Arthur J. Dempster: North America's First Mass Spectroscopist

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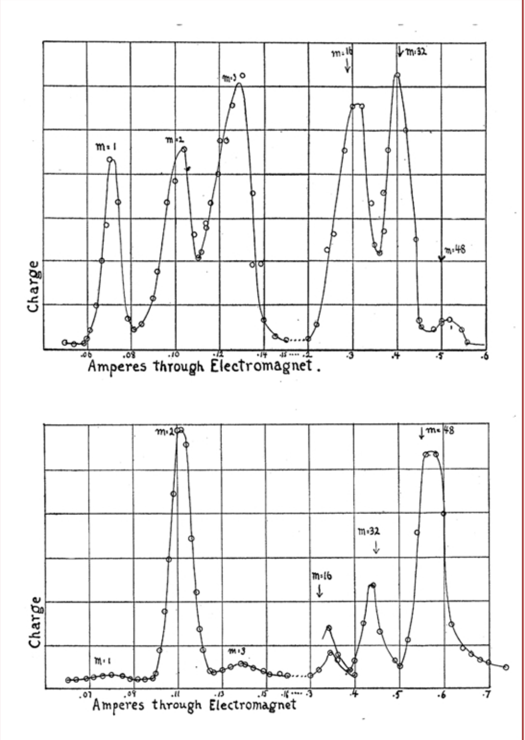
Dempster first ventured into 'positive ray analysis' during his doctoral research in which he studied the properties of slow canal rays[1] (positive ions) using a positive ray analyzer patterned exactly after that described by Thomson[2]. The most popular method of ionization was by gas discharge which produced energetic ions with a wide range of high velocities. Dempster chose instead to ionize gases by electrons emitted from a Wehnelt cathode[3], and was thus able to produce ions whose velocity he could control. Further, he was able to vary the pressure of the gases under investigation while still maintaining ionization of the gas.

Biographical Sketch

Arthur Jeffrey Dempster was born in Toronto in 1886 where he took Bachelors and Masters Degrees at the University of Toronto; completing the latter in 1910. He began his scientific career in 1911 when he was named an "1851 Exhibition Scholar" and chose to work on his doctorate in the laboratory of Professor Wilhelm Wien at the University of Würzburg. Originally intending to study electrical discharges in gases with Wien, he was forced to abandon this plan by the outbreak of hostilities in World War I and return to Canada. He completed his graduate studies in the physics department at the University of Chicago where he received his doctorate in 1916. After becoming a United States citizen and enlisting in the U.S. Army for two years, he returned to the University of Chicago and became a member of the physics faculty in 1919; where he remained until his death in 1950.



THE ORIGIN OF MASS SPECTRAL LINE WITH MASS 3

The ability to control the gas pressure during the ionization process permitted Dempster to make some interesting observations about the ion with mass three observed earlier by Thomson[4].

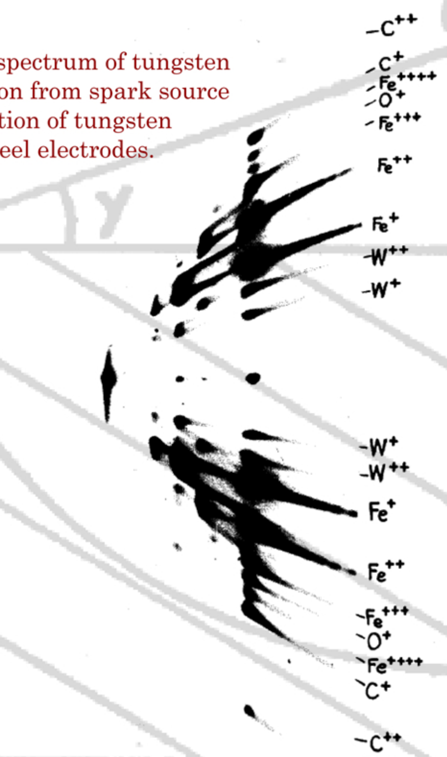
"The electrons cannot dissociate the molecules into atoms, but, when the pressure is taken higher so that the positive(ly charged) molecules make collisions, they dissociate the hydrogen. That H_3 is not present when the gas is not dissociated shows that it is an unstable complex formed in the discharge tube itself, probably a neutral hydrogen molecule to which a charged hydrogen atom has attached itself."

Mass spectra of hydrogen at high pressure *(top)* and low pressure *(bottom)*. Early evidence of chemical ionization?

After his experience with the Thomson design positive ray analyzer, Dempster began in 1917[5] to construct a new instrument based on a completely different form of mass analyzer, a 180° magnetic sector[6]. Returning from his tour of duty in the U. S. Army, he began to use the new instrument to investigate the isotopes of various elements and was the first to report on magnesium[7], zinc[8] and calcium[9] in the early '20s. He was able to study these solid elements by the use of a unique method of ionization in which the anode of the ion source either contained or was composed of the element of interest. This research was ongoing at the same time that Aston was creating his first mass spectrograph[10] at the Cavendish lab in Great Britain. Dempster reported results on lithium[11] and copper[12] within months of the same elements' isotopic composition being reported by Aston[13, 14].

Dempster conceded Aston the role of measuring the isotopes of the elements for the next decade. However, in the mid-30s, he devised a new ionization method to study several elements that had not yet been investigated due to the difficulty in ionizing them. The high frequency oscillating spark source was inspired by work that Millikan had done to enhance spectrum lines of the elements in the far ultraviolet[16]. Adapting this technique to mass spectrometry, Dempster had to deal with the wide energy spread in ions created by the spark source, and at first, resurrected his old Thomson positive ray analyzer, well-suited for mass analysis of energetic ions. However, based on ion optical calculations performed with Bartky[17] in 1929, Dempster created a new mass analyzer incorporating his 180° magnetic sector concept preceded by a 90° electric sector[18].

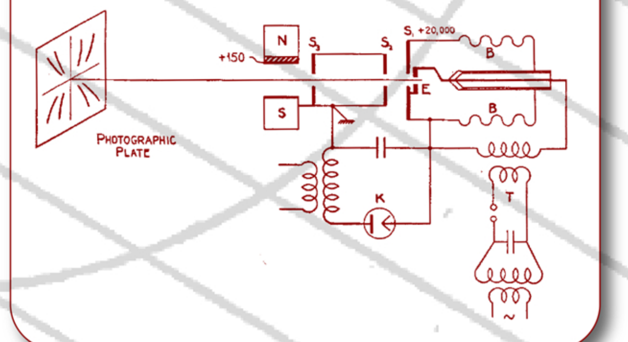
Mass spectrum of tungsten and iron from spark source ionization of tungsten and steel electrodes.



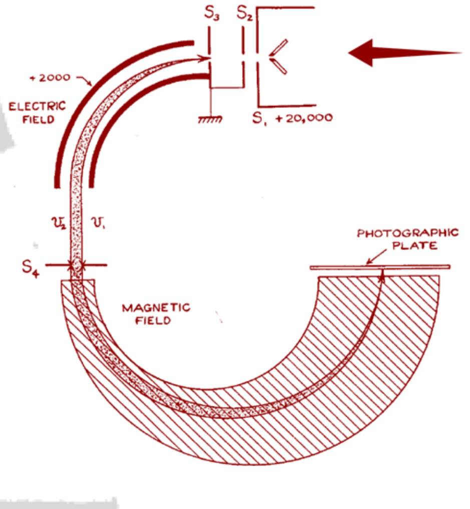
HIGH FREQUENCY SPARK SOURCE

The sample, of necessity, a conducting metal, was shaped into electrodes, (E), one of which was connected to the Tesla circuit (T). The other electrode was grounded. The bellows, (B), permitted movement of the electrified electrode relative to the grounded one thus generating a spark containing ions of both electrodes.

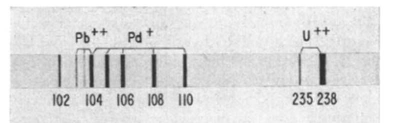
Diagram of original spark source for the ionization of metal electrodes



Using this instrument, Dempster determined that gold was monoisotopic, repeated the analysis of platinum, rhodium and palladium that Aston had performed earlier, and discovered the presence of the ^{235}U isotope of uranium, not previously observed by Aston[19, 20]. Dempster also used this instrument for the discovery of new isotopes of cerium and barium[21].



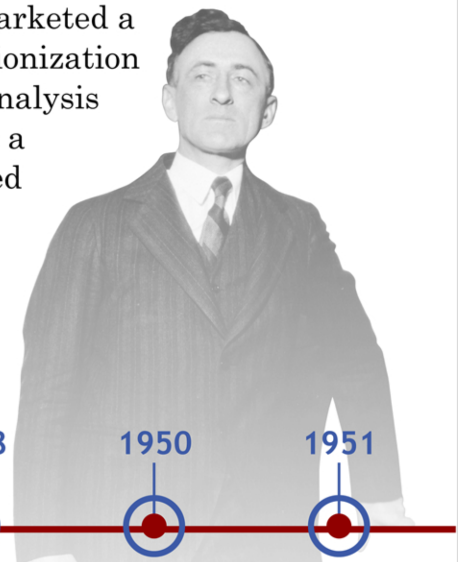
Dempster's double focusing mass spectrograph obtains perfect focusing at only one position on the photographic plate, but this was not considered a problem since accurate mass measurement involved closely matched doublets.



Mass spectrum of uranium showing the faint isotope of mass 235. The palladium is from one electrode and served for calibration. Dempster was the first to report this isotope of uranium.

Bainbridge had provided experimental evidence[22] supporting Einstein's famous equation relating energy to mass by investigating the mass differences between hydrogen, helium and lithium. However, in 1938, Dempster investigated the energy content of the heavy elements[23], providing information about the uranium isotopes that would be important later. In 1941 he became a member of the "Metallurgical Project" at the University of Chicago and subsequent to its success was invited to join the research effort at Argonne National Laboratory[16]. It is interesting to note that his publication record shows only one paper from 1939 to 1947; reflecting the classified nature of his research during that time period. After 1947, his research was devoted to the transmutation of various elements as the result of neutron absorption.

In 1942 Consolidated Engineering Corporation marketed a mass spectrometer based on Dempster's electron ionization method and 180° magnetic sector design for the analysis of hydrocarbons. This mass analyzer concept had a long life, the last such instruments being marketed in the late '60s. The successful introduction of this instrument outside the physics community marked the beginning of the use of analytical mass spectrometry in the chemistry community.



- **1910** Wien reports on Postive Rays (Kanalstrahlen)
- **1913** Thomson publishes monograph *Rays of Positive Electricity and Their Application to Chemical Analysis*
- **1916** Dempster publishes "The Properties of Slow Canal Rays" in Physical Review
- **1918** Dempster publishes "A New Method of Positive Ray Analysis" in Physical Review
- **1919** Aston publishes "Neon" in Nature. Aston publishes "A Positive-Ray Spectrograph" in Philosphical Magazine
- **1922** Aston publishes monograph *Isotopes*
- **1925** Wien reviews "Recent Researches in Positive Rays" in Nature
- **1927** Aston presents Bakerian Lecture on a new mass spectrograph and the whole number rule to the Royal Society of London
- **1929** Bartky & Dempster publish "Paths of Charged Particles in Electric and Magnetic Fields" in Physical Review
- **1930** Bainbridge publishes "Simple Isotopic Constitution of Cesium" in Physical Review
- **1931** Urey discovers isotope of hydrogen
- **1933** Aston publishes monograph *Mass-spectra and Isotopes*. Bainbridge publishes "Equivalence of Mass and Energy" in Physical Review
- **1935** 1935 Dempster describes new mass analyzers and the spark ion source. Nier discovers previously unreported low abundance isotope of potassium
- **1936** Bainbridge & Jordan report new high resolving power mass analyzer
- **1938** Dempster publishes "The Energy Content of Heavy Nuclei" in Physical Review
- **1940** Nier, Dunning, et al publish "Nuclear fission of separated uranium isotopes" in Physical Review
- **1947** Nier publishes "A mass spectrometer for isotope and gas analysis" In Review of Scientific Instruments
- **1948** Dempster reviews "Thirty Years of Mass Spectroscopy" in The Scientific Monthly
- **1950** Dempster dies at age 63
- **1951** U. S. Patent office grants Dempster Patent # 2,572,600 "Mass Spectrograph"