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Charge Detection Mass Spectrometry Using Printed Circuit Board Arrays for the Analysis of Microparticles in the Martian Atmosphere

Elaura LuAnne Gustafson

A dissertation submitted to the faculty of Brigham Young University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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ABSTRACT

Charge Detection Mass Spectrometry Using Printed Circuit Board Arrays for the Analysis of Microparticles in the Martian Atmosphere

Elaura LuAnne Gustafson
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Doctor of Philosophy

Charge detection mass spectrometry (CDMS) is a single particle technique capable of simultaneously measuring charge and mass-to-charge ratios for individual ions or particles. The linear array CDMS design theoretically has no upper mass limit and is therefore a choice method for the analysis of high mass and heterogeneous samples, such as dust microparticles in the Martian atmosphere.

This dissertation describes the development of a novel charge detection mass spectrometer made of printed circuit boards (PCB) for the analysis of dust microparticles in the Martian atmosphere. Development of this device has required investigations in analysis methods and the engineering design of both the PCB device and the vacuum chamber system used in laboratory experiments.

Accurate velocity analysis is crucial in determining correct particle mass in linear array CDMS. By combining the Shockley-Ramo theorem—which allows for the calculation of instantaneous image current for a system of electrodes when a point charge passes them—and SIMION ion optics simulations effective electrode length can be determined for any given charge detector geometry and aid in charge detector engineering and design process. Applying these simulation results to experimental data yields velocity agreement for a PCB charge detector within 0.44% RSD.

The novel PCB CDMS device was demonstrated for the analysis of multiple types of microparticles of varying size and charge similar to that expected of atmospheric Mars dust. This device is able to measure particle charge above 1,500 elementary charges of either polarity. Simulations show that for microparticles having a size and density close to that which is expected for Mars dust, the device is able to ideally measure the mass of particles ranging from 0.2–2.5 µm in diameter, providing broad coverage of particles too small to be observed by optical scattering and other techniques that have been previously used on Mars.

Keywords: image charge, image current, charge detection mass spectrometry, Mars dust
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CHAPTER 1: INTRODUCTION

1.1 SINGLE PARTICLE MASS SPECTROMETRY

Over the last 50 years there has been much interest in extending mass spectrometry (MS) to accurately measure larger and larger high mass and heterogeneous species such as nanoparticles, aerosols, protein complexes, bacteria, and other large supramolecular complexes. However, it seems that the upper mass limit is being approached for conventional MS techniques—where the quantity that is measured is not the mass but rather the mass-to-charge ratio ($m/z$).

Several factors contribute to this upper mass limit in conventional MS. Common detectors used in conventional MS—such as microchannel plates—have low detection efficiencies for high $m/z$ ions. When comparing the most common ionization techniques used for high mass ions, matrix-assisted laser desorption and ionization (MALDI) and electrospray ionization (ESI), detection efficiency is higher for ions charged via electrospray since the charge state is higher. However, this higher charge state makes it more difficult to resolve charge state peaks in a $m/z$ spectrum. For very large ions, peak broadening can occur for ions that are not completely desolvated, leading to a charge state distribution. Peak broadening can also occur for high mass samples with intrinsic heterogeneity that have a broad distribution of possible masses (i.e. nanoparticles, cells, or aerosols), leading to an actual mass distribution. The resulting distribution in a $m/z$ spectrum makes accurate analysis difficult. Additionally, these large, highly charged ions and particles pick up energy through expansion in the vacuum (ESI) or during the laser shot (MALDI) resulting in substantial energy spreads. These energy spreads can lead to ions missing the detector entirely. In order to adjust for the spread in kinetic energy and focus ions for transmission to the detector, ions need to be cooled using background gases in the first couple of regions in the instrument.
One way to overcome these challenges is by performing single particle mass spectrometry. Here the mass of particles (or ions) is measured individually. By analyzing a large number of single particles, a mass histogram can be constructed to give a full mass distribution. From there, insights on heterogeneity, fragmentation, or origin can occur.

Single particle MS is not limited by charge state resolution, so it can be used for high mass and heterogeneous samples. Two basic approaches have been developed for single particle MS. One method involves charge stepping, where mass is determined by taking a very accurate measurement of \( m/z \) for a single particle (ion), shifting the charge, and remeasuring the \( m/z \). This has been performed using quadrupole ion traps (QIT) and using Fourier transform ion cyclotron resonance (FTICR). The other method involves simultaneously measuring charge and \( m/z \) of individual particles then taking the product of the two to determine particle mass. This has been done using direct charge detection in FTICR and Orbitrap instruments as well as time-of-flight (TOF) MS with cryogenic detectors.

Charge detection mass spectrometry (CDMS) is another single particle MS technique which simultaneously measures both charge and \( m/z \) to determine mass. This technique is based on image charge detection. As highly charged particles pass through an image charge detector, particle charge and time-of-flight are measured. The time-of-flight is related to the particle kinetic energy and is influenced by an acceleration of the particles through a known electrostatic voltage. Measurement of time-of-flight and charge allows for the calculation of \( m/z \) for individual particles, which can be converted to mass.
Figure 1. Conventional charge detector. A charged particle passes through three metal cylinders, with the outer cylinders being grounded. As the particle enters the central, sensing cylinder the induced image charge is recorded and amplified by a preamplifier (top signal). A shaping amplifier then differentiates this signal into two peaks, giving the image current (bottom). Reprinted from Barney, B. L.; Daly, R. T.; Austin, D. E., A Multi-stage Image Charge Detector Made from Printed Circuit Boards. Review of Scientific Instruments. 2013, 84 (114101), with the permission of AIP Publishing.

Figure 1 shows the conventional configuration for charge detection. Measurements are made as a multiply-charged particle enters a sensing electrode, traditionally a conducting cylinder, and the induced image charge is amplified and recorded by a charge sensitive pre-amplifier. As the particle exits the sensing electrode the opposite occurs. Typically, a shaping amplifier is used following the pre-amplifier, which differentiates the preamplifier signal resulting in two peaks, positive and negative, yielding the particle image current. Inflection points in the raw image charge signal and/or the peaks in the shaped signal correspond to the
particle’s entrance and exit of the respective sensing electrode and give particle time-of-flight.\(^{19}\) Particle charge corresponds to the amplitude of the image charge signal from the pre-amplifier or the area under the peak of the image current shaped signal. The addition of an electrostatic potential either within or prior to the detection region allows for particle acceleration or deceleration (depending on charge polarity), wherein mass can be determined to perform CDMS.

CDMS can be performed in different ways, such as if the particle passes through the detector once or oscillates back and forth multiple times for continuous analysis. Each will be discussed in greater detail in the next section of this chapter. Briefly, when a charged particle passes through the detection system once (single pass or linear array) the data is typically analyzed in the time domain. If an electrostatic ion trap is used, where the particle oscillates in the trap for a given period, the data is generally analyzed using a Fourier transform to determine mass in the frequency domain (FT-CDMS). Though the work done in subsequent chapters is focused on linear array CDMS in the time domain, it is necessary to include discussion on Fourier transform CDMS when discussing this technique.

The remainder of this chapter is split into two main parts. The first part focuses on how CDMS instrumentation has developed since its invention and is separated into single pass and linear array instruments as well as electrostatic ion trap instruments, including the recently emerging Orbitrap-based CDMS. Since this dissertation is focused on CDMS instrumentation, the dominant discussion of this chapter will be these instrument advancements. However, these advancements have led to incredible work in applying this technique for the analysis of numerous particle types and molecular systems, so it would be remiss not to discuss them. Therefore, a short highlight of CDMS applications will conclude the chapter.
1.2 INSTRUMENTATION DEVELOPMENTS

1.2.1. Single Pass and Linear Array CDMS

Early charge detection and charge detection mass spectrometry works were analyzed in the time domain. As previously mentioned, in CDMS the particle (or ion) time-of-flight and charge are measured as it passes through the detector, and the particle is accelerated (or decelerated) by a known electrostatic potential. Using the particle’s kinetic energy, the \( m/z \) can be determined using the following equation:

\[
\frac{m}{z} = \frac{2V}{v_m^2} \tag{1.1}
\]

Particle mass can then be calculated by taking the product of \( m/z \) and charge \( z \). In this equation \( V \) is the electrostatic acceleration voltage applied either within or prior to the detection system, and \( v_m \) is measured ion velocity. In systems where a single charge detector cylinder is used (single pass), a correction needs to be made to \( v_m \) to account for the particle velocity due to free gas expansion prior to acceleration.\(^{19, 20} \) However, this correction factor is not needed if velocities can be measured before and after acceleration when using multiple charge detector elements (linear array).\(^{21, 22} \) Early charge detection and CDMS work utilized the single pass approach,\(^{19, 23} \) and as instruments matured, multiple detectors in a linear array configuration were used.\(^{21, 24} \)

1.2.1.1. Early Charge Detection and Single Pass CDMS Instrumentation

Charge detection in the United States can be traced back to the space race where there was interest in hypervelocity impacts from micrometeoroids on spacecraft in understanding the associated risk to damage during flight.\(^{23, 25} \) Shelton \textit{et al.}\(^{23} \) invented a way to measure the velocity, mass and surface impact of micrometeoroid simulants traveling at hypervelocities. This
was done by using electric fields to accelerate charged particles prior to detection and led to the emergence of the charge detection technique.

In this work, iron powder served as micrometeoroid simulant. The powder was placed in a conductive cup, and powder particles were surface charged when a positive DC potential exceeding 15 kV was applied to the cup. Once charged by contact, particles accelerated towards the detector as a negative pulse was applied to the region surrounding the conductive cup. The detection system consisted of two orthogonal pairs of parallel plates between two cylinders followed by a surface target for hypervelocity impact analysis. Induced particle charge was amplified by a charge amplifier system, and charge was determined from the amplitude of the signal. Particle time-of-flight was used to calculate velocity. From the charge and velocity measurements mass could be calculated using the equation mentioned above. This simple technique resulted in measured particle charge of 10,000+ charges, velocities between 1-3 km/s, and mass accuracy within 20%.

With microparticle velocities between 1-3 km/s, Shelton’s work did not approach the lower limit of meteoric velocities (11 km/s). Other works attempted to exceed this limit for these micrometeoroid impact studies, but they were unable to accelerate particles much above this limit. Aside from this velocity limitation, scientists determined the risk of damage to spacecraft from hypervelocity impacts of microparticles was small compared to other risks involved in space travel. Therefore, related charge detection experiments were discontinued.

A couple of decades later, in response to a defense program surrounding the question about whether ultrafine particles in exoatmospheric clouds could expose orbital weapons, Keaton and coworkers used a 6 MV Van de Graaff generator to accelerate submicrometer-sized particles to velocities exceeding 100 km/s. Since this work was still focused on particle impacts
rather than mass analysis (which was used as a way to deduce particle size), a single charge detector was used. However, by employing an Amptek A250 preamplifier the limit of detection was reduced to about 2,000 charges.

Particles in all these early charge detection experiments were charged via high voltages applied to conductive surfaces holding the particles. The invention of electrospray ionization (ESI)\textsuperscript{3,4} not only created a way of charging particles and ions to be transferred from solution to gas phase, but it also helped make way to increase the mass range for mass spectrometry. As ESI-MS was emerging with using time-of-flight and FTICR instruments, Fuerstenau and Benner\textsuperscript{19} realized they too could exploit the large amount of charge on ions from electrospray ionization by detecting and quantifying the charge individually using the charge detection technique for mass analysis. As a result, Fuerstenau and Benner termed this “charge detection mass spectrometry”, and the technique started to take flight.

Though previous works had dabbled with determining mass and charge for individual particles, Fuerstenau and Benner were the first to truly focus on both charge and mass with their analysis of DNA ions.\textsuperscript{19} Their charge detector assembly was patterned after that of Keaton,\textsuperscript{28} where a single charge pick-up tube constitutes the detector to measure both particle time-of-flight and charge (Figure 2). In efforts to improve the signal to noise ratio (S/N) a shaping amplifier was implemented after the preamplifier. This reduced the minimum noise level to 150 $\pm 75$ electrons (e\textsuperscript{−}).
The combination of ESI and CDMS to analyze DNA ions yielded results in a fraction of the time compared to other methods such as FTICR or slab-gel electrophoresis. However, the instrument had low mass resolution for ions greater than 10 MDa due to ion kinetic energy spread and sample preparation. Nonetheless, the mass accuracy for DNA ions was relatively high based on averaging single ion mass measurements. A single 1.2-MDa ion was measured with 12.5% (+/- 75 e−) uncertainty in charge leading to 1.2% uncertainty in mass.

From here, Benner continued to use a similar experimental setup to analyze multiple biosystems, including double-stranded and single-stranded circular DNA, polymerase chain reaction products, and intact viruses, extending the mass range and application of this budding technique. These early biosystem experiments showed CDMS as an effective, faster...
alternative to gel electrophoresis since mass spectra could be acquired within minutes. Though this was paving the way for CDMS, the use of only one charge detector electrode for a single measurement was a limitation to both charge and mass accuracy.

1.2.1.2. Linear Array CDMS Instrumentation

As will be discussed throughout the rest of the instrumentation section, CDMS progression has focused on improving accuracy and reducing uncertainty in charge and mass, which can occur with signal averaging by measuring these characteristics multiple times. If a particle or ion passes through a linear array of $n$ detector elements, then mass, charge, and velocity uncertainty as well as S/N improve by a factor of $n^{1/2}$. Additionally, multiple works have focused on reducing the charge limit of detection.

Gamero-Castaño$^{24}$ was the first to describe a linear array charge detector with six charge sensing cylinders. Having all six cylinders connected to the same amplifier would increase input capacitance and the $n^{1/2}$ performance improvement would not be realized. However, having each detector cylinder connected to its own amplifier increases cost and complexity. As a compromise, alternating detector cylinders were connected to two charge amplifiers to help realize the improved performance using a linear array. This linear array was able to achieve a charge limit of approximately 100 electrons.

As previously noted at the beginning of section 1.2.1, an ion velocity correction factor for the initial kinetic energy spread due to free gas expansion is required to determine mass when using a single charge detector. However, when an acceleration potential is implemented within the linear array configuration a velocity shift is realized, and no correction factor is needed. This was seen in the work from Mabbett et al.$^{22}$ where an acceleration tube was sandwiched between two sensing cylinders (Figure 3). Here, as charged water droplets passed through both cylinders the transient time differed and the velocity shifted because of this central acceleration potential.
Mabbett noted that the higher the velocity shift the more accurate $m/z$ measurements became. For a velocity shift of 61 m/s the uncertainty in $m/z$ was 1% whereas for a velocity shift of 6.1 m/s the uncertainty in $m/z$ was 10%.

Figure 3. Schematic diagram of the instrument used in reference 22. The lower portion shows the signal from the first charge detector (top), the acceleration voltage applied (middle), and the second charge detector (bottom). Reprinted with permission from Mabbett, S. R.; Zilch, L. W.; Maze, J. T.; Smith, J. W.; Jarrold, M. F., Pulsed acceleration charge detection mass spectrometry: Application to weighing electrosprayed droplets. Analytical Chemistry 2007, 79 (22), 8431-8439. Copyright 2007 American Chemical Society.

Another way to implement an acceleration potential in a linear array is to split the number of detector elements between two charge amplifiers and having an offset voltage applied to one of the amplifiers, resulting in a particle velocity shift. Smith et al.\textsuperscript{21} designed the longest linear array of 22 detection cylinders (45 total cylinders including those that were grounded) for analysis of 300 kDa poly(ethylene oxide) (PEG) ions. The first eleven cylinders were connected to one amplifier system, and the second set of eleven cylinders were connected to another.
amplifier set to a voltage offset of +1V. This voltage offset enabled ion acceleration through the second half of the detector for this velocity shift to occur.

In this work, \( m/z \) for the electrosprayed PEG ions was centered around 2,000 Da/e\(^{-}\). These ions had between 100–200 electrons with an approximate charge uncertainty of 10%. A velocity shift centered around 145 m/s yielded uncertainty in the velocity determinations that were, at worst, 1.4%. Since velocity and charge uncertainties combine to determine \( m/z \) and mass uncertainty, the maximum \( m/z \) uncertainty was approximately 5% with an 11% mass uncertainty. This uncertainty could have been reduced had a different offset acceleration voltage been applied to give a larger velocity shift.

Assembling, aligning, and connecting multiple charge detector cylinders to an amplifier can present challenges. As a unique way to avoid these challenges, Barney and coworkers\(^{32}\) built charge detectors from printed circuit boards (PCB). Two boards had five copper electrodes patterned onto them to be sandwiched together as the linear array. By putting the PCB detector in series with a conventional cylindrical detector they proved that the signal and data using a PCB detector resembles that of a conventional detector. Additional discussion on the efficacy of PCBs as CDMS detectors will be given in later chapters of this dissertation.

1.2.2. Electrostatic Ion Trap CDMS

1.2.2.1. Ion Trap Improvements

Up to this point only those CDMS instruments that allow for a particle or ion to pass the charge detection system once have been discussed. This next section focuses on CDMS instruments that allow particles to pass through the detector repeatedly using electrostatic ion traps. By trapping charged particles or ions electrostatically for a given time, ions can oscillate within the detector. This way ion charge and velocity can be measured repeatedly, giving way for greater signal averaging than the linear array approach.
In 1997 Zajfman\textsuperscript{33} showed that ions can be trapped electrostatically. Zajfman built a trap made of two cylindrically symmetric “electrostatic mirrors” made from a stack of cylindrical electrodes to trap the particle beam in the direction of the beam.\textsuperscript{33} Here the entrance set of electrodes were set to ground during particle injection, and the exit set of electrodes were set at a potential to focus, stop and reflect charged particles. Once injected particles were reflected back to the entrance electrodes, all electrodes were set to the same potential, thus trapping charged particles electrostatically. This type of electrostatic trap differs from a Kingdon trap in the fact that the central region is field-free so the charged particles travel in straight lines between the “mirrors”. By including a charge detection cylinder in the field-free region (Figure 4) Zajfman...
and collaborators were able to obtain mass spectra from the Fourier transform of the signal from oscillating ions.\textsuperscript{34, 35} This work opened the possibilities of using electrostatic traps for CDMS.

Benner was the first in the United States to build an electrostatic ion trap capable of measuring charge, \( m/z \) and mass.\textsuperscript{36} Electrosprayed DNA ions were accelerated through an ion guide before entering the trap, where they oscillated through the detector cylinder in the field-free region for a few milliseconds. Despite having an oscillation waveform of a few milliseconds, charge and mass were determined using the time domain signal. The longest trapping time reported was 10 ms, resulting in a root-mean-square noise of 2.3 e\(^{-}\) where an ion oscillated within the trap 450 times. However, since the time domain was used for analysis, ions had to possess a charge of at least 250 e\(^{-}\) for the signal to be large enough to trigger the trapping potentials.

In efforts to further reduce limits of detection and improve accuracy Contino and Jarrold\textsuperscript{37} designed an instrument containing an ion trap based on the “cone trap” design of Schmidt \textit{et al.}\textsuperscript{38}—where cone-shaped electrodes are used to trap ions (Figure 1.5)—and a high resolution energy filter. The modifications made to the cone trap design provided more ion oscillations. The energy filter, known as a dual hemispherical deflection analyzer (HDA), was employed to narrow the window of ion kinetic energies entering the trap and reduce the uncertainty in \( m/z \). A fast Fourier transform (FFT) was used to extract the oscillation frequency \( f \) of the trapped ions. The magnitude of the FFT is proportional to ion charge, and mass was determined using the following equation:

\[
\frac{m}{z} = \frac{C}{2E_0 f^2} (1 - 2)
\]
where C is a constant based on their trap geometry, and $E_0$ is kinetic energy selected by the HDA. With this new instrument they were able to reduce the limit of detection to $30 \, e^-$ with a measured charge accuracy of $3.2 \, e^-$. Using this instrument in subsequent work, they reduced the limit of detection to $9 \, e^-$ with a charge root-mean-square deviation (RMSD) of $2.2 \, e^-$ by cryogenically cooling the JFET to around 130 K on the charge amplifier.$^{39}$

Figure 5. Original cone trap design from Schmidt et al. (reference 38) Reprinted from Nuclear Instruments and Methods in Physics B. Vol 173 (4), Schmidt, H. T.; Cederquist, H.; Jensen, J.; Fardi, A., Conetrap: A compact electrostatic ion trap. Pages 523-527, Copyright 2001, with permission from Elsevier.

From here Jarrold and coworkers embarked on a quest to achieve perfect charge accuracy in their CDMS measurements.$^{40, 41}$ To achieve greater charge accuracy ions need to be trapped for longer periods, which can be done by having a more focused ion beam entering the ion trap and/or reducing the pressure of the trapping region to increase trapping time. They first made a few instrument modifications such as better alignment of ion optics, the HDA, and the ion trap. From these adjustments ions were trapped for 391 ms, and by improving their FORTRAN analysis program they reported a limit of detection of seven electrons and a charge RMSD of $0.65 \, e^-$. By isolating the ion trap in an additional differentially pumped region to reduce the operating pressure in the trapping region by two orders of magnitude, trapping time was
extended to 3 s resulting in a charge RMSD of 0.2 e\textsuperscript{−}, a near perfect charge accuracy with an error rate of less than 1 in 15,000\textsuperscript{41}

With reports using both the cone trap design\textsuperscript{38, 40-43} and the ion mirror design,\textsuperscript{33-36, 44} Elliott and Williams et al.\textsuperscript{45} compared the performance of the two using SIMION simulations. These simulations showed that ions penetrated deeper into the cone trapping ends than the ion mirrors, leading to a slower turnaround time in the cone trap and less measurements acquired. However, they realized the cone trap has a higher efficiency at trapping a narrow range of ion energies. Elliott states that as a result, the cone trap can be used as an energy filter\textsuperscript{45} and no prior filtering is needed (further discussion in the next section). Using these simulation results, they designed a CDMS cone trap containing an array of four charge detectors to make additional measurements and overcome the slower turnaround time within the trap. The resulting charge uncertainty for 8 MDa PEG ions was up to ±3 charges, similar to Jarrold et al.\textsuperscript{37} for a similar number of measurements but higher than reports using similar trapping times.\textsuperscript{40}

As mentioned earlier, Jarrold and coworkers have focused their instrument improvements to increase accuracy in CDMS measurements.\textsuperscript{40, 41} Following the significant improvements in charge accuracy from their work as well as that of Elliott et al.,\textsuperscript{45} Jarrold and coworkers shifted their focus to improve \textit{m/z} accuracy and the mass resolving power of CDMS.\textsuperscript{46} Since \textit{m/z} uncertainty is twice the uncertainty of the oscillation frequency (Equation 1-2), a new cylindrical ion trap was designed to reduce changes in the oscillation frequency due to variations in ion kinetic energy and ion entrance trajectories. This trap design, shown in Figure 6, has six cylindrical electrodes sandwiching the field-free region containing a grounded shielding and the charge detector. These electrodes (three on each side of the field-free region) had optimized potentials applied to focus the ions and produce the smallest spread in oscillation frequency. In
SIMION simulations comparing the cylindrical trap to the cone trap, the cylindrical trap showed a 0.0899% change in oscillation frequency. This is an order of magnitude reduction compared to the cone trap. In practice this new trap provided a more than 4-fold improvement in the \( m/z \) resolution.

Johnson et al. realized another way to achieve greater mass resolution with electrostatic linear ion traps (ELIT).\(^\text{47}\) Mass resolution increases linearly with oscillation frequency, so increasing the oscillation frequency by reducing the ion trap length could result in higher mass resolution. By reducing the axial length of their ion mirror trap by a factor of 2, Johnson observed a mass resolution increase of 90%. However, this miniaturization reduced the \( m/z \) range. The upper mass limit is reached when ions with a high \( m/z \) are too slow to enter the trap when ion mirror voltages are switched, and the opposite establishes the lower mass limit when low \( m/z \) ions are too fast to enter the trap.

1.2.2.2. Additional Instrument Improvements

As illustrated, much work has been focused on enhancing the electrostatic ion traps and charge detectors for CDMS. These improvements—including trap and charge detector design
modifications and increased trapping times—have improved charge and \( m/z \) accuracy and reduced uncertainty. Additional instrument adjustments focused on ion transmission, trapping techniques for tandem mass spectrometry, ion-ion interactions within electrostatic traps, amplifier electronics, and data analysis time have helped expand CDMS even further.

With the ability to create highly charged, high mass ions, ESI has remained to be the ionization method of choice for CDMS. Electrospray is an ambient ionization technique, so an interface between ambient pressure and a high vacuum environment is required for mass spectrometry. Upon entering the first vacuum region the gas flow forms a supersonic jet,\(^3\) accelerating ions and creating a wide distribution of energies leading to decreased transmission. Draper and Jarrold \( et \ al. \)\(^{48}\) designed an interface to maximize ion transmission while also minimizing excess kinetic energy. This incorporates a hybrid of both an ion funnel to focus ions and an ion carpet to drive the focused ions to subsequent vacuum regions. This FUNPET, as it is called, helps thermalize and transfer ions ranging from 1 kDa to 1 GDa for CDMS analysis.

Though there is increased transmission of ions on the front end of their instrument, Jarrold and coworkers report that most ions are wasted because the trap is closed most of the time so only about 1 in 620 ions are trapped.\(^{46}\) By storing ions in a hexapole just after the FUNPET interface then pulsing them in a time-compressed ion packet prior to the trap Todd and Jarrold report an increase in CDMS sensitivity by more than 2 orders of magnitude for the analysis of hepatitis B virus \( T = 4 \) capsids.\(^{49}\) This pulsing mode and increased sensitivity allows for lower sample concentrations to be analyzed.

As mentioned earlier, by increasing the trapping time to 3 s, Jarrold and coworkers reported a charge RMSD of 0.2 e\(^-\).\(^{41}\) Though this illustrates that extending the trapping time can increase charge accuracy, both the frequency and intensity of the signal for an ion in an
electrostatic trap can change with time.\textsuperscript{42-44} This makes data analysis more complex. Despite this complexity, Elliott and Williams \textit{et al.}\textsuperscript{42} used the change in frequency and intensity of the signal as a means of observing fragmentation (MS\textsuperscript{n} measurements) and ion mobility in a cone trap. Over a 4 s trapping period the mass, charge, energy, MS\textsuperscript{7}, and ion mobility measurements were made for an 8-MDa PEG ion, expanding the CDMS technique to make additional measurements about analyte structures.

While Williams and coworkers performed MS\textsuperscript{n} measurements by extending the trapping period and observing changes in the signal, tandem MS (MS/MS) can also be accomplished by adding additional MS stages in CDMS instruments. Doussineau \textit{et al.}\textsuperscript{50} integrated a single pass CDMS stage and an ion gate prior to an electrostatic linear ion trap for infrared multiphoton dissociation MS/MS experiments. The first stage and ion gate allowed for m/z and charge selection for the ion of interest. Selected ions were then introduced to the ion trap and irradiated by a cw CO\textsubscript{2} laser to observe changes in ion charge. McLuckey and coworkers have performed MS/MS by coupling an ELIT for mass analysis and a quadrupole linear ion trap (QLIT) to perform mass selection for collision-induced dissociation.\textsuperscript{51-53} By pulsing ions into the ELIT the initial mass spectrum is recorded. The QLIT then recaptures the ions for collisional activation before being injected back into the ELIT for additional mass analysis. McLuckey and coworkers later added a target outside the ELIT for surface-induced dissociation MS/MS analysis.\textsuperscript{53} These MS/MS experiments using CDMS have opened new avenues to large molecule MS and structural properties.

Building their case that no energy filter is needed when using a cone trap mentioned earlier, Harper and Williams \textit{et al.} have designed a method to measure individual ion energy from trapping measurements without a filter.\textsuperscript{54} As ions oscillate within the trap multiple
harmonic frequencies are recorded. These higher order harmonics are not typically used in FT-
CDMS since it is the fundamental oscillation frequency that is used to determine mass.
Nonetheless, fundamental and second order harmonics depend on ion energy, an essential
parameter to measuring ion mass. By taking the ratio of the two they created a method that can
accurately determine ion energy using only the FT of the ion signal. They have also shown that
these ion energies, or frequency shifts, can be used to determine collisional cross section of
single ions using CDMS.55

As has been well discussed throughout this chapter, CDMS is a single ion technique.
However, there are limitations to analyzing single ions. Most ions are eliminated in order to
eliminate potential interferences from multiple ions or ion-ion interactions.5, 56 This means not
only does the majority of ion data go unacquired but it also increases the time required to obtain
a mass histogram with CDMS.

To this end, Harper and Williams et al. have demonstrated a method to determine
individual masses for multiple ions trapped in CDMS using a Python program to identify ion
frequencies for ions inside the trap.56 When multiple ions with similar frequencies are trapped,
they may be unresolved. However, they have proposed that increasing the range of ion
frequencies inside the cone trap enhances multiplexing and reduces measurement time.57

While this approach of multiplexing does reduce acquisition time, Botamanenko and
Jarrold58 have shown that ion-ion interactions cause trajectory and ion energy variations. These
variations reduce precision and accuracy of m/z measurements. Based on their simulations, this
degradation is expected scale with z² and approximately with the square root of the number of
ions trapped. It also depends on the design of the ion trap. Unfortunately, high-resolution CDMS
instruments require focused ion beams and well-defined energies, which promote ion-ion
interactions. However, Botamanenko gives hope in saying that it may be possible to design an ion trap capable of minimizing ion-ion interactions so that “multiple ion trapping and high-resolution m/z measurements are not mutually exclusive.”

Most CDMS instruments up to this point have used the Amptek A250 or CF250 preamplifier systems as the image charge detection circuit. Todd and Jarrold et al. have recently designed a charge sensitive amplifier without a feedback resistor to reduce thermal noise. This design, in connection with the cylindrical trap described earlier shown in Figure 1.6, demonstrated the detection of singly charged bradykinin and angiotensin ions with masses ≤1 kDa in real time using a Fortran analysis program. By calibrating the charge amplifier during a measurement Todd and Jarrold have also been able to achieve charge-state resolution for P22 procapsid ions (24.4 MDa) with 500 charges. These improvements in amplifier design and calibration have resulted in an order of magnitude improvement in mass resolution.

1.2.2.3. Orbitrap-based CDMS

All the CDMS work that has been discussed thus far has been performed using “home-built” instruments because CDMS instrumentation has yet to be widely commercialized. However, in the last couple years Oribtrap-based CDMS has emerged. The Orbitrap mass analyzer is sensitive enough to detect single ions, thus opening up the possibility for Orbitrap-based CDMS.

Two groups have championed Orbitrap-based CDMS analysis methods. In both approaches, analytes are diluted and instrument ion optics are adjusted to reduce ion transmission in the Orbitrap. In the approach from Heck and coworkers, signal intensity from a single ion is used as a correlation to charge. From the analysis of heterogeneous macromolecular assemblies, they were able to demonstrate that signal intensity and charge have a linear relationship (RMSD of 3.5 charges), therefore proving that signal intensity can be used as a
direct measurement of charge. These results led to mass deviations of about 1% for MDa particles. By running calibrants and figuring out the equation to the linear relationship this approach can be applied to a broad range of analytes. The other method comes from Kelleher and coworkers, which uses Selective Temporal Overview of Resonant Ions (STORI) plots rather than signal intensity alone. This method works best with a specialized software as it tracks the temporal evolution of signals. Though sample concentrations are reduced in Orbitrap-based CDMS to limit ion transmission, the STORI plots method can be used when multiplexing—simultaneous trapping of multiple ions—occurs.

While Orbitrap-based CDMS is growing, especially in the field of native mass spectrometry, acquired data can be very complicated to analyze. Recently Kostelic et al. developed the UniDecCD software for computational deconvolution of this data. With this new software providing a “user-friendly” interface it will surely increase the accessibility and feasibility of performing Orbitrap-based CDMS.

1.3 CDMS APPLICATIONS

During the development of CDMS instrumentation described in the previous sections of this chapter, numerous high mass and heterogeneous systems have mostly been used to characterize the technique rather than learning information about each system. However, the accuracy from each study has opened the door to a considerable amount of additional charge detection and CDMS work on charging mechanisms in droplets, nanoparticles, DNA ions, synthetic polymers, proteins (including native MS), viral capsids, gene therapy vectors, and vaccines. A few of these application studies are discussed here. For a more extensive discussion on biomolecular applications of CDMS, refer to the review written by Jarrold.
Electrospray ionization is the most widely used ionization technique for CDMS because solutes can be directly transferred to the gas phase for CDMS analysis. It is assumed that the final ion or charged particle has the same polarity as the voltage applied to the electrospray sample capillary. However, using charge detection, Jarrold and coworkers\textsuperscript{73, 74} observed that up to 1\% of electrosprayed water droplets were negatively charged in positive ESI and that in negative ESI >70\% of water droplets were positively charged. Gao and Austin\textsuperscript{77} also observed that up to almost 24\% of electrosprayed biological and nonbiological particles were negatively charged in positive ESI using a two-stage PCB charge detector.

Because of the inability to directly monitor what occurs in an electrosprayed droplet, multiple theories have been proposed to describe what goes on. The two most widely accepted theories include the charge residue model\textsuperscript{116} and the ion evaporation model\textsuperscript{117, 118} though there are others, including a hybrid of the two Hogan \textit{et al.}\textsuperscript{119} proposed (combined charge residue and field emission model). Multiple charge detection works have sought to explain how charge droplets are generated using CDMS. Based on their results analyzing micrometer-sized biological and nonbiological particles, Gao and Austin\textsuperscript{77} suggest that field-induced charge separation is a likely mechanism for electrosprayed droplets on the micrometer scale. Using an electrostatic ion trap, Harper \textit{et al.}\textsuperscript{78} provided compelling evidence for an ESI charging mechanism of macromolecular complexes in native mass spectrometry that is a hybrid of the charge residue and field emission models by observing charge loss and ion emission of trapped ions. Both works shed light on the mechanism of electrospray ionization, though both works also report that their results apply for their respective experiments rather than for all ESI charging mechanisms.
The accuracy in CDMS mass measurements for heterogeneous samples has been utilized to analyze polymers, which occur in nature and in many everyday objects. Polymers occur at different lengths scales and morphologies, and understanding the two could be helpful in developing new materials. In combination with different imaging techniques such as dynamic light scattering and transmission electron microscopy (TEM), Antoine and coworkers\textsuperscript{86-88} have demonstrated CDMS as a useful technique in relating mass distribution to polymer cluster synthesis and morphology. In particular, CDMS mass distributions of polymer clusters were complementary to TEM in determining the composition of tetrapod, hexapod, and dodecapod composite particles, indicating that “CDMS could become a valuable alternative technique for the direct and fast characterization” of complex polymer objects.\textsuperscript{88}

CDMS has been widely used for the analysis of proteins and protein complexes with a variety of implications and applications. Amyloid fibrils are self-assembled protein structures that play important roles in biology.\textsuperscript{93} Their accumulation is known to be related to Alzheimer’s disease and misfolding of proteins. Building on their work of polymer morphology, Antoine and coworkers\textsuperscript{93, 94} were able to utilize CDMS in determining the presence of different amyloid fiber types as well as population density of each using both mass and charge distributions. These important characteristics of the fibers give important insight into formation mechanisms and maturation during the development of neurodegenerative diseases.

The novel coronavirus, severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2), gave rise to the COVID-19 pandemic.\textsuperscript{120-122} This RNA virus has two structural glycoproteins called the membrane and spike (S) proteins. Miller et al.\textsuperscript{96} assessed the heterogeneity of the SARS-CoV-2 spike protein via CDMS as a “top-down” analysis and compared the results to glycoproteomics studies, a “bottom-up” approach. Interestingly, CDMS measurements on the S
protein gave 35-47% larger masses than the glycoproteomic studies. Their results also showed a broader mass distribution. Miller reports that the heterogeneous distribution found through CDMS “may have evolved as a way of further confounding the host’s immune system.”

Viral capsids, protein shells that surround viral genomes, are assembled from hundreds of identical proteins. How this occurs has not been fully understood. Jarrold and coworkers\textsuperscript{97,106} have used a CDMS electrostatic ion trap to identify intermediates (incomplete capsids) in the assembly of hepatitis B virus $T = 4$ capsids as well as multiple assembly pathways. This was done by observing the heterogeneity in mass distributions acquired by CDMS over a period of capsid incubation time. Charge distribution from CDMS is also useful in determining viral capsid structural information, as reported by Keifer \textit{et al.},\textsuperscript{101} since charge can be related to size and capsid packing.

A successful way to correct defective genes is through gene therapy. Here genetic material is introduced to cells through the transport of a DNA payload. Recombinant adeno-associated viral (AAV) vectors have emerged at the forefront of gene therapy.\textsuperscript{111} However, it is well-known that the preparation of AAV vectors can yield different levels of the payload. Pierson \textit{et al.}\textsuperscript{111} analyzed AAV8 vectors through CDMS to determine the payload packaging efficiency. They were able to resolve the vectors into empty, partial, and full subpopulations, enabling rapid screening of clinical samples. Though each subpopulation has similar charge states, so no charge state resolution is needed, the individual analysis and accuracy of their CDMS measurements provides more reliable information than other techniques used to analyze AAV vectors.

1.4 CHAPTER OVERVIEWS

The incredible application work briefly mentioned in the previous section was made possible by the vast improvements in CDMS instrumentation. As mentioned near the beginning
of this chapter, this dissertation is focused on linear array CDMS instrumentation, which will be evident in the chapters that follow.

In efforts to improve mass accuracy, a lot of work has been done to increase charge accuracy in CDMS, but little has been done to improve velocity accuracy. This is especially important when performing linear array CDMS (refer to Equation 1-1) and will be discussed in detail in Chapter 2. Here, the Shockley-Ramo Theorem—a theorem used to calculate instantaneous electric current induced on an electrode by a moving charge—is applied to SIMION simulations to determine accurate particle position. The simulation results are supported by experiments of electrosprayed droplets.

As mentioned earlier, charge detection and CDMS has been used to analyze extra-terrestrial samples. Chapter 3 will focus on our recent efforts to build a custom CDMS instrument for the analysis of dust microparticles in the Martian atmosphere. The final chapter will present possible future directions for this work on linear array CDMS and how it can continue to prove useful to the area of planetary science.
CHAPTER 2: ACCURATELY MAPPING IMAGE CHARGE AND CALIBRATING ION VELOCITY IN CHARGE DETECTION MASS SPECTROMETRY


2.1 INTRODUCTION

Charge detection mass spectrometry (CDMS) is an emerging technique that has opened the possibility of analyzing complex and high-mass samples where conventional mass spectrometry techniques fall short. CDMS is a technique where the mass is determined for individual nano- or micro-particles in a sample. CDMS analysis has allowed characterization of high-mass and heterogeneous samples including amyloid fibrils, DNA, peptides, polymerase chain reaction products, proteins, synthetic polymers, and viruses.

CDMS measurements are based on image charge detection. As a highly-charged particle passes through the detector consisting of conductive elements, or electrodes, the particle’s image charge is induced onto the detector. This image charge is then amplified using a charge-sensitive preamplifier. In addition, one or more shaping amplifiers (or shapers) are often used to both differentiate and filter the signal, both of which make the signal easier to detect. Charge leakage at the preamplifier results in a slow drop-off of the image charge in the preamplifier output and in a baseline shift in the shaped signal. The output signal from the shaper shows a leading peak as the particle enters the sensing electrode and a trailing peak of opposite polarity as it exits the electrode. Particle charge can be directly determined from this shaped signal, and particle velocity is calculated by dividing the distance the particle traveled by the time between peaks.
The \( m/z \) can be calculated from this velocity if an energy filter has been used to select the ion energy, or if the ion is accelerated through a known potential to give a second measured velocity. With measured values of charge and \( m/z \), absolute mass can be determined for each particle in a sample.

Much has been done to improve charge accuracy in CDMS experiments. This has been achieved by taking replicate measurements of particle charge, which results in reduced noise and increased charge accuracy. Using six co-linear sensing electrodes connected to two amplifiers, Gamero-Castaño\(^{24}\) observed an rms noise of approximately 100 e\(^-\) for the measurement of a droplet with a flight time of 493 \( \mu \)s. Jarrold and coworkers\(^{21}\) used 22 sensing electrodes and reported an rms noise of 10 e\(^-\) for a 500 m/s poly(ethylene oxide) ion. In early work Benner\(^{36}\) used an electrostatic linear ion trap (ELIT) to trap DNA ions and measure particle charge every time they cycled through the detector. Here an rms noise of 2.3 e\(^-\) was reported for a DNA ion that oscillated 450 times. By reducing background pressure and extending trapping time to 3 s, Jarrold and coworkers\(^{41}\) reported an rms deviation in charge uncertainty of less than 0.20 e\(^-\), essentially allowing the exact number of elementary charges to be known for each ion or particle.

To measure \( m/z \) in CDMS, particle velocity must also be measured. Velocity is calculated by dividing the distance the particle traveled by the time between peaks in the amplified, shaped signal. Though velocity is important to determine \( m/z \)—and therefore absolute mass—it is unclear how to accurately determine the distance a particle travels in the time between peaks. Some reports have indicated that the peaks correspond to a particle entering and exiting the detector and have used the physical electrode length to be the peak-to-peak distance.\(^{23, 32, 45, 123}\) Others have reported that the peak-to-peak distance is “approximately” the electrode length, though little is said about an exact length or how to determine it.\(^{19, 20, 29}\) A few reports indicate
that the length of the image charge signal, or effective electrode length, is “slightly longer” than the physical length.\cite{Benner1987, Mabbett2001}

Benner reported that the effective electrode length is longer than the actual electrode length because of the way the image charge is captured by the detector, but provided no other evidence or explanation.\cite{Benner1987} Subsequently, Benner and coworkers\cite{Benner1990} and later Mabbett et al.\cite{Mabbett2001} determined the effective electrode length using a 2-stage charge detector and comparing the event times from both detectors to calculate equal, corrected velocities. In particular, the peaks corresponding to the entrance of the first sensing stage and the entrance of the second sensing stage should cancel out any peak position effects, so the physical distance in this case is known exactly. These reports, though useful for their respective experiments, do not discuss how peak positions from the shaped signal and the effective electrode lengths relate to charge detector geometry, nor do they give details on how to determine these for any other system. This approach cannot be used for a system with a single sensing electrode, for instance.

The Shockley-Ramo Theorem\cite{Shockley1949, Ramo1948} can be used to show that peaks of the shaped image charge signal do occur before a charged particle reaches the physical electrode entrance edge and after the particle has passed the electrode exit edge. The Shockley-Ramo Theorem (SRT) allows calculation of the instantaneous image current for a system of conductors when a point charge passes the conductors at a known velocity. Instantaneous image charge can be calculated by taking the integral of these results. The calculation is based on the following equation:

\[
i = E_v(r) v \quad 2 - i
\]

where \(i\) is the instantaneous current received by the given electrode due to motion of a point charge, and \(v\) is the instantaneous velocity of the point charge. \(E_v\) represents the component—in the same direction as the velocity at point \(r\)—of a hypothetical electric field produced if the
given electrode were to be raised to unit potential with all other electrodes set to zero potential.\textsuperscript{124, 125} The term $E_v$ can be readily determined for all points within a CDMS detector of any geometry, and for a given particle trajectory using SIMION ion trajectory software (Scientific Instrument Services, simion.com) or another finite element or boundary element method.

SIMION can thus be used in combination with SRT to determine both instantaneous image current and image charge for CDMS experiments. The expected signals for a given detector geometry and particle trajectory can then be calculated. SIMION calculates the potential at each point in a potential array for a given electrode geometry (with the hypothetical unit potential on the sensing electrodes) based on a 4th order Runge-Kutta integration. In SIMION, and by implementing the SRT calculation as given above, recording the potential with respect to particle position yields the image charge, and recording the change in the potential with respect to the change in particle position yields the image current. Though the SIMION calculation for SRT requires hypothetical electric fields which do not occur in actual experiments, this method is useful in determining the image charge for any given particle trajectory through any given charge detector. The combination of SRT and SIMION has previously been used to model image charge in Ion Cyclotron Resonance (ICR) mass spectrometry, but the implementation for ICR is somewhat different than reported here.\textsuperscript{126, 127}

In this work we show that SIMION and the Shockley-Ramo Theorem can be used to calculate peak shapes and positions for the shaped image charge signal as well as the effective electrode length for a number of different model charge detector geometries and particle trajectories. The results are supported through laboratory experiments in which electrospray-charged droplets were observed using several charge detector designs. Simulation and
experimental results show excellent agreement. Both simulation and experimental findings in this work focus on the shaped, differentiated signals rather than the raw image charge signals. However, these results are not unique to the shaped signals and can be done with the same accuracy using the raw signals.

2.2 SIMULATION AND EXPERIMENTAL METHODS

Table 1. Dimensions of all six charge detector assemblies.

<table>
<thead>
<tr>
<th>Detector</th>
<th>Type</th>
<th>No. of sensing electrodes</th>
<th>No. of grounded electrodes</th>
<th>Electrode I.D. (mm)</th>
<th>Spacing between electrodes (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>cylinders, equal spacing</td>
<td>5</td>
<td>6</td>
<td>5.0</td>
<td>2.5</td>
</tr>
<tr>
<td>B</td>
<td>cylinders, two different spacings</td>
<td>6</td>
<td>6</td>
<td>5.0</td>
<td>2.5, 5.0</td>
</tr>
<tr>
<td>C</td>
<td>cylinders, three different spacings</td>
<td>4</td>
<td>5</td>
<td>5.0</td>
<td>2.5, 3.75, 5.0</td>
</tr>
<tr>
<td>D</td>
<td>cylinders with different inner diameters</td>
<td>1</td>
<td>2</td>
<td>*11.4, 5.0</td>
<td>3.5</td>
</tr>
<tr>
<td>E</td>
<td>cylinder between two small plates†</td>
<td>1</td>
<td>2</td>
<td>*3.0, 8.0</td>
<td>2.5</td>
</tr>
<tr>
<td>F</td>
<td>printed circuit boards, planar electrodes‡</td>
<td>5</td>
<td>6</td>
<td>5.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>

*indicates inner diameter of grounded electrodes
†small plates are 0.5 mm wide with hole through the center
‡planar electrodes are 20 mm long, 10 mm wide

Six model charge detector geometries were analyzed, as described in Table 1 and illustrated in subsequent figures. Three detectors were built of multiple, identical cylindrical tubular electrodes to observe the effects of different electrode spacings and particle trajectories on image charge. A detector made of cylinders with different diameters and a detector with thin grounded plates were used to observe changes in image charge peak shape and position with these geometries. Additionally, our group has previously reported the use of printed circuit boards (PCB) for charge detectors, so a detector made of two PCBs facing each other with multiple imprinted planar electrodes was also used for analysis of the shaped image charge signal.
Charge detectors were simulated in SIMION 8.1 by setting up finite element arrays with electrodes based on the dimensions described in Table 1. It was important to match each geometry exactly as described to accurately determine the image charge peak position in both simulations and laboratory experiments. To implement Shockley-Ramo Theorem calculations for image charge analysis, 1 V was applied to all sensing electrodes and 0 V was applied to all others in the SIMION models. SIMION calculated the potential at each non-electrode point in the array given these hypothetical applied potentials. The corresponding field values needed for the SRT calculation were extracted for a specific particle trajectory by “flying” a neutral test particle through the detector assembly and recording both the test particle position (x) and the field component (dV/dx) at each point along the particle trajectory. Differentiated image charge signals were determined for each model charge detector and for a variety of possible particle trajectories.

Figure 7 shows a schematic diagram of the custom-built instrument used to evaluate each charge detector geometry. Charged droplets were generated by electrospraying a solution of 80% methanol and 20% water acidified with 3% trifluoroacetic acid. The solution was pumped through a custom-made electrospray needle by a syringe pump operating at 180 µL/hr. The needle was biased at +4200 V relative to the grounded vacuum system. The electrosprayed solution entered the vacuum system through a 200-µm pinhole aperture before passing through a beam tube (4.5 mm I.D.) and two differentially pumped regions separated by conical skimmers before reaching the analysis region. The pressures in the first and second differentially pumped regions (both pumped by rotary vane pumps) were ~ 4.5 Torr and ~ 0.50 Torr, respectively. The pressure in the analysis region (pumped by a turbomolecular pump) was ~ 3 × 10⁻³ Torr. Though the pressure in the analysis region is in the mTorr range, the constant velocity results show this is
below the threshold where collisions with background gas would cause the analyzed droplets to slow down. The analysis region housed the image charge detector and amplifiers. All sensing elements of the charge detectors were connected together to the junction gate field-effect transistor (JFET) input of a charge-sensitive preamplifier. The image charge signal was amplified by an Amptek charge-sensitive preamplifier (A250, Amptek, Bedford, MA) mounted to a PC250 testbed, and three shaping amplifiers (Amptek A275) in series, mounted to a PC275 testbed. Two of the shaping amplifiers are connected as low-pass filters, and one is connected as a high-pass filter. The rise times for the preamplifier and shaping amplifiers are 2.5 ns and 15 ns, respectively, with the shaping amplifier slew rate of 100 V/μs, which are much faster than the change in image charge signal from droplet movement across the detectors in these experiments. The output from the third shaping amplifier was connected to a 200 MHz digital storage oscilloscope (Waverunner 3024, Lecroy, Chestnut Ridge, NY). Based on the triggering level of the oscilloscope, the limit of detection for this system is ~1500 e⁻. The number of charges on the analyzed droplets shown in the results have between a few thousand and tens of thousands of electrons.

Figure 7. Schematic showing an overview of the instrument used for experiments. Particles are charged via electrospray ionization (ESI) and introduced into vacuum. Charged particles are led through the differential pumping system by a beam tube and are analyzed by a charge detector assembly where the
pressure is $\sim 3 \times 10^{-3}$ Torr. Rotary vane pumps (RVP) and a turbomolecular pump (TP) are attached as shown.

For charge detectors with more than one sensing electrode, droplet velocities were calculated across each sensing electrode and across each gap between sensing electrodes (where the grounded electrodes are located). These should each give the same velocity if the correct electrode length is used. For the sake of comparison, velocities were calculated using 1) physical electrode lengths and 2) effective electrode lengths calculated using SRT and SIMION.

2.3 RESULTS AND DISCUSSION
2.3.1. Detector A: Multiple, Identical Cylinder Electrodes with Equidistant Spacing

The geometry of Detector A is shown in Figure 8a, and Figure 8d shows a representative signal from a charged droplet passing through this detector. Figure 8e shows the velocities calculated across each electrode if the assumption were to be made that the measured peaks occur when the particle is at the physical edges of each sensing electrode (square markers and orange trace). Peak times were determined by taking the time derivative of the shaper output signal and calculating the time at which the derivative passed through zero using a linear regression. Uncertainty of the linear regression fit to determine peak time was approximately 200 ns. Velocities were calculated across the length of each sensing electrode and for the spacing between sensing electrodes (including the grounded electrode). Though in reality the particle velocity does not change as it passes the grounded electrodes, these calculations in Figure 8e (square markers, orange trace) show a significant change in apparent velocity across these electrodes. This difference shows that the chosen peak positions in this case are incorrect and confirms that the image current peak does not correspond to the physical edge of the sensing
electrodes. The data in Fig. 8e is from a single droplet; many droplets were examined, and all show the same pattern.

The maximum image current peak positions were determined for the Detector A geometry using SRT-SIMION simulations (Fig. 8b and 8c). The simulated signal in Figure 8c, which looks very similar to that of the shaped signal in Figure 8d, was used in determining effective electrode lengths. The extracted values of image current in Figure 8c for a test particle passing through the center of the detector shows that the image current reaches a maximum exactly halfway between the sensing and grounded electrodes, or 1.25 mm away from the edge of the sensing electrodes. This is where all image current peaks occur for this detector geometry, which results in an effective electrode length greater than the physical electrode length. For this detector the effective electrode length is 15.2 mm, compared with the physical dimensions of the electrodes of 12.7 mm.

Calculated particle velocities using the effective electrode dimensions from the simulation results are shown in the blue trace Figure 8e (triangular markers). Here the velocities across and between all sensing electrodes vary far less and agree within 0.41% relative standard deviation (RSD). This represents an uncertainty of less than 60 µm in the effective length of the electrodes. When precisely, individually measured electrode spacings and lengths are used rather than the nominal values in Table 1 to calculate effective electrode lengths, the consistency among velocity measurements is even better. Calculated velocities agree within 0.25% RSD corresponding to an uncertainty of less than 40 µm in the effective length of the electrodes. This uncertainty is dominated by the noise in the shaped signal when determining the peak centers by linear regression, but it is not much larger than the uncertainty in measured electrode/gap dimensions using digital calipers.
The accurate results from calculating droplet velocities from the shaped signal using the effective electrode lengths show that the peaks from the shaping amplifier occur at the same time as the maximum image current seen in the simulations, or that at least there is a constant offset that cancels out when determining the time/distance between peaks. This goes on to support the simulation results showing that the peak positions from the shaped signal for this detector occur exactly halfway between electrodes rather than at the edges of each sensing electrode. The calculated results and experimental data agree within the 99.9% confidence limit. The close agreement of the simulations and experimental results show that the SRT-SIMION method provides very accurate determination of the effective electrode length.
Figure 8. Detector A simulation and experimental results. (a) Schematic of detector. Light blue boxes are sensing electrodes and gray are grounded. (b) SIMION simulation of the highlighted electrodes showing hypothetical isopotential contours by combining SIMION with SRT (1 V applied to sensing electrodes and 0 V applied to the rest). The maximum occurs midway between electrodes as seen by the extracted values in (c) showing the peak shape with dotted lines indicating the predicted peak positions. (d) Typical signal of a charged droplet from the shaping amplifier. (e) Velocities from the shaped signal of a single droplet are calculated across each electrode using either the physical lengths of electrodes or the effective lengths as determined by simulations. Even electrode numbers refer to measurements as droplets enter and leave the corresponding electrode; odd electrode numbers refer to measurements as droplets leave the preceding sensing electrode and enter the subsequent sensing electrode (i.e., the point at electrode #3 is the measured velocity between the peak as the droplet leaves sensing electrode #2 and enters sensing electrode #4).
When applying the effective electrode lengths determined from SRT-SIMION simulations we have seen consistent patterns (not shown) in the measured velocity across specific electrodes for multiple particles. These patterns reflect imperfect electrode placement and slight variations in the physical dimensions of the electrodes used. These systematic effects are reduced as precisely measured dimensions are used for electrode length and placement in the simulations. It is interesting that the image charge signal is sensitive to slight inconsistencies in electrode position even down to the smallest scale that can be measured using calipers.

2.3.2. Detector B: Cylinder Electrodes with Varied Spacing

Detector B was analyzed to observe the effect of electrode spacing on the effective electrode length. This detector had two different spacing distances between cylinders as shown in Figure 9a and noted in Table 1. Not surprisingly, SRT-SIMION predicts that the peak will coincide with the midpoint between sensing and grounded electrode edges regardless of spacing. As was done with Detector A, a comparison between physical electrode length and SIMION-calculated effective electrode length with Detector B confirms this prediction (Figure 9e). The effective electrode length depends on the size of the gap between a sensing electrode and the adjacent grounded electrode.
Figure 9. Detector B simulation and experimental results. (a) Schematic of detector. (b) SIMION simulation showing hypothetical isopotential contours across electrodes spaced 2.5 mm apart (left) and 5.0 mm apart (right). The maximum occurs at the center between electrodes as seen from the extracted values in (c) showing peak shape with the dotted lines indicating the peak positions. (d) Typical signal from the shaping amplifier of a charged droplet in Detector B. (e) From experimental data of a single, representative droplet, velocities are calculated across each electrode using either the physical lengths of electrodes or the effective lengths as determined by simulations. The decrease in apparent physical edge velocity across electrodes 6 and 8 occur where the electrode spacing is greater.
The hypothetical isopotential contours seen in SIMION are shown in Figure 9b. The extracted values showing the image charge peak positions and shapes are shown in Figure 9c. Peak shape will be discussed in greater detail later. Briefly, as seen in Fig. 9c, the shaped peak amplitude and width is affected by electrode spacing. The electrode spacing also changes the peak position and effective electrode length. Though identical cylinders are used in Detector B there are three different effective electrode lengths because of the varied electrode spacing. Electrodes 2, 3, 4, 10, and 11 have an effective length of 15.2 mm; electrodes 5 and 9 have an effective length of 16.45 mm; and electrodes 6–8 have an effective electrode length of 17.7 mm. Herein we see that peak positions from the shaped signal and the resulting effective electrode lengths are dependent upon electrode spacing.

Effective electrode length can be easily determined when a sensing electrode is placed closely to grounded elements (e.g. between two grounded electrodes or housed in a grounded shielding). As seen in Figures 9b and 9c, the placement of the grounded elements results in defined image current peaks. Electrode 12 from Detector B is not followed by a grounded electrode, nor is the charge detector assembly housed in a grounded shielding. This results in no defined peak following the charged droplet exiting this electrode (Fig. 9d), so the effective length and resulting velocity across this electrode cannot readily be determined.

2.3.3. Detector C: Charge Measurements and Off-Axis Effects

Simulations can also be used to observe how different particle trajectories influence peak shapes. The geometry for Detector C is shown in Figure 10a, and Figure 10d shows a representative experimental signal of a charged droplet passing through this detector where the droplet trajectory was off-center but still parallel to the detector axis. Figure 10d shows that the width of each respective peak is proportional to the electrode spacing, that peak amplitude varies,
and that each peak looks “forked” rather than having one maximum point. As discussed for Detector B, the change in peak amplitude is due to the varied electrode spacing.

Interestingly, the simulations also shed light on the “forked” peak shapes. Figure 10c shows extracted values from simulations when the test particle trajectory is 0.1 mm away from the detector walls and parallel to the detector axis. This simulation looks strikingly similar to the experimental data from the shaped signal in Fig. 10d. Looking closely at the isopotential contour lines where the simulated test particle trajectory occurs (Figure 10b) the lines are bunched together near the electrode corner, indicating a stronger field near the sharp corner compared with elsewhere along the gap between electrodes. This stronger field near the electrode corners results in higher instantaneous image current at these points, and this is seen in both the simulated and experimental signals where the peaks look “forked”. The agreement in both the simulated and experimental data shown in Figures 10c and 10d illustrate the utility of the SRT-SIMION simulations to predict image current peak position and shape for different droplet trajectories.

In the results up to this point, charge measurements have not been addressed. Each peak in the shaped signal gives a charge measurement—two for every sensing electrode—so as a droplet passes through Detector C the charge (which presumably remains unchanged) is measured eight times. The observed measurement corresponding to charge should also remain unchanged. The results in Fig. 8d (earlier) show that the particle signal remains unchanged through each stage, consistent with a particle that is not noticeably losing charge during transit. Both experiments and simulations show that peak amplitudes vary for Detector C as well as Detector B due to electrode spacing. Peak amplitude also varies due to particle trajectory. Since charge should remain unchanged, peak amplitude from the shaped signal cannot correspond to
charge. By integrating the area under each peak for the experimental signal in Fig. 10d, we observed equal areas for all eight peaks agreeing within 2.3% RSD. SRT-SIMION simulations predict that the peak areas from differentiated image charge signal correspond exactly to charge, even for off-axis particles. To the extent that shaped signal corresponds to differentiated signal, the same would be expected in experimental data. The consistent areas for all peaks across Detector C in the experimental droplet signal and the simulated signals confirms that peak area from the shaped image charge signal corresponds to charge. However, for particles that are well-aligned with the detector axis passing through a detector with uniform electrode spacing, the peak widths and corresponding amplitudes are also uniform. In such a case, the peak amplitudes correspond approximately to particle charge.

As seen in Figure 10d there is a baseline shift as well as a change in the amplitude of each “prong” in the forked signal of a single peak. These shifts are due to charge leakage from the JFET on the amplifier. This leakage was taken into account when integrating peaks in the signal and did not affect the area under the peaks. The peak center is shifted slightly by this leakage, though this effect cancels out when calculating effective electrode lengths. However, charge leakage from the JFET is not exactly cancelled out when calculating droplet velocity if the spacing isn’t uniform (e.g. velocity calculated across electrode 3 in Figure 10a).
Figure 10. Detector C simulation and experimental results. (a) Schematic of detector. Three different electrode spacing distances were used as noted in Table 1. (b) Simulation of the highlighted electrode corner showing hypothetical isopotential contours near the detector edge. Dotted line is the particle position and trajectory for the (c) simulated results for a test particle that passed straight through the detector 0.1 mm away from the electrode walls. (d) Signal from a charged droplet where the droplet trajectory was misaligned with respect to the detector.
2.3.4. Detector D: Simulations for Cylinder Electrodes with Different Diameters

Detector D was made of cylinders with different diameters to observe the effect of electrode diameter on the peak position and shape. The geometry for this detector is shown in Figure 11a. The inner diameters for the sensing electrodes (5.0 mm) were smaller than the I.D. for the grounded electrodes (11.4 mm). The simulation results are shown in Figures 11b and 11c. With the grounded electrodes having an I.D. more than twice that of the sensing electrodes, the maximum image current occurs off-center in the gap and closer to the grounded electrodes. This leads to an effective electrode length 22% longer than the physical electrode length for this particular configuration.

Figure 11. Simulations on a charge detector made of cylinders with different diameters. (a) Detector schematic. (b) Isopotential contours across the detector in simulations with hypothetical potential applied and (c) the extracted values of the image current as a test particle passes through the detector. Dotted lines indicate peak positions (where image current is at a maximum).
The different diameter electrodes also change the shape of the simulated peaks, specifically the rise and fall of each peak. Fig. 11c shows that the fall of the second peak and rise of the third peak are similar, and the peaks occur close enough together that there is essentially no defined baseline between them. This could affect accurate charge determination via peak integration. This issue is solved by using electrodes with sufficient aspect ratio.

2.3.5. Detector E: Sensing Cylinder and Grounded Plates with Small Holes

Simulations evaluated a charge detector comprised of a cylinder between two small grounded plates. Each plate had a hole with a smaller I.D. than the cylinder. The cylinder I.D. was 8.0 mm, the holes in the plates had an I.D. of 3.0 mm, and the plates are spaced 2.5 mm away from the cylinder. The geometry is shown in Figure 12a and is similar to that of charge detectors used in electrostatic linear ion traps (ELITs) for Fourier transform CDMS. The hypothetical contours from the simulations are shown in Figure 12b with the extracted values shown in Figure 12c. Simulations show that the peak image current occurs just over 1 mm away from the sensing electrode. Simulations determined the effective electrode length is 14.9 mm or 17% longer than the physical electrode length.

Effective electrode lengths don’t directly affect \( m/z \) measurements in Fourier-transform CDMS but may still have an effect. In FT-CDMS, image charge provides the oscillation frequency as the ion or particle passes back and forth multiple times through a charge detector. Velocity is determined from this frequency, but requires knowing the energy—for instance, using an energy analyzer to constrain the energy of the sampled ion. Harper et al. has shown that the harmonics in the FT signal can also provide enough information to obtain the velocity and \( m/z \). Inasmuch as changing the detector length modifies the resulting signal, a
corrected value for the effective detector length may change the distribution of harmonics used to determine \textit{m/z}.

![Figure 12](image.png)

Figure 12. Simulations for a charge detector made of a cylinder between two thin plates with small holes. (a) Detector schematic. (b) The isopotential contours due to the applied hypothetical potential in the simulations. (c) Extracted image current values. Image current reaches two maxima just over 1 mm away from the sensing electrode edges, resulting in an effective electrode length of 14.9 mm or 17% longer than the physical electrode length.

2.3.6. Detector F: Printed Circuit Boards with Planar Electrodes

Our lab has previously reported the use of printed circuit boards (PCB) for charge detection\textsuperscript{32,128}, so we also examined the application of combining SRT and SIMION in simulations to a 5-stage charge detector made from two PCBs. The PCBs are spaced apart,
parallel, in a sandwich-like assembly. A photograph of one PCB is shown in Figure 13a, and a representative signal from this detector is shown in Figure 13d. All grounded and sensing electrodes on this detector were 20 mm long, 10 mm wide and spaced 2 mm apart with the PCBs spaced 5 mm apart from one another as noted in Table 1. Figure 13b shows the isopotential contours when the hypothetical 1 V is applied in SIMION, and Figure 13c shows the extracted values from a test particle passing through the center of the detector.

Using planar electrodes on two PCBs instead of cylindrical electrodes leads to open sides, whereas a cylindrical detector completely surrounds the charged particle as it passes through. This could result in a different rise time, peak width, peak amplitude, or signal-to-noise ratio when compared to a cylindrical detector with the same electrode lengths, diameters and spacings. However, this should not affect peak position from the shaped image charge signal when compared to a similar cylindrical detector. Not surprisingly, peak position for this PCB detector was determined to be halfway between electrodes, resulting in an effective electrode length 10% longer than the physical electrode length. When using the effective electrode length in velocity calculations the experimental droplet velocities across all electrodes agreed within 0.44% RSD.
Figure 13. Simulation and experimental data for a charge detector made of two printed circuit boards stacked on top of each other with planar electrodes. (a) Picture of one PCB used to make the detector. The two parallel PCBs are spaced 5 mm apart. (b) The isopotential contour lines between two PCBs due to the applied hypothetical potential is applied for the electrodes marked on the PCB pictured above. Hypothetical fields are the same between all congruent electrodes and gaps. (c) Extracted values show maxima halfway between sensing and grounded electrodes indicated by the dotted lines. (d) Representative signal from the shaping amplifier for a charged droplet passing through the PCB detector.

The agreement between the PCB simulation results and the PCB experimental data supports the efficacy of using SRT-SIMION simulations to map image current for a PCB charge detector, and can help explain previous results. For instance, in a previous report from our lab,32
a representative signal of a charged micrometer-sized polystyrene sphere using a PCB with five sensing electrodes showed a change in peak amplitude and shape, which wasn’t able to be explained at the time. Using SRT-SIMION simulations (not shown) we determined the likely particle trajectory for that signal. The particle trajectory was off-axis and at an angle to the PCB detector resulting in the changes of both peak shape and amplitude.

Simulations (Fig. 14) show that the image current peaks should coincide for a cylinder CD and the PCB CD with equivalent dimensions (same electrode length, same gap, and with the PCB spacing the same as the cylinder I.D.). However, the rise-time and amplitudes of the signals differ as a result of the open sides in the PCB charge detector design. The area under the peaks is the same for both designs, confirming and explaining a prior observation in which a single charged particle was measured using both a multi-stage cylindrical-electrode CD and a PCB-based CD.25 The reduced amplitude decreases the charge sensitivity of this design, but this amplitude can be recovered by reducing the gap separating electrodes.

Regardless of the type and extent of signal processing done by the amplifier and the shaping amplifier(s), the distance between peaks in the output signal always corresponds to the distance between points of maximum image current as calculated using the SRT-SIMION method. This effective length can be determined for any electrode combination or geometry, and should be used for calibrating velocity and m/z in CDMS measurements. Whether the shape of experimental signals corresponds to the predicted shape from SRT-SIMION may depend on the amplifier speed and other details; however, agreement between experiental and simulated peak shapes and widths show that there is good agreement across a variety of geometries.
2.4 CONCLUSION

Velocity calculations from experimental data show the distance between peaks from the shaped image charge signal is not the physical length of the sensing electrode, and the peak does not occur at the sensing electrode edge. Through use of simulations combining the Shockley-Ramo Theorem and SIMION, peak positions and effective electrode lengths have been accurately determined for six model charge detectors. These results have been supported by laboratory experiments. We have shown that peak position and shape are dependent upon charge detector geometry (i.e., physical electrode length, diameter, spacing, alignment, and particle trajectory). We have also shown through experiments and simulation results that the area under image current peaks rather than the peak amplitude in the shaped signal corresponds to particle charge. However, in the special case with on-axis particles and uniform electrode spacing, the
amplitude of the shaped signal is also uniform and therefore proportional to charge. These results, including accurate velocity measurements when using the effective electrode lengths, will increase $m/z$ accuracy in CDMS measurements done in the time domain. These results may have an effect on harmonics analyzed in the frequency domain as well. To our knowledge, this is the most rigorous analysis of shaped peak positions and shapes as well as effective electrode lengths for any charge detector geometry as it relates to charge detection mass spectrometry.
CHAPTER 3: CHARGE DETECTION MASS SPECTROMETRY FOR THE ANALYSIS OF ATMOSPHERIC DUST ON MARS

3.1 INTRODUCTION

Dust is a dominant feature of the surface and atmosphere of Mars. Dust suspended in the atmosphere accounts for the majority of the solar IR and UV radiation absorbed,\(^{129-132}\) and therefore drives radiative models, atmospheric dynamics, and climate.\(^{133}\) The atmospheric chemistry on Mars is strongly influenced by the large surface area of these particulates. Dust storms, including dust devils and larger, global dust storms, redistribute dust grains across the Martian surface. These storms have been observed both from orbit and landers, using imaging techniques and by observing the associated drop in local atmospheric pressure.\(^{134-141}\) Global dust storms that expand to encompass the entire planet typically occur every few Mars years and last for weeks to months, with the most recent occurring in 2018.\(^{132,142-145}\)

Atmospheric lift, suspension, and transport of dust during dust devils and storms frequently brings electrification and generation of electric fields.\(^{146-149}\) Electric fields have been observed in the terrestrial atmosphere, and the \(\mu\)ARES instrument on the ill-fated ExoMars 2016 lander was slated to observe evidence of electric fields in the Martian atmosphere.\(^{148,149}\) In the terrestrial atmosphere these electric fields are the result of charged dust grains that are likely charged by some form of contact electrification, such as triboelectric charging.\(^{146}\) Similar triboelectric dust charging, as well as photoelectric charging, likely cause electrification of atmospheric dust grains on Mars. Laboratory evidence shows that dust devil electrification occurs under Martian conditions.\(^{150,151}\)

Aside from dust electrification, dust aerosol transport from dust devils impacts the climate and environment of Mars. The dust load of a dust devil is ultimately dependent on dust aerosol size and surface conditions.\(^{152}\) Numerous Mars missions have used optical scattering instruments to determine dust particle size on the surface and within the atmosphere through imaging means.
Viking, Phobos, Phoenix, Spirit, Opportunity, Mars Science Laboratory, Curiosity, and other missions gave mean particle radii ranging from <1.0 to 2.75 µm that varies throughout the Mars year. The radiation and dust sensor onboard the Mars Environmental Dynamics Analyzer (MEDA) of the Perseverance Rover also operates using optical scattering to measure Mars dust scattering properties in the atmosphere.

In spite of these prior measurements, no instrument has yet measured the electrical charge of individual dust grains in the Mars atmosphere, nor fully characterized the particle size distribution (PSD) or the assortment of particle shapes. However, such measurements are critical factors not only for a complete understanding of dust’s role in Mars atmosphere and climate, but also as a risk factor for future Mars exploration. For example, an In Situ Resource Utilization (ISRU) system to produce oxygen would require filtering dust from the ingested atmosphere, and the size and charge of the dust grains would drive the filter design. The use of solar power on Mars would be improved by a better understanding of the properties of dust that cause it to stick to solar panels. Dust grains clinging to (and potentially abrading) astronaut space suits pose a risk to the health and safety of a crew. The full size distribution and the charge distribution of Mars dust must be determined to retire these risks to future human exploration of Mars.

Image charge detection is a promising option for measuring the electrical charge of individual dust grains. The basic principle of charge detection was first demonstrated during the 1960s when microparticle acceleration experiments were used to simulate micrometeorite impacts on spacecraft. Decades later Fuerstenau and coworkers’ used charge detection for their Mars dust grain particle charge spectrometer to analyze aerodynamic particle diameter and charge for microparticles from various agitated dusts and electrostatic sprays. In this technique, particle image charge is recorded as individual particles pass through a detection
electrode. The opposite charge is induced on the electrode, and this charge is amplified and recorded by a charge-sensitive amplifier (Figure 15). The resulting signal amplitude is proportional to the particle charge. The particle velocity can also be determined as the time required for the particle to pass through or across the detection electrode (Figure 15). Charge detection mass spectrometry (CDMS) takes this process one step further, by measuring the change in velocity of a particle in response to an applied electric field. The change in velocity is a function of the charge-to-mass ratio of the particle, and this value combined with the measured particle charge yields the particle mass. If particle aerodynamic size can also be determined, the relationship between size and mass gives some information about particle density and shape. Other particle sizing and aerosol techniques, such as differential mobility analysis, are able to give aerodynamic size, but are not alone able to determine the charge or other particle parameters.

Charge detection mass spectrometry (CDMS) is a single particle technique that is useful for the analysis of microparticles of varying mass, size, and charge. This allows for the direct measurement and calculation of charge, $m/q$, and absolute mass of every particle analyzed. Measurements of these characteristics allow for both a charge distribution (magnitude and polarity) and a correlated mass distribution of a given species to be constructed, wherein the complete PSD can be determined. CDMS can measure suspended microparticles in the Martian atmosphere, providing direct analyses of vital parameters that have not been determined on previous Mars missions.

We report on the development a CDMS instrument to measure both the mass and the electrical charge on individual dust particles in the Mars atmosphere. This instrument is centered around a charge detection mass spectrometer made using a novel approach consisting of two
printed circuit boards. Sets of electrodes are patterned onto the facing surfaces of the PCBs, with the dust grains being drawn through the space between the boards. Electrode and detector design has been optimized based on results from our previously published work.164

**3.2 PCB CDMS ANALYZER DESIGN AND SIMULATED PERFORMANCE SETUP**

Figure 15 shows the PCB electrode layout (a) and detector assembly (c) of the CDMS Mars dust analyzer. Two PCBs are assembled in a sandwich-like array spaced 5 mm apart to make the complete analyzer. Each PCB has copper electrodes patterned onto FR4 board material. Dimension of the two end electrodes are 8 mm × 12 mm, and all other electrodes are 16 mm × 12 mm. Spacing between all electrodes is 2 mm.

Charged particles are drawn through the assembly from left to right. The odd electrodes (blue in top image) are those connected to the charge amplifier system and are referred to as “sensing” electrodes. Electrode 4 (green) has a DC voltage applied which creates an electric field and changes particle velocity across this electrode based on the charge polarity and $m/q$ of the particle. All other electrodes are grounded (gray).

An example of the observed signal output as a charged particle passes through the dust analyzer is shown in the middle of Figure 15. Velocities are calculated across each sensing electrode and those grounded electrodes between two sensing ones. These particle velocities—across both sensing and grounded electrodes 1–3 and 5–7 in the figure—are expected to remain the same since no electric field is acting on the particle as it crosses them (velocities are measured across electrodes 2 and 6 to increase the number of measurements). Particle velocity is also calculated across the central region (electrode 4) where there is a shifted velocity from acceleration or deceleration across the central DC electrode. The plot in (d) of Figure 15 illustrates the expected velocity trend for a particle traveling through the analyzer with an acceleration spike across the central region. This spike or shift in velocity is dependent upon
charge polarity, \( m/q \), and the applied DC voltage. From these charge and velocity measurements, mass can then be determined using the following equation:

\[
m = \frac{2qV}{v_2^2 - v_1^2}
\]

Here, \( q \) is particle charge, \( V \) is the DC voltage applied to the central region, \( v_1 \) is the average particle velocity across electrodes 1–3 and 5–7, and \( v_2 \) is the shifted particle velocity across the central DC region.

Dust analyzer performance has been simulated with finite element calculations in SIMION 8.0 ion trajectory software\textsuperscript{165} and accompanying analysis in Microsoft Excel. Microparticles of varying charge, \( m/q \), and mass were “flown” through the CDMS analyzer model in SIMION. Particle position, time-of-flight, and velocity were recorded to determine velocity change across the central region of the analyzer. Initial particle velocity was estimated based on expected gas flow and acceleration due to free gas expansion in the vacuum system. Dust grain mass, derived using density data obtained from the Mars Pathfinder Rover\textsuperscript{166}, is larger than the mass that can be given as an input to SIMION, so trajectory modeling was done using particles with the same \( m/q \), but with lower mass and unit charge. No adjustments for initial particle velocity were needed for the simulations.
3.3 EXPERIMENTAL METHODS

For experimental analysis and development of the CDMS dust analyzer, microparticle simulants were used to mimic Mars dust. Several types of microparticles were used, including a Mars regolith simulant (MMS-1), olivine powder, polystyrene microspheres, and chalkboard
chalk dust. Olivine was chosen because of the chemical composition it shares with Mars dust. Olivine, an iron-magnesium silicate, was observed by the Thermal Emission Spectrometer (TES) on the Mars Global Surveyor orbiter \(^{168, 169}\) and has been used in previous experiments as an analogue for interstellar dust.\(^{170}\) The latter two microparticle samples were chosen based on their size, affinity for charging, and availability, although the material density differs significantly from the expected composition of dust grains in the Martian atmosphere.

Olivine was obtained as a 1 cm\(^3\) mineral specimen and was ground and micronized using a mortar and pestle followed by a micronizing mill. A solvent of 80% methanol and 20% water was used during the milling process. Mineral samples were then separated into narrow size bins using centrifugation—a common filtration mechanism for mineral analysis\(^{171, 172}\)—and dried. Following these preparation steps, scanning electron microscopy (SEM) helped determine that mineral particle sizes were in the micrometer size range prior to CDMS analysis. Amino-terminated polystyrene microspheres (Spherotech, Lake Forest, IL) were purchased in the size range of interest and did not require the size reduction steps.

In order to mimic the natural charge of dust grains on Mars, triboelectric charging of dry samples was used. MMS-1 and olivine particles were charged by vortexing each simulant powder in polyethylene pipettes for 30 seconds. Chalkboard erasers were clapped to charge and release chalk dust for analysis.

Electrospray charging using an acidified 4:1 methanol:water solvent was also used as part of the experiments for the amino-terminated polystyrene spheres. However, upon data analysis it was evident that the polystyrene was not fully desolvated from the electrosprayed solvent, thus interfering with accurate characterization of the PCB CDMS device. Therefore, we did not utilize this charging mechanism in the results displayed in this chapter.
Although the atmospheric pressure on Mars is much lower than that of Earth, CDMS for particles of this size requires an operating pressure even lower—typically below 500 mTorr in the analyzer. For instrument demonstration using microparticle samples initially at Earth atmospheric pressure, a laboratory vacuum system with a 2-stage differentially pumped inlet was used to simulate operation under Mars-like conditions. The first vacuum region was held slightly lower than Mars atmosphere at ~2.4 Torr (rotary vane pump), and the second vacuum region where CDMS analysis was performed was pumped down to ~5.5×10^{-2} Torr (turbomolecular pump). As shown in Figure 16, charged particles entered the vacuum system through a 250-µm pinhole aperture and passed through a PTFE-lined beam tube (15 mm I.D) before reaching the CDMS analyzer.

![Figure 16](image)

Figure 16. Schematic of laboratory vacuum instrument setup for CDMS experiments. Microparticle powders were charged via vortexing and introduced into the two-stage vacuum system. Charged particles were guided through a PTFE-lined beam tube in the differentially pumped vacuum system before CDMS analysis. Pressure in the analysis region was ~5.5×10^{-2} Torr. A rotary vane pump (RVP) and turbomolecular pump (TP) were attached as shown.

The analysis region housed the PCB CDMS Mars dust analyzer and charge amplifier. All sensing elements of the charge detector were connected to the junction gate field-effect transistor.
(JFET) input of a charge-sensitive preamplifier. The image charge signal was amplified by a CoolFET charge sensitive preamplifier (A250CF, Amptek, Bedford, MA) containing an A250 preamplifier and JFET cooled to -50°C by a Peltier cooler. The amplifier output was connected to a 200 MHz digital storage oscilloscope for data acquisition (Waverunner 3024, Lecroy, Chestnut Ridge, NY). Signals were recorded by the oscilloscope using the charge trigger tool. Based on the triggering level of the oscilloscope, the limit of detection for this system is ~1500 elementary charges (e) of either polarity. It is possible to observe particles with less charge than this by continuously recording data.37 Data was analyzed using a MATLAB code used to extract both 1) the signal amplitude (to determine particle charge using the amplifier charge-to-voltage gain) and 2) the inflection points, when the particle is midway between adjacent electrodes electrodes (used to determine particle time-of-flight and velocity). Mass could then be calculated using Equation 1.

3.4 SIMULATION AND EXPERIMENTAL RESULTS
3.4.1. Simulation Results
Figure 17 shows the SIMION simulation results defining mass accuracy ranges for different particle size and charge combinations beyond the ±1500 e⁻ triggering limit of detection for the charge amplifier used in our experiments. This detection limit could be lowered by reducing electrical noise or by continuously acquiring data rather than using a trigger. Optimal mass accuracy occurs when the particle velocity changes by more than 10%.21 The central DC potential was stepped between 200–1,000 V. This maximum voltage of 1,000 V is the highest applied voltage possible to prevent damage to the charge amplifier and is below the Paschen curve for the CDMS detector geometry and expected vacuum conditions.
Figure 17. SIMION simulation results for PCB CDMS analysis of microparticles having varying size and charge (triggering limit ± 1500 e). With a DC voltage range between 200–1,000V, the optimal mass accuracy occurs for particles with a radius roughly between 0.2–1.5 µm.

For a given acceleration voltage, dust grains too high in mass or too low in charge are not accelerated or decelerated enough for the resulting signal delay to be discernable. The charge can still be measured, but only a lower limit to the grain’s mass determined. Dust grains too low in mass are deflected onto the circuit board and bounce, producing an erratic signal that will not be usable for analysis at a given voltage. Lower voltages allow measurement of particles with lower mass and/or higher charge. Between the extremes described is a range of \( m/q \) values that will produce analyzable signals. Simulation results illustrated in Figure 17 show that the optimal region for mass accuracy across the DC voltage range up to 1,000 V occurs when particles are less than 1.5 µm in radius.

3.4.2. Experimental Results

Figure 18 shows an SEM image of the olivine sample showing successful size reduction steps prior to CDMS analysis. Figure 19 shows an image charge signal for a negatively charged olivine particle passing through the PCB CDMS detector array having the central DC voltage set
to 950 V. Based on the charge-to-voltage gain, average measured particle charge was -49,300 e. Average particle velocity across sensing electrodes was 24.9 ± 0.4 m/s at the 95% confidence level. Despite successful size reduction steps (shown through the SEM in Figure 18), there was not a shift in particle velocity across the central DC electrode as expected based on the anticipated particle $m/q$. Therefore, CDMS could not be performed to determine particle mass and size. This is most likely due to formation of a charged particle conglomeration within our laboratory inlet.

![SEM image](image.png)

Figure 18. SEM image taken of olivine mineral following the size reducing and separation steps. Scale bar is 5 µm.

As seen in Figure 19, the shapes of the image charge peaks are skewed from parallel in comparison with the illustrated example signal in Figure 15b. This creates uncertainty in the voltage (y-axis in the signal), which is the measurement used to determine particle charge in connection with the charge-to-voltage gain. The source of this uncertainty is current leakage, or an undesirable current path, within the Amptek charge amplifier. Reduction of this leakage would increase charge accuracy and can be achieved by integrating a charge amplifier that
utilizes a differential input to increase sensitivity, has an active reset, and has a smaller feedback capacitance.\textsuperscript{173}

![Amplitude vs Time Graph](image.png)

Figure 19. Experimental signal from a negatively charged olivine particle. Applied DC voltage across the central electrode was set to 950 V. Average velocity for this particle was 24.9 ± 0.4 m/s with an average charge of -49,300 e.

Like olivine, analysis of both MMS-1 and chalk dust data showed no shift in velocity across the central electrode region when the DC voltage was applied, which is likely due to the same development of particle conglomeration mentioned. With a DC voltage of 950 V, average MMS-1 particle average velocity was 28.3 ± 0.9 m/s with an average charge of +10,300 e. With the DC voltage set to 800 V, average chalk velocity was 23.1 ± 0.3 m/s with an average charge of +24,500 e.

Figure 20 shows measured velocities for two chalk dust particles across all electrodes of the detector when the central DC region had 0 V and 800 V applied (refer to Figure 15a for electrode illustration). As noted earlier, no velocity shift is seen across electrode 4 when a DC voltage is applied. However, both data sets in Figure 20 show a slight decrease in velocity between electrodes 1 and 7. This is due to collisions with background gas within the chamber at the given pressure (~55 mTorr). The impact of background gas collisions depends on particle
size rather than mass and therefore will vary with each passing particle. With this in mind, it may be possible to exploit this phenomena to calculate an aerodynamic particle size and shape to determine PSD.

Figure 20. Chalk dust velocity analysis. Two chalk dust velocities measured across each electrode when 0 V and 800 V were applied to the central DC region of the PCB CDMS device.

For Earth laboratory experiments aimed at demonstrating analyzer performance, we have used an inlet suitable for those conditions; however, an inlet for Mars operations would obviously be of different design. For example, the inlet for a flight instrument would need to prevent changes to the charge state of dust grains (as opposed to trying to charge them, as in lab experiments), and would need to account for differences in conductance of the inlet, pressure on both sides of the inlet, gas composition, humidity, gravity, and other factors. It would also be essential to prevent or to calibrate for any bias against particles due to size or charge. The analyzer itself would be of the same design or could be optimized for specific measurement conditions or science objectives.
3.5 CONCLUSION

Dust charge and particle size are important characteristics in understanding the Martian atmosphere and climate. Image charge detection is a method capable of measuring charge of individual dust grains. Charge detection mass spectrometry utilizes this method to determine particle charge in addition to $m/q$ and mass. If aerodynamic size can be determined, then the relationship between mass and size can give information on particle density and shape. We have reported simulation and experimental results for the development of a CDMS analyzer comprised of a printed circuit board array for the analysis of individual dust grains within the Martian atmosphere. We have shown through SIMION simulations that optimal analysis of both mass and charge occurs for particles ranging below 2.5 µm in diameter. Charge can be measured for larger particles, but mass cannot be determined. We have also shown through laboratory experiments that particle charge can be measured using the PCB CDMS device described. Additional instrument advancements, including those for the inlet, would be required for Mars operation of this instrument.
CHAPTER 4: FUTURE DIRECTIONS

Most of the work described focused on the engineering and design aspects of developing a PCB CDMS instrument system. As per the nature of this process, many trade spaces needed to be explored. This included exploring different sample preparation steps and ionization techniques, multiple atmospheric pressure inlet designs, vacuum chamber designs best coupled with a given inlet and ionization technique while achieving the desired pressure in the CDMS analysis region, a slew of PCB analyzer designs, and the charge amplifier integration along with the required shielding to reduce electrical noise. Modification of each subsystem in the PCB CDMS instrument system led to a “domino effect” on the performance of the rest of the instrument, making it more difficult than anticipated to successfully perform CDMS with the designed analyzer.

Performing computational fluid dynamics (CFD) to better understand the fluid flow of the gas and particles in the vacuum system would be a very useful tool for continuing development of this instrument. To this point, we have only made assumptions about the fluid flow through different vacuum chamber designs, and SIMION simulations are unable to simulate microparticle flow at the vacuum pressure of operation. By combining CFD and SIMION simulations, a level of understanding concerning the gas and particle flow would be discovered, which would help optimize the laboratory instrument design.

In connection with the developments in PCB CDMS charge detector designs shown in this work, more PCB detector geometries and configurations could be explored. One such configuration would be using a rolled-up PCB CDMS detector, which would prove easy fabrication for future study. Looking back to the discussion on the difference in raw signal rise time and shaped signal peak height when comparing the PCB sandwich and cylindrical detectors
(Section 2.3.6.), a rolled-up PCB CDMS detector would enable the charged particle to be fully enclosed by a PCB image charge detector while still maintaining the benefits of using printed circuit board materials. Bunching or stacking rolled-up PCB detectors could also prove useful for a tubular Mars dust analyzer configuration to perform multiple particle analyses.

Aside from Mars, there has been growing interest in icy worlds\textsuperscript{174, 175} and gaining “a deeper understanding of the physical . . . mechanisms that occur during hypervelocity impact.”\textsuperscript{176} The work in chapter 2 laid a foundation that enables image charge detectors to be used in determining particle trajectories for such studies. Different charge detector geometries could be designed and used as surface targets for hypervelocity impacts of ice grains, and the resulting trajectories could be observed to help determine these physical mechanisms. Though some work has been done in this realm,\textsuperscript{177, 178} the image charge detectors used have been stainless steel ring electrodes. In contrast, the wide variety of possible PCB designs creates limitless possibilities of image charge detector configurations that could lead to additional information acquired that ring electrodes otherwise could not. One such design would be to have a PCB sandwich array in the direction of the particle beam with another array orthogonal to it at the end of the beam path where the particle impact and resulting shatter trajectories could be recorded.

A future application of the work described herein could be the analysis of microplastics in liquid samples. There is much interest in microplastics contaminating liquid samples for metabolomics, proteomics, and human consumption. There is also much interest in the effect plastics have in the oceans and other bodies of water on Earth. It would be interesting to use electrospray PCB CDMS to analyze microplastics in these samples.
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