Mass Spectrometry: The Historical Development and Modern Applications in Nuclear Physics

Garrett King

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Abstract

In this paper, the historical development of Mass Spectometry (MS) techniques is discussed. The physical principles and mathematical models that made these advancements possible are discussed in tadem with the progress of the method. Specific experiments that applied MS in nuclear physics are discussed. The importance of a precision mass measurement technique in the Long Range Plan of Nuclear Science is touched upon and connected to its previous applications.

1 Introduction

Mass spectrometry (MS) is a technique that was introduced by J.J. Thompson in the early 1900s that has continued to grow and develop since. Although the method was originally used to understand a particular phenomenon, its applications have grown over the years to encompass multiple scientific discplines and commercial purposes. Early work in MS involved leveraging electricity and magnetism to create more sensitive tools and to select for different qualities. It was realized that the dynamics of particles could be taken into account in order to create mass spectra, a strategy that will be discussed in detail later on in the report. [1] Mass spectra have turned out to be useful in many areas, but nuclear physics is one subfield in particular that makes use of the capabilities of MS and could benefit from further use of the technique.

Before discussing the development of MS, it is import to detail the typical process that all of the methods follow in order to create mass spectra. All of the methods analyze substances to create a spectrum of their masses through the application of principles of electromagnetism and mechanics to select for certain qualities.[1] While it is common to select for the charge to mass ratio, m/z, there are other detectors that can select for velocity, energy, and mass times energy over the charge squared.[2] Looking at trajectories of particles and using the relevant equations to determine their masses is another way to create a mass spectrum. A majority of the methods involve the ionization of particles in vacuo prior to entering into one or more selection devices, which are typically in regions of low pressure. Once the particles pass through the mass analyzer regions, they go on to the detectors and the signals measured are used to create a spectrum for the given particles.[1]

2 Techniques and Development

While MS has grown in its applications and techniques, it began in J.J. Thompson's quest to understand "canal rays" at the start of the 1900s. These rays were found to carry the same charge as cathode rays, but with the opposite sign; however, unlike the cathode rays, its constituents did not have a uniform m/z. This inspired Thompson to create a parabola spectrograph. This device was the first to scan for different mass to charge ratios in order to create a spectrum of the masses contained in the substance being studied. Using a Faraday cup to detect ions and get counts for how many were present, it was possible to plot the intensity of the different m/z in a sample. To scan for ions of different masses, Thompson tuned magnetic fields to select for certain m/z to pass through a slit on a metal sheet. This process of selecting certain ions and getting counts to determine their m/z gave birth to all of the concepts that make up MS.[1]

After Thompson's initial work on the subject, most of the development that followed involved buidling upon his methods in order to get better resolutions and measurements. Aston followed up Thompson's work and made measurements that confirmed the existence of hundreds of isotopes. Dempster refined Thompson's method by using the knowledge that a particle with a given m/z at a constant velocity v in a constant magnetic field B would follow a uniqe radius r, given by:

$$\frac{m}{z} = \frac{Br}{v} \tag{1}$$

These particles were taken along a 180 degree turn at this radius to get to a detector. Selecting for B, v, and r allowed him to scan for different m/z and create a spectrum. The velocity selector made use of Wein's crossed E and B fields.[1] In the set up of crossed E and B fields, it is possible to select for a charged particle that experiences zero net force at a certain velocity in that region. Particles with other velocities experience a force and be moved off of the trajectory that would carry them through the slit.[2] Wein's crossed fields rely on the application of $F = q(v \times B + E)$ for a charged particle moving through this region. Balancing the direction and magnitudes of the electric and magnetic forces allows for the selection of a given velocity to make it through into Dempster's detector.

While much of the early work involved using electricity and magnetism as the main tools for the selection of particles, more methods were pioneered that involved the use of dynamics. Wolfgang Pauld developed many different methods that leveraged the particles motion in a given field in order to create mass spectra. Two methods of his that are similar in their approach are the quadrupole mass spectrometer and the ion trap. Both of these techniques arise from the idea that a particle is confined when it is bound elastically to a central axis. In order to have this elasticity, it is necessary that a restoring force of the form $F = -cr$ acts on a particle to pull it back as it moves away from the origin. To have a force of this form, one should have a potential that looks like:

$$\Phi \sim (\alpha x^2 + \beta y^2 + \gamma z^2) \tag{2}$$

Paul chose a quadrupole set up knowing that the electostatic potential behaved like $r^{m/2}$, where m was the number of poles in his mass analyzer set up. The condition that $\nabla^2\Phi = 0$ imposed another condition on the set up of the instrument. One option that satisfied this equation was $\alpha = -\gamma = 1, \beta = 0$, which is used in quadrupole MS. His set up involved two pairs of hyperbolic poles on a given axis being separated by a distance r_0 and with potentials of $\pm\Phi_0$ applied on either end, giving rise to the following equation:

$$\Phi = \frac{\Phi_0(x^2 - z^2)}{r_0^2} \tag{3}$$

And causing electrostatic fields of $E_x = -\frac{\Phi_0}{r_0^2}x, E_y = 0, and E_z = \frac{\Phi_0}{r_0^2}z$. In this set up, particles enter the mass analyzer region moving along the y-axis and have the following equations of motion in x and z:

$$\begin{aligned}
\ddot{x} + \frac{e}{mr_0^2}(U + Vcos(\omega t))x &= 0 \\
\ddot{z} - \frac{e}{mr_0^2}(U + Vcos(\omega t))z &= 0
\end{aligned}$$

Where U is the value of an electrostatic potential, V is the amplitude of an rf voltage oscillating at ω, m is the mass of the particle, and e is its charge. Using the following dimensionless parameters, $a = \frac{4eU}{mr_0^2\omega^2}, q = \frac{2eV}{mr_0^2\omega^2}$, and $\tau = \frac{\omega t}{2}$, the equations can be rewritten as:

$$\begin{aligned}
\frac{d^2x}{d\tau^2} + (a + 2qcos(2\tau))x &= 0 \\
\frac{d^2z}{d\tau^2} - (a + 2qcos(2\tau))z &= 0
\end{aligned}$$

Which are in the form of the Mathieu equations. These equations have two solutions, which are stable and unstable motion. Particles that satisfy the conditions for stability in the set up will have limited oscillations in x and z, which is what this set up was intended to do. If a particle does not meet the stability criteria, then it will oscillate without bound in either x, z, or both x and z and hit the walls of the set up, not making it to the detector. Because of this fact, if one understands the conditions for stability, it is possible to make a device that analyzes the different masses contained in a substance. According to Paul, particles with the same m/z lie on the stable operating line a/q = 2U/V = constant. It is detailed that, for U = 0, 0 <q <0.92 are stable and that by changing U and V together to keep their ratio constant, different masses on the operating line can be focused and analyzed.

Another case that satisfied the condition of the Laplacian being zero is $\alpha = \beta = 1, \gamma = -2$, which is used in the ion trap. This device consists of a hyperbolic cap surrounded by a hyperbolic ring in the x-y plane. While the set up is different, it follows the same principles of stability to trap charges. The ion trap equation is given by:

$$\Phi = \frac{\Phi_0(r^2 - 2z^2)}{r_0^2 + 2z_0^2} \tag{4}$$

In this case, the factors of z in those equations are scaled up by 2 and the x equations are replaced by ones in r, the radius in cylindrical coordinates. Particles with a given m/z will lie on the stable operating line and oscillate in the ion trap. By setting the rf voltage frequency to the frequency that a particle with a given mass oscillates in the trap, resonance will occur. Scanning for multiple masses can thus be used to create a mass spectrum.[3]

Another method of detection that makes use of the dynamics of a given particle is the Time of Flight (TOF) detector. This technique uses the knowledge that a partcile with a give m/z moves a certain distance under the influence of an electrostatic potential U in a time t such that:

$$t \propto \sqrt{m/z}\frac{1}{\sqrt{U}} \tag{5}$$

Using this relationship and analyzing the trajectories of different particles in a detector, it is possible to create a mass spectrum. Because of this fact and the equationst that govern them, cyclotrons make for MS detectors in addition to particle accelerators. This is possible because particles of a given m/z have a given cyclotron frequency f that satisfies[1]

$$\frac{m}{z} = \frac{B}{2\pi f} \tag{6}$$

Keeping track of a particles frequency with a time of flight detector or tuning the cyclotron so that one particular particle resonants are two ways that this equation could be leveraged to create a mass spectrum.

3 Applications to Nuclear Physics

While MS has grown to give various methods of creating mass spectra, it is fair to wonder where applying these techniques is useful and more than just interesting physics. One subfieldthat provides examples of the method being useful is Nuclear Physics. In 2015, the Nuclear Long Range plan was released, containing a number of objectives seen as important to advance the field. According to this long range plan, Nuiclear Physics seeks to understand the the basic fundamental interactions governing the arrangement of subatomic matter and the limits of nuclear existence. One way the plan mentions advancing the thoery governing nuclear structure and fundamental interactions is by making precision measurements of masses near the proton and neutron drip lines, as well as of superheavy nuclei, in order to understand how the strong force works in these extreme regions. An MS technique was specifically mentioned in this plan was the use of the ion trap for the measurement of superheavy nuclei. This technique adavanced the knowledge of masses from Z=110 to Z=111. The plan indicated that the goal was to make measurements up to Z=114 to understand the interplay of the strong and Coulomb forces in this region. As far as the other two regions of interest, mass measurements had been made along the proton drip line for elements up to Z=83 when this plan was published, but measurements had only been made along the neutron drip line up to Z=8. Making measurements of key isotopic chains near the neutron drip line will give insight into the magic numbers of nuclear shells. At the time of the plan, the concept of magic numbers was being challenged by the discoveries of ^{24}O and ^{26}O, which suggested possible N=14 and 16 magic numbers for neutron rich nuclei. Results like this indicate the need for precision mass measurements in these regions of exotic nuclei to understand their binding energies, how these nuclei structure themselves, and what keeps them together.[4]

One experiment by Gaudefroy et al., while performed prior to this plan, seemed to line up well with these objectives. In it, the masses of 16 light exotic nuclei near the neutron drip line were measured. The setup used for this experiment involved a TOF detector in combination with a loss of energy (ΔE) detector. TOF detectors obey the model given by Equation (6), where a given m/z corresponds to particular cyclotron frequency. Keeping track of the number of revolutions made per second by particles in the accelerator with a given magnetic field allowed the researchers to figure out what m/z were in the sample. In this particular study, exotic nuclei which form halo structures had their masses determined for the first time. Using the precision mass data in combination with nuclear matter radii determined by interaction cross section measurements, the researchers were able to constrain the model of halo formation for these nuclei. This experiment is an example of where good measurements can inform our understanding of how nuclear structures exist in the limits of stability. [5]

Sun et al. provide an another example of the use of TOF in combination with cyclotron MS to measure the masses of other exotic nuclides. In this experiemnt, heavier exotic nulcides than those produced in Gaudefroy et al. were created by high energy collisions of ^{238}U with a Be target. The TOF detector observed how many revolutions per second different particles in the accelerator made and used this information to determine the different m/z in the sample. This experiment demonstrated both the power and the possible limitations of the method. The researchers were able to identify 71 nuclides, with 35 of them hitting typical precison for one of these measurements; however, the fact that two different particles could have the same charge to mass ratio led to the contamination of some of the peaks of the mass spectrum. Because of this, they could only indentify the 71 nuclies mentioned in their publication, even though much more were observed to have been created. Even without all of the peaks, it was possible to compare to the theoretical predictions of the previously unknown massses and determine their predictive power. Looking at where theory failed to match up with the data, the researchers were able to account for the features of the theory that were causing it to not quite describe the data.[6]

In a pioneering paper on the use of cyclotrons for MS, R.A. Muller described using loss of energy detectors, like in Gaudefroy et al., to limit the contamination of various peaks for light nuclei at low beam energies. Additionally, in this range, the use of foils that can stop contaminants and let deisred particles pass, while also avoiding spurious creation of the desired particle throguh reactions, helps to limit the contamination of peaks.In the Muller study, he was discussing the separation of stable C and ^{14}C isotopes via tuning cycltron parameters for use in radiocarbon dating. A small error in the measurement of ^{14}C would lead to a large uncertainty in the predicted age of the sample being date. For this reason, he was seeking to eliminate the contamination of ^{14}N, another particle common in samples being studied, in the ^{14}C peaks[7] The fact that this paper existed well before Sun. et al.and the lack of their application in that study makes it reasonable to question if such techniques are not feasible for cyclotron MS for heavy nuclei at high beam energies. The cycltron gives the advantage of operating at higher energies and being able to create the exotic nuclei that were seen in Sun et al, so if there are uncertainties related to the method, its effectiveness could be limited; however, the number of distinct peaks that were resolved from the detectors in Sun et al. is promising and could suggest that better resolution of the TOF detectors is the key for the future of this method. As far as the presence of MS in general, the fact that ion traps were used for the Z=111 measurements suggests that it will play an important role in various forms.

Sobiczewski and Litvinov provide an example of why refined mass measurements are important for the development of nuclear structure theory. In this study, an analysis of 10 different mass models was conducted to understand if there was a connection between how well they described the data and how well they predicted new mass measurements beyond the region used to create the model. It was found that these models did very well for the data in the region that was used to create them, which did not seem unsurprising. The most striking part of the report was the finding that there was no connection between a model that described known data well and one that made accurate predictions for new data. [8] The take away from this article was that it does not seem wise to rely solely on theoretical predictions in order to inform our models of nuclear structure. Instead, it seems that there should be an initiative to make more precision mass measurements in these important regions in order to create robust theories of nuclear structure.

4 Outlook

Although MS began as just the solution to one problem, innovative developments upon the original technique have made it a powerful tool not only in physics, but in various scientific domains, as well. The isotopic separation techniques, like the one used by Muller, have proven useful in biomedicine for the detection of different drugs. Finding precise rations of ^{14}C and ^{13}C in urine is a way to determine the presence of performance enhancing drugs. In the future, its possible that small scale MS devices could be used by law enforcement to test for the presence of illicit substances by separting a sample into its constituents and precisely determining what makes it up. MS can also be used to test for the presence of different proteins and could detect biomarkers in tissues that serve as early signals of chronic heart failure. The use of MS to image certain substances, like proteins, is also a possibility. This imaging technique would be superior to others, since it also provides an indication of the chemical make up of different substances. The wide range of applications of MS shows how innovative advancements of the method over the years have turned it into a versatile tool. Given all of the possible and important applications of this tool, MS should continue to be studied and developed upon to improve its precision and resolution.

5 Conclusion

MS has grown from Thompson's studies on canal rays into its own field of study with many diverse applications. Levaraging what was known about electricty, magnetism, and particle dynamics, researchers were able to push the technique into the frontiers it has reached today. MS shows up in many disciplines of science, but in Nuclear Physics in particular, it could prove useful in refining theories about nuclear structure by providing precision measurements of masses and information on binding energies at the limits of nuclear stability. Nuclear mass models used to inform these theories tend to break down outside of the regions where they were originally created to describe, so it is important that we are relying on accurate information in this region as opposed to theoretical predictions that might not hold up. To continue developing the usefulness of the tecnhique, it is important that the methods continue to be refined in order to get higher resolving power and to limit uncertainties in data.

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