

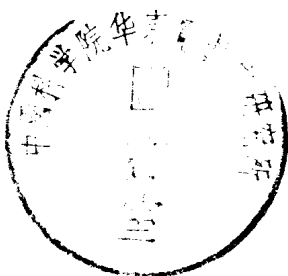
ADVANCES IN MASS SPECTROMETRY

PROCEEDINGS OF A JOINT CONFERENCE ORGANISED BY THE HYDROCARBON
RESEARCH GROUP, INSTITUTE OF PETROLEUM, AND A.S.T.M. COMMITTEE E.14
AND HELD IN THE UNIVERSITY OF LONDON, 24TH-26TH SEPTEMBER, 1958.

Edited by

J. D. WALDRON

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ADVANCES IN
MASS SPECTROMETRY



FOREWORD

THIS conference is the third to be held in Great Britain on Mass Spectrometry, the previous conferences being held in 1950 and 1953. The present conference, however, marks a departure from those held previously in that it has been organised jointly with the A.S.T.M. E.14 Committee on Mass Spectrometry. The suggestion for a joint conference came originally from A.S.T.M. E.14, and in view of the success which attended this suggestion, the conference marks the beginning of a series of such conferences.

The object of the conferences is to review the major developments in Mass Spectrometry over a period of years, and it is considered that three year intervals would be appropriate for this purpose. The next joint conference will, therefore, be held in 1961, probably in Great Britain.

Some 200 people representing ten countries attended the conference. This was a most gratifying response and augurs well for the success of the series. I am indebted to Professor Sir Cyril Hinshelwood, P.R.S., for his opening address, to Mr. W. Priestley, Jnr., and Dr. R. A. Friedel of A.S.T.M. E.14, to Dr. C. J. Danby and Mr. A. Quayle of the Mass Spectrometry Panel for their assistance in organising the conference, and to the Session Chairmen on whom depended the smooth running of the various Sessions. Above all, I pay tribute to the great contribution made by Dr. Waldron in editing the papers and this final publication, and to Mr. W. J. Brown to whom fell the administrative work of the conference.

ROY R. GORDON

Chairman

Mass Spectrometry Panel

Hydrocarbon Research Group

EDITOR'S NOTE

THE original title of the conference was simply "Mass Spectrometry" but on reading through the papers afterwards the present title seemed more appropriate, particularly in view of the many papers which described new instruments, techniques and applications for the first time.

A feature of the conference was the discussion which followed each paper. These were most interesting and informative and contributed greatly to the success of the meeting but, unfortunately, the verbatim record which was taken was too voluminous to publish in full. It is hoped that the present version does not detract too seriously from the cogency of the remarks made. In order to reduce the delay in publication, it has not been possible for all contributors to the discussion to check their remarks and I would ask readers to bear this in mind. It is too much to hope that the record is completely free from errors and I apologise for any that remain.

I should like to express my sincere thanks to numerous colleagues in the Research Department of Metropolitan-Vickers for the help they have given in preparing the bibliography and with the editorial work in general. In particular, the efforts of Mrs. A. Buckley, Mrs. P. Jones, Messrs. R. M. Elliott and I. S. Simpson are much appreciated and I am indebted to Mrs. J. M. Roberts who typed the bibliography, the discussion and many of the papers. Grateful thanks are also due to the publishers for the assistance they have so readily given in preparing this volume.

J. D. WALDRON

OPENING REMARKS

by

Professor Sir CYRIL HINSELWOOD, *President of the Royal Society*

THE MOST senior people present probably made their first acquaintance with the possibilities of mass spectrometry when they saw reproduced in a text book a photograph, with two not very impressive looking smudges which were the visual demonstration by J. J. Thomson's positive ray analysis that isotopes of neon really exist. The difference between the germ and the developed organism is very great. Then, the marvel was not that it was done badly but that it was done at all.

Today mass spectrometry, achieving higher and higher resolution, is no longer a *tour de force* of the general physicist but a highly developed field of specialised scientific technology. It was possible to foresee something of this evolution after Aston's great advance just about the end of the First World War, when accurate determinations of atomic masses gave a new significance to nuclear theory, but the great break through to all the modern potentialities is almost certainly something which it owed to the taking over of physics in large measure by the experts in electronics.

We are coming to expect more and more from the technique, and our demands seem to be satisfied. At first we were thrilled if we identified an isotope: next reasonably accurate atomic weights became possible. The big invasion into everyday chemistry came when fairly complex mixtures could be analysed. This did not come all at once. In the early forties I took good industrial opinion about the value of a mass spectrometer for the analysis of the products from hydrocarbon pyrolysis and similar chemical reactions and received discouraging advice, which I may say I was led to disregard (at any rate much earlier than I should have done otherwise) by the enthusiasm and foresight of my friend, H. C. Urey. Now we representatives of the "user" class take gas analysis for granted, and are even able to have separated for us constituents such as N_2 and CO with only fine structure mass differences.

The progress towards the satisfaction of more and more exacting technical demands is perhaps one of the major themes of the present conference, and it is clear from the list of papers that the subject is still rapidly on the move. Analysis of solid samples, or of high molecular weight compounds is now moving into the forefront. All these matters involve the most elaborate studies of the ion optics of the focusing processes, and naturally tend to pass more and more from the ken of the layman.

Mass spectrometry, I may remark, complicates life for the ordinary chemist in several ways. It is not merely that the machines become more and more complicated to understand: to that we are resigned. Shutting one's eyes, crossing one's fingers and trusting to the expert is in any event one of

the major features of modern life, and nobody looking at the programme of this conference could have doubts about the intense and high powered work on which he is relying. But oddly enough the accurate and detailed analyses which mass spectrometry provides are showing us that the things going on in our own fields are often very much more complicated than we thought they were. Where the process will stop I do not know, but that is the concern of other conferences than the present one.

There is one aspect of mass spectrometry where the cleavage into laymen and experts does not yet apply. This is, I should like to emphasise, a good thing, because the most live and truly scientific parts of any subject are those which excite the attention of the layman and the expert equally. I am referring now to the fundamental physics and chemistry of the processes by which the ions are formed, and in which they fragment to give the characteristic pattern shown in the mass spectrum of a complex molecule. The whole sequence of events is still in many ways rather a mysterious one, but it is of fundamental interest, and, indeed the behaviour of molecules in this fragmentation is a new and self-contained chapter of chemical kinetics. I am glad to note that there are a number of communications in the present symposium which touch on this topic.

Here perhaps I am indulging a certain personal bias. But the range of mass spectrometry is now so wide that it penetrates into fields as separate as surface chemistry, nuclear physics, geology, as other communications bear witness. It is evident that a very full and expertly documented discussion lies before you in the next three days.

CONTENTS

	Page
Foreword	xi
Editor's Note	xii
Opening Remarks	xiii
Professor Sir CYRIL HINSHELWOOD	

SESSION A

HIGH RESOLUTION MASS SPECTROMETRY

Chairman: A. O. NIER

Some New Atomic Mass Determinations Made with a Large Single-focusing Mass Spectrometer <i>J. T. Kerr, G. R. Bainbridge, J. W. Dewdney and H. E. Duckworth</i>	1
The Performance and Image Error Correction of the New Stigmatic Focusing Mass Spectrograph <i>H. Ewald, G. Sauermann and H. Liebl</i>	10
Mass Spectrometers and Mass Spectrographs Corrected for Image Defects <i>H. Hintenberger and L. A. König</i>	16
Correction of Second Order Aberrations in Inhomogeneous Magnetic Sector Fields <i>H. A. Tasman</i>	36
Theoretical and Experimental Study of High-mass High-resolution Mass Spectrometers <i>H. G. Voorhies, C. F. Robinson, L. G. Hall, W. M. Brubaker and C. E. Berry</i>	44
Design and Performance of a Double-focusing Mass Spectrometer for Analytical Work <i>R. D. Craig and G. A. Errock</i>	66

SESSION B

MASS SPECTROMETRY OF SOLIDS

Chairman: J. BLEARS

High Sensitivity Solid Source Mass Spectrometry <i>G. H. Palmer</i>	89
--	----

	Page
Isotope Dilution Analysis <i>R. K. Webster</i>	103
Ionization of Silver and Copper in a Triple-filament Ion Source <i>W. Weiershausen</i>	120
Investigation of the Time Variation of Alkali Ion Emission from Solid Specimens on Glowing Metal Surfaces <i>M. Kaminsky</i>	125
Determination of Impurities in Solids by Spark Source Mass Spectrometry <i>R. D. Craig, G. A. Errock and J. D. Waldron</i>	136
The Analysis of Non-conducting Solids by the Mass Spectrometer <i>J. A. James and J. L. Williams</i>	157
The Application of Mass Spectrometry to the Study of Surfaces by Sputtering <i>R. E. Honig</i>	162

SESSION C

APPLICATION OF THE MASS SPECTROMETER IN ORGANIC CHEMISTRY

I. Analysis and Instrumental Techniques

Chairman: H. POWELL

Status of Application of Mass Spectrometry to Heavy Oil Analysis <i>A. Hood and M. J. O'Neal</i>	175
Use of Rhenium Filaments and Low Ionizing Voltages for Analysing Liquid Products from Coal Hydrogenation by Mass Spectrometry <i>A. G. Sharkey, Jr., C. F. Robinson and R. A. Friedel</i>	193
The Analysis of Corrosive Gases with a Mass Spectrometer <i>P. G. Bentley, A. N. Hamer and P. B. F. Evans</i>	209
Mass Spectrometric Identification of Impurities in Organic Substances by Means of Additional Fractionation at the Inlet System <i>C. Bokhoven and H. J. Theeuwen</i>	222
Digitization of Mass Spectra <i>B. F. Dudenbostel, Jr., and P. J. Klaas</i>	232
The Time-of-flight Mass Spectrometer <i>D. B. Harrington</i>	249
A High Speed Cycloidal Mass Spectrometer <i>L. G. Hall, C. K. Hines and J. E. Slay</i>	266

II. Mass Spectra and Their Interpretation*Chairman: F. P. LOSSING*

	Page
Ion Dissociation Reactions in the Mass Spectrometer <i>A. L. Wahrhaftig</i>	274
Theoretical Aspects of the Mass Spectra of Polyatomic Molecules <i>G. R. Lester</i>	287
Ion-molecule Reactions in the Gas Phase <i>J. L. Franklin, F. H. Field and F. W. Lampe</i>	308
High Resolution Mass Spectrometry of Organic Materials <i>J. H. Beynon</i>	328
Interpretation of Mass Spectra of Organic Molecules <i>F. W. McLafferty</i>	355
The Mass Spectra of Some Organic Phosphates <i>A. Quayle</i>	365
Study of Rearrangement Processes in Mass Spectrometry by Means of Labelled Compounds <i>J. Collin</i>	384

SESSION D**IONIZATION AND ELECTRON IMPACT STUDIES***Chairman: A. L. WAHRHAFTIG*

Study of Multiple Ionization in Helium and Xenon by Electron Impact <i>R. E. Fox</i>	397
Recent Electron Impact Studies on Simple Molecules <i>D. C. Frost and C. A. McDowell</i>	413
Ionization Potentials of Alkyl and Halogenated Alkyl Free Radicals <i>F. P. Lossing, P. Kebarle and J. B. de Sousa</i>	431
Electron Impact Studies of Hydrazine and the Methyl-substituted Hydrazines <i>V. H. Dibeler, J. L. Franklin and R. M. Reese</i>	443
Negative Ion Formation and Electric Breakdown in Some Halogenated Gases <i>W. M. Hickam and D. Berg</i>	458
A Modification of the R.P.D. Method for Measuring Appearance Potentials <i>G. G. Cloutier and H. I. Schiff</i>	473

Kinetic Energy of Fragment Ions <i>R. Taubert</i>	Page 489
--	-------------

SESSION E

USE OF THE MASS SPECTROMETER IN
FUNDAMENTAL RESEARCH*Chairman: C. J. DANBY*

Isotopic Analysis of Trace Quantities of Rare Gases <i>A. O. Nier</i>	507
Mass Spectrometric Analysis of Simple Hydrogen Compounds <i>G. Nief and R. Botter</i>	515
The Mass Spectrometer as a Geological Instrument <i>R. D. Russell</i>	526
Mass Spectrometric Studies of the Thermodynamic Properties of Group III-V and Group II-VI Compounds and the Group V and VI Elements <i>P. Goldfinger and M. Jeunehomme</i>	534
Absorption and Desorption of Gases in the Ionized State on Metal and Glass Surfaces <i>J. H. Leck</i>	547
The Investigation of Certain Surface Processes by Mass Spectrometry <i>A. J. B. Robertson</i>	559
A Mass Spectrometer with a Low Temperature Ionization Chamber to Study Heterogeneous Reactions of Atoms and Free Radicals (Example: Iodine Atoms) <i>L. P. Blanchard and P. Le Goff</i>	570

BIBLIOGRAPHY ON MASS SPECTROMETRY

Introduction	593
Section A: Instrument Design	595
Section B: Operating Techniques	620
Section C: Applications to Isotopic Problems: Ca Atomic weights and isotopic constitution of the elements Cb Isotopes used as tracers	630 649
Section D: Applications to Organic Chemistry	651

CONTENTS

ix

	Page
Section E: Ionization and Dissociation of Molecules	665
Section F: General Applications in Engineering and Physics	677
Section G: Applications to Solids	687
Name Index	690

SOME NEW ATOMIC MASS DETERMINATIONS MADE WITH A LARGE SINGLE-FOCUSING MASS SPECTROMETER*

By J. T. KERR†, G. R. BAINBRIDGE‡, J. W. DEWDNEY§
and H. E. DUCKWORTH

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Hamilton, Ontario, Canada

Summary—A large semi-circular magnetic analyser with a resolving power (at the base of the peaks) of ~ 9000 has been used to determine the atomic masses of ^{84}Kr , ^{86}Kr , ^{129}Xe , ^{132}Xe , ^{200}Hg , ^{201}Hg and ^{204}Hg to a precision of $\sim 1/2,000,000$. In this work the necessary doublet spacings were determined by a beam modulation technique. This technique and certain other details of the apparatus are described.

INTRODUCTION

THE determination of atomic masses by mass spectroscopic methods has usually involved the use of either a double-focusing or cyclotron-resonance type of mass spectroscopy. Aston's work, done with an instrument possessing velocity-focusing alone, is a notable exception. Also, a single example appears in the literature in which a direction-focusing instrument was used for this purpose. In this latter instance, Ney and Mann⁽¹⁾ employed a small sector-type mass spectrometer to determine the mass ratio $\text{He}^{++}/\text{H}_2^+$. As this instrument possessed no velocity-focusing property, the attainable accuracy (1 part in 80,000) was limited not only by the geometrical resolution, but also by the energy spread that characterized the ion beam.

A large Dempster-type double-focusing mass spectroscopy has been under construction in this laboratory. We have used the magnetic-analyser portion of this instrument as a single-focusing, semi-circular mass spectrometer and with it have made a number of atomic mass comparisons that are similar in principle to that done by Ney and Mann. The actual resolution of this instrument (at the base of the peaks) is $\sim 1/9000$. This, plus a special beam-modulation technique, has enabled us to determine the masses of ^{84}Kr , ^{86}Kr ,

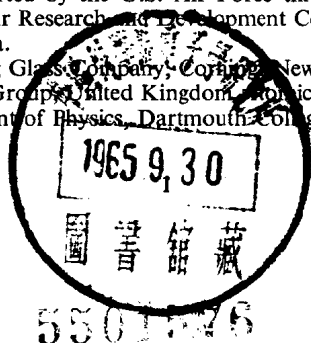
* This work was supported by the U.S. Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, and by the National Research Council of Canada.

† Now with the Corning Glass Company, Corning, New York, U.S.A.

‡ Now with Industrial Group, United Kingdom Atomic Energy Authority.

§ Now in the Department of Physics, Dartmouth College, Hanover, New Hampshire, U.S.A.

B



^{129}Xe , ^{132}Xe , ^{200}Hg , ^{201}Hg and ^{204}Hg with a precision of approximately one part in two million.

THE MASS SPECTROMETER

The mass spectrometer is shown schematically in Fig. 1. Ions formed in an electron bombardment source are accelerated between S_1 and S_2 to an energy of $\sim 50n$ keV, when n is the number of charges carried by the ion. They are then collimated by slits S_2 and S_3 and are deflected in the homogeneous magnetic field so that those with a particular value of specific charge reach the collector slit S_C . Those that pass through the slit emerge from the magnetic field and enter, via the slit S_M , a 14-stage Allen-type electron multiplier, where they are detected.

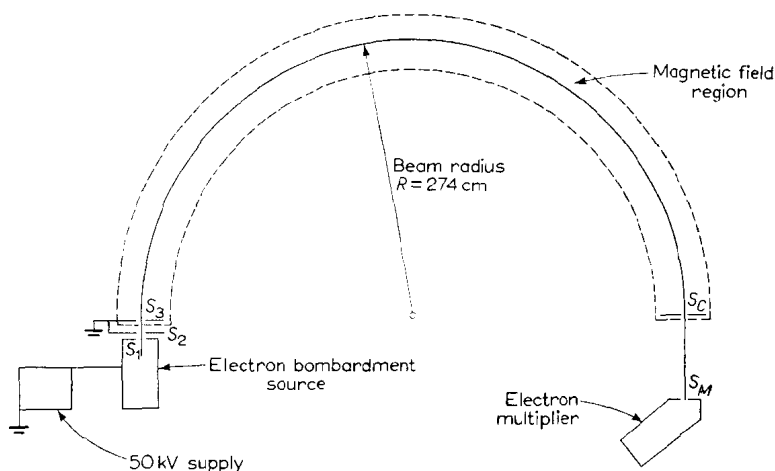


FIG. 1. Schematic diagram* of the mass spectrometer

$S_1 = 0.006$ in., $S_2 = 0.007$ in., S_3 is variable,
 $S_4 = 0.005$ in. and $S_M = 0.25$ in. Interslit
 distances are $S_1-S_2 = 0.5$ in. and $S_2-S_3 = 2.5$ in.

The magnet of the analyser is a composite structure, consisting of twenty-eight separate C-shaped electromagnets placed side by side so as to provide a semi-circular annular field of median radius 274 cm. A stabilized flux of 500–1600 oersteds can be established in the 2 cm gap. Stabilization is accomplished either by controlling the current to the coils of the magnet or by using proton-resonance control*. In the latter case the probe is located in the gap of one of the twenty-eight magnets. Current control is used when an extended portion of the mass spectrum is being scanned, while proton-resonance control is employed when mass determinations are being made. The proton-resonance control provides a stability of about one part in a million over periods of several minutes.

* The control systems were designed by Dr. H. E. Petch of this University.

A rectangular copper pipe, 4 in. \times 0.75 in. in cross-section, especially drawn for us by the Anaconda Copper Company of Canada Ltd., is located in the pole gap of the magnet and serves as the vacuum chamber. Three oil diffusion pumps, located at the 45°, 90° and 135° positions and supplemented by liquid-air traps, establish a pressure of $\sim 10^{-6}$ mm Hg*.

The accelerating voltage is provided by a locally-modified, high-voltage unit (Beta Electric Corporation of New York) which is capable of supplying a 2 mA current in the range 40–100 kV. This unit is operated at ~ 50 kV and is stable (a.c. and d.c.) to one part in 100,000 for several minutes at a time. For shorter periods, but sufficiently long to permit a mass comparison to be made, the d.c. stability of the accelerating voltage must be, and is, higher than this figure by at least an order of magnitude.

Adequate monochromaticity in the ion beam, as required by the absence of velocity-focusing, was achieved in this work by using parent ions only. All materials that were used as sources of ions, with the exception of mercury, were either gaseous at STP or possessed a sufficiently high vapour pressure that they could be introduced into the ionization chamber of the source through a conventional leak system. To secure mercury ions, a drop of mercury was placed in the gas inlet system in a position, near the ionization chamber, where the temperature was considerably above room temperature. Thus, its vapour pressure was increased to a value at which the desired mercury ion current could be obtained.

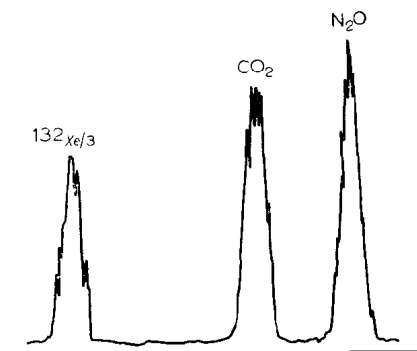


FIG. 2. Chart recorder trace of the mass triplet. $\text{N}_2\text{O}-\text{CO}_2-^{132}\text{Xe}/3$

The resolving power of the instrument is illustrated by Fig. 2, which shows a chart-recorder trace of the triplet at mass number 44 formed by singly-charged N_2O and CO_2 and triply-charged ^{132}Xe . For the values of S_3 and S_C used to obtain Fig. 2, the theoretical resolving power (at the foot of the peaks), calculated on the basis of first-order focusing theory and a monochromatic ion beam, is 1/9800. The actual resolving power, as deduced from Fig. 2, and many other similar traces, is about 1/9000. Most of the fluctuations on the trace are caused by small changes in the accelerating voltage.

* Dr. B. G. Hogg, now at the University of Manitoba, was largely responsible for the vacuum system.

Some of the small irregularities are due to the random arrival of ions at the multiplier. The maximum ion current recorded in Fig. 2 was about 1000 ions/sec. Further evidence that the actual resolving power is comparable with the calculated value was provided by the mass spectral doublet formed by singly charged- C_2F_4 and doubly-charged ^{200}Hg . These two doublet members differ in mass by one part in 10,000 and have been almost completely resolved.

METHOD OF DETERMINING ATOMIC MASS DIFFERENCES

It will be recalled that the effective mass M^* of an ion that traces an orbit of radius R in a mass spectrometer is given by:

$$M = \frac{150 e B^2 R^2}{V c^2} \quad \dots(1)$$

where e is the electronic charge in e.s.u., B is the magnetic induction in oersteds, R is the radius of the semi-circular orbit terminating at S_C and V is the total accelerating voltage. In the "doublet" method of mass comparison, two ions whose specific charges are almost, but not quite, equal are brought in turn to the collector by appropriately varying either B or V . The difference in the effective mass, ΔM , between the two ions in question is then obtained from:

$$\frac{\Delta M}{M_2} = \frac{M_2 - M_1}{M_2} = 2 \frac{(B_2 - B_1)}{B_2} = 2 \frac{\Delta B}{B_2} \quad \dots(2)$$

keeping V constant, or from

$$\frac{\Delta M}{M_2} = \frac{M_2 - M_1}{M_2} = \frac{V_1 - V_2}{V_2} = \frac{-\Delta V}{V_2} \quad \dots(3)$$

keeping B constant. If M_2 is accurately known, the mass, M_1 of the other member of the doublet may be determined in terms of the measureable quantities B_1 and B_2 or V_1 and V_2 .

We have, in an earlier publication, described⁽²⁾ preliminary experiments, based upon the use of expression (2), in which the flux values necessary to bring M_1 and M_2 in turn to the collector slit were obtained in terms of the proton resonance frequency. It has since been discovered that hysteresis effects in the individual magnets comprising the momentum analyser invalidate the mass difference values that are obtained in this manner. In the work described in this paper the mass difference values have been obtained in terms of accelerating voltages, using expression (3). We have checked the validity of this relationship for our instrument by determining thereby, by direct measurement of V_1 and V_2 , a known mass difference of ~ 7 amu.

* The effective mass of a singly-charged ion is simply its mass; for multiply-charged ions, it is given by the actual mass of the ion divided by the number of charges it carries.