



# The Evolution of Mass Spectrometry: 1910 to 1940

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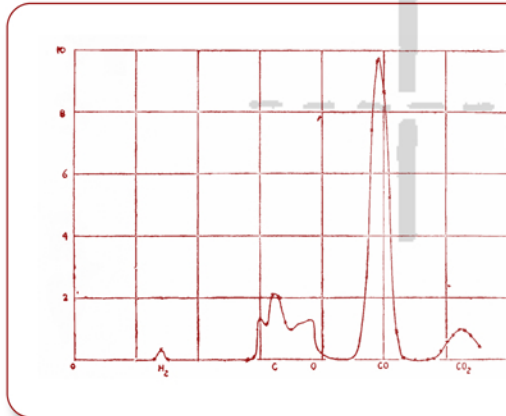
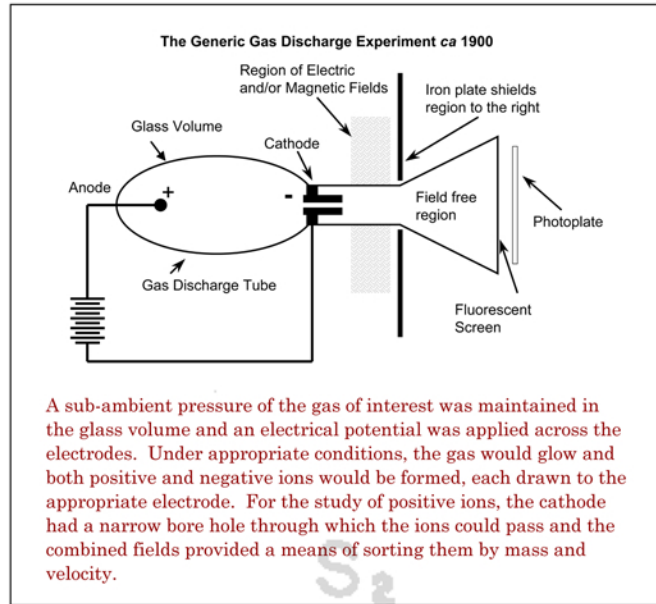
## Investigation of 'RAYS POSITIVE OF ELECTRICITY'

### WHAT ARE THEY?

Slow canal rays, anode rays, positive rays, *kanalstrahlen*, rays of positive electricity, canal rays – they all stood for the same thing, what we call today, positive ions. The uncertainty as to what was being observed in gas discharge experiments during the 19th century led investigators, frequently working alone and in different countries, to name things in their observations as they felt.

As with studies of cathode rays, the gas discharge apparatus was used to create ions for the investigation of rays of positive electricity.

Wilhelm Wien investigated *kanalstrahlen* by setting the electric and magnetic fields of his apparatus at right angles to each other. He made two important observations: 1) much stronger magnetic fields were required to deflect the *kanalstrahlen* compared to cathode rays; and 2) several 'lines' appeared on the screen, suggesting that the rays were not all the same mass – as was observed in the case of cathode rays. Wien continued experimenting with *kanalstrahlen* until the mid 1920s, but he didn't pursue the analytical capabilities of his apparatus. However, the arrangement of the electric and magnetic fields used in his early experiments is in use today in nuclear physics as a velocity filter for ions, the Wien Filter.



**The 'First' Mass Spectrum from a Mass Spectrometer?**

The spectrum shown here, published in 1912<sup>28</sup> is probably the first mass spectrum obtained from a mass spectrometer. It was recorded with Thomson's parabola mass analyzer, but instead of holding the fields constant and recording the spectrum on a photographic plate – the ion detection method of the mass spectrograph – Thomson placed a parabolic shaped slit in front of a Faraday cage and measured the ion current as he varied the magnetic field.



Wilhelm Wien



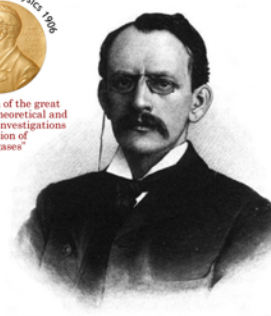
"for his discoveries regarding the laws governing the radiation of heat"

### Contemporaries and Competitors

Some maintain that Wien preceded Thomson in the creation of the first mass spectrograph. They certainly performed many similar experiments and each was aware of the other's work. Perhaps Wien was first, but Thomson's Cavendish lab group used his positive ray apparatus to begin the analysis of the elements; a pursuit that lasted into the 1940s.

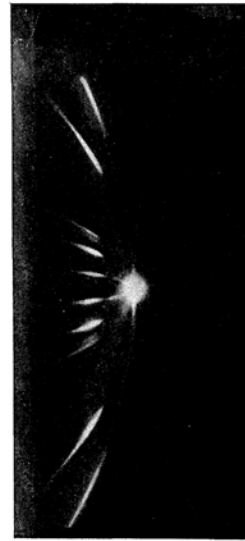


"in recognition of the great merits of his theoretical and experimental investigations on the conduction of electricity by gases"



Sir J.J. Thomson

In 1906, the same year that J. J. Thomson was awarded the Nobel Prize in Physics for determining the properties of the electron; he turned his attention to the investigation of 'rays positive of electricity'. In his experiment, the electric and magnetic fields of the apparatus were parallel.



A parabola mass spectrum recorded with the apparatus to the right. A photographic plate replaced the fluorescent coating.<sup>1</sup>

His initial results perplexed him, being primarily artifacts of the poor vacuum of his apparatus and the nature of the material used for the fluorescent screen. Upon Aston's arrival in 1909, the first interesting results were obtained from the experiment. Once the vacuum had been improved, several different parabolas were observed on the fluorescent screen, indicating that positive rays had different  $e/m$  ratios, reflecting the presence of different gases in the discharge. In essence, Thomson's apparatus for the analysis of positive rays was the first mass spectrograph<sup>1</sup>.

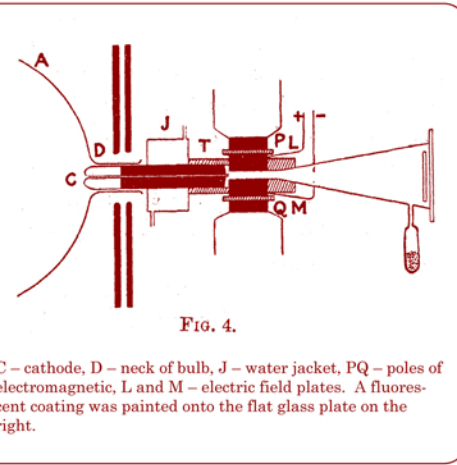


Fig. 4.

C – cathode, D – neck of bulb, J – water jacket, PQ – poles of electromagnetic, L and M – electric field plates. A fluorescent coating was painted onto the flat glass plate on the right.

## THE NEXT GENERATION BUILDS BETTER MASS ANALYZERS

While Thomson foresaw the analytical utility of the positive ray apparatus and promoted it in both the literature<sup>2</sup> and a book<sup>3</sup> Aston was acutely aware of the limitations of the positive ray analyzer. Consequently, he chose to construct a different mass analyzer, the first in a series of three instruments based on the same design that gave ever increasing performance with refinements in succeeding decades. With the first of these instruments, Aston unequivocally showed that the line at  $m/e$  22 was due to an isotope of neon.



"for his discovery, by means of his mass spectrograph, of isotopes, in a large number of non-radioactive elements, and for his enunciation of the whole-number rule"

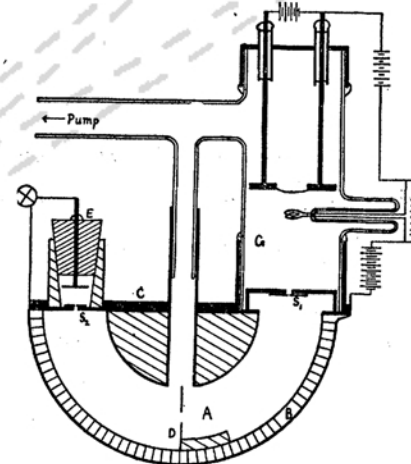
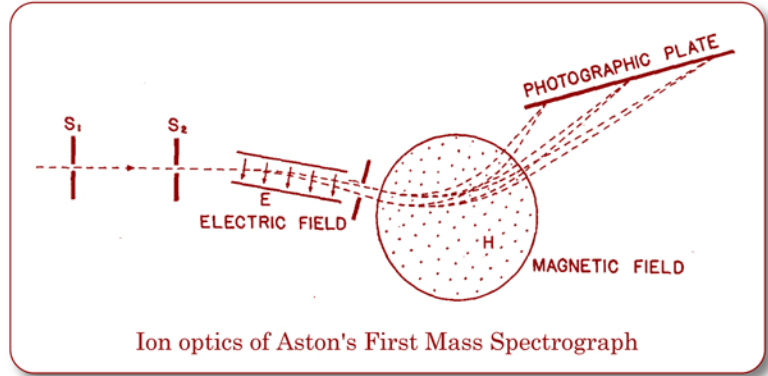


Fig. 1.

With this simpler mass analyzer design, Dempster began his own research into the mass and relative abundance of the elements and their isotopes. He heated salts of the elements of interest placed on platinum ribbons (Region G). The slits S1 and S2 were adjustable, and a screen placed at D "was . . . to prevent reflected rays from getting into the second slit." The semicircular analyzer tube was placed between the poles of a powerful electromagnet. Both Wien and Thomson feared that the fringe field from the magnet would skew the path of the ions prior to entering the analyzer region, but Dempster conducted measurements to show the effect to be negligible. This fundamental design was adopted by several later researchers and served as the basis for the Consolidated Engineering Corporation's 21-102, -103, and -104 analytical mass spectrometers.

Using this instrument and improved variations of it, Dempster competed with Aston in the business of determining the masses and relative abundances of the elements and their isotopes over the next several decades.



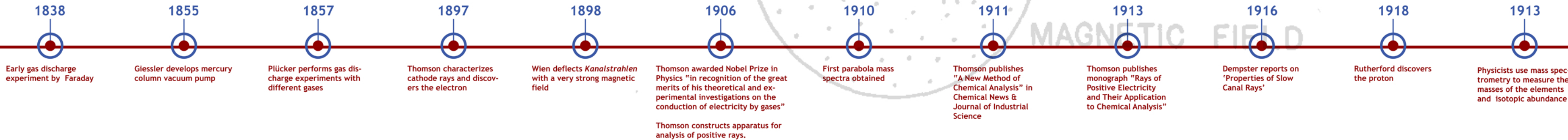
Ion optics of Aston's First Mass Spectrograph

Using this basic design, Aston began investigating the mass and relative abundance of the elements and their isotopes.

As the table shows, Aston was not alone in this work. As early as 1916 Arthur J. Dempster, who had studied under Wien at the University of Wurzburg, proposed a different approach to the analysis of positive rays. He initially duplicated Thomson's positive ray analysis instrument; but soon abandoned it for a simpler approach. He designed an ion source that produced ions with a low, controllable energy and a small energy spread compared to the ions produced by the more

Year	Elements	Investigator	References
1919	Neon, Chlorine, Mercury	Aston	(4), (5)
1920	Argon, Helium, Hydrogen, Nitrogen, Krypton, Xenon	Aston	(6), (7)
	Boron, Fluorine, Silicon, Bromine, Sulphur, Phosphorus, Arsenic	Aston	(7)
	Iodine	Aston	(8)
	Magnesium	Dempster	(9), (10)
1921	Lithium	Aston & G. P. Thomson	(11)
	Lithium	Dempster	(12), (13)
	Sodium, Potassium, Rubidium, Cesium	Aston	(14)
	Nickel	Aston	(15)
	Beryllium	G. P. Thomson	(16), (17)
	Zinc	Dempster	(18)
1922	Calcium	Dempster	(19)
	Xenon (new isotopes), Iron,	Aston	(20)
	Selenium, Aluminum	Aston	(21)
	Xenon (additional rare isotopes)	Aston	(22)
	Antimony	Aston	(23)
1923	Germanium	Aston	(24)
	Copper	Aston, Dempster	(25), (26)
1924	Scandium, Titanium, Vanadium, Chromium, Manganese, Cobalt, Gallium, Strontium, Yttrium, Silver	Aston	(27)
	Barium, Lanthanum, Praesodymium, Neodymium, Zirconium, Cerium, Cadmium, Tellurium, Bismuth	Aston	(22)

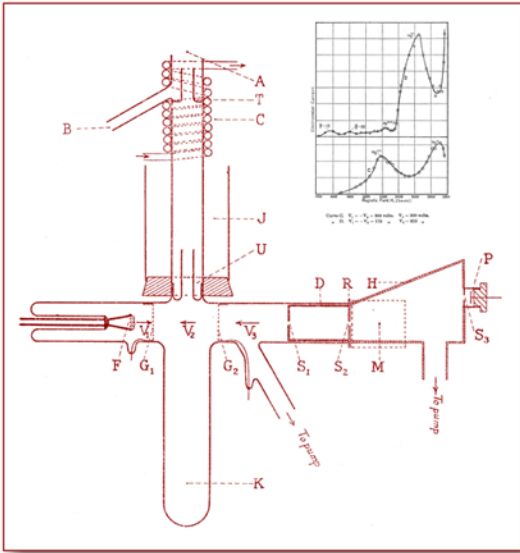
robust gas discharge ionization method. Consequently, he was able to use a single magnetic sector mass analyzer for mass separation of these 'slow canal rays', rather than the two sectors required in Aston's apparatus.





## BETTER WAYS TO MAKE IONS

Interest in the ionization potential of the elements, the photoelectric effect and the formation of X-rays were all intertwined in physics research beginning in the late 19th century. Obviously, the gas discharge method of ionization did not lend itself to such studies! While a variety of experiments were used to investigate ionization potentials, the first to utilize a mass spectrometer, albeit a crude one, was performed by Smyth in 1922 working as a National Research Fellow in Aston's lab<sup>29</sup>. With this apparatus, he was able to determine the first and second ionization potentials of mercury.

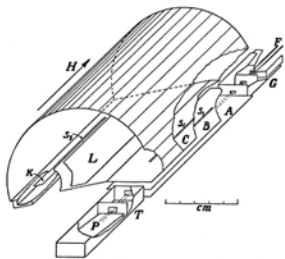


### Smyth's Simple 'Mass Spectrometer'

The electrically heated filament at F provided a source of electrons and the voltages on the grids at G1 and G2 controlled their energy in the cross section of the apparatus. The vertical apparatus supplied a constant, low velocity stream of mercury atoms, entering at A and passing between the grids where they would undergo ionization. Positive mercury ions were accelerated by a voltage on the slit system S1 and S2. A magnet located at M directed ions to the detector, P, behind slit S3. By varying the magnetic field singly, doubly, and triply charged ions could be observed depending upon the electron energy in the ionization region.

Walker Bleakney, working under John Tate at the University of Minnesota in 1929, was charged with revisiting the ionization potentials of mercury<sup>30</sup>. The novel idea in his ion source was to use a stream of electrons generated by an electrically heated filament and accelerated through a potential difference, just as Smyth had done, BUT collimated by a co-linear magnetic field. The same magnetic field was then used to mass analyze the mercury ions. This instrument was not specifically designed as an analytical mass spectrometer, but in a later publication<sup>31</sup> Bleakney described a modified version of this instrument that he refers to as a "mass spectrograph" for the study of the ionization potential of molecular hydrogen.

While this mass analyzer design saw limited use, the production of ions from gases by an electron beam collimated by a magnetic field was quickly adopted by other workers in the field.



Isometric drawing of the apparatus with sections cut away to show the interior. All dimensions are to scale except the widths of the slits which are 1.0, 0.2, and 0.5 mm for S<sub>1</sub>, S<sub>2</sub> and S<sub>3</sub> respectively.

An electrically heated filament, F, provided a source of electrons that were accelerated through the ionization region, A, to the electrode at P. Ions were accelerated by voltages on the plates B and C with slits S1 and S2. The whole apparatus was placed in the core of a solenoid providing the magnetic field H. Thus, ions followed a circular path through slit S3 to the collector K.

## EARLY ADOPTERS OF ANALYTICAL MASS SPECTROMETRY

Beginning around 1930, the development of more sensitive and higher resolving power mass analyzers was pursued in labs around the world. Physicists remained the dominant users and pursued the development of better instruments for the study of the elements and their isotopes. A core group of physicists pursued the development and application of mass spectrometry to problems of interest in the physics community.

Investigator	Affiliation
Aston	Cambridge UK
Bainbridge	Bartold Research Foundation of the Franklin Institute, Harvard University
Bleakney	University of Minnesota, Princeton University
Dempster	University of Chicago
Henneberg	Berlin
Mattauch	University of Vienna
Mohler	National Bureau of Standards
Tate	University of Minnesota

A number of hardy souls outside of the physics community decided to apply the analytical capabilities of mass spectrometry in their research. They were mostly biologists, drawn to the idea that stable isotopes could be used to track metabolic processes in living organisms; an approach preferred over the use of radioactive isotopes.

These early adopters did not have the luxury of purchasing instrumentation from a company. They relied in large part on the good will of their colleagues in nearby, and not so nearby, physics departments. In this letter, Harold Urey, having won the Nobel Prize in Chemistry in 1934 is requesting help with his instruments from Al Nier.

For the most part, their physicist colleagues responded favorably to these requests for help, but not without asking for some financial remuneration. In August 1942, Nier sent Urey a bill for "the construction of three mass spectrometer tubes" in the amount of \$257. Most of that was for 100 hours of machinist time at \$1.50 per hour. The Minnesota physics department levied a 10% overhead charge of \$15.00 for the machinist's time!



"for his discovery of heavy hydrogen"

Columbia University  
in the City of New York  
Department of Chemistry

March 5, 1941

Prof. H. O. Nier  
University of Minnesota  
Minneapolis, Minnesota

Dear Professor Nier:

Neither Professor Taylor nor my men here have been able to get our mass spectrometer of the type which you recently described, running. We finally gave it up and went back to using the old one. From what I hear from Taylor he is unable to get his going, though he has had it going in excellent shape for short periods of time.

We need both of these mass spectrometers very badly on National Defense work. In fact, the bottleneck on our work is at the mass spectrometer.

I am wondering whether it would be possible for you or perhaps one of your well-trained assistants, to come to Columbia and to produce for a couple of weeks if necessary, and help us to locate the difficulty with these instruments. It would be very glad to pay you for the time if this is necessary.

We need these mass spectrometers for a program which we wish to have completed in the next two months, and hence some action on our bottlenecks in the near future would be highly desirable. May I say that this work is regarded as of first importance in National Defense.

Would you please consider our proposition and let us know if you can help us out.

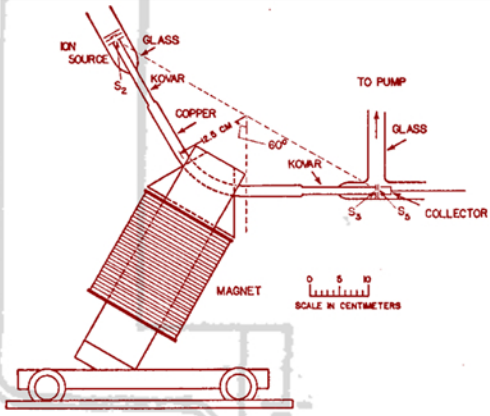
Very sincerely,  
Harold C. Urey

Harold C. Urey

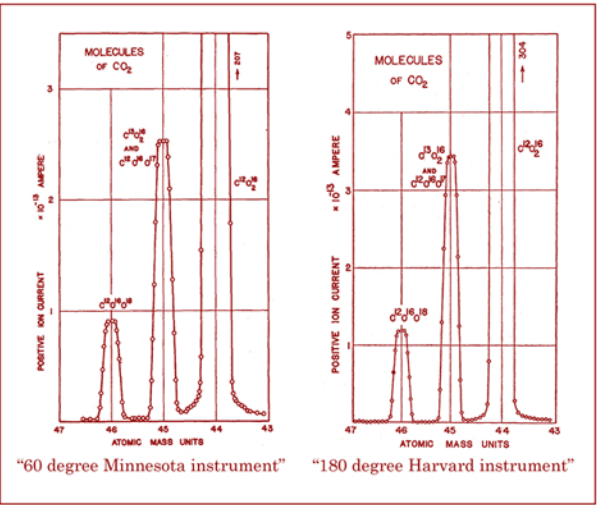
AIR MAIL

## SYNTHESIS OF PROGRESS

The most important figure in the evolution of mass spectrometry from a cantankerous tool used primarily by physicists investigating the elements and their isotopes to an analytical tool for chemists was Alfred Otto Carl Nier. Earning both Bachelors and Masters degrees in Electrical Engineering at the University of Minnesota, he then turned to the Physics Department for his doctorate which he obtained in 1936. After completing a National Research Council Fellowship at Harvard in 1938; Nier returned to the Physics Department at Minnesota to begin his academic career. Faced with limited resources compared to those available to him at Harvard, Nier focused on creating small, rugged, inexpensive instruments that consumed less power and were easy to fabricate.

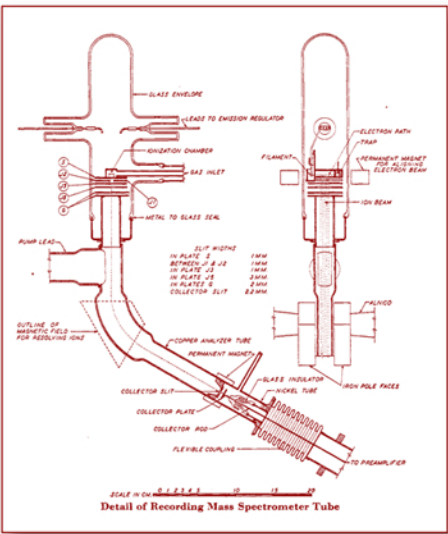


Nier's 60° magnetic sector instrument required a smaller magnet, simpler electronics, and included all of the recent advances in electron bombardment ionization in his ion source. In his 1940 publication<sup>32</sup> he asks the reader to compare the carbon dioxide spectrum obtained with this instrument to that obtained with the instrument he used at Harvard that was much more expensive and complicated.



Nier used his simple 60° instrument to conduct a series of experiments with his colleague at Iowa State University, Harland Wood, investigating the metabolic pathways of carbon dioxide in bacteria. This collaboration resulted in more than a dozen publications in the span of a few years.

In 1943, Nier was 'drafted' into the Manhattan Project and charged with the task of analyzing contaminants in the process stream of the gaseous diffusion plant at Oak Ridge. He adapted his 60° design to the specific requirements of that task. Two instruments were required at each of the fifty stages in the diffusion plant<sup>34</sup>; one on-line and the other ready to go on-line if needed.



The details of the process stream mass spectrometer are shown. This information wasn't published until 1948 since all work on the Manhattan Project was held in strictest secrecy during the war years.

Nier also created the helium leak detector while working at the diffusion plant. Air and moisture had to be avoided at all costs in the working parts of the diffusion system, otherwise reactions with uranium hexafluoride would plug the pores of the diffusion membranes. His helium leak checking method had sufficient sensitivity to find the smallest and most damaging leaks. His interest in helium piqued as a result of this work, he proceeded to publish 20 papers on the element and its isotopes in the atmosphere, stratosphere, and extraterrestrial matter from the end of the Manhattan Project until 1994!

By synthesizing critical developments in the field, such as the simple magnetic sector analyzer and the electron bombardment ion source, along with technical developments in vacuum systems and electronics, he used his superior command of electronic circuits to build easy to use, reliable instruments with high sensitivity and improved resolving power. Through Nier's efforts, it was clear by the beginning of the '40s that mass spectrometry was poised to become the analytical tool for the chemist that Thomson had long ago envisioned. It only awaited a daring entrepreneur.

Alfred Otto Carl Nier, ca 1940, at the console of his 60° instrument. Here, he is preparing to manually record a mass spectrum point-by-point in the manner of the spectra of carbon dioxide shown to the left.



"for (their) experimental discovery of the diffraction of electrons by crystals"



1922



Aston publishes the 1st Edition of "Isotopes"

1924



Aston publishes the 2nd Edition of "Isotopes"

1925



International Committee on Chemical Elements issues report on atomic weights

Mohler begins photoionization studies at National Bureau of Standards

1929



Bleakney reports on 'A New Method of Positive Ray Analysis . . .'

Bainbridge issued patent for 'Photoelectric Tubes'

1930



Atanasoff reports on 'The Dielectric Constant of Helium'

1931



Bleakney at Minnesota uses his 'new mass spectrograph' to study the ionization potential of molecular hydrogen

1932



Chadwick discovers the neutron

1933



Urey publishes 'A Name and Symbol for H<sup>2</sup>'

Bainbridge publishes 'Equivalence of Mass and Energy'

1935



Dempster publishes 'Table of Nuclear Transformations'

Schoenheimer & Rittenberg publish series of articles on 'Deuterium as an Indicator in the Study of Intermediary Metabolism'

1936



Mattauch publishes 'A Double-Focusing Mass Spectrograph and the Masses of N<sup>15</sup> and O<sup>18</sup>'

1938



Nier completes National Research Council Fellowship at Harvard and returns to Minnesota

1939



Clifford Berry completes his undergraduate study in Electrical Engineering at Iowa State College



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