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

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March 1, 2018

Abstract

In this paper, the historical development of Mass Spectometry (MS) is discussed. The physical principles and mathematical models for some of the major models are outlined. Specific examples of the use of MS in Nuclear Physics are detailed after the development of the models. 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. An outlook for the future of MS in physics and other domains is given.

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] This fact has turned out to be useful in many different disciplines, but nuclear physics is one in particular that makes use of the capabilities of MS and could benefit from further applications of its techniques.

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. In every case, substances are analyzed 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 where signals are measured and used to determine the presence of various substances.[1]

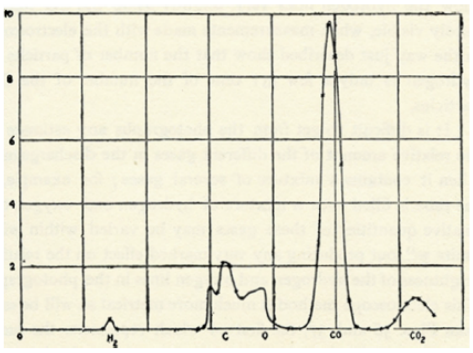

Figure 1: Thompson's Mass spectrum of Carbon Monoxide found in Reference [1]

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 an 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 m/z in order to create a spectrum. Using a Faraday cup to detect ions and get counts for how many of each one 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 a specific 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 was the inception of MS and its core principles.[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 that selector, it is possible to pick out a charged particle that experiences zero net force at a certain velocity in the region of crossed E and B fields. Particles with other velocities experience a force and will be deflected away from 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 techniques that leveraged the motion of particles in a given field in order to create mass spectra. Two similar approaches 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 requirement that $\nabla^2\Phi = 0$ imposed another condition on the instrument: $\alpha + \beta + \gamma = 0$. One option that satisfied this 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 have two solutions, which are stable and unstable motion. Particles that satisfy the conditions for stability 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.

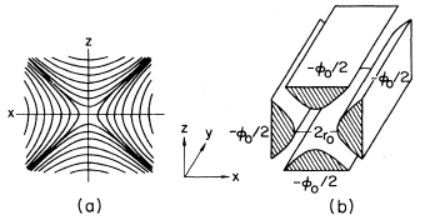

Figure 2: A visual representation of the Quadrupole Mass Spectrometer potential and its set up. In (a), the equipotential lines are pictured. A schematic of the set up is pictured in (b).

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:

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

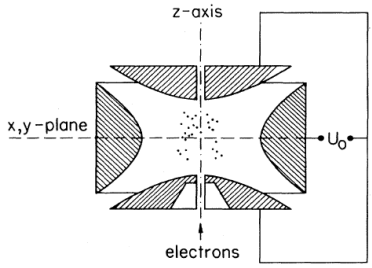

Figure 3: A schematic of the ion trap.

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 resonance frequency of a given particle, it will exit out of a bore hole in the trap and go on to a detector. Scanning for multiple masses can thus be used to create a mass spectrum. Paul discusses a mechanical analog to the ion trap, shown in Figure 4. The ion trap's constant voltage will have equipotential lines that look like a saddle, similar to the one in the mechanical analog. If a steel ball is placed on that saddle, it will be unstable and roll off; however, if the saddle is rotated at the right angular frequency for the potential parameters and mass of the ball, then it will make small oscillations about the saddle point and be confined to the device for an extended period of time. As long as the ball has the right Mathieu parameter for stability, it will be trapped in the set up. This idea of using the appropriate frequency for the problem parameters is the same as what is being done with electricity and magnetism in the ion trap.[3]

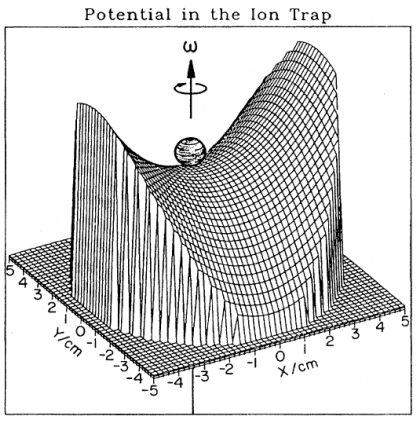

Figure 4: The mechanical analog of the ion trap. The steel ball represents a particle being trapped and the rotation of the potential is analogous to the use of an rf voltage to confine particles on the stable operating line.

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, cyclotrons make for MS detectors in addition to particle accelerators, since certain particles have certain frequencies in them. From the equations of motion in a cyclotron, 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 particle's frequency with a time of flight detector or tuning the cyclotron to resonate with one in particular are two ways that this equation could be leveraged to create a mass spectrum.

3 Applications to Nuclear Physics

While MS has developed many techniques over the years, it is fair to wonder where applying this method is useful and more than just interesting physics. One subfield that 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, Nuclear 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 theory in these areas is by making precision measurements near the proton and neutron drip lines, as well as in the region of superheavy nuclei. Knowing about the masses and binding energies in these regions should give insight into the workings of the strong nuclear force. An MS technique 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 for 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 only to Z=8 along the neutron drip line. Mak-

ing 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]

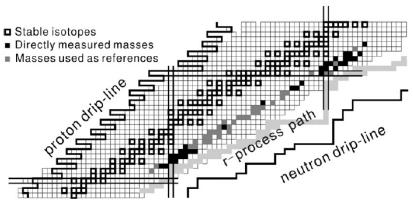

Figure 5: A visual of the masses measured in Sun et al. and where they fall on the Chart of the Nuclides relative to the stable isotopes and the neutron drip line.

One experiment by Gaudefroy et al., while performed prior to this plan, seemed to line up well with these objectives. In that study, the masses of 16 light exotic nuclei near the neutron drip line were measured. The set up 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 nuclides mentioned in their publication, even though many 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 accuracy. Looking at where predictions failed to match up with the data, the researchers were able to account for the features of the theory that were causing the discrepancy.[6]

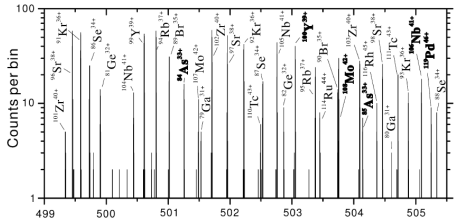

Figure 6: The mass spectrum generated in the Sun et al. measurements.

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 helps to keep unwanted signals out of certain peaks. When selecting a foil for a given beam energy, it is important that it does not react with the beam to make more of the particles being searched for than was originally present. In the Muller study, the concept of contamination was important because he was discussing the separation of stable C and ^{14}C isotopes 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 dated. For this reason, he was seeking to eliminate the contamination from ^{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 the application of these techniques in that study makes it reasonable to question if those measures are not feasible for heavy nuclei at high beam energies. The cycltron gives the advantage of operating at higher energies and being able to create exotic nuclei like those seen in Sun et al. If there are uncertainties inherent in the method at those energies, then 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 some sort of MS will play a role in advancing Nuclear Physics.

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 develop them. It was found that these models did very well for data in the range that was used to create them, which was not surprising. 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 other domains, as well. The isotopic separation techniques, like the one used by Muller, have proven useful in biomedicine. Finding precise ratios 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 its possible and important applications, 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 electricity, 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 they were originally created to describe, so it is important that we are relying on accurate information in this region as opposed to 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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