons, Inc., New York), p. 664.

Michelson, A.A. (1911). Science, 23, 901.

Mohler, O.C. (1966).The Encyclopedia of Physics, ed. by R.M. Besancon (Reinhold Publishing Corp., New York), p. 659.

Nakai, K. (1971). Phys. Lett. 34B, 269.

Nier,A.O., Quisenberry, K.S. and Scolman, T.T. (1957). Nuclear Masses and their Determinations, ed. by H. Hintenberger, (Pergamon Press, London), p. 49.

Nilsson, S.G., Nix, J.R., Moller, P. and Ragnarsson, I. (1974). Nucl. Phys. A, 222, 221.

Ogata, K. and Matsuda, H. (1957). Nuclear Masses and their Determinations, ed. by H. Hintenberger, (Pergamon Press, London), p. 202.

Oothoudt, M.A. and Hiztz, N.M. (1973). Nucl. Phys. A 213, 221.

Petit-Clerc, Y. and Carette, J.D. (1968). Vacuum, 18,7

Petit-Clerc, Y. and Carette, J.D. (1970). Abst. of 38 th ACFAS Congress, Quebec, Canada.

Quisenberry, K.S., Scolman, T.T. and Nier, A.O.(1956). Phys. Rev. 102, 1071.

Reasenberg, R.D. and Shapiro, I.I. (1976). Atomic Masses and Fundamental Constants Vol 5, ed. by J.H. Sanders and A.H. Wapstra (Plenum Publishing Corp., London), p. 643.

Roll, P.G., Krotkov, R. and Dicke, R.H. (1964). Ann. Phys. 26, p. 442.

Rytz, A., Grennberg, B. and Gorman, D.J. (1972). Atomic Masses and Fundamental Constants, Vol 4, ed. by J.H. Sanders and A.H. Wapstra (Plenum Publishing Corp., London), p. 1.

Schult, O.W.B., Kane, W.R., Mariscotti, M.A.J. and Simic, J.M. (1967). Phys. Rev. 164, 1548.

Sharma, K.S. (1978). PhD. Thesis, U. of Manitoba.

Sharma, K.S., Kozier, K.S., Barnard, J.W., Barber, R.C., Haque, S.S. and Duckworth, H.E.(1977 a).Can.J.Phys. 55,506.

Sharma, K.S., Meredith,J.O., Barber, R.C., Kozier, K.S., Haque, S.S., Barnard, J.W., Southon, F.C.G., Williams, P. and Duckworth, H.E. (1977 b). Can. J. Phys. (in press).

Smith, L.G. (1971). Phys. Rev. C, 4, 22.

Smith, L.G. and Damm, C.C. (1953). Phys. Rev. 90, 324.

Smith, L.G. and Damm, C.C. (1956). Rev. Sci. Instr. 27, 638.

Smith, L.G. and Wapstra, A.H. (1974). Phys. Rev. C 11, 1392.

Snedecor, G.W. and Cochran, W.G. (1967). Statistical Methods (Iowa State Univ. Press, Ames), p. 550

Southon, F.C.G. (1973). PhD. Thesis, U. of Manitoba.

Southon, F.C.G., Meredith, J.O., Barber, R.C. and Duckworth, H.E. (1977). Can. J. Phys. 55, 383.

Stevens, C.M., Terandy, J., Lobell, G., Wolfe, J., Beyer, N., and Lewis, R. (1964). Proc. of the Int. Conf. on Nuclidic Masses, ed. by H.E. Duckworth (Univ. of Toronto Press), p. 403.

Stevens, C.M. and Moreland, P.E. (1967). Proc. 3 rd Int. Conf. on Atomic Masses, ed. by R.C. Barber, (Univ. of Manitoba Press, Winnipeg), p. 673.

Swann, W.F.G. (1931). J. Franklin Inst. 212, 439.

Thibault, C., Klapisch, R., Rigaud, C., Poskanzer, A.M., Prieels, R.,Lessard, L.,and Reisdorf, W. (1976). Atomic Masses and Fundamental Constants, Vol 5, ed. by J.H. Sanders, and A.H. Wapstra (Plenum Publishing Corp, London), p.205.

Thomson, J.J. (1907). Phil. Mag. S6 13, 561.

Tripathi, K.D., Bljchert - toft, P.H. and Boreving, S. (1969). Proc. Int. Symp. on Neutron Capture Gamma Ray Spectroscopy, Studsvik, Sweden (International Atomic Energy Agency, Vienna, Austria), p. 183.

Von Ardenne, M. (1962). Tabellen Zur Angewandten Physik, Band 1 (veb Deutscher Verlag der Wissenschaften, Berlin).

Wapstra, A.H. (1967). Proc. Third Int. Conf. on Atomic Masses, ed. by R.C. Barber (Univ. of Manitoba Press, Winnipeg), p. 831.

Wapstra, A.H. Kurzeck, C. and Anisimoff, A. (1967). Proc. Third Inter. Conf. Atomic Masses, ed. by R.C. Barber (University of Manitoba Press, Winnipeg), p. 152.

Wapstra, A.H. and Gove, N.B. (1971). Nucl. Data Tables, A9, 267.

Wapstra, A.H. and Bos, K. (1976). Nucl. Data Tables, 17,474.

Wichers, E. (1962). Nature, 194, 621.

Willet, J.B. and Spejewski, E.H. (1967). Nucl. Instrum. Methods, 52, 77.

Williams, P. and Duckworth, H. E. (1972). Sci, Prog., Oxf. 60, 319.

Wollnik, H., Siegert, G., Greif, J., Fiedler, G., Ashgar, M., Bailleul, J.P., Bocquet, J.P., Chauvin, M., Decker, R., Pfeiffer, B. and Schrader, H. (1976). Atomic Masses and Fundamental Constants, Vol 5, ed. by J.H.Sanders and A.H. Wapstra (Plenum Publishing Corp., London), p.218.

Wong, C.Y. (1972). Phys. Lett. 41 B, 451.

Wong, C.Y. (1973). Ann. Phys. 77, 279.

PREVIOUSLY COPYRIGHTED MATERIAL

AT END OF THESIS, (3 REPRINTS)

NOT MICROFILMED

Reprinted from Canadian Journal of Physics

Precise single neutron separation energies of Ti, Fe, and Zn

J. W. Barnard, P. Williams, R.C. Barber,
S. S. Haque, K. S. Kozier, K. S. Sharma,
and H. E. Duckworth
Volume 55 Number 3, 1977 Pages 200-205
National Research Council Canada.

Reprinted from Canadian Journal of Physics

Precise atomic masses and mass differences for W and Re

K. S. Sharma, K. S. Kozier, J. W. Barnard,
R. C. Barber, S. S. Haque, and H. E. Duckworth
Volume 55 Number 6, 1977 Pages 506-511
National Research Council Canada.

Reprinted from Canadian Journal of Physics

Nucleon separation and pairing energies, decay energies, and atomic masses for $68 \leq Z \leq 72$

K. S. Sharma, J. O. Meredith, R. C. Barber,
K. S. Kozier, S. S. Haque, J. W. Barnard,
F. C. G. Southon, P. Williams, and,
H. E. Duckworth
Volume 55 Number 15, 1977 Pages 1360-1378
National Research Council Canada.

Reprinted from

Canadian Journal of Physics

Réimpression du

Journal canadien de physique

Nucleon separation and pairing energies, decay energies, and atomic masses for 68 $\leq Z \leq 72$

K. S. Sharma, J. O. Meredith, R. C. Barber,
K. S. Kozier, S. S. Haque, J. W. Barnard,
F. C. G. Southon, P. Williams, and,
H. E. Duckworth

Volume 55 • Number 15 • 1977

Pages 1360–1378

National Research Council Canada
Conseil national de recherches Canada

Nucleon separation and pairing energies, decay energies, and atomic masses for $68 \le Z \le 72$[1]

K. S. SHARMA, J. O. MEREDITH,[2] R. C. BARBER, K. S. KOZIER, S. S. HAQUE,
J. W. BARNARD, F. C. G. SOUTHON,[3] AND P. WILLIAMS[4]
Department of Physics, University of Manitoba, Winnipeg, Man., Canada R3T 2N2
AND
H. E. DUCKWORTH[5]
University of Winnipeg, Winnipeg, Man., Canada R3B 2E9

Received February 18, 1977

A set of 24 precise determinations of mass spectroscopic doublet spacings, including a new determination of the $^{176}Hf^{35}Cl - {}^{174}Hf^{37}Cl$ mass difference, has been combined with nuclear reaction and decay Q values in a least squares adjustment of the atomic mass differences in the region $68 \le Z \le 72$. The following quantities have been calculated for each nuclide: separation energies for the last neutron and last pair of neutrons (S_n, S_{2n}), the neutron pairing energy (P_n), separation energies for the last proton and last pair of protons (S_p, S_{2p}), the proton pairing energy (P_p), Q values for α and β^- decays, and the mass defect. The systematic variations of these quantities with N and Z are discussed.

Une série de 24 déterminations précises des écarts de masse de doublets, incluant une nouvelle mesure de la différence de masse $^{176}Hf^{35}Cl - {}^{174}Hf^{37}Cl$, a été combinée avec des valeurs Q de réactions nucléaires et de désintégration dans un ajustement par moindres carrés des différences de masse atomique dans la région $68 \le Z \le 72$. Les quantités suivantes ont été calculées pour chaque noyau: énergies de séparation pour le dernier neutron et la dernière paire de neutrons (S_n, S_{2n}), l'énergie de paire des neutrons (P_n), les énergies de séparation pour le dernier proton et la dernière paire de protons (S_p, S_{2p}), l'énergie de paire des protons (P_p), les valeurs de Q pour les désintégrations α et β^-, et le défaut de masse. Les variations systématiques de ces quantités avec N et Z sont discutées.

[Traduit par le journal]

Can. J. Phys., **55**, 1360 (1977)

Introduction

For several years we have been undertaking a systematic program of atomic mass determinations by means of high resolution mass spectrometry in order to investigate precisely the variation of nucleon binding energies for naturally occurring isotopes in the region between 82 and 126 neutron shells. Initially the 2.7 m radius mass spectrometer, then located at McMaster University, Hamilton, Ont., and now at the University of Manitoba ('Manitoba I'), was used to investigate the nature of the mass effect associated with the onset of nuclear deformation in the region $N \sim 90$ (Barber *et al.* 1964*a*; Barber *et al.* 1964*b*). Subsequently a general survey was made of the more abundant even-N, even-Z nuclides throughout the region (Duckworth *et al.* 1969; Macdougall *et al.* 1970; McLatchie *et al.* 1970; Whineray *et al.* 1970).

More recently, a 1.0 m radius, second order double focusing mass spectrometer ('Manitoba II', Barber *et al.* (1968); Barber *et al.* (1971)) has been used to extend this study by the determination of many additional mass differences and by the redetermination with improved precision of some of the doublets studied previously. These data, combined with the McMaster data, then provide mass spectroscopically derived links amongst all of the naturally occurring nuclides in the region $59 \le Z \le 69$ (Pr to Tm) (Barber *et al.* 1972). In order to obtain 'best' values for the mass differences amongst all nuclides in the region, these mass spectroscopic values were then combined with all existing nuclear reaction and decay Q values in a least squares evaluation of the atomic mass differences for the region $59 \le Z \le 69$ (Meredith and Barber 1972).

TABLE 1. Values of constants

	Experimental	Adopted
$^{37}Cl - {}^{35}Cl$	$1.997\,049\,85 \pm 13$ u[a] $050\,11 \pm 30$ u[b] $049\,74 \pm 10$ u[c]	$1.997\,049\,802 \pm 76$ u
$^{1}_{1}H$	$1.007\,825\,05 \pm 1$ u[a] 07 ± 3 u[b]	$1.007\,825\,052 \pm 11$ u
$^{4}_{2}He$	$4.002\,602\,94 \pm 27$ u[a]	$4.002\,602\,94 \pm 27$ u
$^{1}_{0}n$	$1.008\,665\,02 \pm 4$ u[a]	$1.008\,665\,02 \pm 4$ u
Mass to energy conversion	$0.931\,493\,4 \pm 28$ keV/μu[d]	
S_n ($^{2}_{1}H$)	2224.64 ± 0.04 keV[a]	
S_n ($^{3}_{1}H$)	6257.51 ± 0.12 keV[a]	

[a] 1971 Mass Evaluation with Smith (Wapstra and Gove (1971), p. 168).
[b] Katakuse and Ogata (1972).
[c] Southon *et al.* (1977).
[d] e from Cohen and Taylor (1973). N_A from Deslattes (1976). c from Cohen (1976).

We have extended this investigation to the adjoining region and have presented (Barber *et al.* 1974) a series of 17 new determinations of mass doublets in the region $68 \le Z \le 72$ (Er to Hf). In addition we have redetermined, and report in this work, the value for one doublet studied previously by us (Barber *et al.* 1973) involving the $^{176}Hf - {}^{174}Hf$ mass difference which was in disagreement with some other work. All of the doublets studied are of the types

$$[1] \qquad {}^{A+2}X^{35}Cl - {}^{A}Y^{37}Cl = \Delta_1$$

$$[2] \qquad {}^{A+4}X^{35}Cl_2 - {}^{A}Y^{37}Cl_2 = \Delta_2$$

where X and Y may or may not be the same element. The measured values are combined with the known $^{37}Cl - {}^{35}Cl$ mass difference (Table 1) to derive mass differences between pairs of nuclides for which A is either even or odd. These data thus provide mass links between the naturally occurring isotopes throughout this region and relate it to the one previously studied.

The precision associated with the doublet values is in the range of 0.70 to 3.0 μu (0.65 to 2.8 keV) except for two doublets which involve the relatively rare isotope ^{168}Yb (0.14%) and which carry lower precision (~8 keV). As will be apparent, the precision of these determinations compares favourably with that of the determinations of nuclear reaction or decay Q values.

Following the same general procedure used in our earlier work (Meredith and Barber 1972) we have combined the new mass spectroscopic determinations for $68 \le Z \le 72$ with the nuclear reaction and decay Q values in a least squares evaluation of the atomic mass differences and here report the 'best' values so obtained for the nucleon separation and pairing energies, the decay energies, and the atomic masses in the region.

General Description of the Least Squares Evaluation

The experimental data under consideration, whether derived from mass spectrometry or from nuclear reaction or decay Q-value determinations, may be expressed as mass differences between pairs of nuclides. Thus each measured value is a linear combination of n atomic masses, and the whole set of N observations may be written in the following way:[6]

$$[3] \qquad \sum_{j=1}^{n} A_{Ij} M_j = y_I \pm s_I$$

where $I = 1, 2, \ldots, N$ and $j = 1, 2, \ldots, n$, the coefficients A_{Ij} are, in general, either 0 or 1 and each s_I is the standard deviation associated with the measured value of y_I.

This corresponds to the general linear model of the form

$$[4] \qquad y = X\boldsymbol{\mu} + \boldsymbol{\varepsilon}$$

where y is an N vector of observed results, X is a full rank $N \times n$ matrix of coefficients, $\boldsymbol{\mu}$ is an

---

[1] Work supported by the National Research Council of Canada.

[2] Now with the Canadian Grain Commission, Winnipeg, Man., Canada.

[3] Now with the Division of Medical Physics, Prince of Wales Hospital, Randwick, N.S.W., Australia.

[4] Now with the Institute of Materials Research, University of Illinois, Urbana, IL.

[5] Adjunct Professor of Physics, University of Manitoba, Winnipeg, Man., Canada.

[6] Lower case subscripts run from 1 to n; upper case subscripts run from 1 to N.

n vector of unknown parameters, *i.e.*, the atomic masses, and $\boldsymbol{\varepsilon}$ is an N vector of unknown residuals.

This form is well known, and specific variations of it have been investigated by Ellenberg (1973) and by Hartley and Jayatillake (1973). The use of the method of least squares for estimations of the parameter of [4] is well documented. Subject to the assumption that the residuals are normally distributed with a mean zero and a standard deviation, σ, *i.e.*

$$\boldsymbol{\varepsilon} = N(0, \sigma^2) \tag{5}$$

the standard results are:

$$\boldsymbol{\mu}^* = (X^{\mathrm{T}}X)^{-1}X^{\mathrm{T}}y \tag{6}$$

$$\boldsymbol{\varepsilon}^* = y - X\boldsymbol{\mu}^* \tag{7}$$

where X^{T} is the transpose of X.

The assumption of [5] is a special case. In a more general case considered by Hartley and Jayatillake (1973), the N vector $\boldsymbol{\varepsilon}$ has independent elements e_i, each of which has a mean of zero and its own unknown variance σ_I^2.

In some cases, as in the present study, there are independent experimental estimates of the σ_I. Thus, one may solve the system [3] of N linear equations in n unknown experimental values, making use of the experimental estimates, s_I, for weighting the equations (for example, Mattauch (1960); Wapstra and Gove (1971); Meredith and Barber (1972)). Each observational equation is multiplied by a weight

$$\omega_I = 1/s_I^2 \tag{8}$$

and the solution M^* is that which minimizes the sum of the weighted squares of the residuals, *i.e.*

$$\sum_{I=1}^{N} \omega_I r_I^2 \quad \text{or} \quad \sum_{I=1}^{N} (r_I/s_I)^2 \tag{9}$$

is a minimum.

Often the assumption is made that the normalized residuals (r_I/s_I) of each equation now satisfy [5] but this is not strictly necessary. The general validity of weighting least squares evaluations by using the variances of the experimental observations has been discussed recently by Taylor *et al.* (1970), Eisenhart (1971), and Cohen (1971).

The set of equations [3] can now be written as:

$$(\omega_I A_{Ij})M_j = \omega_I y_I \tag{10}$$

and the standard solution [6] becomes

$$M^* = [X^{\mathrm{T}}X]^{-1}\cdot X^{\mathrm{T}}(S\cdot y) \tag{11}$$

where $X = (S)\cdot A$ and $S = (1/s_I)$.

The matrix $(X^{\mathrm{T}}X)^{-1}$ is known as the variance–covariance matrix, with elements v_{ij}. The standard deviation associated with a particular adjusted mass M_j^* is $e_j^* = \sqrt{v_{jj}}$, and the standard deviation associated with a particular mass difference $(M_i^* - M_j^*)$ is:

$$e_{ij} = \sqrt{v_{ii} + v_{jj} - 2v_{ij}} \tag{12}$$

The distribution of the square of the normalized residuals should be compared to χ^2 for the $f = (N - n)$ degrees of freedom to help determine whether all input values and assigned errors are consistent with the assumption of [5]. As was the case in our previous evaluation (Meredith and Barber 1972), the quantity $\sqrt{\chi^2/f}$ should be unity with the limits $\pm\sqrt{1/2f}$. If this quantity is significantly greater than 1.0, the input data are examined and grossly inconsistent data may be identified and dealt with before the final calculation is performed.

New Determination of Mass Difference

As described in our recent work (Barber *et al.* 1974; Barber *et al.* 1976; Sharma *et al.* 1977) we have improved the procedure for accumulating the mass spectra in the signal averager. Previous to making this change, we studied and reported (Barber *et al.* 1973) values for two such doublets involving the relatively rare isotopes ^{180}W (0.13%) and ^{174}Hf (0.17%). However, a recent redetermination of the tungsten doublet (Sharma *et al.* 1977), made with the modified apparatus, has resulted in a significantly different and substantially more precise value.

Accordingly we have made a new determination of the hafnium doublet, using the apparatus and experimental procedures described in detail by Sharma *et al.* (1977) and have obtained the value

$$^{176}\mathrm{Hf}^{35}\mathrm{Cl} - {}^{174}\mathrm{Hf}^{37}\mathrm{Cl} = 4314.21 \pm 0.86\ \mu\mathrm{u} \tag{13}$$

as compared to the earlier value (Barber *et al.* 1973) of 4106 ± 16 μu. We also note that, in the light of the large change in the value, we have measured this difference at three widely different mass numbers by using the fragments $\mathrm{HfCl_2}$, $\mathrm{HfCl_3}$, and $\mathrm{HfCl_4}$, and have obtained consistent results.

TABLE 2. Double neutron separation energies

Code	Nuclide	Reference	S_{2n} (keV)	Input (keV)	Output (keV)	r_I (keV)	$(r_I/s_I)^2$
X′	^{164}Er	a	15 748.7 ± 1.2				
P_1		b	15 744 ± 10				
				15 748.6 ± 1.2	15 748.6 ± 1.2	0.0	0.000
W′	^{166}Er	a	15 126.9 ± 1.2				
P_2		b	15 123 ± 5				
				15 126.7 ± 1.2	15 126.2 ± 1.1	−0.5	0.174
P_3	^{167}Er	b	14 909 ± 6				
		c	14 912 ± 5				
				14 910.8 ± 3.8	14 912.0 ± 1.3	1.2	0.100
U′	^{168}Er	a	14 206.6 ± 1.3				
P_4		b	14 205 ± 6				
				14 206.5 ± 1.3	14 207.1 ± 0.7	0.6	0.213
T′	^{170}Er	a	13 258.3 ± 1.6				
P_5		b	13 267 ± 5				
				13 259.1 ± 2.5	13 260.7 ± 1.3	1.6	0.410
P_6	^{168}Yb	b	16 129 ± 7				
				16 129 ± 7.0	16 125.0 ± 6.7	−4.0	0.327
S	^{170}Yb	a	15 345.7 ± 7.1				
P_7		b	15 343 ± 6				
				15 344.1 ± 4.6	15 337.6 ± 3.0	−6.5	2.000
P_8	^{171}Yb	b	15 081 ± 5				
				15 081 ± 5.0	15 084.8 ± 3.1	3.8	0.578
Q	^{172}Yb	a	14 635.4 ± 1.9				
P_9		b	14 643 ± 5				
				14 636.4 ± 1.8	14 634.8 ± 0.8	−1.6	0.790
C	^{173}Yb	a	14 386.9 ± 1.5				
P_{10}		b	14 395 ± 5				
				14 387.6 ± 2.2	14 387.1 ± 0.6	−0.5	0.012
P	^{174}Yb	a	13 832.7 ± 1.0				
P_{11}		b	13 841 ± 5				
				13 883.0 ± 1.6	13 833.4 ± 1.1	0.4	0.063
N	^{176}Yb	a	12 690.6 ± 1.3				
P_{12}		b	12 698 ± 5				
				12 691.1 ± 3.3	12 690.4 ± 1.2	−0.7	0.045
M	^{176}Hf	a	14 872.6 ± 0.8				
P_{13}		b	14 879 ± 5				
				14 872.6 ± 1.0	14 872.4 ± 1.0	−0.2	0.040
P_{14}	^{177}Hf	b	14 533 ± 5				
				14 533 ± 5	14 547.9 ± 1.5	14.5	8.410
L	^{178}Hf	a	14 010.4 ± 1.0				
P_{15}		b	14 013 ± 5				
				14 010.5 ± 1.0	14 009.7 ± 0.9	−0.8	0.640
A	^{179}Hf	a	13 726.4 ± 0.7				
P_{16}		b	13 731 ± 5				
				13 726.5 ± 0.7	13 726.6 ± 0.6	0.0	0.000
J	^{180}Hf	a	13 489.8 ± 0.7				
P_{17}		b	13 493 ± 5				
				13 489.9 ± 0.7	13 489.1 ± 0.6	−1.0	2.041

NOTES: a, Mass spectroscopic measurements (Barber *et al.* 1974). b, Oothoudt and Hintz (1973). c, Debenham *et al.* (1974).

This doublet, as originally measured as the fragment HfCl, is badly mismatched (96:1) and also relatively narrow ($\Delta M/M \sim 1/50\,000$). At the time of the earlier determination we were unaware of the presence of low level modulation of the baseline of the signal which quite sabotaged the result and which has since been corrected. Moreover, the new determination benefited from an improved signal-to-noise ratio and from higher intensity and instrumental resolution.

This value may be combined with the values given in Table 1 to derive the double neutron separation energy (S_{2n}) of ^{176}Hf. As is shown in Table 2, the new value is in satisfactory agreement with the reaction Q value of Oothoudt and Hintz (1973).

TABLE 3. Other mass spectroscopic differences and α decay

Code	Nuclides	Input (keV)	Output (keV)	r_I (keV)	$(r_I/s_I)^2$
B	^{175}Lu – ^{173}Yb	2n – 13 760.9±1.3	13 759.3±1.1	−1.6	1.515
E	^{171}Yb – ^{169}Tm	2n – 14 175.8±1.6	14 175.4±0.7	−0.4	0.074
G′	^{169}Tm – ^{167}Er	2n – 14 128.0±1.0	14 127.6±0.7	−0.4	0.128
I′	^{167}Er – ^{165}Ho	2n – 14 532.0±1.1	14 533.3±0.8	1.3	1.304
D	^{173}Yb – ^{169}Tm	4n – 28 561.6±1.1	28 562.5±0.8	0.9	0.703
F	^{171}Yb – ^{167}Er	4n – 28 301.2±1.6	28 303.0±0.8	1.8	1.275
H′	^{169}Tm – ^{165}Ho	4n – 28 661.7±1.0	28 660.9±0.8	−0.8	0.648
K	^{180}Hf – ^{176}Hf	4n – 27 501.9±3.0	27 498.7±1.0	−3.2	1.142
O	^{176}Yb – ^{172}Yb	4n – 26 521.2±2.2	26 523.8±1.4	2.6	1.413
R	^{172}Yb – ^{168}Er	4n – 28 553.9±1.6	28 552.2±0.9	−1.7	1.092
V*	^{168}Yb – ^{168}Er	1 414.9±8.7	1 420.2±3.1	5.3	0.367
α	^{174}Hf – ^{170}Yb[a]	4n – 27 301±30	27 366.9±2.4	65.9	4.822

[a] MacFarlane and Kohman (1961).

Input Data

As indicated in the tables, we have transformed the experimental data so that they are all expressed in keV as mass excesses, energy differences, or particle separation energies (S_n, S_{2n}, Q_β, etc.). The values for the various constants used in making the transformation are given in Table 1.

Mass differences derived from mass spectroscopic doublet values reported by this group (Barber *et al.* 1974) are given in Tables 2 and 3 in terms of the neutron rest mass, *n*, and a separation energy in keV. The values which appear here are the experimental values given in Table 1 of Barber *et al.* (1974) and are not the least squares adjusted values shown in Table 6 of that paper, because the present adjustment requires linearly independent data for input. Also shown for each datum in Table 2 and 3 are the corresponding output values for the separation energies with the associated error, the residual (*i.e.*, the difference between input and output values r_I), and the square of the normalized residuals $(r_I/s_I)^2$.

In Tables 4, 5, 6, and 7 are compiled the mass difference data which derive from nuclear reaction and decay *Q* values. Where several determinations of the same mass difference exist, a weighted mean was calculated and used as the 'input' value shown in the table. At this stage, some discrepant data may be identified and investigated. Generally an offending datum can be rejected on reasonable grounds, *e.g.* where it might be concluded that a transition to the ground state had not been observed. Such inconsistent data have been deleted, and a new weighted mean and standard deviation calculated. As in Tables 2 and 3 the output values, residuals, and squares of normalized residuals are shown for each input quantity involved in the overdetermined set of mass differences in the adjustment.

The nuclides and the connections between them, involved in the present adjustment, are shown in Fig. 1, and identified by the code used in the tables. The mass spectroscopic connections are indicated by upper case letters, reactions yielding S_n values by r, and (p,t) reactions yielding S_{2n} by p. After the elimination of b_{32}, it can be seen from Fig. 1 that 87 of the total of 109 remaining mass differences form an overdetermined set of differences involving 43 of the 67 known nuclides in the region. (We note that the values for the relative *Q* values of Burke and Balogh (1975) are not shown in this figure.)

Results and Discussion

The squares of the normalized residual, $(r_I/s_I)^2$ or $\omega_I r_I^2$, for the above 109 input values are shown as a frequency histogram in Fig. 2 and are summarized, according to type of input, in Table 7. The sum of the squares of the normalized residuals, which corresponds to the χ^2 for this adjustment is 73.47. Inasmuch as there are 44 degrees of freedom in this adjustment, the consistency factor, or generalized Birge ratio, $\sqrt{\chi^2/f}$, is 1.29. The probability of equalling or exceeding this value is <5%. This might be interpreted as reflecting a general underestimation of the size of the errors for all of the input values, in which

TABLE 4. Neutron separation energies

Code	Nuclide	Reaction	Reference	S_n	Input	Adjusted value	$R(I)$	$(r_I/s_I)^2$
r_1	^{166}Ho	d,p	a	6250 ± 7				
		n,γ	b	6243 ± 3				
		n,γ	c	6243.0± 1.0				
		n,γ	d	6248 ± 5	6243.4± 0.9	6243.4± 0.9	0.0	0.000
r_2	^{162}Er	d,t	e	9215 ±10	9215 ±10	—	—	—
r_3	^{163}Er	d,p	e	6904 ±10	6904 ±10	6900.8± 7.1	−3.2	0.102
r_4	^{164}Er	d,t	e	8851 ±10	8851 ±10	8847.8± 7.1	−3.2	0.102
r_5	^{165}Er	d,p	e	6657 ±10				
		n,γ	f	6650.1± 0.7	6650.1± 0.7	6650.3± 0.7	0.2	0.056
r_6	^{166}Er	d,t	g	8473 ±10				
		d,t	e	8476 ±10	8474 ± 7	8476.0± 1.3	2.0	0.094
r_7	^{167}Er	d,p	g	6434 ±10				
		d,p	e	6439 ±10				
		d,p	h	6434 ±10				
		n,γ	i	6436.2± 0.5				
		n,γ	j	6436 ± 3.0	6436.2± 0.5	6436.1± 0.5	−0.1	0.001
r_8	^{168}Er	d,p	k	7763 ± 3				
		d,t	g	7778 ±10				
		d,t	e	7781 ±10				
		n,γ	l	7766 ± 4				
		n,γ	c	7712.0± 1*				
		n,γ	m	7771.2± 0.5	7771.0± 0.7	7771.1± 0.6	0.1	0.029
r_9	^{169}Er	d,p	h	5988 ±12				
		d,t	g	6001 ±10				
		d,t	e	6006 ±10				
		n,γ	n	6003.1± 0.3				
		n,γ	f	6002.7± 0.8	6003.0± 0.3	6003.1± 0.3	0.1	0.028
r_{10}	^{170}Er	d,t	g	7265 ±10				
		d,t	e	7268 ±10				
		d,t	n	7207 ±30	7263 ± 9	7257.6± 1.3	−5.4	0.360
r_{11}	^{171}Er	d,p	g	5678 ±10				
		d,p	e	5683 ±10				
		d,p	h	5674 ±10				
		n,γ	o	5681.5± 0.5	5681.5± 0.5	5681.6± 0.5	0.2	0.160
r_{12}	^{169}Tm	γ,n	p	8000 ±50				
		γ,n	p	8110 ±50				
		d,t	q	8034 ±15	8036 ±14	8033.4± 1.2	−2.6	0.035
r_{13}	^{170}Tm	d,p	r	6594 ±15				
		n,γ	r	6595.0± 2.5				
		n,γ	c	6552.9± 1.0*				
		n,γ	s	6593.9± 1.5	6594.2± 1.3	6593.0± 1.0	−1.2	0.852
r_{14}	^{168}Yb	d,t	t	9055 ±12	9055 ±12	9055.8± 9.2	0.8	0.004
r_{15}	^{169}Yb	d,p	t	6861 ±12				
		n,γ	u	6859 ± 4				
		n,γ	v	6867.2± 0.5	6867.1± 1.1	6867.3± 1.1	0.2	0.030
r_{16}	^{170}Yb	d,t	t	8469 ±12	8469 ±12	8470.4± 3.1	1.4	0.013

TABLE 4 (*Continued*)

Code	Nuclide	Reaction	Reference	S_n	Input	Adjusted value	$R(I)$	$(r_I/s_I)^2$
r_{17}	^{171}Yb	d,t	t	6617 ±12				
		d,p	t	6614 ±12				
		n,γ	w	6616 ± 3				
		n,γ	at	6614.7± 0.8				
					6614.8± 0.8	6614.5± 0.7	−0.3	0.141
r_{18}	^{172}Yb	d,t	t	8030 ±12				
		d,p	t	8022 ±12				
		n,γ	w	8023 ± 3				
		n,γ	ba	8020.1± 0.5				
					8020.2± 0.5	8020.3± 0.4	−0.1	0.045
r_{19}	^{173}Yb	d,t	t	6372 ±12				
		d,p	t	6370 ±12				
		n,γ	y	6365 ± 3				
		n,γ	o	6367.3± 0.5				
					6367.2± 0.5	6366.8± 0.5	−0.4	0.729
r_{20}	^{174}Yb	d,t	t	7476 ±12				
		d,p	t	7463 ±12				
		n,γ	w	7465 ± 3				
					7465.5± 2.8	7466.7± 1.1	1.0	0.128
r_{21}	^{175}Yb	d,p	t	5820 ±12				
		n,γ	y	5822 ± 5				
		n,γ	w	5819 ± 2.0				
		n,γ	z	5822.6± 0.5				
					5822.4± 0.5	5822.6± 0.5	0.2	0.163
r_{22}	^{176}Yb	d,t	t	6879 ±12	6879 ±12	6868.0± 1.3	−11.2	0.871
r_{23}	^{177}Yb	d,p	aa	5565 ±16				
		d,p	t	5562 ±12				
		n,γ	ab	5566.8± 1.2				
					5566.7± 1.2	5566.7± 1.2	0.0	0.000
r_{24}	^{175}Lu	γ,n	ae	7770 ±50				
		d,t	ad	7658 ±10				
					7662 ±22	7665 ± 1.5	6.6	0.090
r_{25}	^{176}Lu	d,t	ae	6282 ±15				
		d,p	af	6295 ± 8				
		d,p	ag	6295 ±15				
		n,γ	ah	6293.2± 1.2				
		n,γ	au	6292.5± 4				
					6293.1± 1.1	6293.2± 1.0	−0.6	0.298
r_{26}	^{177}Lu	n,γ	ae	7072.7± 2.0				
		d,p	ai	7073 ± 5				
		n,γ	aj	6890.3± 2.0*				
		n,γ	av	7072.5± 1.0				
		n,γ	ax	7072.4± 0.6				
					7072.4± 0.5	7072.4± 0.5	0.0	0.000
r_{27}	^{175}Hf	n,γ	o	6708.8± 0.5	6708.8± 0.5	6708.9± 0.5	0.1	0.040
r_{28}	^{176}Hf	d,t	bb	8183 ± 8	8183 ± 8	8163.5± 1.1	−19.5	5.941
r_{29}	^{177}Hf	d,p	ak	6374 ± 7				
		γ,n	al	6400 ±30				
		d,t	az	6384 ±11				
					6378 ± 6	6385.1± 1.1	5.9	0.967
r_{30}	Hf	n,γ	am	7623 ± 3				
		n,γ	an	7619 ± 5				
		d,t	ak	7621 ± 9				
		n,γ	ao	7625.5± 1.0				
		d,p	ai	7621 ±10				
					7625.0± 0.9	7625.6± 0.6	0.8	0.790

TABLE 4 (*Concluded*)

Code	Nuclide	Reaction	Reference	S_n	Input	Adjusted value	$R(I)$	$(r_I/s_I)^2$
r_{31}	^{179}Hf	d,p	aa	6102 ±14				
		n,γ	am	6098 ± 3				
		n,γ	ap	6098.0± 1.5				
		n,γ	ab	6099.5± 1.5				
					6098.5± 1.0	6100.7± 0.6	2.2	4.840
r_{32}	^{180}Hf	n,γ	am	7383 ± 3				
		d,t	ak	7381 ± 6				
		n,γ	aq	7387.5± 0.5				
		d,p	az	7392 ± 7				
					7387.4± 0.6	7388.2± 0.5	0.8	1.778
r_{33}	^{181}Hf	d,p	as	5665 ±25				
		n,γ	am	5693 ± 3				
		d,p	ak	5700 ±10				
		n,γ	ap	5694.5± 1.5				
					5694.2± 1.3	—	—	—

*Excluded from calculation on the assumption that the ground state transition was not observed.

NOTES: a, 65 St 06, references in this format are from the *Nuclear Data Tables*. b, 67 Mo 05. c, Rasmussen *et al.* (1968). d, Motz and Jurney (1964). e, 69 Tj 01. f, 70 Bo 16. g, 67 Tj 01. h, 68 Ha 10. i, 68 Mi 08. j, 67 Pt 11. k, 67 Ha 25. l, 65 Ar 32. m, 70 Mi 09. n, 70 Mu 15. o, 71 Al 01. p, 66 MTW 3. q, 71 Jo 18. r, 66 Sh 03. s, 67 Ra 33. t, 66 Bu 16. u, 67 Mi 12. v, 68 Mi 08. w, 69 Na 08. x, 69 Na 08. y, 67 Bo 19. z, 71 Al 14. aa, 63 Ve 09. ab, 72 Al 12. ac, 59-2-91, *Nuclear Data Sheets*. ad, 70 Jo 08. ae, 71 Mi 01. af, 67 St 14. ag, 70 Wh 01. ah, 70 Wa 20, 69 Mi 21. ai, 69 Mi 11. aj, 67 Ra 33. ak, 68 Ri 07. al, 60 Ge 1, 60 HA 18. am, 66 Na 03. an, 64 Gr 22. ao, 69 Fa 01, 67 Ra 33. ap, 67 Ra 33, 66 Na 03. ar, 70 Bu 05, 66 Na 03. aq, 72 Al 19. as, 66 Ga 06. at, 72 Wa 10. au, 72 Fu 06. av, 72 Fu 12. ax, 72 Me 16. az, 72 Za 04. ba, Greenwood and Reich (1974). bb, 73 Za 08.

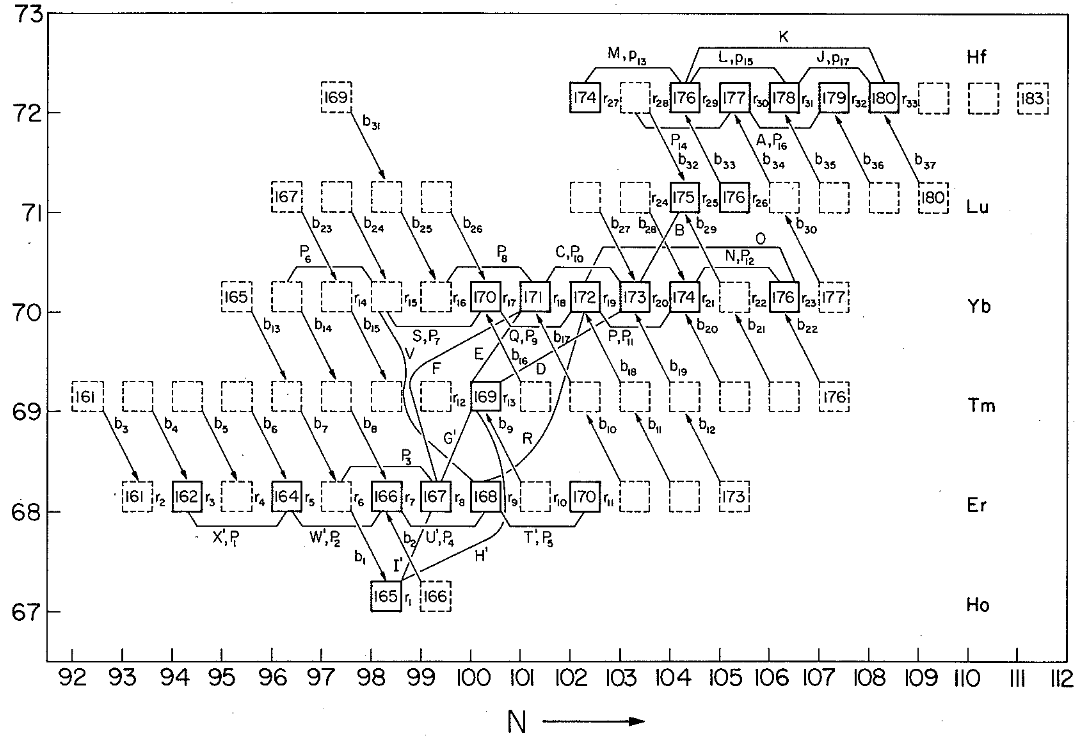


FIG. 1. Schematic diagram of the input data. Naturally occurring nuclides are indicated by solid squares with the mass number. The mass difference connections are identified by the code.

TABLE 5. Beta decay Q values in keV

Code	Decay	Reference	Q values	Input	Adjusted value	$R(I)$	$(r_I/s_I)^2$
b_1	^{165}Er(e.c.)^{165}Ho	a	371± 6	371± 6	378.8± 1.5	7.8	1.690
b_2	^{266}Ho$(\beta^-)^{166}$Er	b	1847± 5				
		c	1857± 3				
				1854± 4	1854.2± 1.2	0.2	0.003
b_3	^{161}Tm$(\beta^+)^{161}$Er	d	3520±100	3520±100			
b_4	^{162}Tm$(\beta^+)^{162}$Er	e	4890±100				
			4700±100				
		aw	4705± 70	4750± 50			
b_5	^{163}Tm$(\beta^+)^{163}$Er	f	2270± 30*				
		g	2417± 20				
				2417± 20			
b_6	^{164}Tm$(\beta^+)^{164}$Er	h	3962± 20	3962± 20			
b_7	^{165}Tm(e.c.)^{165}Er	i	1565± 30	1565± 30	1591.6± 2.3	26.6	0.786
b_8	^{166}Tm$(\beta^+)^{166}$Er	j	2980± 50				
		k	3035± 12				
				3032± 13	3046 ± 11	13.7	1.111
b_9	^{169}Er$(\beta^-)^{169}$Tm	l	344± 4	344± 4	353.5± 0.8	9.5	5.641
b_{10}	^{171}Er$(\beta^-)^{171}$Tm	m	1490± 2.0	1490± 2.0	1492.4± 1.1	2.4	1.440
b_{11}	^{172}Er$(\beta^-)^{172}$Tm	n	891± 10	891± 10			
b_{12}	^{173}Er$(\beta^-)^{173}$Tm	o	2800±300	2800±300			
b_{13}	^{165}Yb$(\beta^+)^{165}$Tm	p	2752± 20*				
		q	2922± 10				
				2922± 10			
b_{14}	^{166}Yb(e.c.)^{166}Tm	r	260± 20	260± 20	292.0±120	32.4	2.624
b_{15}	^{167}Yb$(\beta^+)^{167}$Tm	s	1960± 20				
		t	2015± 70				
		u	1955± 20				
				1960± 14	1959 ± 9	−1.1	0.006
b_{16}	^{170}Tm$(\beta^-)^{170}$Yb	v	970± 2				
		w	968± 0.7				
				968.2± 0.7	967.9± 0.6	−0.3	0.184
b_{17}	^{171}Tm$(\beta^-)^{171}$Yb	x	97± 1	97± 1	97.2± 0.9	0.2	0.040
b_{18}	^{172}Tm$(\beta^-)^{172}$Yb	y	1869± 9	1869± 9			
b_{19}	^{173}Tm$(\beta^-)^{173}$Yb	z	1320± 30	1320± 30			
b_{20}	^{174}Tm$(\beta^-)^{174}$Yb	aa	3060± 40	3060± 40			
b_{21}	^{175}Tm$(\beta^-)^{175}$Yb	ab	2400± 50	2400± 50			
b_{22}	^{176}Tm$(\beta^-)^{176}$Yb	ac	4200±100				
		ad	4140± 70				
				4160± 60			
b_{23}	^{167}Lu$(\beta^+)^{167}$Yb	ae	3070± 70	3070± 70			
b_{24}	^{168}Lu$(\beta^+)^{168}$Yb	af	4360± 80	4360± 80			
b_{25}	^{169}Lu$(\beta^+)^{169}$Yb	ag	2293± 70				
		ah	2270± 30				
				2274± 28			
b_{26}	^{170}Lu$(\beta^+)^{170}$Yb	ai	3465± 20				
		aj	3440± 20				
				3453± 13			
b_{27}	^{173}Lu(e.c.)^{173}Yb	ak	690± 30	690± 30	669.7± 1.7	−20.3	0.458
b_{28}	^{174}Lu$(\beta^+)^{174}$Yb	al	1372± 11	1372± 11	1375.8± 2.4	3.8	0.119
b_{29}	^{175}Yb$(\beta^-)^{175}$Lu	am	467± 2	467± 2	470.2± 1.3	3.2	2.560
b_{30}	^{177}Yb$(\beta^-)^{177}$Lu	an	1400± 20	1400± 20	1400.6± 2.7	0.6	0.001
b_{31}	^{169}Hf$(\beta^+)^{169}$Lu	q	3365±200	3365±200			
b_{32}	^{175}Hf(e.c.)^{175}Lu	ao	590± 30				
		ap	607± 8	606± 8*			
b_{33}	^{176}Lu$(\beta^-)^{176}$Hf	aq	1195± 8				
		aq	1193± 5				
				1193.6± 4.2	1185.9± 1.5	−7.7	3.361
b_{34}	^{177}Lu$(\beta^-)^{177}$Hf	ar	497± 1	497± 1	497.4± 1.0	0.4	0.160
b_{35}	^{178}Lu$(\beta^-)^{178}$Hf	as	2250± 50*				
		ax	2050± 50	2050± 50			
b_{36}	^{179}Lu$(\beta^-)^{179}$Hf	as	1350± 40	1350± 40			
b_{37}	^{180}Lu$(\beta^-)^{180}$Hf	at	3060±100				
		ac	3300±100				
		au	3100±100				
		au	3200±100				
				3165± 50			

TABLE 5 (*Concluded*)

*Excluded from calculation on the assumption that the ground state transition was not observed.

NOTES: a, 63 Ry 01 63ZY01. b, 55 Gr 07. c, 66 Da 04. d, 64 ab 03. e, 63 ab 02, 72 De 57. f, Gromov *et al.* (1963). g, 67 Gn 01. h, 67 Vr 04. i, 65 Pr 02. j, 63 Dz 07. k, 61 Zy 02, 61 Gr 33. l, 56 Bi 30, 65 Du 02. m, 61 Ar 15. n, 62 Gu 03. o, 68 Ih 01. p, 67 Pa 04. q, 70 Ar 16, 69 Ar 23, 73 Me 09. r, 63 Ja 06, 73 De 22. s, 64 Ag 03. t, 65 Ta 01. u, 65 Gr 20. v, 54 Po 26. w, 69 Va 17. x, 57 Sm 73. y, 66 Ha 15, 60 Vo 08. z, 63 Or 01, 63 Ku 22. aa, 67 Gu 12, 64 Ka 16. ab, 66 Wi 04. ac, Takahashi *et al.* (1961). ad, 67 Gull. ae, 64 Ag 03, 65 Gr 20. af, 70 Ch 28. ag, 70 Ba 09. ah, 60 Dz 2. ai, 71 Bo 09. aj, 65 Ha 30. ak, 59 Bi 11, 73 Ko 10. al, 68 Li 01. am, 62 Ba 32, 56 Co 13. an, 64 Jo 03. ao, 65 Fu 11. ap, 68 Ja 11. aq, 71 Be 10, 69 Pr 11. ar, 62 El 02. as, 61 Ku 10, 67 Ta 09. at, 71 Sw 01. au, 71 Gu 02. av, 74 De 47. ax, 75 Ka 15.

TABLE 6. Mass differences via (α,t) reactions*

Nuclides	Input (keV)	Output (keV)	r_I (keV)	$(r_I/s_I)^2$
^{164}Er − ^{165}Tm − ^{168}Er + ^{169}Tm	−1298.0± 2.0	−1297.9±2.0	0.1	0.003
^{166}Er − ^{167}Tm − ^{168}Er + ^{169}Tm	−666.5± 1.0	−666.5±1.0	0.0	0.000
^{167}Er − ^{168}Tm − ^{168}Er + ^{169}Tm	−262.3± 1.0	−262.3±1.0	0.0	0.000
^{170}Er − ^{171}Tm − ^{168}Er + ^{169}Tm	817.9± 1.0	818.3±0.9	0.4	0.168
^{169}Tm − ^{168}Er	n − 6332.8±15	6356.6±0.8	23.8	2.508
^{170}Yb − ^{171}Lu − ^{174}Yb + ^{175}Lu	−1156.2± 2.0	−1156.2±2.0	0.0	0.000
^{171}Yb − ^{172}Lu − ^{174}Yb + ^{175}Lu	−791.9± 2.0	−791.9±2.0	0.0	0.000
^{172}Yb − ^{173}Lu − ^{174}Yb + ^{175}Lu	−595.6± 1.0	−595.6±1.0	0.0	0.001
^{173}Yb − ^{174}Lu − ^{174}Yb + ^{175}Lu	−202.1± 1.0	−202.1±1.0	0.0	0.002
^{176}Yb − ^{177}Lu − ^{174}Yb + ^{175}Lu	674.1± 1.0	674.5±0.9	0.4	0.158
^{175}Lu − ^{174}Yb	n − 6274.8±15	6292.8±1.3	18.0	1.434

*Burke and Balogh (1975).

TABLE 7. Summary of adjustment of input data

Table	Nature of input	Number of data	Average r_I	Contribution to χ^2
2	S_{2n} (Mass spec. and (p,t))	17	0.37 ± 1.06	15.843
3	Mass spec. diff.	11	0.35 ± 0.71	9.661
	α decay	1	65.88	4.822
4	S_n	31	−0.82 ± 0.83	18.687
5	β decay Q values	16	4.46 ± 3.08	20.184
6	Mass diff. from (d,t) Q values	11	3.80 ± 2.57	4.274
	Total	87		73.471

case self consistency may be achieved by increasing all of the errors by 29%. It is more likely that it arises from some *systematic* biases, either in certain groups of data or in a few particular items. However, the size of this adjustment is sufficiently small that it is difficult to identify the source of such inconsistency.

The results of the calculation are presented in Tables 8 and 9 in terms of the particle separation and pairing energies, the alpha and beta decay

TABLE 8. Separation and pairing energies (keV)

A	Element	Z	S_{2n}	S_n	P_n	S_{2p}	S_p	P_p
161	Er	68	*	*	*	10 619 ± 12	6110 ± 50	
	Tm	69	*	*			*	*
162	Er	68	*	9215 ± 10	*	11 244.3 ± 1.7	6430 ± 50	1050 ± 39
	Tm	69	*	7990 ± 110		9 750 ± 110	3680 ± 50	
163	Er	68	16 116 ± 12	6901 ± 7	1065 ± 6	11 688 ± 5	6437 ± 30	
	Tm	69	17 220 ± 100	9230 ± 50		10 130 ± 60	3701 ± 21	*
164	Er	68	15 748.6 ± 1.2	8848 ± 7	1036 ± 5	12 342.8 ± 2.1	6857.7 ± 3.5	980 ± 8
	Tm	69	16 540 ± 50	7303 ± 29		10 540 ± 36	4103 ± 21	
165	Er	68	15 498 ± 7	6650.2 ± 0.7	1005.8 ± 1.9	12 726.1 ± 4.7	6884 ± 21	
	Tm	69	16 323 ± 21	9021 ± 20		11 170 ± 30	4276 ± 2.1	1055 ± 40
	Yb	70	*	*	*	9 420 ± 12	5316 ± 22	
166	Er	68	15 126.2 ± 1.1	8476.0 ± 1.3	966.4 ± 0.7	13 588.4 ± 2.4	7313.5 ± 1.4	873 ± 21
	Tm	69	16 043 ± 23	7022 ± 11		11 550 ± 50	4648 ± 11	
	Yb	70	*	9651 ± 13	*	10 223 ± 7	5947 ± 8	1100 ± 19
167	Er	68	14 912.0 ± 1.3	6436.0 ± 0.5	843.7 ± 0.4	14 261.5 ± 2.8	7506.3 ± 1.6	
	Tm	69	15 757.6 ± 2.5	8736 ± 11		12 222 ± 20	4907.6 ± 1.3	953 ± 25
	Yb	70	16 721 ± 14	7069 ± 11	1142 ± 9	10 642 ± 9	5994 ± 14	
	Lu	71	*	*		9 160 ± 70	3220 ± 70	1020 ± 50
168	Er	68	14 207.1 ± 0.7	7771.1 ± 0.6	775.8 ± 0.3	14 978 ± 5	7961 ± 20	833 ± 15
	Tm	69	15 576 ± 11	6840.2 ± 1.5		12 620 ± 60	5311.8 ± 1.3	
	Yb	70	16 125 ± 7	9056 ± 9	1044 ± 7	11 222.1 ± 3.1	6314.5 ± 3.3	978 ± 7
	Lu	71	*	7770 ± 110		9 910 ± 80	3910 ± 80	
169	Er	68	13 774.1 ± 0.6	6003.0 ± 0.3	755.7 ± 0.4	*	8520 ± 100	
	Tm	69	14 873.6 ± 1.2	8033.4 ± 1.1		13 532 ± 20	5574.1 ± 0.8	897 ± 23
	Yb	70	15 923 ± 9	6867.3 ± 1.1	947.9 ± 2.4	11 653.4 ± 3.1	6341.6 ± 3.3	
	Lu	71	16 720 ± 80	8950 ± 80		10 125 ± 28	3811 ± 28	*
	Hf	72	*	*	*	8 720 ± 200	4810 ± 220	
170	Er	68	13 260.7 ± 1.3	7257.6 ± 1.3	707.6 ± 0.7	*	8580 ± 100	*
	Tm	69	14 626.4 ± 1.5	6593.0 ± 0.9		13 532 ± 20	6164.1 ± 1.1	
	Yb	70	15 337.6 ± 3.0	8470.3 ± 3.1	864.7 ± 1.6	12 352.6 ± 1.1	6778.5 ± 0.9	907.2 ± 0.8
	Lu	71	16 240 ± 80	7291 ± 31		10 576 ± 13	4235 ± 13	
	Hf	72	*	*	*	*	*	
171	Er	68	12 929.3 ± 1.4	5681.6 ± 0.5	686.1 ± 3.4	*	9100 ± 100	
	Tm	69	14 078.2 ± 1.1	7485.1 ± 1.2		14 960 ± 100	6391.6 ± 1.1	780 ± 100
	Yb	70	15 084.8 ± 3.1	6614.4 ± 0.7	815.4 ± 0.9	12 964.0 ± 0.9	6799.9 ± 0.9	
	Lu	71	15 881 ± 28	8590 ± 13		11 132.7 ± 2.5	4354.1 ± 2.4	*
	Hf	72	*	*	*	*	*	

TABLE 8 (*Concluded*)

A	Element	Z	S_{2n}	S_n	P_n	S_{2p}	S_p	P_p
172	Er	68	12 532 ± 14	6850 ± 14	750 ± 80	*	*	*
	Tm	69	13 734 ± 9	6248 ± 9		*	6958 ± 9	
	Yb	70	14 634.8 ± 0.8	8020.3 ± 0.4	764.8 ± 0.3	13 726.7 ± 1.4	7335.1 ± 1.0	840.9 ± 0.7
	Lu	71	15 568 ± 13	6978.7 ± 2.9		11 518.4 ± 2.6	4718.4 ± 2.4	
	Hf	72	*	*	*	*	*	*
173	Er	68	11 860 ± 300	5010 ± 300	*	*	*	
	Tm	69	13 164 ± 30	6916 ± 31		*	7024 ± 33	*
	Yb	70	14 387.1 ± 0.6	6366.8 ± 0.4	688.3 ± 0.4	14 411.9 ± 1.5	7453 ± 9	
	Lu	71	15 195.3 ± 2.4	8216.6 ± 2.3		12 249.8 ± 1.9	4914.7 ± 1.7	939.5 ± 1.2
	Hf	72	*	*	*	*	*	
174	Tm	69	12 642 ± 41	5730 ± 50		*	7740 ± 300	
	Yb	70	13 833.4 ± 1.1	7466.5 ± 1.1	685.9 ± 0.6	15 029 ± 14	8004 ± 30	868 ± 23
	Lu	71	14 977.0 ± 2.3	6760.4 ± 1.5		12 762 ± 9	5308.3 ± 1.6	
	Hf	72	*	*	*	11 167.3 ± 2.3	6252.6 ± 2.4	*
175	Tm	69	12 210 ± 60	6480 ± 60		*	*	*
	Yb	70	13 289.1 ± 1.2	5822.6 ± 0.5	672.3 ± 0.5	15 840 ± 300	8100 ± 40	
	Lu	71	14 429.0 ± 1.5	7668.6 ± 1.5		13 514 ± 30	5510.3 ± 1.3	920 ± 8
	Hf	72	*	6708.9 ± 0.5	*	11 509.3 ± 2.3	6201.0 ± 2.4	
176	Tm	69	11 590 ± 70	5110 ± 80		*	*	
	Yb	70	12 690.4 ± 1.2	6867.8 ± 1.3	586.6 ± 0.8	*	8490 ± 50	*
	Lu	71	13 961.1 ± 1.7	6292.5 ± 1.0		14 080 ± 40	5980.3 ± 1.7	
	Hf	72	14 872.4 ± 1.0	8163.5 ± 1.1	808.6 ± 0.7	12 206.3 ± 2.3	6696.0 ± 1.7	*
177	Yb	70	12 434.5 ± 1.8	5566.7 ± 1.2	*	*	8940 ± 60	
	Lu	71	13 364.9 ± 1.1	7072.4 ± 0.5		14 670 ± 50	6184.8 ± 1.6	864 ± 13
	Hf	72	14 547.4 ± 1.5	6383.9 ± 1.1	755.4 ± 0.7	12 767.6 ± 2.0	6787.3 ± 1.1	
178	Lu	71	13 150 ± 50	6070 ± 50		15 640 ± 80	6690 ± 50	
	Hf	72	14 009.7 ± 0.9	7625.8 ± 0.6	691.7 ± 0.6	13 525.6 ± 1.9	7340.8 ± 1.1	*
179	Lu	71	12 874 ± 40	6800 ± 60		*	*	*
	Hf	72	13 726.5 ± 0.6	6100.7 ± 0.6	703.2 ± 0.5	14 059.6 ± 2.3	7370 ± 50	
180	Lu	71	12 370 ± 70	5570 ± 60		*	*	
	Hf	72	13 488.9 ± 0.6	7388.2 ± 0.5	745.4 ± 0.5	*	7956 ± 40	*
181	Hf	72	13 082.4 ± 1.4	5694.2 ± 1.3	650 ± 200	*	8080 ± 50	
182	Hf	72	12 280 ± 200	6590 ± 200	530 ± 200	*	*	*
183	Hf	72	11 974 ± 27	5390 ± 200	*	*	*	

*Values cannot be calculated from the information available in this adjustment.

TABLE 9. Decay energies and masses

A	Element	Z	$Q(\beta^-)$ (keV)	$Q(\alpha)$ (keV)	Mass excess	
					(keV)	μu
161	Er	68	−3520 ± 100	1795 ± 13	−65 203 ± 12	−69 998 ± 13
	Tm	69	*	*	−61 680 ± 100	−66 220 ± 110
162	Er	68	−4750 ± 50	1636.8 ± 2.7	−66 347 ± 6	−71 226 ± 6
	Tm	69	*	2480 ± 100	−61 600 ± 50	−66 130 ± 50
163	Er	68	−2417 ± 20	1563 ± 8	−65 176 ± 9	−69 969 ± 10
	Tm	69	*	*	−62 759 ± 22	−67 374 ± 24
164	Er	68	−3962 ± 20	1301.0 ± 2	−65 953 ± 6	−70 802 ± 7
	Tm	69	*	1960 ± 50	−61 991 ± 21	−66 549 ± 22
165	Er	68	−1591.6 ± 2.3	1098.7 ± 4.8	−64 531 ± 6	−69 277 ± 7
	Tm	69	−2922 ± 10	1800 ± 60	−62 940 ± 6	−67 568 ± 7
	Yb	70	*	2761 ± 14	−60 018 ± 12	−64 431 ± 13
166	Er	68	−3046 ± 11	825.8 ± 2.3	−64 936 ± 6	−69 711 ± 7
	Tm	69	−292 ± 12	1640 ± 60	−61 890 ± 13	−66 441 ± 14
	Yb	70	*	2324 ± 7	−61 598 ± 10	−66 127 ± 10
167	Er	68	−746 ± 1.3	665.9 ± 2.4	−63 301 ± 6	−67 955 ± 7
	Tm	69	−1959 ± 9	*	−62 555 ± 6	−67 154 ± 7
	Yb	70	−3070 ± 70	2156 ± 12	−60 596 ± 11	−65 051 ± 12
	Lu	71	*	2810 ± 70	−57 530 ± 70	−61 760 ± 80
168	Er	68	−1676.8 ± 1.6	548.5 ± 2.5	−63 000 ± 6	−67 633 ± 7
	Tm	69	256.7 ± 3.3	1220 ± 60	−61 323 ± 6	−65 833 ± 7
	Yb	70	−4360 ± 80	1948.1 ± 3.3	−61 580 ± 7	−66 108 ± 7
	Lu	71	*	2350 ± 80	−57 220 ± 80	−61 430 ± 90
169	Er	68	353.5 ± 0.9	258.6 ± 2.9	−60 932 ± 6	−65 412 ± 7
	Tm	69	−909.4 ± 3.1	1212.1 ± 1.8	−61 285 ± 6	−65 792 ± 7
	Yb	70	−2274 ± 28	1731.0 ± 3.4	−60 376 ± 7	−64 815 ± 7
	Lu	71	−3370 ± 200	2413 ± 28	−58 102 ± 29	−62 374 ± 31
	Hf	72	*	2860 ± 200	−54 740 ± 200	−58 760 ± 220
170	Er	68	−311.1 ± 1.6	56 ± 6	−60 118 ± 6	−64 539 ± 7
	Tm	69	967.9 ± 0.6	850.7 ± 3.2	−59 807 ± 6	−64 205 ± 7
	Yb	70	−3453 ± 13	1736.7 ± 1.1	−60 775 ± 6	−65 244 ± 7
	Lu	71	*	2144 ± 17	−57 322 ± 14	−61 537 ± 16
	Hf	72	*	*	*	*
171	Er	68	1492.4 ± 1.1	*	−57 728 ± 6	−61 973 ± 7
	Tm	69	97.2 ± 0.9	687 ± 21	−59 220 ± 6	−63 575 ± 7
	Yb	70	−1477.9 ± 2.5	1558.3 ± 0.8	−59 318 ± 6	−63 679 ± 7
	Lu	71	*	2290.2 ± 2.8	−57 840 ± 7	−62 093 ± 7
	Hf	72	*	*	*	*
172	Er	68	891 ± 10	*	−56 506 ± 15	−60 662 ± 16
	Tm	69	1869 ± 9	*	−57 397 ± 11	−61 618 ± 12
	Yb	70	−2519.4 ± 2.4	1309.0 ± 0.9	−59 266 ± 6	−63 624 ± 7
	Lu	71	*	2151.6 ± 2.8	−56 747 ± 7	−60 920 ± 7
	Hf	72	*	*	*	*
173	Er	68	2800 ± 300	*	−53 440 ± 300	−57 370 ± 320
	Tm	69	1320 ± 30	*	−56 242 ± 31	−60 377 ± 33
	Yb	70	−669.7 ± 1.7	945.2 ± 1	−57 562 ± 6	−61 794 ± 7
	Lu	71	*	1968.4 ± 1.8	−56 892 ± 7	−61 076 ± 7
	Hf	72	*	*	*	*
174	Tm	69	3060 ± 40	*	−53 897 ± 41	−57 860 ± 43
	Yb	70	−1375.8 ± 2.4	736.3 ± 1.8	−56 957 ± 6	−61 145 ± 7
	Lu	71	274.6 ± 2.4	1801.1 ± 1.9	−55 581 ± 7	−59 668 ± 7
	Hf	72	*	2494.4 ± 2.4	−55 856 ± 7	−59 963 ± 7
175	Tm	69	2400 ± 50	*	−52 310 ± 50	−56 150 ± 50
	Yb	70	470.2 ± 1.4	595.4 ± 1.8	−54 708 ± 6	−58 731 ± 7
	Lu	71	−685.2 ± 2.0	1617.6 ± 1.6	−55 178 ± 6	−59 236 ± 7
	Hf	72	*	2400.0 ± 2.4	−54 493 ± 7	−58 500 ± 7
176	Tm	69	4160 ± 60	*	−49 340 ± 60	−52 970 ± 60
	Yb	70	−105.1 ± 1.6	577 ± 14	−53 504 ± 6	−57 439 ± 7
	Lu	71	1185.8 ± 1.5	1574 ± 9	−53 399 ± 6	−57 326 ± 7
	Hf	72	*	2256.7 ± 2.1	−54 585 ± 7	−58 599 ± 7
177	Yb	70	1400.6 ± 2.0	20 ± 300	−51 000 ± 7	−54 750 ± 7
	Lu	71	497.4 ± 1.0	1417 ± 30	−52 400 ± 6	−56 253 ± 7
	Hf	72	*	2239.7 ± 1.8	−52 898 ± 7	−56 787 ± 7
178	Lu	71	2050 ± 50	1070 ± 60	−50 400 ± 50	−54 110 ± 50
	Hf	72	*	2080.4 ± 2.1	−52 452 ± 7	−56 309 ± 7
179	Lu	71	1350 ± 40	750 ± 60	−49 131 ± 41	−52 744 ± 44
	Hf	72	*	1802.2 ± 2.1	−50 481 ± 7	−54 193 ± 7
180	Lu	71	3170 ± 50	290 ± 80	−46 630 ± 50	−50 060 ± 50
	Hf	72	*	1281.9 ± 2.0	−49 798 ± 7	−53 460 ± 7
181	Hf	72	*	1154.4 ± 2.6	−47 421 ± 7	−50 908 ± 7
182	Hf	72	*	*	−45 950 ± 200	−49 320 ± 210
183	Hf	72	*	*	−43 258 ± 27	−46 439 ± 29

TABLE 9 (*Concluded*)

*Values cannot be calculated from the information available in this adjustment.

energies, and the mass excesses. In Table 8 the separation and pairing energies were calculated according to the definitions:

$$[14]\qquad S_{2n}(Z, N) = 2n - [M(Z, N) - M(Z, N - 2)]$$

$$[15]\qquad S_n(Z, N) = n - [M(Z, N) - M(Z, N - 1)]$$

$$[16]\qquad P_n(Z, N) = (-1)^N \tfrac{1}{4}[2S_n(Z, N) - S_n(Z, N - 1) - S_n(Z, N + 1)], \quad Z \text{ even}$$

$$[17]\qquad S_{2p}(Z, N) = 2M_H - [M(Z, N) - M(Z - 2, N)]$$

$$[18]\qquad S_p(Z, N) = M_H - [M(Z, N) - M(Z - 1, N)]$$

$$[19]\qquad P_p(Z, N) = (-1)^Z \tfrac{1}{4}[2S_p(Z, N) - S_p(Z - 1, N) - S_p(Z + 1, N)], \quad N \text{ even}$$

In Table 9 we give the Q values for α and β^- decays in keV and the mass excesses in μu and keV. The latter may be used to calculate other mass differences of interest and an upper limit on the error may be obtained by ignoring the term v_{ij} in [12].

Asterisks are inserted in the table where the quantities called for cannot be calculated from the available information. For errors in the range 1.0 to 4.9 (and multiplied by factors of 10) two significant digits are quoted, while in the range 5 to 9 one is given.

Inasmuch as the data consist of mass differences, it is necessary to assume one known mass excess in order to calculate mass excesses for the nuclides in this region. For this purpose ^{162}Er was taken to have the value $^{162}\text{Er} = 162\text{u} - (66\,347 \pm 6)$ μu, as reported by Meredith and Barber (1972) and which, in turn, was determined by a series of mass differences which link ^{162}Er to the 'absolute' masses of neodymium reported by Benson and Johnson (1966).

We show the double neutron separation energy as a function of neutron number for even N in Fig. 3 and for odd N in Fig. 4. As in previous work (Duckworth *et al.* 1969; Meredith and

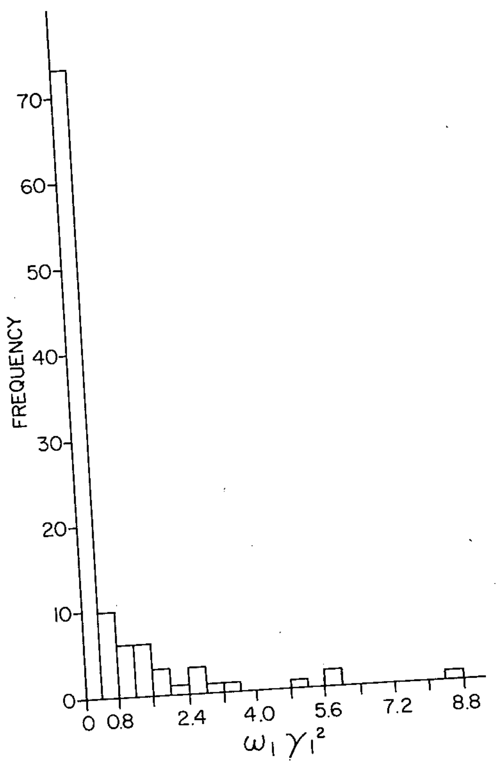


FIG. 2. Frequency histogram for the normalized residuals.

Barber 1972; Barber *et al.* 1973) the separate presentation of the curves for even-*N* and for odd-*N* nuclides emphasizes the underlying systematic behaviour. In this region, as in the region immediately below it, the systematic variation of S_{2n} is such that, when viewed over an interval of two neutron numbers, the segments of adjacent curves tend to be almost parallel. As a result, irregularities which appear in one curve are reproduced in other elements at the same neutron numbers.

In particular, we have noted the downward breaks in the even-*N* curves at $N = 98$, 104, and 108. These changes are reminiscent of the large changes in similar curves that occur at the major shell closures and indicate that the energy difference between the ground states (*e.g.* $E(N = 110) - E(N = 108)$) is greater than that 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 ($N = 108$)) with somewhat smaller gaps for $5/2^-$ [523] ($N = 98$) and for $1/2^-$ [512] ($N = 104$). 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 with larger gaps than usual above these levels.

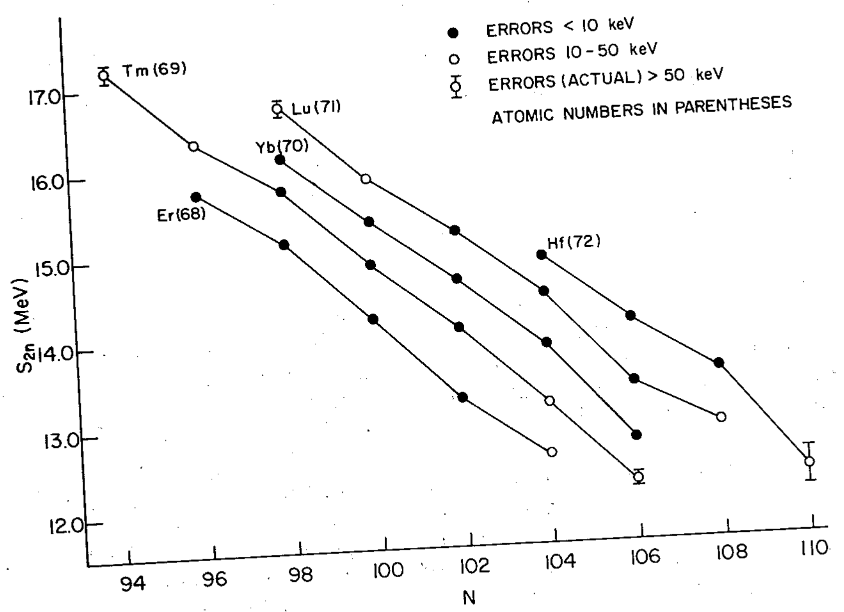


FIG. 3. Double neutron separation energies, S_{2n}, for even-*N* nuclides.

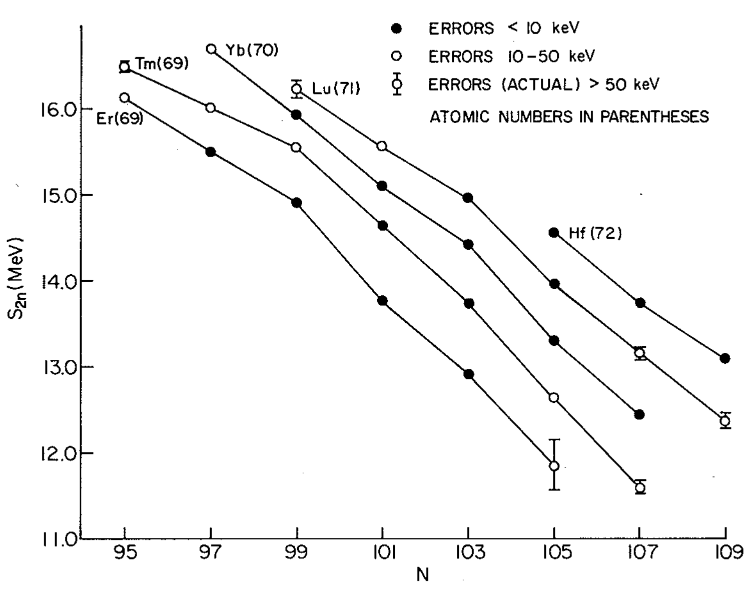


FIG. 4. Double neutron separation energies, S_{2n}, for odd-*N* nuclides.

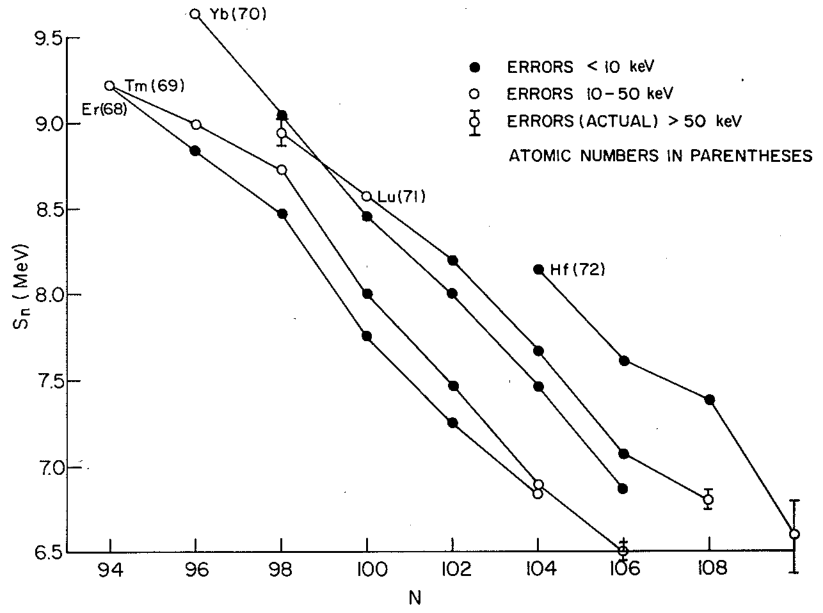


FIG. 5. Single neutron separation energies, S_n, for even-*N* nuclides.

The S_{2n} curves for odd N (Fig. 4) represent the energy required for both the separation of the pair of neutrons from the next-to-last occupied level and the transfer of the last odd neutron to the next lower energy level. Thus the interpretation of these curves is less certain than in the even-*N* case. Nevertheless, they reflect the discontinuities noted above for the even-*N* curves and show downward breaks at $N = 99$ and 103.

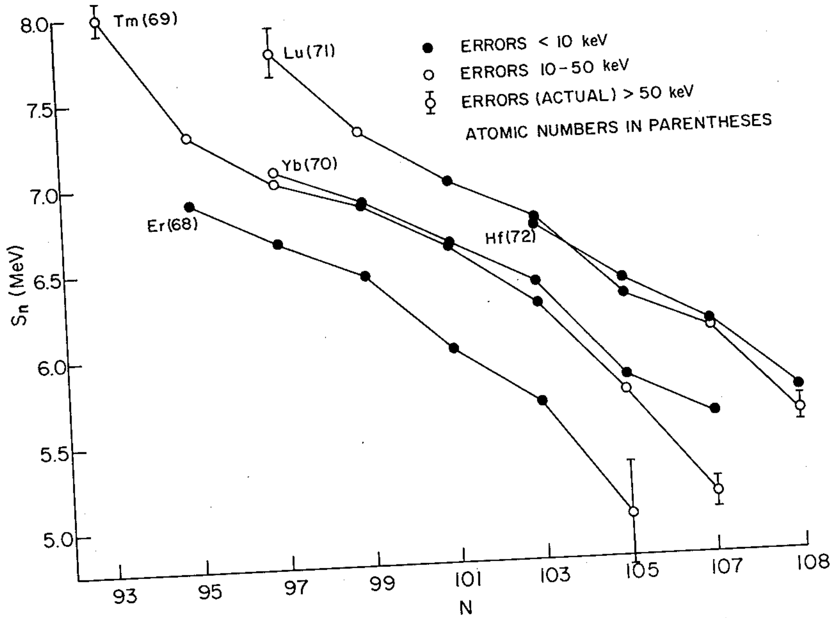


FIG. 6. Single neutron separation energies, S_n, for odd-N nuclides.

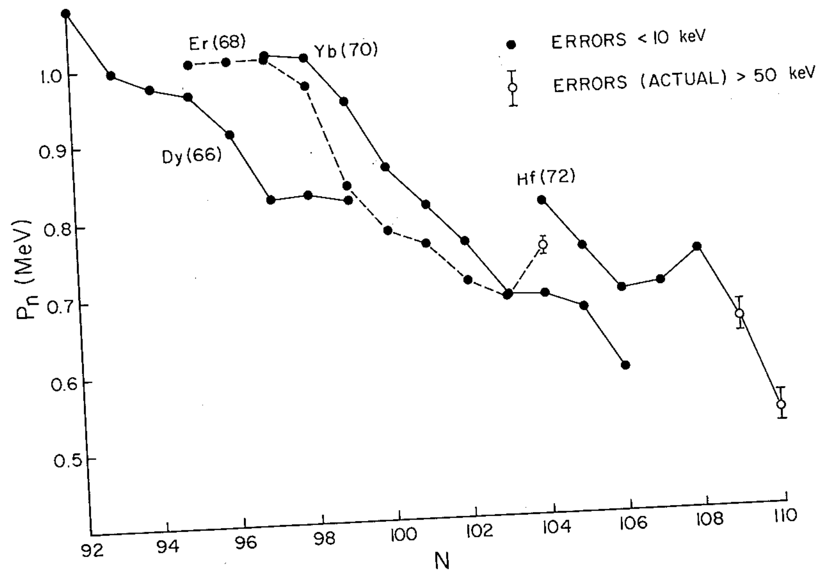


FIG. 7. Neutron pairing energies.

Presumably the fact that in the one case the break in the odd-N curve is at a neutron number one higher than the corresponding break in the one even-N curve, while in the other case it is one lower, results from small shifts in the energies of the levels, associated with the pairing interaction.

Figures 5 and 6 show the variation of the single neutron separation energies as a function of N for even-N and for odd-N nuclides. Again these curves extend the information given previously in similar plots by Meredith and Barber (1972) into the region described in this work. Some of the same systematic features referred to in that work are again evident here.

(*i*) A comparison of the even-N and odd-N curves shows that the average slope of the even-N curves is somewhat greater than that of the odd-N curves. That is, with increasing neutron number, the last neutron in an odd-N nucleus is relatively more tightly bound than the last neutron in an even-N nucleus. This may suggest that odd-N nuclei in this region are somewhat more deformed than even-N nuclei.

(*ii*) In odd–odd nuclides the neutron–proton interaction is ~300 keV and occurs throughout the region $95 < N < 109$, as shown in Fig. 6. The effect of the neutron–proton interaction can also be seen in the curves of odd Z and even N, where the removal of a neutron leaves an odd–odd nucleus. In this case the odd-Z curves are displaced downward by the effect.

(*iii*) The departure of the points for ^{172}Er ($N = 104$), ^{163}Tm ($N = 94$), and ^{169}Lu ($N = 98$) from the expected systematic behaviour may indicate errors in the input data which are larger than the stated errors.

Neutron pairing energies are plotted in Fig. 7 as a function of N for both even and odd N. Also shown in the figure are the P_n values for Dy ($Z = 66$) taken from Meredith and Barber (1972). In the region immediately below the one shown here, at $N = 90$, the neutron pairing energy reaches maximum value of ~1.3 MeV, independent of Z, and, in the region shown here, experiences a steady overall decrease. However, in each element there is evidence for a small but distinct increase in P_n in the neighbourhood of $N = 98$, 104, and 108 at which points the S_{2n} curves indicated enhanced stability.

In the region covered in this work it is found that the double proton separation energies, S_{2p}, and the single proton separation energies, S_p, do not show evidence of nuclear structure effects apart from the neutron–proton interaction mentioned above. Similarly, the proton pairing energy, P_p does not exhibit a clear dependence on N or Z, in contrast with the situation in the region $N \sim 90$ where a strong dependence on N was noted (Meredith and Barber 1972). Accordingly these quantities are not presented graphically.

Summary

(*a*) A new precise value of the double neutron separation energy of ^{176}Hf has been measured by a mass spectroscopic doublet.

(*b*) This value has been combined with a set of mass spectroscopic doublet determinations reported previously from this laboratory and with related nuclear reaction and decay Q values in a least squares adjustment in order to derive improved values of the mass differences and masses for $68 \leq Z \leq 72$.

(*c*) The mass differences derived, expressed in terms of the neutron separation and pairing energies show somewhat enhanced stability for neutron numbers $N = 98$, 104, and 108.

BARBER, R. C., DUCKWORTH, H. E., HOGG, B. G., MACDOUGALL, J. D., MCLATCHIE, W., and VAN ROOKHUYZEN, P. 1964*a*. Phys. Rev. Lett. **12**, 597.

BARBER, R. C., BISHOP, R. L., CAMBEY, L. A., DUCKWORTH, H. E., MACDOUGALL, J. D., MCLATCHIE, W., ORMROD, J. H., and VAN ROOKHUYZEN, P. 1964*b*. Proceedings of the Second International Conference on Nuclidic Masses. Springer Verlag, Berlin. p. 393.

BARBER, R. C., MEREDITH, J. O., BISHOP, R. L., DUCKWORTH, H. E., KETTNER, M. E., and VAN ROOKHUYZEN, P. 1968. Proceedings of the Third International Conference on Atomic Masses. University of Manitoba Press, Winnipeg, Manitoba. p. 717.

BARBER, R. C., BISHOP, R. L., DUCKWORTH, H. E., MEREDITH, J. O., SOUTHON, F. C. G., VAN ROOKHUYZEN, P., and WILLIAMS, P. 1971. Rev. Sci. Instrum. **42**, 1.

BARBER, R. C., BISHOP, R. L., MEREDITH, J. O., SOUTHON, F. C. G., WILLIAMS, P., DUCKWORTH, H. E., and VAN ROOKHUYZEN, P. 1972. Can. J. Phys. **50**, 34.

BARBER, R. C., MEREDITH, J. O., SOUTHON, F. C. G., WILLIAMS, P., BARNARD, J. W., SHARMA, K., and DUCKWORTH, H. E. 1973. Phys. Rev. Lett. **31**, 728.

BARBER, R. C., BARNARD, J. W., BURRELL, D. A., MEREDITH, J. O., SOUTHON, F. C. G., WILLIAMS, P., and DUCKWORTH, H. E. 1974. Can. J. Phys. **52**, 2386.

BARBER, R. C., BARNARD, J. W., HAQUE, S. S., KOZIER, K. S., MEREDITH, J. O., SHARMA, K. S., SOUTHON, F. C. G., WILLIAMS, P., and DUCKWORTH, H. E. 1976. Atomic masses and fundamental constants 5. Plenum Press, New York and London. p. 170.

BENSON, J. L. and JOHNSON, W. H. 1966. Phys. Rev. **141**, 1112.

BURKE, D. G. and BALOGH, J. M. 1975. Can. J. Phys. **53**, 948.

COHEN, E. R. 1971. Natl. Bur. Stand. U.S., Spec. Publ. No. 343, 499.

——— 1976. Atomic masses and fundamental constants 5. Plenum Press, New York and London. p. 674.

COHEN, E. R. and TAYLOR, B. N. 1973. J. Phys. Chem. Ref. Data, **2**, 663.

DEBENHAM, P., FALK, W. R., and CANTY, M. 1974. Can. J. Phys. **52**, 1416.

DESLATTES, R. D. 1976. Atomic masses and fundamental constants 5. Plenum Press, New York and London. p. 552.

DUCKWORTH, H. E., BARBER, R. C., VAN ROOKHUYZEN, P., MACDOUGALL, J. D., MCLATCHIE, W., WHINERAY, S., Bishop, R. L., Meredith, J. O., Williams, P., Southon, G., Wong, W., Hogg, B. G., and Kettner, M. E. 1969. Phys. Rev. Lett. **23**, 592.

Eisenhart, C. 1971. Natl. Bur. Stand. U.S., Spec. Publ. No. 343, 509.

Ellenberg, J. H. 1973. J. Am. Stat. Assoc. **68**, 941.

Greenwood, R. C. and Reich, C. W. 1974. Nucl. Phys. A, **223**, 66.

Gromov, K. Ya., Dzhelepov, B. S., Zvol'ska, V., Zvol'skii, I., and Kalimnikov, V. G., 1963. Izv. Akad. Nauk SSSR Ser. Fiz. **27**, 182.

Hartley, H. O. and Jayatillake, K. S. E. 1973. J. Am. Stat. Assoc. **68**, 189.

Katahuse, I. and Ogata, K. 1972. Atomic masses and fundamental constants 4. Plenum Press, London and New York. p. 153.

Macdougall, J. D., McLatchie, W., Whineray, S., and Duckworth, H. E. 1970. Nucl. Phys. A, **145**, 223.

MacFarlane, R. D. and Kohman, T. P. 1961. Phys. Rev. **121**, 1758.

Mattauch, J. H. E. 1960. Proceedings of the International Conference on Nuclidic Masses. University of Toronto Press, Toronto, Ontario. p. 126.

McLatchie, W., Whineray, S., Macdougall, J. D., and Duckworth, H. E. 1970. Nucl. Phys. A, **145**, 244.

Meredith, J. O. and Barber, R. C. 1972. Can. J. Phys. **50**, 1195.

Motz, H. T. and Jurney, E. T. 1964. Bull. Am. Phys. Soc. **9**, 31.

Ogle, W., Wahlborn, S., Piepenbring, R., and Fredrikson, S. 1972. Rev. Mod. Phys. **43**, 424.

Oothoudt, M. and Hintz, N. M. 1973. Nucl. Phys. A, **213**, 221.

Rasmussen, N. C., Orphan, V. J., and Hukai, Y. 1968. Proceedings of the Second International Conference on Atomic Masses. University of Manitoba Press, Winnipeg, Manitoba. p. 278.

Sharma, K. S., Kozier, K. S., Barnard, J. W., Barber, R. C., Haque, S. S., and Duckworth, H. E. 1977. Can. J. Phys. **55**, 506.

Southon, F. C. G., Meredith, J. O., Barber, R. C., and Duckworth, H. E. 1977. Can. J. Phys. **55**, 383.

Takahashi, K., Kuroyanagi, T., Yuta, H., Kotajima, K., Nagatini, K., and Morinaga, H. 1961. J. Phys. Soc. Jpn. **16**, 1664.

Taylor, B. N., Parker, W. H., and Langenberg, D. N. 1970. The fundamental constants and quantum electrodynamics. Academic Press, New York, NY.

Wapstra, A. H. and Gove, N. B. 1971. Nucl. Data Tables, **A9**, 267.

Whineray, S., Macdougall, J. D., McLatchie, W., and Duckworth, H. E. 1970. Nucl. Phys. A, **151**, 377.

Reprinted from

**Canadian
Journal of
Physics**

Réimpression du

**Journal
canadien
de physique**

Precise atomic masses and mass differences for W and Re

K. S. Sharma, K. S. Kozier, J. W. Barnard,
R. C. Barber, S. S. Haque, and H. E. Duckworth

Volume 55 • Number 6 • 1977

Pages 506–511

National Research Council Canada
Conseil national de recherches Canada

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

Received October 18, 1976

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.

[Traduit par le journal]

Can. J. Phys., **55**, 506 (1977)

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] $${}^{A}\mathrm{X} - {}^{A}\mathrm{Y} = \Delta M_1$$

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

[3] $${}^{A+4}\mathrm{X}^{35}\mathrm{Cl}_2 - {}^{A}\mathrm{Y}^{37}\mathrm{Cl}_2 = \Delta M_3$$

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] $${}^{A+1}\mathrm{X}^{16}\mathrm{O}_2{}^{37}\mathrm{Cl} - {}^{A}\mathrm{Y}^{35}\mathrm{Cl}_2 = \Delta M_4$$

[5] $${}^{A+3}\mathrm{X}^{16}\mathrm{O}_2 - {}^{A}\mathrm{Y}^{35}\mathrm{Cl} = \Delta M_5$$

[6] $${}^{A}\mathrm{X}^{16}\mathrm{O} - \mathrm{C}_2\mathrm{Cl}_5 = \Delta M_6$$

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] $$MV_i = M'V_i'$$

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] $$\Delta M/M' = \Delta V/V$$

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

---

[1] Work supported by the National Research Council of Canada.

[2] Adjunct Professor of Physics, University of Manitoba, Winnipeg, Man., Canada.

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)

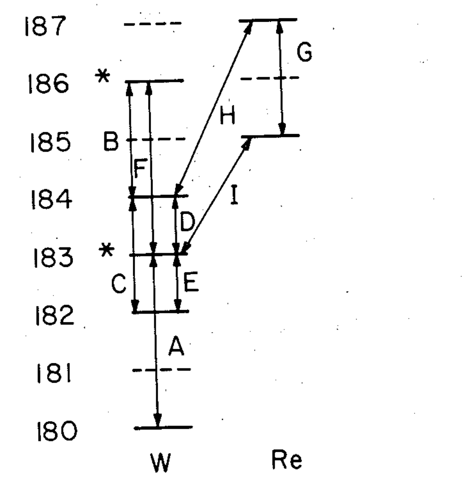


FIG. 1. Schematic diagram of atomic mass differences in W and Re. The letters refer to the doublets in Table 1. The symbol * indicates a doublet by which an absolute mass is determined.

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

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

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] 223 ± 11[d]	14 732.9 ± 5.6	14 700 ± 200[a] 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] 950 ± 9[d]	13 603.2 ± 1.6	13 602.5 ± 1.9[a] 13 609 ± 7[b] 13 606 ± 5[c] 13 603 ± 11[a]
^{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] 372 ± 9[d]	12 945.4 ± 1.4	12 951.8 ± 3.4[a] 12 956 ± 5[c] 12 955 ± 11[d]
^{187}Re	186.955 730 8 ± 2.6	186.955 791 ± 14[a] 759 ± 9[d]	13 539.7 ± 1.0	13 550.4 ± 3.4[a] 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[c]
^{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 5461 ± 5	5465.0 ± 4.0	5465 ± 10[c]

[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(β^-)^{185}Re (Willett and Spejewski 1967).
[f] Calculated with Q_β = 1312 ± 2 keV for ^{187}W(β^-)^{187}Re (Wapstra and Gove 1971).

with the precise (n,γ) Q value

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

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

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

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

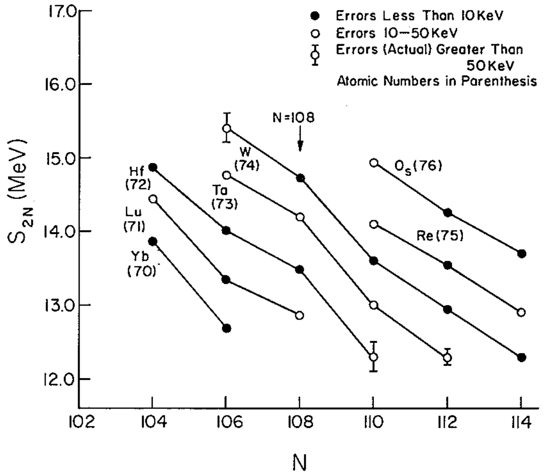


FIG. 2. Double neutron separation energies (S_{2n}) vs. neutron number (N).

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 $N = 108$.

Acknowledgements

We are grateful to Mr. V. P. Derenchuk and Mr. R. E. Ellis for their assistance in certain parts of the experimental work reported here.

Barber, R. C., Bishop, R. L., Cambey, L. A., Duckworth, H. E., Macdougall, J. D., McLatchie, W., Ormrod, J. H., and Van Rookhuyzen, P. 1964. Proc. Second Int. Conf. Nuclidic Masses, *ed. by* W. H. Johnson, Jr. (Springer-Verlag, Vienna), p. 363.

Barber, R. C., Meredith, J. O., Bishop, R. L., Duckworth, H. E., Kettner, M. E., and Van Rookhuyzen, P. 1968. Proc. Third Int. Conf. Atomic Masses, *ed. by* R. C. Barber (University of Manitoba Press, Winnipeg, Man.), p. 717.

Barber, R. C., Bishop, R. L., Duckworth, H. E., Meredith, J. O., Southon, F. C. G., Van Rookhuyzen, P., and Williams, P. 1971. Rev. Sci. Instrum. **42**, 1.

Barber, R. C., Bishop, R. L., Meredith, J. O., Southon, F. C. G., Williams, P., Duckworth, H. E., and Van Rookhuyzen, P. 1972. Can. J. Phys. **50**, 34.

Barber, R. C., Meredith, J. O., Southon, F. C. G., Williams, P., Barnard, J. W., and Sharma, K. S., and Duckworth, H. E. 1973. Phys. Rev. Lett. **31**, 728.

Barber, R. C., Barnard, J. W., Burrell, D. A., Meredith, J. O., Southon, F. C. G., Williams, P., and Duckworth, H. E. 1974. Can. J. Phys. **52**, 2386.

Barber, R. C., Barnard, J. W., Haque, S. S., Kozier, K. S., Meredith, J. O., Sharma, K. S., Southon, F. C. G., Williams, P., and Duckworth, H. E. 1976. Atomic masses and fundamental constants, Vol. 5, *ed. by* J. H. Sander and A. H. Wapstra (Plenum Publishing Corporation, London), p. 170.

Benson, J. L. and Johnson, W. H. 1966. Phys. Rev. **141**, 1112.

Bishop, R. L. and Barber, R. C. 1970. Rev. Sci. Instrum. **41**, 327.

Bleakney, W. 1936. Am. Phys. Teach. **4**, 12.

Casten, R. F., Kleinheinz, P., Daly, P. J., and Elbek, B. 1972. K. Dan. Vidensk. Selsk. Mat.-Fys. Medd. **38**, No. 13.

Casten, R. F., Burke, D., and Hansen, O. 1976. Nucl. Phys. A, **261**, 445.

Cohen, E. R. 1976. Atomic masses and fundamental constants, Vol. 5, *ed. by* J. H. Sanders and A. H. Wapstra (Plenum Publishing Corporation, London), p. 674.

Cohen, E. R. and Taylor, B. N. 1973. J. Phys. Chem. Ref. Data, **2**, 663.

Deslattes, R. D. 1976. Atomic masses and fundamental constants, Vol. 5, *ed. by* J. R. Sanders and A. H. Wapstra (Plenum Publishing Corporation, London), p. 552.

Duckworth, H. E., Barber, R. C., Van Rookhuyzen, P., Macdougall, J. D., McLatchie, W., Whineray, S., Bishop, R. L., Meredith, J. O., Williams, P., Southon, G., Wong, W., Hogg, B. G., and Kettner, M. E. 1969. Phys. Rev. Lett. **23**, 592.

Greenwood, R. C. and Reich, C. W. 1974. Nucl. Phys. A, **223**, 66.

Groshev, L. V., Demidov, A. M., Pelekhov, V. I., Sokolevskii, L., Kurchatov, I. V., Bartholomew, G. A., Doveika, A., Eastwood, K. M., and Monaro, S. 1969. Nucl. Data Tables, **A5**, 243.

Katakuse, I. and Ogata, K. 1972. Atomic masses and fundamental constants, Vol. 4, *ed. by* J. H. Sanders and A. H. Wapstra (Plenum Publishing Corporation, London), p. 153.

Meredith, J. O. and Barber, R. C. 1972. Can. J. Phys. **50**, 1195.

Meredith, J. O., Southon, F. C. G., Barber, R. C., Williams, P., and Duckworth, H. E. 1972. Int. J. Mass Spectrom. Ion Phys. **10**, 359.

Ogle, W., Wahlborn, S., Piepenbring, R., and Fredrikson, S. 1972. Rev. Mod. Phys. **43**, 424.

Oothoudt, M. A. and Hintz, N. M. 1973. Nucl. Phys. A, **213**, 221.

Sharma, K. S., Meredith, J. O., Barber, R. C., Kozier, K. S., Haque, S. S., Barnard, J. W., Southon, F. C. G., Williams, P., and Duckworth, H. E. 1977. (To be published.)

Southon, F. C. G., Meredith, J. O., Barber, R. C., and Duckworth, H. E. 1977. Can. J. Phys. **55**, 383.

Wapstra, A. H. and Bos, K. 1976. Nucl. Data Tables, **17**, 474.

Wapstra, A. H. and Gove, N. B. 1971. Nucl. Data Tables, **A9**, 267.

Willett, J. B. and Spejewski, E. H. 1967. Nucl. Instrum. Methods, **52**, 77.

Reprinted from

Canadian
Journal of
Physics

Réimpression du

Journal
canadien
de physique

Precise single neutron separation energies of Ti, Fe, and Zn

J. W. BARNARD, P. WILLIAMS, R. C. BARBER, S. S. HAQUE, K. S. KOZIER, K. S. SHARMA, AND H. E. DUCKWORTH

Volume 55 • Number 3 • 1977

Pages 200–205

National Research
Council Canada

Conseil national
de recherches Canada

Precise single neutron separation energies of Ti, Fe, and Zn [1]

J. W. BARNARD, P. WILLIAMS[2], R. C. BARBER, S. S. HAQUE,
K. S. KOZIER, AND K. S. SHARMA
Department of Physics, University of Manitoba, Winnipeg, Man., Canada R3T 2N2
AND
H. E. DUCKWORTH[3]
Department of Physics, University of Winnipeg, Winnipeg, Man., Canada R3B 2E9

Received August 13, 1976

Six precise single neutron separation energies have been derived from doublets determined using Manitoba's 2.73 m mass spectrometer. In addition, Manitoba's 1 m instrument has been used to corroborate certain of these new values. The new S_n values, which are generally in good agreement with precise nuclear reaction data, are accurate to 0.9 keV or better. These values may be suitable as calibration standards for nuclear reaction studies in the 5 to 10 MeV region.

On a obtenu de façon précise six énergies de séparation d'un seule neutron, à partir de doublets déterminés en utilisant le spectrographe de masse de 2.73 m de l'Université du Manitoba. De plus, l'instrument de 1 m du même laboratoire a été utilisé pour corroborer certaines de ces nouvelles valeurs. Les nouvelles valeurs S_n, qui sont généralement en bon accord avec les données précises de réactions nucléaires, sont déterminées à 0.9 keV près ou mieux. Elles peuvent servir comme étalons de calibration pour les études de réactions nucléaires dans la région de 5 à 10 MeV.

[Traduit par le journal]

Can. J. Phys., **55**, 200 (1977)

Introduction

For many years, the efforts of this laboratory have been directed to the measurement of precise double neutron separation energies (S_{2n}) by determining mass differences between doublet members of the type

[1] $$^{A+2}X^{35}Cl - {}^{A}Y^{37}Cl$$

[2] $$^{A+4}X^{35}Cl_2 - {}^{A}Y^{37}Cl_2$$

where X and Y may or may not be different elements. In such studies the chlorine mass difference, which is now known to a precision of 65 nu (1 nu = 10^{-9} u) (Barber *et al.* 1972*a*, 1974), becomes the secondary standard against which X and Y are compared. It has been found that very few elements between titanium and bismuth do not form chloride doublets suitable for mass spectroscopic evaluation.

This study of S_{2n} values was originally carried out using a 2.73 m double focusing mass spectrometer located at McMaster University. The work at that time included a general survey of the region from $N = 30$ to $N = 126$ (Duckworth *et al.* 1969; Macdougall *et al.* 1970; McLatchie *et al.* 1970; Whineray *et al.* 1970). Later a second order double focusing instrument of 1 m radius in the electrostatic analyser (Manitoba II) was constructed at the University of Manitoba (Barber *et al.* 1968, 1971) and used to perform a detailed survey of the S_{2n} values of naturally occurring isotopes mainly in the rare earths from neodymium to hafnium (Barber *et al.* 1972*b*, 1974).

The S_{2n} studies, which are currently being extended to the region beyond the rare earths, have demonstrated the utility of the chloride technique for the determination of S_{2n}'s. This success has inspired a search for a similar general method for the determination of single neutron separation energies (S_n). Such mass spectroscopic determinations would not only lend completeness to the chloride work by connecting even and odd A isotopes but also provide a number of precise reaction Q values suitable for use as calibration standards in nuclear reaction studies.

The purpose of this paper is to report a number of S_n determinations for some isotopes of the transition metals. All but one of these values have been determined using a technique which appears to possess widespread applicability to mass spectroscopic determinations of S_n's.

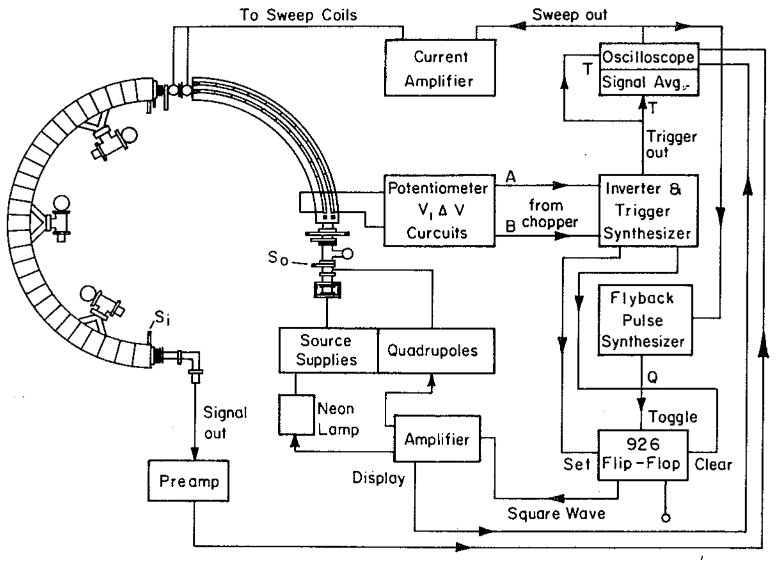


FIG. 1. Schematic of Manitoba I.

Experimental Method

The 2.73 m instrument mentioned previously has been moved from McMaster University and subsequently reassembled in the Physics Department at the University of Manitoba. This instrument (now referred to as Manitoba I) has been used to determine most of the S_n values reported here. However, as noted below, two determinations of overlapping or confirming value have been determined using Manitoba II.

The structure, geometry, and important associated circuitry of Manitoba I are illustrated in Fig. 1. This instrument, first described in its present form by Barber *et al.* (1963), has as its main analysing elements a 90° radial electric field and 180° uniform magnetic field. The optic axis has the same radius of curvature in both fields. Each analyser is positioned so that the object and direction focus are equidistant from the field boundaries. Such a field arrangement is first order double focusing and the second order coefficients have been shown to be small (Hintenberger and König 1959). The theoretical resolving power of 100 000 (calculated assuming principal slit S_0 and the image slit S_i are both about 14 μm wide) has been exceeded on occasion (Barber *et al.* 1963).

Helmholtz coils located between the electrostatic and magnetic analysers are driven by a sawtooth current so that the beam is modulated across S_i in phase with the oscilloscope. The ions which pass through S_i are amplified and the output is observed on the oscilloscope. The resulting trace is a cross section of the beam, or a limited mass spectrum.

To date determinations of atomic mass differences between doublet members have been performed with Manitoba I by the 'visual null' method, as described by Barber (1972*b*). On every other sweep the potential fields experienced by the ions are altered by the correct fractional amounts so that ions of mass M and M' are made alternately to follow identical paths through the instrument. For such conditions to be satisfied Bleakney's theorem (Bleakney 1936) requires that

[3] $$MV_j = M'V_j'$$

where V_j is the voltage of the jth electrode. Because of the velocity focusing properties of the instrument this process, which is very sensitive to adjustment of the electrostatic analyser potential, V, is very insensitive to adjustments of the source potential. Adjustment of ΔV, the amount by which V and V' differ, will bring M and M' to the same point in alternate sweeps. The mass difference ΔM may then be calculated from:

[4] $$\Delta M = (\Delta V/V)M'$$

For the visual null method a 1024 channel

---

[1] Work supported by National Research Council of Canada.

[2] Now at Institute for Materials Research, University of Illinois, Urbana, IL, U.S.A.

[3] Adjunct Professor, Department of Physics, University of Manitoba.

signal averager is used to help the operator judge the matched condition. The slit located at the intermediate direction focus enables the operator to confirm that the paths of the two ion groups coincide at this location as well as at S_0 and S_i.

A number of recent modifications to Manitoba I includes the addition of a potentiometer circuit for the precise measurement of the ratio $\Delta V/V$. This circuit is similar to one reported by Bishop and Barber (1970) and is designed to match or exceed the best expected precision of the instrument.

Before new mass measurements were attempted using Manitoba I its performance was evaluated by redetermining several well-known neodymium chloride doublets. This study revealed the existence of a proportional systematic error similar to that first reported by Southon (Southon 1973; Southon *et al.* 1976) and later by Barber *et al.* (1972*a*, 1974) in their work with Manitoba II. They attributed this systematic error to the presence of surface charges on the plates of Manitoba II's electrostatic analyser and were, in fact, able to reduce it to zero for a short time by carefully cleaning the plates with ether, absolute alcohol, distilled water, and a low pressure discharge in an argon atmosphere.

Although Manitoba II's systematic error has always been of the same sign, the sign and magnitude of the systematic error associated with Manitoba I have been found to depend on the material being mass analysed. A cleansing of the electrostatic analyser plates similar to that applied by Southon (1973) to Manitoba II has succeeded in altering the systematic error but not in removing it entirely.

Studies of the doublet $^{132}Xe - {}^{131}Xe$ (Barnard 1976) indicate that the main systematic error for Manitoba I may result from the accretion of deflected ions on the walls of the magnetic analyser. Such charged surfaces would create an unswitched potential causing a deviation from Bleakney's theorem during peak matching. The systematic error of +200 ppm for the neodymium chloride doublets dwindled to near zero when xenon replaced neodymium chloride in the source. Presumably other ions, both heavier and lighter, would not be present if only xenon were being produced by the source.

It has now become standard practice with Manitoba I to perform a series of matches on a well-known doublet one or two mass units wide to determine a correction to the narrow doublet of interest. This calibration doublet is chosen from among the same set of ions as the unknown so that the magnet setting need not be changed. For doublets of types given by [1] and [2], the correction derived by this method is usually only slightly larger than the final standard deviation assigned to the doublet value.

Success in the determination of S_n values has been achieved using both cyanides and cyclopentadienyl samples. However, the cyclopentadienyl method has proven to be the most widely applicable.

The cyanide samples provided doublets of the form:

$$[5] \qquad {}^{A}X^{15}N - {}^{A+1}X^{14}N$$

Since the precise mass standard was to be the $^{15}N - {}^{14}N$ mass difference, it was necessary to prepare the samples from ^{15}N-enriched potassium cyanide. It was discovered, furthermore, that many of the ions of interest preferred to form negative cyanide complexes. Despite such disadvantages one precise S_n was determined using this technique.

Doublets such as

$$[6] \qquad {}^{A}X({}^{13}C^{12}C_4H_5) - {}^{A+1}X({}^{12}C_5H_5)$$

and

$$[7] \qquad {}^{A}X({}^{13}C^{12}C_5H_5)(C_5H_5) - {}^{A+1}X({}^{12}C_5H_5)_2$$

are provided by cylopentadienyl compounds. Moreover, from certain chemical compounds involving trivalent metals we can obtain complexes such as $X(C_5H_5)_2Cl^+$ and $X(C_5H_5)Cl_2{}^+$. In these cases the metal chloride doublets are also produced so that both single and double neutron separation energies can be determined using the same sample. Exactly such a combination of the two techniques has made possible the determination of mass differences linking all the naturally occurring titanium isotopes.

For the cyclopentadienyl determinations the precise mass standard is the $^{13}C - {}^{12}C$ difference. The natural abundance ratio of $^{13}C - {}^{12}C$ is 98.9 to 1.1. However, for ions containing the (C_5H_5) group there are five ways to choose the heavy carbon. This improves the ratio of the ^{13}C-bearing member in relation to its companion to a tolerable 1:18. For the dicyclopentadienyl doublets the 10 ways available to choose ^{13}C improve this still further to 1:9. Thus, the need for enriched samples is obviated.

TABLE 1. Doublets determined with Manitoba I and Manitoba II

	Doublet	ΔM (μu)
	Manitoba I	
A	$^{67}Zn^{12}C^{14}N - {}^{66}Zn^{12}C^{15}N$	4060.21 ± 0.25
B	$^{56}Fe^{13}C^{12}C_9H_{10} - {}^{57}Fe^{12}C_{10}H_{10}$	2897.67 ± 0.47
C	$^{48}Ti^{13}C^{12}C_4H_5 - {}^{49}TiC_5H_5$	3432.64 ± 0.80
D	$^{46}Ti^{37}Cl^{35}Cl - {}^{48}Ti^{35}Cl_2$	1730.29 ± 0.87
E	$^{46}Ti^{13}C^{12}C_4H_5{}^{35}Cl - {}^{47}Ti^{12}C_5H_5{}^{35}Cl$	4218.03 ± 0.94
F	$^{49}Ti^{13}C^{12}C_4H_5{}^{37}Cl - {}^{50}Ti^{12}C_5H_5{}^{37}Cl$	6440.47 ± 0.88
	Manitoba II	
G	$^{56}Fe^{13}C^{12}C_9H_{10} - {}^{57}Fe^{12}C_{10}H_{10}$	2897.68 ± 0.40
H	$^{47}Ti^{35}Cl^{37}Cl - {}^{49}Ti^{35}Cl_2$	944.46 ± 0.35

New Data

The six new doublets, which have been determined by the techniques just described, are listed in Table 1. Also listed are two overlapping or related doublets determined with Manitoba II.

The iron values (B and G), as determined on the two instruments, are in excellent agreement. These two values have been combined to obtain a best value which is listed in Table 2.

Note further that doublet H, determined with Manitoba II, forms a closed loop with doublets C, D, and E, determined using Manitoba I. This loop closes to 0.4 ± 1.6 μu. This loop was subjected to a least squares adjustment in order to derive the best values for these doublets. These also are listed in Table 2.

All the best values derived from these new data were converted to the six mass differences of Table 3. The three mass standards used to generate the values of Table 3 are: (1) $^{15}N - {}^{14}N$ = 997 034.90 ± 0.43 μu from the mass table by Wapstra and Gove (1971), (2) 2 − ($^{37}Cl - {}^{35}Cl$) = 2950.276 ± 0.064 from Southon (1973) and Barber *et al.* (1972*a*), and (3) $^{13}C - 13$ = 3 354.831 ± 0.010 μu from Smith and Wapstra (1975).

TABLE 2. Adjusted values based on new data

Doublet	ΔM (μu)
$^{56}Fe^{13}C^{12}C_9H_{10} - {}^{57}Fe^{12}C_{10}H_{10}$	2897.68 ± 0.30
$^{48}Ti^{13}C^{12}C_4H_5 - {}^{49}TiC_5H_5$	3432.26 ± 0.69
$^{47}Ti^{35}Cl^{37}Cl - {}^{49}Ti^{35}Cl_2$	944.53 ± 0.34
$^{47}Ti^{37}Cl^{35}Cl - {}^{48}Ti^{35}Cl_2$	1730.29 ± 0.87
$^{46}Ti^{13}C^{12}C_4H_5{}^{35}Cl - {}^{47}Ti^{12}C_5H_5{}^{35}Cl$	4218.56 ± 0.75

TABLE 3. New atomic mass differences

Mass difference	ΔM (μu)
$^{67}Zn - {}^{66}Zn$	1.001 094 93 ± 43
$^{57}Fe - {}^{56}Fe$	1.000 457 16 ± 38
$^{47}Ti - {}^{46}Ti$	0.999 136 80 ± 75
$^{48}Ti - {}^{47}Ti$	0.996 183 00 ± 77
$^{49}Ti - {}^{48}Ti$	0.999 922 19 ± 69
$^{50}Ti - {}^{49}Ti$	0.996 914 36 ± 88

Six S_n values generated from the isotopic mass differences of Table 3 appear in Table 4. These separation energies have been evaluated using the neutron mass that was derived by Wapstra from his mass adjustment (Wapstra and Gove 1971) after the Smith (1971) data had been included in the input. This value is

$$n - 1 = 8665.02 \pm 0.04$$

The value for the mass-to-energy conversion

$$c^2/N_A e = 931.4940 \pm 26 \text{ MeV/u}$$

results from recent precise determinations of N_A by Deslattes *et al.* (1974).

The new S_n values agree with the mass table by Wapstra and Gove (1971) in all cases. The agreement with the neutron capture values is particularly good wherever the (n, γ) data are precise. The one exception is the S_n for ^{50}Ti. However, in this case the new value lies between the recent (n, γ) value and that of the mass table by Wapstra and Gove (1971).

Wapstra and Gove (1971) have noted that all the titanium (d, p) values appearing prior to 1971 seem to be high. The new S_n values tend to confirm this. Jolivette *et al.* (1975) have also found this to be the case. Their Q values for $^{46}Ti(d, p)^{47}Ti$ and $^{48}Ti(d, p)^{49}Ti$ are directly comparable to the new values for $S_n{}^{47}Ti$ and

TABLE 4. Single neutron separation energies

	S_n values (keV)				
	(n, γ)	(d, p)	Wapstra and Gove (1971)	Minnesota[d]	This work
^{67}Zn	7 052.4±1.5[a]	7 045±7[a]	7 053.9±1.2	7 058.71±8.57	7 051.49±0.46
^{57}Fe	7 646.0±0.5[a]	7 650±8[a]	7 646.2±0.5	7 646.26±1.30	7 645.57±0.35
^{50}Ti	10 949±2[b]	10 961±4[a]	10 948.0±2.0	10 937.88±2.20	10 945.67±0.82
^{49}Ti	8 142.3±1.0[a]	8 143.0±1.7[c]	8 143.4±0.8	8 145.73±1.97	8 143.14±0.64
^{48}Ti	11 627.6±1.3[a]	11 647±6[a]	11 628.1±1.0	11 623.46±3.27	11 626.93±0.71
^{47}Ti	8 884±7[a]	8 879.0±1.7[c]	8 875.1±1.5	8 884.68±3.27	8 875.47±0.69

[a] Input data to Wapstra and Gove (1971).
[b] Tripathi *et al.* (1969).
[c] Jolivette *et al.* (1975).
[d] Derived from doublets determined by Giese and Benson (1958).

$S_n{}^{49}$Ti. The agreement is excellent for $S_n{}^{49}$Ti but the new S_n for ^{47}Ti differs from Jolivette's value by +4 ± 2 μu.

Nevertheless, the consistency achieved between Manitoba's two instruments and the good agreement with nuclear data suggest that the new S_n's are reliable. They are, in every case, more precise than any of the comparable nuclear data. Moreover, the two most precise values (those for ^{57}Fe and ^{67}Zn) are only surpassed in precision by the five recent S_n values for ^{15}N, ^{14}C, ^{13}C, ^{3}H, and ^{2}H measured by Smith (Smith and Wapstra 1975) which are all precise to 30 eV. Because of the high precision of our Zn and Fe values they are suitable as calibration standards for capture gamma studies in the range 5 to 10 MeV. Although the Smith and Wapstra values for S_n (^{14}C) and S_n (^{3}H) fall within the 5 to 10 MeV range, the low abundances of the nuclides involved may make them less convenient reaction standards.

Summary

Six new mass differences connecting some naturally occurring isotopes of titanium, iron, and zinc have been determined using Manitoba I. These determinations enable the calculation of four precise S_n values connecting all naturally occurring isotopes of titanium as well as precise S_n values for ^{57}Fe and ^{67}Zn. The precision in all cases is better than 0.9 keV. Two doublets determined using Manitoba II show good agreement with the Manitoba I values.

The ion fragments involved in these determinations were provided by samples of metal chlorides, cyclopentadienyl metals, and metal cyanides. It appears that the cyclopentadienyl method will provide a general technique for determining precise neutron separation energies.

Barber, R. C., Bishop, R. L., Cambey, L. A., Duckworth, H. E., MacDougall, J. D., McLatchie, W., Ormrod, J. H., and van Rookhuyzen, P. 1963. Proc. Second Int. Conf. Nuclidic Masses, *ed. by* Walter H. Johnson Jr. (Spring-Verlag, Wien), p. 393.

Barber, R. C., Meredith, J. O., Bishop, R. L., Duckworth, H. E., Kettner, M. E., and van Rookhuyzen, P. 1968. Proc. Third Int. Conf. Atomic Masses, *ed. by* R. C. Barber (University of Manitoba Press, Winnipeg, Manitoba), p. 717.

Barber, R. C., Bishop, R. L., Duckworth, H. E., Meredith, J. O., Southon, F. C. G., van Rookhuyzen, P., and Williams, P. 1971. Rev. Sci. Instrum. **42**, 1.

Barber, R. C., Barnard, J. W., Bishop, R. L., Burrell, B. A., Duckworth, H. E., Meredith, J. O., Southon, F. C. G., and Williams, P. 1972*a*. Atomic mass and fundamental constants, Vol. 4, *ed. by* J. H. Sanders and A. H. Wapstra (Plenum Press, London), p. 141.

Barber, R. C., Bishop, R. L., Meredith, J. O., Southon, F. C. G., Williams, P., Duckworth, H. E., and van Rookhuyzen, P. 1972*b*. Can. J. Phys. **50**, 34.

Barber, R. C., Barnard, J. W., Burrell, D. A., Meredith, J. O., Southon, F. C. G., Williams, P., and Duckworth, H. E. 1974. Can. J. Phys. **52**, 2386.

Barnard, J. W. 1976. Ph.D. Thesis, University of Manitoba, Winnipeg, Man., Canada.

Bishop, R. L. and Barber, R. C. 1970. Rev. Sci. Instrum. **41**, 327.

Bleakney, W. 1936. Am. Phys. Teach. **4**, 12.

Deslattes, R. D., Henins, A., Bowman, H. A., Schoonover, R. M., Carroll, C. L., Barnes, I. L., Machlan, L. A., Moore, L. J., and Shield, W. R. 1974. Phys. Rev. Lett. **33**, 463.

Duckworth, H. E., Barber, R. C., van Rookhuyzen, P., MacDougall, J. D., McLatchie, W., Whineray, S., Bishop, R. L., Meredith, J. O., Williams, P.,

Southon, H., Wong, W., Hogg, B. G., and Kettner, M. E. 1969. Phys. Rev. Lett. **23**, 592.

Giese, C. F. and Benson, J. L. 1958. Phys. Rev. **110**, 172.

Hintenberger, H. and König, L. A. 1959. Advances in mass spectrometry, *ed. by* J. D. Waldron (Pergamon Press, London), p. 16.

Jolivette, P. L., Goss, J. D., Marolt, G. L., Rollefsun, A. A., and Browne, C. P. 1975. Atomic masses and fundamental constants, Vol. 5, *ed. by* J. H. Sanders and A. H. Wapstra (Plenum Press, London), p. 133.

MacDougall, J. D., McLatchie, W., Whineray, S., and Duckworth, H. E. 1970. Nucl. Phys. A, **145**, 223.

McLatchie, W., Whineray, S., MacDougall, J. D., and Duckworth, H. E. 1970. Nucl. Phys. A, **145**, 244.

Smith, L. G. 1971. Phys. Rev. C, **4**, 22.

Smith, L. G. and Wapstra, A. H. 1975. Phys. Rev. **11**, 1392.

Southon, F. C. G. 1973. Ph.D. Thesis, University of Manitoba, Winnipeg, Man., Canada.

Southon, F. C. G., Meredith, J. O., Barber, R. C., and Duckworth, H. E. 1977. (In press).

Tripathi, K. C., Bljchert-toft, P. H., and Boreving, S. 1969. Proc. Int. Symp. on Neutron Capture Gamma-Ray Spectroscopy, Studsvik, Sweden (International Atomic Energy Agency, Vienna, Austria), p. 183.

Wapstra, A. H. and Gove, N. B. 1971. Nucl. Data Tables, **A9**, 357.

Whineray, S., MacDougall, J. D., McLatchie, W., and Duckworth, H. E. 1970. Nucl. Phys. A, **151**, 377.