DEVELOPMENT OF MASS-DEPENDENT FOCUSING TECHNIQUES IN QUADRUPOLE MASS FILTERS

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Abstract

A new mass-separation technique based on mass-dependent focusing in radio-frequency (RF) quadrupoles is presented. The focusing effect was originally observed during ion-optical simulations for the definition of the low-energy beamline of the S3 spectrometer and was subsequently developed further during a maturation project funded by SATT Conectus. The novel technique can be combined with the standard operating principle of quadrupole mass filters (QMF), which is based on the stability of ion-motion. The expected gain in performance, in terms of mass resolution and transmission, exceeds an order of magnitude compared to current quadrupole mass filters. Recent simulations have shown that the technique can simultaneously achieve resolving powers above 10000 (FWHM) and transmission efficiencies above 80 % over a broad mass range from 80 u to 2000 u and for ion kinetic energies up to several hundred eV. Experimental verification using a dedicated quadrupole prototype validated the focusing principle and enabled resolving powers of 14300 for Cs^+ ions. The compactness, simplicity, speed, and low cost of quadrupoles, together with the expected performance gains, make the technique particularly attractive for isobaric separation of short-lived exotic nuclei. Several related projects are currently under preparation, including collaborations on short-lived radioactive ion beam identification and implementation of the technique in commercial mass spectrometry (MS) filters and analyzers.

RF QUADRUPOLE OPERATION

Stability-Based Operation

RF quadrupoles have been a cornerstone of mass spectrometry since their introduction in the 1950s, serving both as standalone analyzers and as mass filters in hybrid MS instruments [1, 2]. Their operating principle is based on the stability of motion for ions with specific mass-to-charge ratios, as described by the Mathieu equations and stability diagrams (Fig. 1).

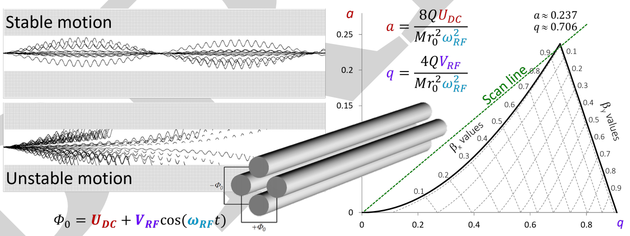

Figure 1: Mathieu equations and motion stability diagrams define standard, stability-based operation of QMF.

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In standard operation, the stability range is determined by the intersection of the scan line with the apex of the stability region, which depends on the ratio between the RF and DC potentials. Mass resolution can be increased by operating at higher DC potentials, resulting in a narrower stability overlap and therefore a smaller mass range of ions in stable motion. However, this increase in resolution is associated with reduced ion acceptance and transmission.

Mass-Dependent Focusing

In both transverse planes, the oscillatory motion of ions passing through the QMF can be described by ω_{RF} and secular frequencies ω_0, ω_1, ω_2, etc. [2]:

$$\omega_0 = \frac{\beta}{2}\omega_{RF},\ \omega_1 = \left(1 - \frac{\beta}{2}\right)\omega_{RF},\ \omega_2 = \left(1 + \frac{\beta}{2}\right)\omega_{RF},$$

where β_x and β_y ($0<\beta_x,\beta_y<1$) are the iso-lines passing through the operating point corresponding to a reference ion mass (Fig. 1). Fine tuning of the RF and DC parameters allows an oscillation node (or beat minimum) to be formed at the same longitudinal position in both transverse planes. The focal position can then be further adjusted through the kinetic energy of the ions to match a small exit aperture. Due to the strong mass dependence of the focal position, only a narrow mass range of ions is transmitted (Fig. 2).

EXPERIMENTAL VERIFICATION

Prototype Quadrupole and Experimental Setup

After extensive SIMION [3] simulations for performance optimization and error studies, a high-precision prototype quadrupole was built and installed to verify the focusing technique. The prototype featured exceptional machining precision and custom electronics with improved RF stability. The experimental setup (Fig. 3) consisted of a Cs+ source and a six-element focusing lens for precise injection into the entrance aperture. After selection by the QMF, the ions were detected using a Faraday cup, a two-plate MCP detector with a phosphor screen, and a zoom-lens camera.

Experimental Results

The experimental verification of the focusing technique was achieved by measuring the node-related multi-peak structure during RF scans using single-mass Cs+ ions. This characteristic structure represents a unique mass-dependent fingerprint associated with multiple focusing nodes in both transverse planes (Fig. 4, left panel). A fine multi-parameter sweep was implemented in the system control in order to achieve simultaneous focusing in both planes. This enabled signals as narrow as 20 Hz to be obtained, corresponding to

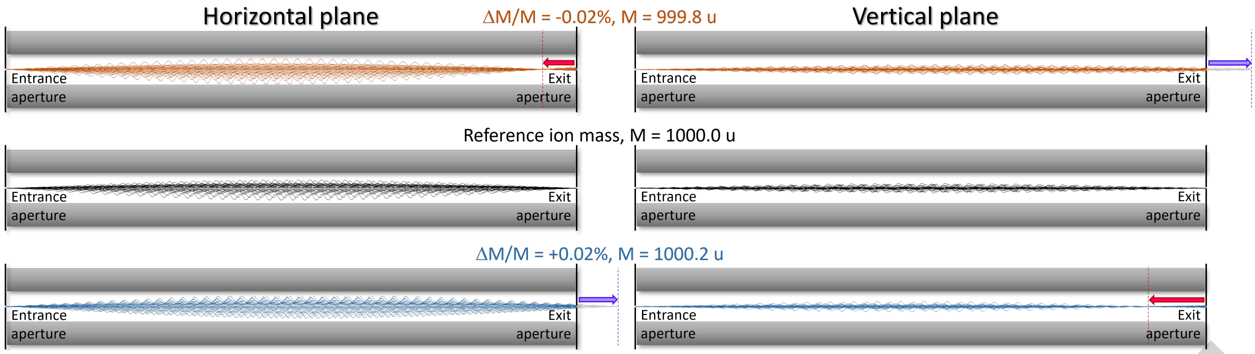

Figure 2: Mass-depending trajectory oscillations of a reference ion mass (middle) adjusted to focus at an exit aperture compared to slightly off-mass ions (top and bottom). The ion trajectories were produced using SIMION [3] and the left and right panels show the horizontal and vertical planes respectively.

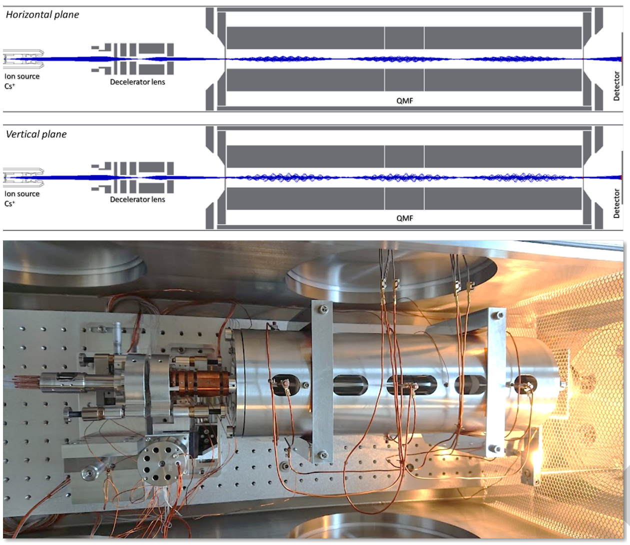

Figure 3: Configuration of the main elements in the experimental setup. The top panel shows the SIMION model with ion trajectories in both transverse directions.

a resolving power (FWHM) of 14300 (Fig. 4, right panel) and matching the values predicted by the simulations [4].

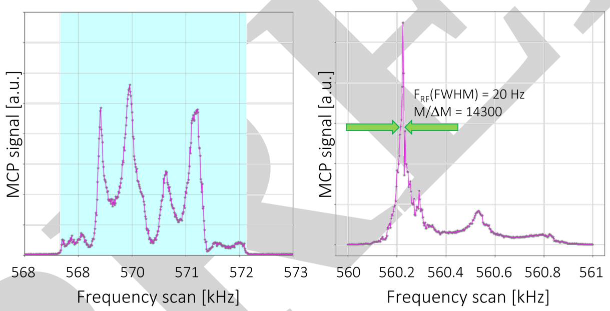

Figure 4: The left panel shows a frequency scan with multi-peak structures corresponding to multiple focusing nodes for a single ion mass (Cs^+). The blue background represents the transmission window corresponding to the stability-based operation. The peak width on the right panel corresponds to a resolving power of 14300 (FWHM).

The ion images recorded on the phosphor screen during the scans also enable phase-space tomography, allowing further exploration of the advantages of the focusing technique.

HIGH-RESOLUTION OPERATION WITH COOLED ION BEAMS

Simulations with Realistic Ion Distributions

A collaboration with Waters Corporation was initiated to explore the application of the focusing technique to buffer-gas cooled ion beams, aiming for resolving powers above 10000 while keeping efficiency above 80 %. Realistic ion-beam distributions provided by Waters were reproduced in SIMION together with extraction, focusing, and injection optics to generate realistic quadrupole input conditions. In addition, digital-waveform (e.g. rectangular) operation was applied successfully. The results from the latter are shown as square markers in the right panel of Fig. 5 fitting the overall performance with the focusing technique. Using digital RF allows extending the mass range of the quadrupole. The simulations show a major improvement over standard quadrupole operation across a broad mass range, reaching performance comparable to high-end hybrid mass spectrometry systems (Fig. 5) while retaining the compactness and transmission advantages of quadrupoles.

RF Monopoles for Isobaric Identification

The exceptional results obtained with cooled beams using the focusing technique initiated studies on possible applications for isobaric identification and separation, as well as mass spectrometry in space missions, benefiting from the compact size of quadrupoles. A simplified variant of a quadrupole is the RF monopole [1, 5], corresponding to one quarter of a quadrupole (Fig. 6). RF monopoles feature simplified RF electronics and mechanical design while retaining a compact footprint. First simulation results indicate resolving powers approaching 10^5, making these devices particularly promising for isobaric identification of short-lived exotic beams. With suitable modifications of the operating kinetic energy, they could also be adapted as high-resolution mass separators.

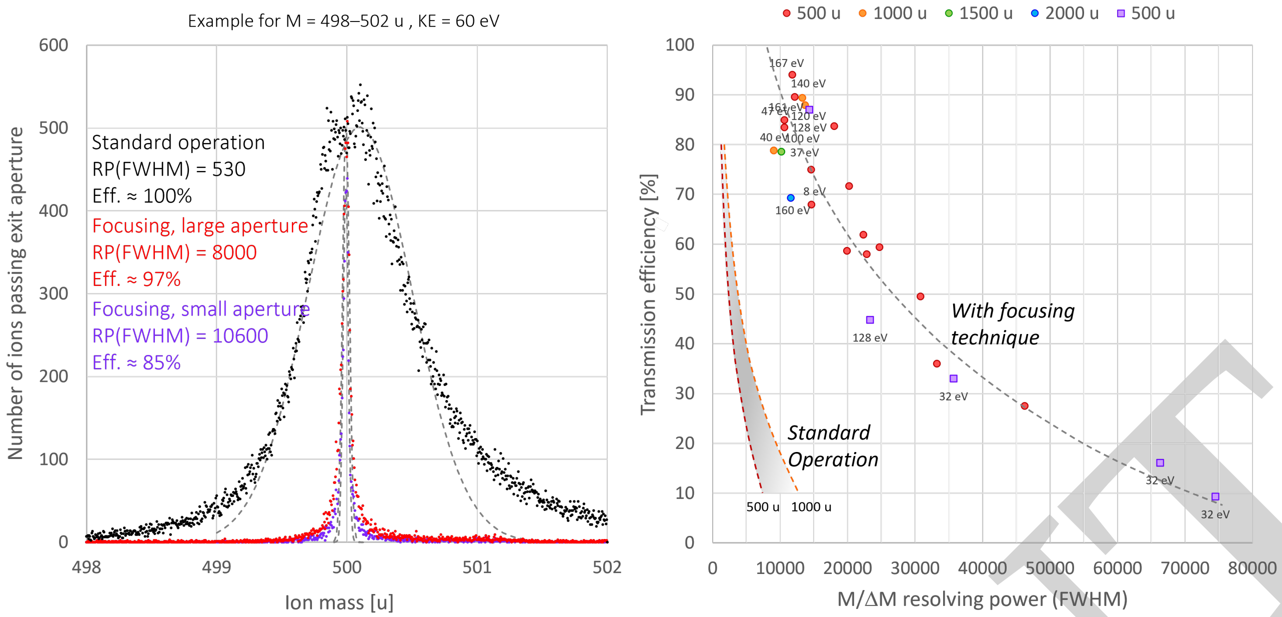

Figure 5: The left panel shows a comparison of the mass filtering based on standard operation (black points) and with the addition of the focusing technique for two different exit aperture sizes (red and purple points). The right side shows a collection of data points for a large variety of ion masses and energies comparing the operation without and with the use of the mass-dependent focusing selection. The square points correspond to operation with digital waveform RF.

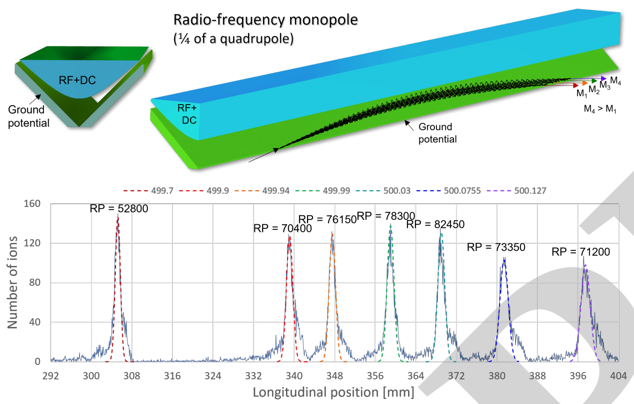

Figure 6: The RF monopole is one quadrant of a quadrupole with a 90-degree V-shaped grounded electrode placed along the symmetry planes that can incorporate the entrance and exit apertures (top panel). Resolving powers up to 80000 according to the results from SIMION simulations with cooled ion beams. The example shows the longitudinal distribution of multiple ion masses in the range between 499.7 u and 500.127 u for a 40 cm long monopole.

CONCLUSION

A novel mass-dependent focusing technique for RF quadrupoles has been developed and experimentally validated, demonstrating performance far beyond that of standard QMFs. Originally observed during simulations for the S3-LEB beamline and subsequently optimized through dedicated simulation and prototype studies, the method combines ion-motion stability filtering with mass-dependent focusing to achieve exceptional selectivity and transmission. Experimental measurements with a high-precision prototype quadrupole confirmed the predicted focusing behavior and showed resolving powers up to 14300 for surface-ionized Cs^+ ions. Recent simulations using realistic buffer-gas cooled ion beams indicate that resolving powers above 10000 can be achieved while maintaining transmission above 80 % over a broad mass range, making the approach attractive for mass filtering in hybrid MS. Additional studies on RF quadrupoles and RF monopoles suggest that resolving powers approaching 10^5 may be achievable for compact devices, enabling the use of focusing RF quadrupoles as the main mass analyzer in standalone and hybrid spectrometers. The achieved resolution and transmission could also make the technique suitable for isobaric identification and separation of short-lived radioactive ion beams. The performance, combined with the compactness, speed, simplicity, and low cost of quadrupole-based systems, could significantly impact the MS market and enable a wide range of applications relying on high performance and compact instrumentation.

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