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Walter Bleakney and His Contributions to Mass Spectroscopy

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Mass spectrometry is a fundamental analytical technique that revolutionized atomic and molecular physics by allowing the precise measurement of the mass-to-charge ratio of ions. Since its early development and the foundational improvements in calculating atomic masses by pioneers such as A. J. Dempster and F. W. Aston in the early 20th century, the field has continuously evolved toward higher sensitivity and resolution. This paper presents a historical overview of Dr. Walker Bleakney (1901–1992), a professor of physics at Princeton University, whose innovative research significantly advanced these capabilities. Dr. Bleakney made pivotal contributions to the field, ranging from the confirmation of the existence and abundance of deuterium to the discovery of rare isotopes such as Sr^{84} and Ba^{134}. Special emphasis is placed on his development of the "Bleakney-Hipple" analyzer, which utilized crossed electric and magnetic fields (E×B) to generate trochoidal ion paths, thereby establishing the theory of velocity-independent perfect focusing. Additionally, the review covers his introduction of automatic recording systems and improvements in vacuum technology. These innovations not only solved significant questions in gas ionization and shock waves during his time but also laid the theoretical and experimental groundwork for modern ion optics and spectroscopic methods still in use today.

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1. Introduction

Walker Bleakney's work as an Experimental Physicist is defined by his ability to command the respect and admiration from the students and colleagues he has influenced; Bleakney's intuitive ability combined with technical skill allowed him to make notable contributions to a broad range of disciplines. Additionally, his interpersonal sensitivity enabled him to be viewed by his students and colleagues as both a scientist and a humanist [1].

In the early part of his professional life, Bleakney had pursued both an undergraduate and graduate degree in Physics at Princeton University (where he earned his Ph.D.) in the 1920s. The majority of Bleakney's early scientific contributions were made while he worked with various experimental techniques in the areas of atomic and molecular physics. While working in these areas, Bleakney made substantial contributions to the area of molecular physics through developing instrumentation and conducting some of the first experiments related to the ionization potential of gases. This technology that he developed is now referred to as the Mass Spectrograph. At least seven years after he began using the technology, Bleakney named it the "Mass Spectrograph." He made substantial improvements to the Mass Spectrograph during the mid-1930s. Bleakney began building instrumentation capable of better resolving and being more sensitive than before in Minnesota in 1925, after earlier improvements of mass spectrometry methods were made by A. J. Dempster and F. W. Aston for calculating atomic and molecular masses in 1916 [2].

Bleakney's research during the 1930s at Princeton was focused primarily on improving the performance (i.e., the sensitivity, resolution, and ability to detect) of the mass spectrometer. As such he made substantial progress with respect to all three of those objectives and received recognition for his experimental work. His contributions however were not simply for the sake of making improvements in technique; they were based upon a desire to investigate a number of significant questions in atomic and molecular physics. Bleakney generated over thirty peer-reviewed articles and gave sixteen talks on the isotopic content of all elements from hydrogen to platinum as well as the ionic fragments formed by decomposing organic compounds. At least half of his research during this period was focused on hydrogen. He said later that one of the greatest achievements of this period was to confirm the existence of deuterium, measure it’s natural abundance, and determine the chemical properties of deuterium. Additionally, he produced early reliable data about the concentration of tritium in natural hydrogen and demonstrated that hydrogen was radioactive. In early 1938, Bleakney published a very influential paper titled "A New Mass Spectrometer With Improved Focusing Characteristics" which included initial findings of the mass spectrum of ethane. Bleakney described how he had developed a new mass spectrometer that employed an arrangement of overlapping electric (E) and magnetic (B) fields to generate complex ion trajectories in the plane perpendicular to the magnetic field; consequently the "focusing characteristics were superior". Bleakney concluded by expressing optimism, stating that "It is expected that a much larger unit will be completed shortly." This larger unit would have been considered state-of-the-art for mass spectrometers at that time. During this period of developing instrumentation seven PhD candidates completed their thesis under his supervision. Each of these individuals went on to establish themselves as prominent researchers in the area of physics [3-5].

2. Walker Bleakney’s Contributions to Mass Spectroscopy

In his article published in 1929 Walker Bleakney developed an entirely new analytical technique that utilized positive ray analysis in order to determine the identities of ions produced via single electron collisions in gases, efficiency of their formation and the ionization potential for those same ions. His method used a unique means of generating a uniform magnetic field using a very large solenoid which acted like an electromagnet and compressed a beam of electrons into a line resulting in a high degree of linearity and uniformity of positively charged ions, which were then passed through the magnetic field and separated based on the ratio of charge to mass (e/m) via a specially built analyzer [6].

Electrons from the filament F are accelerated from the potential V_1 through the slit system S; they then enter the area between plates A and B in which ion formation takes place (Figure 1). Electrons newly forming positively charged ions are extracted from this space with a small extraction potential V_2. The very strong magnetic field H confines the electrons to a well-focused electron beam. At low gas pressures the number of electrons colliding along the path of the electron beam is minimal. Upon exiting the trap T the electron beam terminates, and secondary electrons cannot pass back into the trap as the result of a holding potential on plate P. By controlling the magnetic field confinement, the direction of the cross-field applied across A and B does not significantly alter the position or velocity of the electron beam. Therefore, it produces a linear, uniform ion distribution. An applied cross-field will deflect the ions from the electron beam, but because the electron beam is confined within the magnetic field, the deflection is at no cost to either the electron beam's position or its velocity. A long narrow slit is cut into plate B, perpendicular to the electron beam, to allow a wide band of ions to exit and be analyzed using the principles of e/m separation (Figure 1).

In order to obtain the first four ionization energies of mercury, an analyzer was used which most closely approximated the physical size of the other pieces of available equipment as depicted in Figure 2. The magnetic field direction of the solenoid is perpendicular to the page. The electron beam (dots) has been resolved into a ribbon shape — this was done by stretching a tungsten filament along the slit length for the initial slit (as seen in Figure 1). Almost all of the apparatus was made of copper with insulation being provided using Pyrex parts. During operation, the magnetic field and the voltages V_1 and V_2 are held constant, but varying voltage E allows one to study the production of ions. By analyzing the amount of ionization occurring during the chosen length of the path, one can measure the current going to plate B and thus determine the relative abundance of each of the different ionic species that were produced.

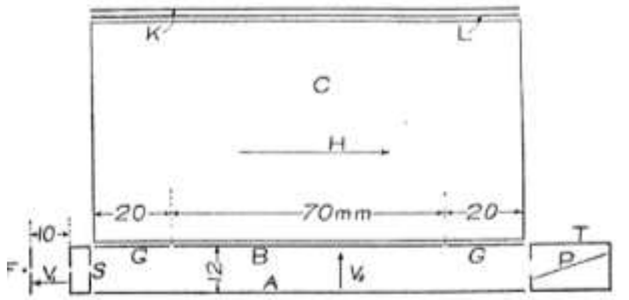

Figure 1. Side view of apparatus [6].

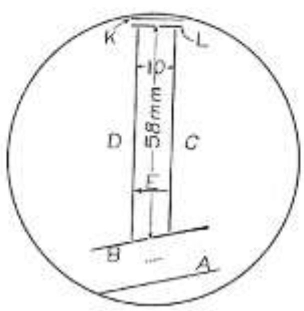

Figure 2. End view. [6]

It was thought important to find the number of charge per ion (i.e., how many times charged) for every particular electron velocity as a basis for studying the relative efficiencies of ionization in mercury vapor; based on some early studies with mercury vapor, preliminary data showed that the ionization voltages of the Hg+ Hg2+ and Hg4+ ions are 30, 71 and 143 volts, respectively.

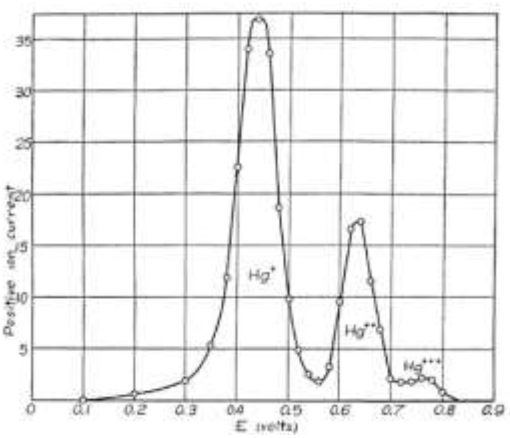

Figure 3. A typical e/m analysis curve.

This technique has several advantages compared to other positive ray analysis methods: the velocity of electrons in the field is both uniform and well defined; it provides conditions that are favorable for studying ionizations at extremely low-pressure and extremely low-current-density conditions which permits the study of the results of a single collision; because of its design, the pressure of gas is uniform throughout the length of the tube and thus can be precisely measured; finally, the entire apparatus can be enclosed in a glass tube that can be evacuated (baked out) and then sealed.

He developed a special type of a low-pressure mass spectrograph with a magnetic field for a study he began in 1932. Both helium and hydrogen have roles as fundamental building blocks in all physical theories; therefore, it has been of interest whether there are isotopes of each. There had been some suggestions that there might be two or more isotopes for each element and several experiments had been performed over the years to try and demonstrate this. The first proof that hydrogen had an isotope (mass 2) was found by Urey, Brickwedde, and Murphy [7].

Gases entered the tube via very small (fine) capillary tubes or from a palladium tube; they exited the tube via a diffusion pump. When an equilibrium existed between the gas inside the tube and the gas outside of the tube, it was assumed that there would be no variation in the relative amounts of the isotopes contained within the ionization chamber throughout the experiment. No difference occurred between the experiments using hydrogen when a palladium tube was used instead of a capillary tube.

The first to show that in addition to the "resolution" (or "resolving power") of a mass spectrometer, the isotopic composition of elements can be determined from the pressure-dependent characteristics of the formation of ions in the instrument; independent verification of the existence of deuterium; determination of the maximum abundance of helium; provided stimulus for subsequent generations of high resolution instruments [8].

In 1933, he attempted to establish the actual abundance ratio of the naturally existing isotopic forms of H_2 (heavy hydrogen) and H_1 (light hydrogen), by measuring the respective proportions. By heating samples of rain water, which had been collected in Princeton, to a temperature of 510 °C in a beaker containing a few grams of iron turnings, the hydrogen was separated from the other constituents. The resultant hydrogen was subsequently analyzed using a mass spectrograph to measure the H_2/H_1 abundance ratio. An earlier determination of the H_2/H_1 abundance ratio, by means of electrolysis, had resulted in a value of 1:30,000. However, the present study indicated that a commercially available sample of electrolytically generated hydrogen produced a ratio of approximately 1:25,000. Bleakney's contributions included establishing the mass spectrograph as a primary analytical tool for measuring the abundance ratios of isotopic forms, developing a pressure dependent separation method, and providing the first accurate quantitative abundance ratio of the deuterium form. The methodology developed in this work has formed the foundation for many of the methods used in contemporary isotope analysis [9].

Blewett and Jones were successful in developing high quality ion sources for elements of Barium (Ba), Strontium (Sr), and Indium (In) during the same year (1936) [10], therefore, in order to assess the quality of the results obtained with less than ideal sources, it was decided to replicate the examination of some of the elements already studied; additionally, a more complete study of the newly discovered isotopes of these elements would be conducted.It was also the intent of the investigators to examine the heavier elements in order to verify the data reported by Brewer on Li^5 and Na^{22} and to determine the most accurate upper limits of the possible abundance of other isotopes of Lithium (Li) and Sodium (Na) [11].To accomplish this, a mass spectrograph was built, which included a 22 cm diameter and 180 degrees focusing circle. Figure 4a shows both the ion path and the mechanical configuration of this mass spectrograph. The intended function of this instrument is to separate ions based upon their m/e ratio by deflecting them in a semicircle, utilizing a magnetic field, and then measuring the separated ions at a collector. A magnetic field of 1400 gauss was created by using permanent magnets and an accelerating potential of approximately 2000 volts, developed from a stabilized rectifier, was used to accelerate the ions.

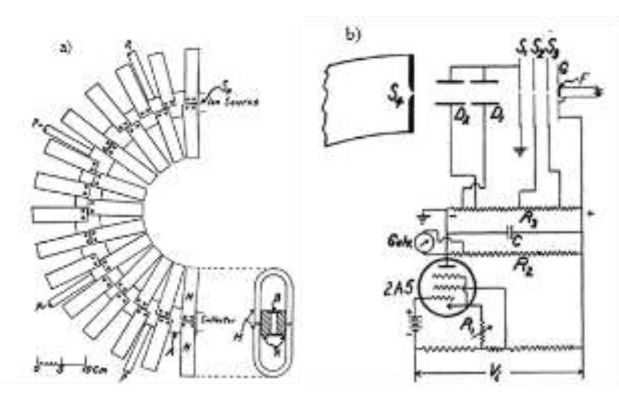

Figure 4. a) Magnetic analyzing chamber b) Diagram showing arrangement of ion gun and connection to the

voltage regulator. V_1 is the filtered output of the rectifier unit. [12].

Mass analyses of Ba, Sr, In, Li, and Na were carried out using ions produced from coated filaments. Spectra obtained from $SrCl_2$ and $BaCl_2$ are presented in Figure 5a and 5b. The first discovery of Sr^{84} is demonstrated here; although the peak is very small, it is nevertheless stable. The spectrum clearly indicates that the resolving power of the instrument is exceptionally high. The existence of Ba^{134} is also confirmed here for the first time, and the peak intensities are consistent with the theoretical atomic abundances. Indium is known to consist of two isotopes in nature, and Bleakney and Sampson investigated whether a third isotope might exist; however, none was observed. Figure 5c strongly supports the absence of such a third isotope.

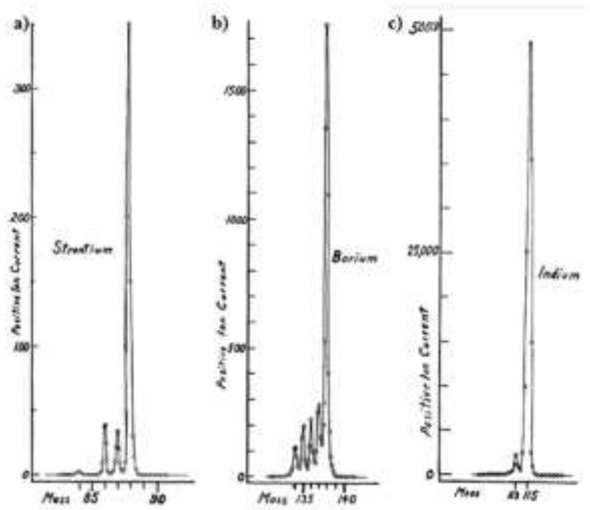

Figure 5.. Mass spectrum of Sr, Ba and In [12].

Brewer had previously claimed the existence of a Li^5 isotope, but the present measurements demonstrate that Li^5 does not occur. Brewer also asserted the presence of a Na^{22} isotope; yet, as seen in Figure 6a and 6b , only the peak corresponding to the 100% abundant and stable isotope Na^{23} is observed.

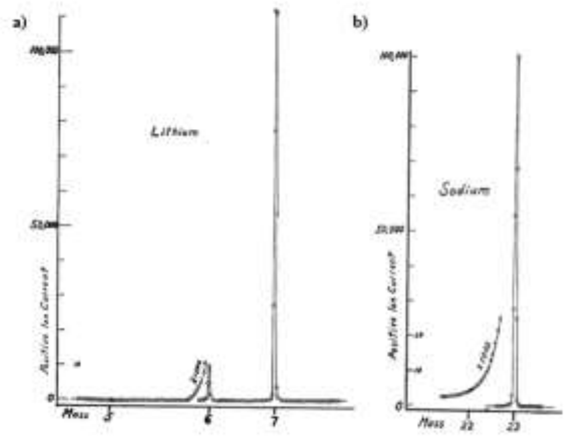

Figure 6. Mass spectrum of a) Li and b) Na [12].

The resolution into two clearly separated isotopes of even neighboring masses, which Bleakney was able to accomplish with his instrument, indicates that it has a 180° focusing capability and that the resolving power of this device exceeded that of other spectrographs available during the time that it was developed. The proper operation of the apparatus is also demonstrated through the identification of the potassium isotope at mass 40—and recently reported by Nier—that had been isolated from all others completely and as per the expected abundance [13]. A brief overview of the findings of the work conducted in this study are shown in Table 1 [12].

Table 1. Investigation of Na, Ba, Sr, In, Ga and Li using a Mass Spectrograph.

Element	Mass	Relative Abundance(%)	Description
Ba	**134**	**1.8**	**New isotope. Previously unreported.**
Ba	**135**	**Small and irregular.**	
Ba	**137**	**Small and irregular.**	
Sr	**84**	**0.5**	**New isotope. Previously unreported.**
In	**114, 116**	**0**	**A third isotope could not be found.**
Ga	**69**	**38.8**	
Ga	**71**	**61.2**	**Ga^{71}/Ga^{69} 1.577±0.005**
Li	**5**	**<Li^7's 1/50.000**	**Brewer's Li^5 finding was not confirmed.**
Li	**4**	**< Li^7's 1/1000**	**Brewer's Li^4 finding was not confirmed.**
Na	**22**	**<Na^{23}'s 1/50.000**	**Brewer's Na^{22} finding was not confirmed.**

In the study conducted in 1937, he introduced one of the earliest automatic recording systems in the history of mass spectrometry [14]. The primary objective in the measurements performed with this mass spectrograph was to determine the ion current being analyzed as a function of the potential applied to an electrode within the instrument. To obtain this information mechanically, a motor-driven, continuously variable potentiometer was synchronized with a moving photographic plate. In this way, the position of the light spot reflected from the galvanometer mirror could be recorded as a function of the potential produced by the potentiometer. The arrangement is shown in detail in Figure 7.

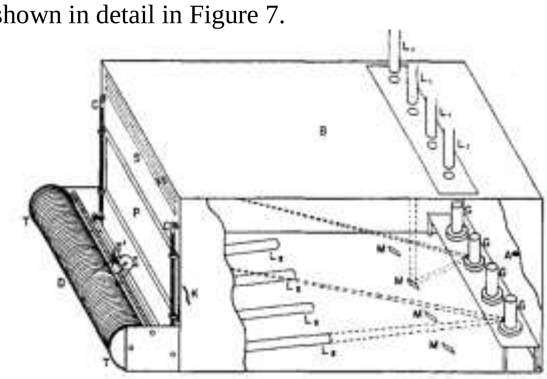

Figure 7. The automatic recorder [14].

The work carried out by Bleakney and his team represented a turning point in enhancing the sensitivity of the instrument and reducing human error. It is regarded as a precursor to the transition of mass spectrometry, in the subsequent decades, toward modern electronic data recording.

The orthogonal combination of electric and magnetic fields was first introduced to a new analyzer design in 1938 by Walker Bleakney and J. A. Hipple. They demonstrated both the theoretical basis for and an experimental demonstration of this new type of analyzer [15]. It has been considered one of the milestones in the development of mass spectrometry. Ions traveling in the Bleakney-Hipple analyzer travel in a unique path called a trochoid due to the circular motion imposed upon them by the magnetic field and the drift caused by the electric field (see Figure 8). One of the primary characteristics of the motion of the ions in the Bleakney-Hipple analyzer is that the focal points of the ions are completely independent of their velocity at time zero. Therefore, it can be used as a completely focusing analyzer and can obtain high resolution regardless of the size of the variation in the ion velocity.

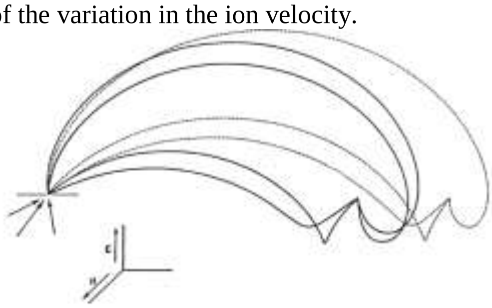

Figure 8. Trochoidal paths corresponding to various initial conditions. The two foci represent two diferent values of m/e [15].

There are two types of Trochoids: Curtate (see Figure 9) and Prolate (see Figure 10). A comparison of these two types shows that a curtate type produces sharp cusp points (leading to loss of ionized particles); whereas a prolate produces a very smooth surface which allows for the ion beam to travel with minimal distortion and provides very stable focusing, as demonstrated in both theoretical calculations and experimental results. As such, the final optical design of the instrument was based on the prolate type of Trochoidal curve.

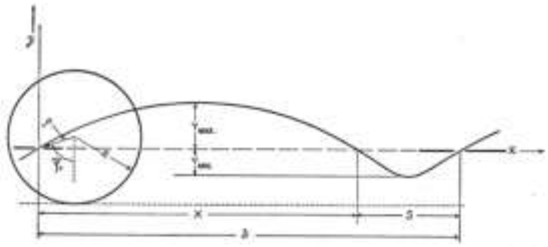

Figure 9. The curtate cycloid [15].

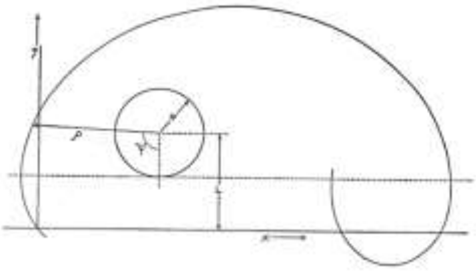

Figure 10. The prolate cycloid [15].

The performance of this newly built spectrometer is illustrated with a set of mass spectra from ethane (C_2H_6) (Figure 11). The ability to detect both singly charged ions ($C_2H_6^+$, $C_2H_5^+$, $C_2H_4^+$, etc.) and doubly charged ions ($C_2H_6^{2+}$, $C_2H_4^{2+}$), which were previously impossible for many instruments of the time to distinguish between, clearly demonstrates the high resolving power of the new instrument. The doubly charged peaks seen on the spectrum at m/e values of 14.5 and 13.5 are two of the clearest evidence of the high resolving power of the new instrument. The fact that the sharpness of the peaks did not change regardless of whether the ion energy varied by as much as 50%, is a clear indication that the theoretically predicted concept of velocity-independent focusing is indeed valid.

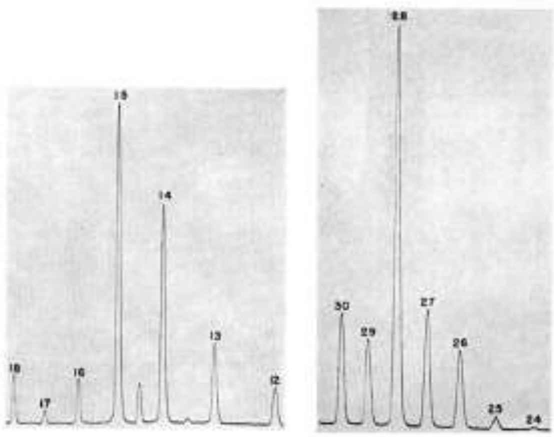

Figure 11. Mass spectra obtained with ethane in the prolate instrument. The peaks at masses 14.5 and 13.5 are due to C_2H_5++ and C_2H3++ , respectively [15].

Bleakney and Hipple made a significant contribution to the development of mass spectrometers by demonstrating an application of the trochoidal motion of ions, from a conceptual (theoretical) and experimental perspective. Their successful demonstration of this type of motion, led to the design of a new type of analyzer that provided the advantages of high resolution, a linear mass scale, and focused performance regardless of the ion velocity distribution. The contributions of Bleakney and Hipple, are also recognized as being among the most significant technological developments in the history of mass spectrometry; contributing to the establishment of many of the fundamental principles used in the design of Wien filters, trochoidal analyzers, ion optical systems and modern mass analyzers.

The 1949 publication by Bleakney and Mariner details the design, construction, and initial performance results of a very large-scale crossed electric and magnetic field (E \B) mass spectrometer [16]. The article aimed to demonstrate the feasibility of implementing trochoidal focusing, the theoretical foundations of which were established in 1937, in a true full-scale instrument.

The foundation of the design is based on the idea that ions will travel in trochoidal paths under the influence of E and B fields and when those paths are correctly selected, they provide excellent focusing capabilities regardless of the ions' velocity distributions. In order to evaluate each type of trochoid, a prolate and curtate trochoid were studied. The full scale, magnified drawings of each of these paths were developed. An evaluation was made to determine which of the two geometries were physically possible for the instrument and which would provide the best focusing capability; ultimately, it was demonstrated that either design could be utilized. Theoretical resolving power for the prolate trochoid was found to be approximately 26000 while that for the curtate trochoid was found to be 34000. These numbers demonstrate the high resolving power that could be obtained if the instrument were manufactured with all idealized conditions.

The Vacuum Chamber - The instrument is contained in a substantial vacuum chamber made up of a wide diameter steel shell, Armco iron end-plates, and sufficient space inside the chamber for the placement of the analyzer. The electric field is created by two large parallel plates held in place by many (approximately 30) "guard ring" supports, placed at one-centimeter intervals from each other. This design allows for virtually perfect homogeneity of the electric field across a relatively large area. The magnetic field is created by large coils of heavy copper wire wrapped around a large solid iron core with large pole faces. These coils produce a very stable and nearly uniform magnetic field of about 10 to 18 kilogauss. The specific geometry of the electric and magnetic fields are critical for obtaining the necessary focusing conditions for operation of the E x B analyzer.

It utilized a standard design for the electron-bombardment ion source; that is to say, it had two stages for accelerating electrons toward the ionization chamber so as to optimize ion formation. The redesign of the inlet system for gas produced a higher ion density than before. Once the ions had been analyzed, they were then detected by an electrometer capable of detecting very low levels of ion current. These electrical signals were recorded using a galvanometer.

Under testing conditions, the theoretical resolution (81%) of the instrument was very close to experimental values (with deviations of approximately 5%). As a result of these findings, it can be determined that the analyzer's design was highly accurate. Additionally, as slits are made narrower, the resolving capability will increase greatly. Therefore, there is no reason to believe that the theoretical maximum resolution of 25,000 cannot be attained.

As stated, the article describes the first complete instrumentation of a large mass spectrometer using the E×B principle. In addition to providing evidence of the focusing theory and proving the high degree of the analyzer's stability, the article provides data on the instrument's resolving capabilities which were found to be significant. These findings provided a basis for the development of later crossed field analyzers and furthered the development of the principles used in today's ion optics.

3. Conclusion

Walter Bleakney was among the leading physics innovators who led the early stages of mass spectrometry through his ability to translate his theoretical ideas into actual instrumentation designs. He was the first to demonstrate that ions traveling within crossed electric and magnetic (E×B) fields traveled in a path resembling a trochoid; he established the theory of "perfect focusing" irrespective of velocity distribution; and then successfully implemented the above concepts using a large scale spectrometer in 1949. All three of the above concepts are the foundation of modern ion optics. Bleakney also created an entirely new level of resolving capability for the mass spectrometer through the integration of many different technologies such as vacuum purifying systems which were better than previous generations; electric-magnetic field configurations which produced a homogeneous configuration; highly stable voltage dividers; refined slit assembly techniques; and highly sensitive electrometer technology. The trochoidal focusing principle and E×B configuration used by Bleakney is the direct inspiration behind all subsequent derivative Wien filter devices, ion lenses, and modern time-of-flight and electromagnetic analyzers. Thus, Bleakney played an instrumental role in the theoretical and experimental development of mass spectrometry.

Author Contributions

A.O.E.: Conceptualization, writing, Editing,

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