



Mass Resolution of Ca, K Isotopes and CO, N₂ and C₂H₄ Isobars in Isotopes Separator On-Line trap Mass spectrometry

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Abstract

In Isotopes separator on-line trap, ions are trapped, cooled, accumulated, bunched and isotopes or isobars are separated, cyclotron frequencies are determined, which are followed by time of flight mass resolution. The mass resolution of isotopes in Penning trap mass spectrometry is achieved by the direct excitation of axial motion of ions, driven by RF field at the pure cyclotron frequencies of ions. The design and working of Isotopes separator on-line trap which is used for high-accuracy mass spectrometry in the mass resolution of calcium isotopes (⁴⁰Ca⁺, ⁴²Ca⁺, ⁴⁴Ca⁺), potassium isotopes (³⁹K⁺, ⁴¹K⁺) and [²⁸(CO)]⁺, [²⁸N₂]⁺, [²⁸(C₂H₄)]⁺ isobars found in mixtures is achieved from time of flight mass spectrometry are presented here.

Keywords: Mass spectrometry, Mass resolution, Isotope online Penning trap, Resonance spectrum, RF excitation.

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1. Introduction

The stable six isotopes of calcium are ⁴⁰Ca, ⁴²Ca, ⁴³Ca, ⁴⁴Ca, ⁴⁶Ca and ⁴⁸Ca out of which ⁴³Ca, ⁴⁶Ca, ⁴⁸Ca are rare isotopes found in trace amounts and hence cannot be identified in the isotope-ratio mass spectrum obtained from stimulations. The mass resolving powers of ⁴⁰Ca⁺, ⁴²Ca⁺, ⁴⁴Ca⁺ are determined from [1, 2, 3]

$$(M.R.P.)_{Ca^+} = \frac{m_{Ca^+}}{\delta m_{Ca^+}} \quad (1)$$

where m_{Ca^+} → mass of Ca^+ and δm_{Ca^+} → full width at half maximum in mass spectrum. The mass spectrum of ions [²⁸(CO)]⁺, [²⁸N₂]⁺ and [²⁸(C₂H₄)]⁺ of isobars is obtained by time of

flight mass spectrometry simulations. The isobars are identified from identifying the values of time of flight in mass spectrum and calculating the mass from [4, 5]

$$m = 2qV \left[\frac{t_f}{d} \right]^2, \quad (2)$$

where m → mass of ion, q → charge state of ion, t_f → time of flight of ion, d → distance travelled by the ion before reaching the detector. This is compared with the estimated values of masses of the isobars and the corresponding isobar is identified from approximately equating to the estimated value of its mass. The mass determination of ⁴¹K⁺ isotope in Penning trap mass spectrometry is achieved by the excitation of axial motions of same charge state of ³⁹K⁺ and ⁴¹K⁺ ions by driving Radio Frequency (RF) field at the pure cyclotron frequencies $f_{c_{19}^{39}K^+}$, $f_{c_{19}^{41}K^+}$ of ³⁹K⁺ and ⁴¹K⁺ ions respectively as the

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magnetic field is known. The mass of most abundant isotope $m_{(19}^{39}K^+)$ = 38.963707 amu is well known and hence the mass of less abundant isotope $m_{(19}^{41}K^+)$ of $^{41}_{19}K^+$ can be determined from the following equation [6]:

$$m_{(19}^{41}K^+) = \frac{f_{c_{(19}^{39}K^+)}}{f_{c_{(19}^{41}K^+)}} m_{(19}^{39}K^+). \quad (3)$$

2. Theory

The isotope-ratio mass spectrum of Ca isotopes is drawn by using data from the Mass Spectrometry Data Base. The accuracy of mass measurements in penning trap is determined by the resolving power of masses of isotopes. The resolving power of masses of isotopes of ions is defined as the ratio of the centre frequency of the resonance line to the full width at half maximum of the resonance line. Therefore the mass resolving power (M.R.P.) of masses of isotopes of ions is given by [1, 2, 3]

$$(M.R.P.)_{ion} = \frac{m}{\delta m} = \frac{f_0}{\Delta f_{1/2}}, \quad (4)$$

where $m \rightarrow$ mass of ion and $\delta m \rightarrow$ full width at half maximum in mass spectrum, $f_0 \rightarrow$ centre frequency of the resonance line, $\Delta f_{1/2} \rightarrow$ full width at half maximum of the resonance line. The mass spectrum of ions $[^{28}(\text{CO})]^+$, $[^{28}\text{N}_2]^+$ and $[^{28}(\text{C}_2\text{H}_4)]^+$ of isobars is obtained by time of flight mass spectrometry simulations. In time of flight mass spectrometry ions are accelerated by an electric field of known strength E with potential V and all those ions which have the same charge state q , will have same kinetic energy with velocity v due to the acceleration. The specific charge (q/m) of ions is given by [7]

$$\frac{q}{m} = \frac{1}{2} \left[\frac{E^2}{B^2 V} \right] = \frac{1}{2} \left[\frac{v^2}{V} \right], \quad (5)$$

where $q \rightarrow$ charge state of ion, $m \rightarrow$ mass of ion, $B \rightarrow$ Magnetic field, $E \rightarrow$ Electric field, $V \rightarrow$ electric potential, $v \rightarrow$ velocity of ion. The velocity of the ion accelerated by electric field depends upon its specific charge q/m the time taken by the particle to reach the detector is called time-of-flight t_f and it can be measured. The specific charge of ions is determined through the measurement of time to reach the detector in time-of-flight mass spectrometry. Heavier ions reach the detector slower than the lighter ones as the mass of moving ion is $m \propto t_f^2$. The time is measured from the instant the ion leaves the cooler ion trap to the instant that reaches the detector, it is used to find specific charge of it and the ion is determined from the known parameters. The time-of-flight is given by [4]

$$t_f = \frac{d}{\sqrt{2V}} \sqrt{\frac{m}{q}} \Rightarrow \frac{m}{q} = 2V \left[\frac{t_f}{d} \right]^2 \Rightarrow \frac{q}{m} = \frac{1}{2V} \left[\frac{d}{t_f} \right]^2. \quad (6)$$

$$\therefore m = 2qV \left[\frac{t_f}{d} \right]^2, \quad (7)$$

where $d \rightarrow$ distance traveled by the ion, $V \rightarrow$ electric potential, m is mass and q is charge state of ion. When the ions are excited by continuously sweeping the RF field, the motional frequencies of ions respond to the external RF at a given step, consequently some of the ions gain enough energy to escape the trap. This change in the motion of ions due to RF field drive causes increase in kinetic energy in the radial plane and can be detected by a time-of-flight technique. The mass resolution of isotopes of ions is related to specific charge and cyclotron angular frequency as [6]

$$\begin{aligned} \frac{m}{\delta m} &\propto \frac{q}{m} B (t_{RF} \sqrt{N}) \\ &= \omega_c (t_{RF} \sqrt{N}) = 2\pi f_c (t_{RF} \sqrt{N}) \\ &\Rightarrow f_c \propto \frac{1}{m}, \end{aligned} \quad (8)$$

where $q \rightarrow$ charge state of ion, $m \rightarrow$ mass of ion, $B \rightarrow$ Magnetic field, $t_{RF} \rightarrow$ time of RF drive, $N \rightarrow$ number of cycles of RF field, $\omega_c \rightarrow$ cyclotron angular frequency. The resolving power of masses of isotopes of ions is proportional to the time of excitation of RF field, which results in the motional resonances of the isotopes of ions that can be observed in motional resonances spectrum. The lifetime of unstable isotopes limit the time of excitation as they are in very short duration of time. The temporal stability of the magnetic field due to shielding current in pair of coils of wire limit the radial confinement of the stable and long-lived isotopes. The exchange of the ions of isotopes in the trap is required for comparison of cyclotron frequencies of two different ions and measured at different times during which the magnetic field strength changes. Superconducting magnets require temperature and pressure stabilization to reduce temporal variation of the magnetic field strength. The mass determination in isotopes separator on-line trap is on the basis of the fact that the two ions of isotopes whose charge state is same but their masses are different. The ratio of their cyclotron frequencies is equal to the inverse of ratio of their masses kept in the same magnetic field [6]. Therefore if the charge state of two ions of isotopes is $q_1=q_2$ kept in the same magnetic field B then

$$\frac{f_{c1}}{f_{c2}} = \frac{m_2}{m_1}, \quad (9)$$

where f_{c1} and f_{c2} are cyclotron frequencies of isotopes of ions of an element with masses m_1 and m_2 respectively.

3. Experimental Procedure

3.1. Design

The isotopes separator on-line trap consists of three ion traps connected end to end together in an order of RF Paul trap, Cooler Penning trap and Precision Penning trap as shown in Figure 1 [8, 9]. The RF quadrupole ion trap consists of 4 rods structure to which a RF field is applied for alternate rods, and

this is used for beam preparation and hence it is also called beam buncher. The Cooler Penning trap is a large cylindrical Penning trap which is placed in the homogeneous magnetic field of superconducting magnets, which is used to cool the ions. The Precision Penning trap is a Quadrupole Penning trap in which ions are detected through time of flight.

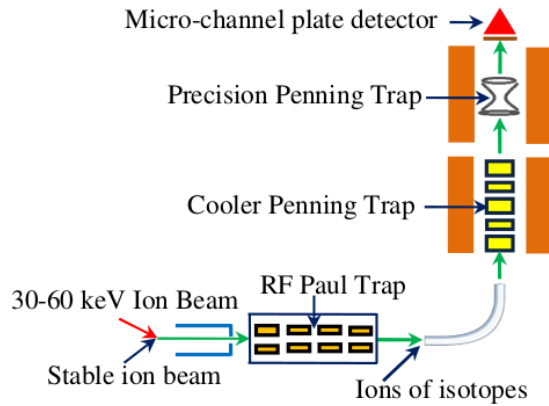


Figure 1. Schematic diagram of Isotopes separator on-line trap [8, 9]

3.2. Working

A quadrupole Penning trap is designed with three-electrode infinite hyperboloid revolution of structure, which consists of two end-cap electrodes and a ring electrode, a homogeneous magnetic field is superposed on electrostatic quadrupole field. The magnetic field B confines ion beam of isotopes of charge state q and different masses in the radial direction, while the electric field quadrupole potential V_{DC} , confines ions in the axial direction, as it prevents the ions from escaping along the magnetic field lines. The motion of trapped ions in a Penning trap is not a simply pure cyclotron motion with frequency f_c but a combination of three harmonic Eigen motions, viz. an axial oscillatory motion with frequency f_z , two circular motions called modified cyclotron motion with frequency f'_c and magnetron motion with frequency f_m which are related to each other as [1]

$$f_c = f'_c + f_m. \quad (10)$$

The precise value of pure cyclotron frequency in an isotope separator on-line trap is [6]

$$f_c = \left(\frac{q}{m}\right) \frac{B}{2\pi} \Rightarrow f_c \propto \frac{1}{m} \quad (\because B, q \rightarrow \text{constants}) \quad (11)$$

The motion of ions of isotopes can be driven by oscillating electric field which changes the amplitudes of the oscillatory motion of ions and azimuthal electric quadrupole field causes the excitation of ion oscillatory motion directly at the side band frequency f_c . The mass determination of ion of unknown isotope in isotopes separator on-line trap mass spectrometry is achieved

by the direct excitation of axial oscillatory motions of same charge state ions of isotopes at their pure cyclotron frequencies from the relation $m_2 = m_1 \frac{f_{c1}}{f_{c2}}$ as the magnetic field is known [6].

3.3. Cooling and bunching in RF quadrupole ion trap

A RF field is applied to the 4 rods structure which creates an oscillating quadrupole electric field that confines the ions of isotopes or isobars along the symmetry axis of trap. The rods are segmented and an appropriate shape DC potential is applied to the segments to drag the ions close to the end of the 4-rods structure where the ions are trapped. The first step is stopping and preparation of the high energy of $\approx 30 - 60 \text{ keV}$ ion beam of isotopes or isobars. The ions of isotopes or isobars are decelerated electro statically by applying repelling potential and then injected into the central region of 4-rods structure being filled with buffer gas. The RF quadrupole ion trap cools the ion beam of isotopes through buffer gas cooling by collisions. The ions of high energy of $\approx 30 - 60 \text{ keV}$ lose kinetic energy up to a few keV due to the collision with the buffer gas, and then finally accumulated as a small ion cloud of isotopes or isobars in the trapping region. Thus cooled ions of isotopes or isobars are accumulated in beam buncher and enter into cooler Penning trap later, where contaminants are removed. The cold ion cloud bunch of selected isotopes or isobars of an element can be ejected out off the trapping region, transported and then injected into the cooler trap through a potential adaption in a pulsed drift tube.

3.4. The cooler trap

The cooler trap is a large cylindrical Penning trap placed in the homogeneous magnetic field of $\approx 5 \text{ T}$ superconducting magnets. The ions transported from the RF quadrupole ion trap are captured in the cylindrical Penning trap and cooled through mass selection technique. The cooler cylindrical Penning trap is optimized for high quality mass selection to resolve isotopes or isobars. Isotopes are different species of the same element with same atomic number (same number of protons and electrons) but differ in mass number (the number of nucleons) and hence specific charge (charge to mass ratio) will be different for different isotopes with same charge state, therefore the isotopes travel with different velocities and take different time durations to reach the detector. When ions of isotopes which have same charge state but different masses are trapped in constant magnetic field, then heavier ions of the same charge state reach at lower speeds as [6]

$$f_c = \frac{q}{m} B \propto \frac{1}{m} \propto v \propto \frac{d}{t} \quad (\because B, q \text{ are constants}) \quad (12)$$

$$\therefore m \propto t \quad (\because d \text{ is constant}) \quad (13)$$

Isobars are different elements with same mass numbers (same number of nucleons) but differ in atomic number (the number

of protons and electrons) and hence specific charge (charge to mass ratio) will be different for different isobars, therefore the isobars travel with different velocities and take different time durations to reach the detector. For ions of isobars which have same mass but different charge state in constant magnetic field, the velocity of ions with higher charge state will also increase [6].

$$f_c = \frac{q}{m} B \propto q \propto v \propto \frac{d}{t} \quad (\because B, m \text{ are constants}) \quad (14)$$

$$\therefore q \propto \frac{1}{t} \quad (\because d \text{ is constant}) \quad (15)$$

The cooled and clean bunches of ions are transferred into the precision Penning trap, which are used for highly accurate mass measurements.

3.5. Precision Penning trap mass spectrometer

An azimuthal RF field of frequency f_{RF} drives the motion of ions, the amplitude of the cyclotron motion of the stored ions increases due to resonance of driving frequency of RF field with cyclotron frequency ($f_{RF} = f_c$) in Quadrupole Penning trap. The RF generator switched to sweep mode is used to feed RF energy into the trap through the antenna. The RF power is kept very low of the order of a few mV to weakly probe the motion of the trapped ion cloud. If the RF power is kept high, then it will resonantly drives the trapped ion cloud in the trap and causes to escape from the trap. When the ions are excited by continuously sweeping the RF field, the motional frequencies of ions respond to the external RF at a particular step, consequently some of the ions gain enough energy to escape from the trap, then the signal height is reduced and appears as a dip in the motional resonance spectrum, which is directly proportional to the number of ions lost from the trap. The cooled ions are ejected from the trap due to the excitation of the motion of ions by RF field, and drift through the inhomogeneous fringe magnetic field B to reach the detector of ions. The magnetic moments of the orbits of ions also increase due to magnetic field. An axial force arising from the inhomogeneous magnetic field increases the axial momenta of the ions by orbital magnetic moments. The time-of-flight of ions is determined as a function of the frequency of the RF field, as ions in resonance with the RF field reach the detector faster than those ions that are not in resonance. The mass can be extracted in conjunction with a reference mass measurement after the determination of the frequency of stored ion from the time-of-flight detection technique .

4. Results and Discussion

4.1. Mass spectrum of Calcium isotopes

The isotope ratio mass spectrum of Calcium isotopes shows 3 peaks as shown in Figure 2. The tallest peak corresponds to

Ions of Calcium isotopes	Mass Resolving Power
$^{40}_{20}\text{Ca}^+$	794.0675
$^{42}_{20}\text{Ca}^+$	789.60086
$^{44}_{20}\text{Ca}^+$	900.089

$^{40}\text{Ca}^+$ as specific charge of it is lesser than that of both of $^{42}\text{Ca}^+$ and $^{44}\text{Ca}^+$, the second short peak next to it corresponds to $^{42}\text{Ca}^+$ as its specific charge is greater than that of $^{40}\text{Ca}^+$ and the third short peak next to it corresponds to $^{44}\text{Ca}^+$ as its specific charge is greater than that of $^{42}\text{Ca}^+$. The mass resolving powers of $^{40}\text{Ca}^+$, $^{42}\text{Ca}^+$, $^{44}\text{Ca}^+$ are [10]

$$\begin{aligned} (M.R.P.)_{^{40}\text{Ca}^+} &= \frac{m_{\text{Ca}^+}}{\delta m_{\text{Ca}^+}} = \frac{39.961765}{39.981125 - 39.9307996} \\ &= 794.06751 \approx 794.0675 \quad (16) \end{aligned}$$

$$\begin{aligned} (M.R.P.)_{^{42}\text{Ca}^+} &= \frac{m_{\text{Ca}^+}}{\delta m_{\text{Ca}^+}} = \frac{41.9586}{41.9802842 - 41.9271452} \\ &= \frac{41.9586}{0.053139} \approx 789.60086 \quad (17) \end{aligned}$$

$$\begin{aligned} (M.R.P.)_{^{44}\text{Ca}^+} &= \frac{m_{\text{Ca}^+}}{\delta m_{\text{Ca}^+}} = \frac{43.9555}{43.9763821 - 43.9275475} \\ &= \frac{43.9555}{0.0488346} \approx 900.089 \quad (18) \end{aligned}$$

Therefore the mass resolving powers of $^{40}\text{Ca}^+$, $^{42}\text{Ca}^+$, $^{44}\text{Ca}^+$ as calculated from equation (1) are 794.0675, 789.60086 and 900.089 respectively as presented in Table 1.

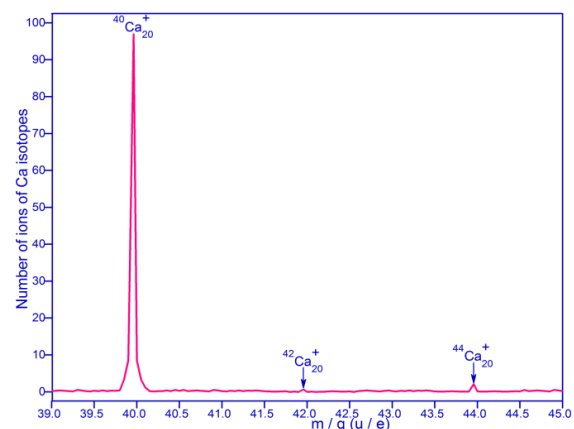


Figure 2. Isotope ratio mass spectrum of ions of $^{40}\text{Ca}^+$, $^{42}\text{Ca}^+$, $^{44}\text{Ca}^+$ isotopes drawn by using isotope-ratio Mass Spectrometry Data Base

4.2. Mass spectrum of CO, N₂ and C₂H₄ isobars

The ions $^{28}(\text{CO})^+$, $^{28}(\text{N}_2)^+$ and $^{28}(\text{C}_2\text{H}_4)^+$ of isobars can be produced by collisions of isobars with electrons. The

Table 2. Masses of Isobars calculated from Mass spectrum of ions

Ions of Isobars	Mass (amu)
$[^{28}\text{(CO)}]^+$	27.99489
$[(^{28}\text{N}_2)]^+$	28.00699
$[^{28}\text{(C}_2\text{H}_4)]^+$	28.031297

mass spectrum of ions $[^{28}\text{(CO)}]^+$, $[(^{28}\text{N}_2)]^+$ and $[^{28}\text{(C}_2\text{H}_4)]^+$ isobars obtained by time of flight mass spectrometry simulations is shown in Figure 3. The mass spectrum consists of three peaks, one corresponds to each of ions $[^{28}\text{(CO)}]^+$, $[(^{28}\text{N}_2)]^+$ and $[^{28}\text{(C}_2\text{H}_4)]^+$ of isobars [11]. The isobars are identified from identifying the values of time of flight of isobar in mass spectrum and the mass of corresponding isobar is calculated from the value of time of flight. This accurate value of mass is compared with the estimated values of masses of the isobars and the corresponding isobar is identified from approximately equating it to the estimated value of its mass. The masses of ions $[^{28}\text{(CO)}]^+$, $[(^{28}\text{N}_2)]^+$ and $[^{28}\text{(C}_2\text{H}_4)]^+$ of isobars are calculated from time of flight using equation (19) as shown below. From Figure 3 the time of flight that corresponds to first peak is $t_f = 762.27882\text{ ns}$, then

$$m = 2qV \left[\frac{t_f}{d} \right]^2 \quad (19)$$

$$m = 2 \times 1.6 \times 10^{-19} \times 25 \left[\frac{762.27882 \times 10^{-9}}{10 \times 10^{-3}} \right]^2 \quad (20)$$

$$\Rightarrow m = 46.48552 \times 10^{-31} \text{ kg} = 27.99489 \text{ amu} = m_{\text{CO}} \quad (21)$$

From Figure 3 the time of flight that corresponds to second peak is $t_f = 762.43137\text{ ns}$, then

$$m = 2 \times 1.6 \times 10^{-19} \times 25 \left[\frac{762.43137 \times 10^{-9}}{10 \times 10^{-3}} \right]^2 \quad (22)$$

$$\Rightarrow m = 46.504128 \times 10^{-31} \text{ kg} = 28.00699 \text{ amu} = m_{\text{N}_2} \quad (23)$$

From Figure 3 the time of flight that corresponds to third peak is $t_f = 762.77432\text{ ns}$, then

$$m = 2 \times 1.6 \times 10^{-19} \times 25 \left[\frac{762.77432 \times 10^{-9}}{10 \times 10^{-3}} \right]^2 \quad (24)$$

$$\Rightarrow m = 46.54597 \times 10^{-31} \text{ kg} = 28.031297 \text{ amu} = m_{\text{C}_2\text{H}_4} \quad (25)$$

The ions of isobars $[^{28}\text{(CO)}]^+$, $[(^{28}\text{N}_2)]^+$ and $[^{28}\text{(C}_2\text{H}_4)]^+$ are identified from mass spectrum as shown in Figure 3. The mass of the isobar that corresponds to the first, second and third peaks were calculated using equation (19) as 27.99489 amu, 28.00699 amu and 28.031297 amu with corresponding time of flight of 762.27882 ns, 762.43137 ns and 762.77432 ns respectively as presented in Table 2.

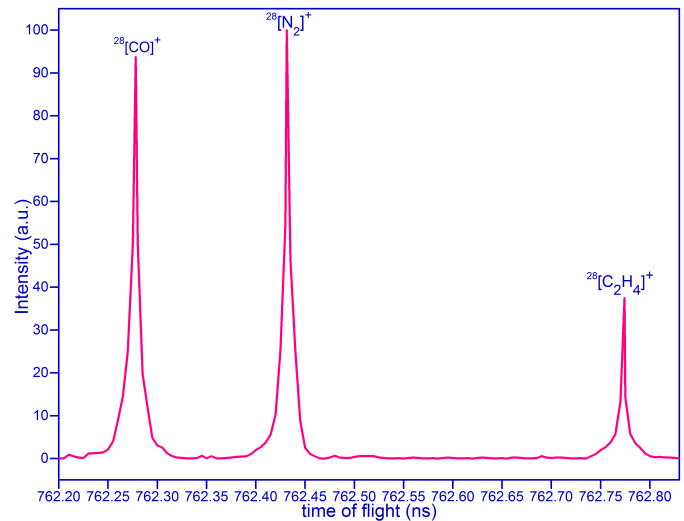


Figure 3. Mass spectrum of ions $[^{28}\text{(CO)}]^+$, $[(^{28}\text{N}_2)]^+$ and $[^{28}\text{(C}_2\text{H}_4)]^+$ of isobars drawn by using Mass Spectrometry Data Base

4.3. Mass spectrum of K isotopes

The mass determination of $^{41}_{19}\text{K}^+$ isotope in Penning trap mass spectrometry is achieved by the excitation of axial motions of same charge state of $^{39}_{19}\text{K}^+$ and $^{41}_{19}\text{K}^+$ ions by driving RF field at the pure cyclotron frequencies $f_{c_{19}^{39}\text{K}^+}$ and $f_{c_{19}^{41}\text{K}^+}$ respectively as the magnetic field is known. As the mass of most abundant isotope $m_{19}^{39\text{K}^+} = 38.963707\text{ amu}$ is well known, and hence the mass of less abundant isotope $m_{19}^{41\text{K}^+}$ can be determined. The pure cyclotron frequencies of $f_{c_{19}^{39}\text{K}^+}$ and $f_{c_{19}^{41}\text{K}^+}$ from Figure 4 are 98.426156 kHz and 93.624975 kHz respectively. The mass of ion $^{41}_{19}\text{K}^+$ of potassium isotope is given by [6]

$$\frac{f_{c_{19}^{39}\text{K}^+}}{f_{c_{19}^{41}\text{K}^+}} = \frac{m_{19}^{41\text{K}^+}}{m_{19}^{39\text{K}^+}} \quad (26)$$

$$\begin{aligned} \Rightarrow m_{19}^{41\text{K}^+} &= \frac{f_{c_{19}^{39}\text{K}^+}}{f_{c_{19}^{41}\text{K}^+}} m_{19}^{39\text{K}^+} \\ &= \frac{98.426156 \times 10^3}{93.624975 \times 10^3} \times 38.963707 \times 1.66 \times 10^{-27} \quad (27) \end{aligned}$$

$$\therefore m_{19}^{41\text{K}^+} = 67.996595 \times 10^{-27} \text{ kg} = 40.9618\text{ amu} \quad (28)$$

The mass of $^{41}_{19}\text{K}^+$ calculated using equation (27) is 40.9618 amu as presented in Table 3.

5. Conclusion

The mass resolving powers of $^{40}\text{Ca}^+$, $^{42}\text{Ca}^+$, $^{44}\text{Ca}^+$ are 794.0675, 789.60086 and 900.089 respectively. The ions of isobars $[^{28}\text{(CO)}]^+$, $[(^{28}\text{N}_2)]^+$ and $[^{28}\text{(C}_2\text{H}_4)]^+$ are identified in mass spectrum which correspond to time of flights of 762.27882 ns, 762.43137 ns and 762.77432 ns respectively. The pure cyclotron frequencies

Table 3. Masses of potassium isotopes calculated from Mass spectrum of potassium ions

Ions of Potassium isotopes	Interchange Cyclotron frequency values	Mass (amu)
$^{39}_{19}\text{K}^+$	98.426156 kHz	38.963707
$^{41}_{19}\text{K}^+$	93.624975 kHz	40.9618

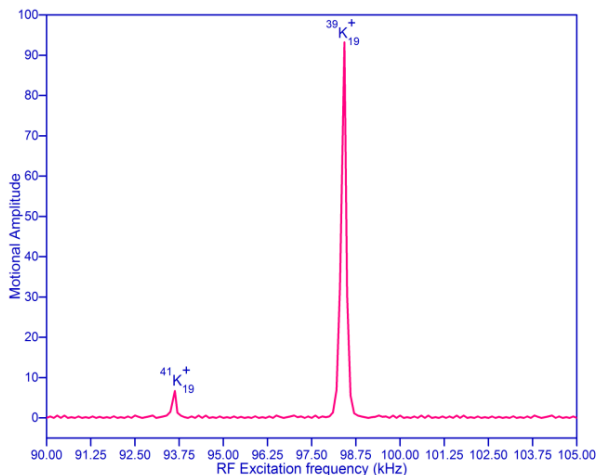


Figure 4. Time of flight detection of cyclotron resonance of isotopes of potassium ions $^{39}_{19}\text{K}^+$ and $^{41}_{19}\text{K}^+$ at magnetic field 0.25T by RF excitation from 90-105 kHz drawn by using Mass Spectrometry Data Base

of ions $^{39}_{19}\text{K}^+$ and $^{41}_{19}\text{K}^+$ from motional resonance spectrum are 98.426156 kHz and 93.624975 kHz respectively and hence the mass of ion of less abundant potassium isotope $^{41}_{19}\text{K}^+$ is determined to be 40.9618 amu.

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