Measurements of exotic calcium isotopes
by multi-reflection time-of-flight mass spectrometry
and further developments and applications

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Nomenclature & Abbreviations

\( A \) ...................... Mass number
\( c \) ...................... speed of light
\( D_{2n} \) ................. Empirical two-neutron shell gap
\( D_{2p} \) ................. Empirical two-proton shell gap
\( E_{\text{tot}} \) ............. Total energy of the system
\( M \) ....................... Mass of an atomic nucleus
\( M_n \) ...................... Mass of the neutron
\( M_p \) ...................... Mass of the proton
\( ME \) ..................... Mass excess
\( N \) ....................... Neutron number
\( S_{2n} \) .................... Two-neutron separation energy
\( S_{2p} \) .................... Two-proton separation energy
\( t_{1/2} \) .................... Half life
\( Z \) ....................... Proton number

BigRIPS ................ Large-acceptance superconducting fragment separator at RIKEN

DOTA ..................... 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid
DOTATOC .............. DOTA-(Tyr\(^3\))-octreotide or edotreotide
GPS ..................... General Purpose Separator of ISOLDE/CERN
HRS ..................... High Resolution Separator of ISOLDE/CERN
IGISOL ................. Ion Guide Isotope Separator on-line
IoI ....................... Ion of Interest
ISOLDE ................. Isotope Separator On Line DEvice
MR-ToF MS ............. Multi-Reflection Time-of-Flight Mass Spectrometry or Mass Spectrometer
List of Figures

MS ..................... Mass Spectrometry or Mass Spectrometer
PET ..................... positron emission tomography
PI ....................... Proportional–integral
radiotheragnostics ...... radio therapy and diagnostics
RIBF ..................... Radioactive Isotope Beam Factory at RIKEN
RILIS .................... Resonance Ionization Laser Ion Source
SHARAQ .................. The high-resolution RI-beam spectrometer at RIKEN
SPECT .................... single photon emission computed tomography
TISD ..................... Target and ion source development
ToF ....................... Time-of-Flight
1 Introduction

Since the discovery of radioactivity by Antoine Henri Becquerel [Béc96] 1896 and the work by Marie and Pierre Curie during which they discovered radium and coined the term radioactivity [CS98], many more radioactive nuclei were discovered. The term isotope for an element ("same place" in the periodic table) with different number of neutrons in its nucleus was introduced by Frederick Soddy in 1913 [Sod13a] after he realized that, although chemically equal, atoms of the same element can have different nuclear characteristics, like decay energy, mass and half life [Sod13b]. For a recent overview with detailed information on the discovery of the different nuclides see ref. [Tho16]. In the late 19th and the beginning of the 20th century, radioactivity could be studied of only the naturally occurring radioactive nuclides and their daughters. That changed with the development of particle accelerators. With time, different techniques based on the concept of "smashing" particles onto each other, were developed, which allowed to produce nuclei that are close to or even exactly at the proton or neutron drip lines.

![Chart of nuclides](image)

**Figure 1.1:** Chart of nuclides including currently known and extrapolated nuclides and their decay modes. The data was taken from [Hua17; Wan17]. The predicted two-proton as well as the two-neutron drip line are added to the figure [Erl12]. Those define the (theoretical) boundaries in which the nuclei are expected to have positive separation energies.
1 Introduction

Being able to produce nuclei "on-demand" paved the way to systematically investigate the properties of the elements for different neutron number, which is a key ingredient to have a closer look at the nuclear many body problem, still one of the not yet fully understood fields in physics research.

A typical representation known as a chart of nuclides, which presents the different nuclei in a graphical manner, is shown in Fig. 1.1. Here, the different isotopes and their decay channels (color coded) are shown as boxes in a matrix. Each horizontal line is occupied by a chemical element where the atomic nucleus has \( Z \) protons and the numbers of neutrons \( N \) varies along the line.

Mass spectrometry played a key role in the discovery of new nuclides right from the beginning of nuclear research. In 1913 Joseph John Thomson and Francis Aston discovered that neon must be a mixture of at least two different particle species which were later identified to be \( ^{20}\text{Ne} \) and \( ^{22}\text{Ne} \) [Tho13]. At the time were not able to also distinguish the much less abounded \( ^{21}\text{Ne} \). New mass spectrometers, with higher sensitivity and resolving power, had to be introduced. In Fig. 1.2 the chart of nuclides is shown again, this time the colour code represents the year of the discovery of the different nuclides [Aud17].

![Figure 1.2: Year of the discovery of the different isotopes according to [Aud17].](image)

Recently, the suggestion and the introduction of fast, sensitive and high resolution multi-reflection time-of-flight (MT-ToF) mass-spectrometers by Wollnik and co-workers [WP90] has triggered developments from different groups to apply it in different fields of physics. In the present work, the application of MR-ToF mass-spectrometry (MS) in the field of high precision mass measurements for nuclear physics research will be addressed. New measurements as well as new developments to increase the stability and reliability of the apparatus will be presented.
2 Masses of exotic nuclides

As already stated in the introduction, mass spectrometry has played and plays a key role in nuclear physics research not only for the discovery of new isotopes but also to further our understanding in nuclear structure, nuclear astrophysics and other fields since the mass of different nuclei is a key ingredient for many theoretical calculations. From the knowledge of the precise mass of the nucleus its binding energy $B(Z, N)$ can be deduced which is a measure on how much energy is needed to dismantle a system of nucleons (protons and neutrons) into its constitutions:

$$B(Z, N) = (Z \cdot M_p + N \cdot M_n) \cdot c^2 - M(Z, N) \cdot c^2,$$

(2.1)

where $A$ is mass number of the nucleus, $Z$ is the proton number, $N$ is the neutron number, $M_p$ and $M_n$ are the mass of the proton and the neutron, $c$ is the speed of light and $M(Z, N)$ is mass of the nucleus. For nuclei which are particle stable, the binding energy is positive. For the presentation of the mass data, the mass excess of a nucleus is very often used which is defined as:

$$ME(Z, N) = M(Z, N) - (Z + N) \cdot u,$$

(2.2)
where \( u \) is the unified mass unit, defined as the 1/12 of the mass of the atom of the carbon isotope \(^{12}\text{C}\). This is also the way the data is presented in the "atomic mass evaluation" (AME) [Wan17], which lists the mass data (among others) for all known nuclides. In the graphical representation of the available binding energy data from the AME, one can only distinguish areas in which this quantity is more or less positive or negative but hardly any "fine structure", see Fig. 2.1.

**Neutron and Proton binding energies and shell gaps**

From the differences of nuclear binding energies or mass excesses, one can learn how much energy is needed to remove a neutron or a proton form the nucleus, i.e. information about the underlying nuclear structure. To remove the odd-even staggering [Dob01; HJR13] from the data, the two-neutron and the two-proton separation energies

\[
S_{2n}(Z,N) = B(Z,N) - B(Z,N-2)
\]

\[
S_{2p}(Z,N) = B(Z,N) - B(Z-2,N)
\]

are used. The graphical representation of these are presented in Fig. 2.2. To determine the amount in which the two-neutron or two-proton separation energies vary the empirical two-neutron shell gap and the two-proton shell gap

\[
D_{2n}(Z,N) = S_{2n}(Z,N) - S_{2n}(Z,N+2)
\]

\[
= 2 \cdot B(Z,N) - (B(Z,N+2) + B(Z,N-2))
\]

\[
D_{2p}(Z,N) = S_{2p}(Z,N) - S_{2p}(Z+2,N)
\]

\[
= 2 \cdot B(Z,N) - (B(Z+2,N) + B(Z-2,N))
\]

are determined. In this representation of the nuclear chart 2.3, one can clearly see the appearance of the nuclear magic numbers as well as the \( N = Z \) Wigner effect [Wig37] or the mid-shell regions where the shell gap becomes negative. The so called regions of on-set of deformation, were the nuclei start to gain energy through deformation, become visible. These regions are of great interest, for example, with respect to the persistence or disappearance of classical or new magic numbers [SP08], regions of deformation [Möl16] or regions through which the rapid neutron capture process for the synthesis of heavier elements than iron is going through [Mar16].

Many masses are still not determined with sufficient relative precision (\( \leq 1 \cdot 10^{-6} \)) and only extrapolations from the trend are applied to estimate the binding energy of the very exotic nuclei.
Figure 2.2: Chart of nuclides of two-neutron separation energy (top) and two-proton separation energy (bottom). Data as in Fig. 2.1.
Figure 2.3: Chart of nuclides of two-neutron shell gap (top) and two-proton shell gap (bottom). Data as in Fig. 2.1
In Fig. 2.4 the absolute uncertainty of the mass excess of all nuclei (extrapolated and measured) is represented in color code. There are more than 350 isotopes for which their masses has to be determined experimentally or their precision can still be improved, not counting those which have not been extrapolated towards the drip-lines yet.

Figure 2.4: Chart of nuclides with uncertainty of the mass excess taken from the recent version of the AME2016 [Hua17; Wan17].
3 Production of exotic nuclides

The radioactive isotopes that were studied within the frame of the present work were produced at the ISOLDE (Isotope Separator On Line DEvice) facility at CERN [Kug92; BJ17] which takes advantage of CERN’s proton beam that is accelerated and directed onto a thick target (several centimeters) within the ISOLDE complex. The reactions of the high energy protons (1.4 GeV, as a pulsed beam of up to 2.1 µA DC beam equivalent) with the target material cause the fragmentation of the precursor nuclei through fission and spallation reactions. Since the target container itself is heated to high temperatures (≈ 2000 K) the atoms are defusing out of the material into the ion source section. Depending on the goal of the experiment and the nature of the elements of interest, different ion sources can be used to ionize the atoms [Kös01]. Due to its selectivity, the Resonance Ionization Laser Ion Source (RILIS) of ISOLDE is commonly used [Fed17]. The ions are then accelerated to up to 60 kV. Two different magnetic mass separators can be used, a general purpose separator (GPS) with lower mass resolving power ($R \approx 500 − 1500$) and the high resolution separator (HRS) using two electric dipole magnets which achieve a mass resolving power of up to $R \approx 5000$ depending on the emittance of the incoming ion beam. The magnetic separators allow the selection of a certain mass range from the ions that are produced and, thus, the removal of unwanted ions that are usually accompanying the ion of interest due to the non-selective production mechanism. The ions of interest can then be send to the different experiments located in the ISOLDE hall to study their properties [BB17].

A mayor disadvantage of ISOL-type facilities is the relatively long diffusion time of the isotopes out of the target material which ultimately limits the minimal half life of the isotopes that can be studied ($t_{1/2} \approx 10 − 50$ ms). Additionally, due to the refractory nature (high melting point) of some elements, the process is chemically selective, meaning that some elements (like vanadium and molybdenum and others) can be only very inefficiently or not at all extracted from the target.

To be able to study the isotopes that cannot be extracted from a thick target unit, other methods have been introduced at other facilities like the IGISOL (ion guide isotope separator on-line) method, which is successfully used in Jyväskylä in Finland [Ärj86; Moo13]. There, a thin target (few mg/cm$^2$) is used. The isotopes, produced by similar processes as at ISOLDE facilities, are recoiling from the material into a helium atmosphere were they are slowed down and send to the experimental stations.

Furthermore, in-flight production techniques can be used at facilities like the FRS separator at the GSI Facility [Gei92; Pla13], the ARIS separator at the Michigan State University (MSU) Facility for Rare Isotopes Beams (FRIB) [Hau13] and the BigRIPS separator at the RIKEN RI Beam Factory (RIBF) [Kub16]. Heavy ion reactions at high energy are used to produce the radioactive ions through projectile fragmentation [Gol74] and in-flight fission reactions [Ber94].
4 The MR-ToF device of ISOLTRAP and its applications

ISOLDE’s ion beam of short-lived nuclei can be sent to the ISOLTRAP setup. The latter consists of four different ion traps to decelerate, bunch and clean the beam and to subsequently perform high precision mass measurements, beam analysis, support decay spectroscopy experiments and in-source laser spectroscopy [Muk08; Kre13]. One of ISOLTRAP’s main components, that was installed in 2009 [Wol13c], is the MR-ToF mass separator and analyzer [Wol13b], depicted in Fig. 4.1. The MR-ToF device can be used to separate the ion beam and identify its constituents and their production yield [Got14], to collect the time-of-flight information and, thus, to determine the mass of an unknown ions [Wie13] and to remove unwanted species from the IIs which can then be forwarded to Penning traps for high precision mass measurements with the ToF-ICR [GKT80] or the recently introduced PI-ICR [Eli13; Eli14] technique [Wol13a]. A complete list on how the MR-ToF device at ISOLTRAP has been used, is presented in one of the papers that is part of this thesis [Wie18].

A comparison of the achievable mass resolving power and the improvement factor (ratio of the different resolving powers) between the different techniques is presented in Fig. 4.2. Especially for short observation times, in case the half life of the ions is particularly small, the MR-ToF technique is favorable to the Penning-trap based approaches. If the mass resolving power needed to remove contaminates is very high or the relative precision which is needed to sufficiently address the physics case exceeds $10^{-7}$ the PI-ICR technique becomes the method of choice provided the half life of the ion of interest is sufficiently long.

Figure 4.1: Schematic overview of the MR-ToF MS including the ion detector and a pictorial representation of the ion separation.
4 *The MR-ToF device of ISOLTRAP and its applications*

![Figure 4.2: Mass resolving power (left) and improvement factor (right) as a function of the observation time of the ions for the different techniques available at ISOLTRAP. See also text.](image)

In addition the complexity and the time that has to be invested for the preparation of the measurements is significantly reduced if only the MR-ToF device is used. For the Penning trap based techniques, more time and effort has to be considered, which makes the MR-ToF MS the method of choice if a fast response to the changing availabilities of exotic ion beams, due to the constraints at an online facility like ISOLDE, is needed.

In the following, some of the main applications of the MR-ToF device that were pioneered at ISOLTRAP, in the context of the present work are briefly presented and the publications of this cumulative thesis are introduced.
4.1 Application I: Precision mass measurement of the $N=32$ sub-shell of calcium

With its closed proton shell ($Z = 20$), the calcium isotopic chain is an ideal test bench to investigate how adding neutrons to the nucleus and thus increasing the proton-to-neutron asymmetry influences its nuclear structure. Mass measurements in this region challenge the different mass models available and lead to a better understanding of the underlying nuclear forces.

The first Penning-trap measurements in the region of the neutron-rich calcium isotopes up to $^{50}$Ca were performed by Lapierre and co-workers [Lap12] with the TITAN Penning-trap mass spectrometer [Kwi13]. Those lead the way to investigate the predicted sub-shell closings at $N = 32$ [Hol12] and $N = 34$ [Hon04]. The measurements could be extended further by the same group [Gal12] in 2012 in which significant deviations from the AME2003 [WAT03; AWT03] were found. Since the calcium nuclei with $N > 32$...

![Figure 4.3: Two-neutron separation energy as a function of neutron number $N$ in the region where the ISOLTRAP experiments were performed. The AME2003 and 2016 as well as the recent measurements in the area are highlighted. The established neutron magic numbers $N=20$ and $N=28$ are indicated with vertical black lines, the suggested sub-shell closing $N = 32$ by a dot-dashed line.](image-url)
could still not be reached with high precision mass measurements techniques and thus the open questions regarding the proposed \( N = 32 \) sub-shell could not be addressed, a new experimental proposal at ISOLDE/CERN was submitted and measurements in a dedicated beam-time were performed. These measurements, which are part of this thesis as paper I, extend further up to \( ^{54}\text{Ca} \) [Wie13] and allowed a comparison of the predictive power of different state-of-the-art nuclear models and furthermore allowed to give hints to the magic nature of the neutron number \( N = 32 \) in this exotic part of the chart of nuclides.

Very recent measurements at the RIKEN Radioactive Isotope Beam Factory (RIBF) using the time-of-flight magnetic-rigidity method [Gil86] with a flight path of approximately 100 m from the large-acceptance superconducting fragment separator BigRIPS [Kub03] to the SHARAQ spectrometer [Ues12], have confirmed those mass measurements and extended the knowledge up to \( ^{57}\text{Ca} \) [Mic18].

The results of the just mentioned measurements, together with mass data taken from the AME2017 [Wan17] for the neighboring nuclei are comprised in Fig. 4.3. The established magic numbers \( N = 20 \) and \( N = 28 \) are marked with solid vertical lines. They are clearly visibly as a faster decrease of the two-neutron separation energies after the crossing of the sub-shell closing.

\[\text{Figure 4.4: The empirical two-neutron shell gap as a function of the proton number } Z \text{ for } N = 20, 28 \text{ and } 32.\]

The decrease is not only visible for the calcium isotopes, but, less pronounced, also for the neighbouring isotope chains. The position of the \( N = 32 \) sub-shell closing is marked with a dot-dashed vertical line. The drop of the \( S_{2N} \) is clearly visible for the calcium
4.1 Application I: Precision mass measurement of the $N=32$ sub-shell of calcium

[Wie13] as well as for the potassium [Ros15] chain, both measured at ISOLTRAP. But also the scandium [Xu15] as well as the titanium chains [Lei18] show signs that the sub-shell closure is persisting for nuclei with $Z > 20$. The quenching of the $N = 32$ shell closure was reported recently for vanadium isotopic chain [Rei18].

To further illustrate the strength of the shell closing for $N = 32$ in comparison to $N = 20, 28$ the empirical two-neutron shell gap is plotted in Fig. 4.4. For proton magic calcium isotopes, this quantity is particularly high. It is difficult to state whether the shell gap is maximal for the calcium chain for $N = 32$ due to the big uncertainty of masses of the scandium isotopes, thus more precise measurements in this area are needed.
4.2 Technical developments of the MR-ToF component

One of the main parameters of a mass spectrometer is the ability to separate ions of different masses from each other. As already stated, this is characterized by the mass resolving power that can be achieved by the device. To be competitive in nuclear research, the device has not only to be able to reach high resolving power but at the same time also as fast as possible to be able to investigate nuclei with short half-lives. In the second paper of this thesis [Wie15] the resolving power (more then $3 \times 10^5$), that was achieved with the device is demonstrated with offline measurements on stable potassium ions.

Additionally, the device has to be able to selectively deliver only the ion of interest after they have been separated from the contaminating ions to be able to send clean beams to the adjunct Penning-traps. A detailed description of a new mass selective ejection technique is discussed in detail in paper III [Wie17]. The technique utilizes the in-trap lift [Wol12b; Wol12a] and does not rely on any other devices like the Bradbury-Nielsen beam gate [BN36] used earlier. Furthermore, in paper IV, the stability of the time-of-flight of the ions in the MR-ToF MS was improved significantly by stabilizing the voltage applied to mirror electrode 5 using a software based PI-algorithm [Wie18]. Figure 4.5 illustrates the effect on the ion time-of-flight with the PI loop on and off. For the measurements, $^{85}$Rb ions were used and the time of flight of the ions after 1000 revolutions in the MR-ToF MS was recorded.

![Figure 4.5: Color-coded plot of time-of-flight spectra of $^{85}$Rb$^+$ after 1000 revolutions in the MR-ToF MS with the PI regulation on and off.](image-url)
4.3 Application II: Ion-beam analysis for the optimization of ISOLDE operation

The mass spectrometry techniques that were used to study the basic nuclear forces and the structure of the nuclei, can also be applied to support other experiments, in particular if the knowledge about the beam composition if relevant. A typical example is the determination of yields of different nuclides to support target and ion source development (TISD) activities [Got14].

Another important example is the support of campaigns in which the collection of isotopes relevant for the application in medical science was the main interest. An overview plot of isotopes used in medical applications can be found in Fig. 4.6. Some

![Chart of nuclides in which all isotopes currently used for medical applications are highlighted, taken from [Ass19].](image)

Figure 4.6: Chart of nuclides in which all isotopes currently used for medical applications are highlighted, taken from [Ass19].

of the radioactive terbium isotopes are of particular interest because of there specific properties that makes same suitable not only for diagnostic but also for therapeutic applications in cancer treatment.

The use of $^{149}$Tb was suggested by Allen et al. [AB96] as the preferred isotope for $\alpha$-radionuclide therapy. $^{149}$Tb is not easily produced at facilities specialist for medical isotope production as described in [Bey02]. That is why the ISOLDE facility was used to produce sufficient amounts of radioactive terbium using a thick $^{181}$Ta foil target for initial tests. The beam composition of the isotopes that were collected and analyzed with the MR-ToF MS is presented in Fig. 4.7. The terbium isotopes are indirectly produced by collecting dysprosium which ionization can be selectively enhanced using the RILIS lasers [Fed05]. The dysprosium subsequently decays then to the desired terbium isotopes. Those isotopes are accompanied by isobars and pseudo-isobars (molecular ions) like
cerium oxide which can cause a significant part of the collected activity that is, due to legal restrictions, ultimately limiting the amount of dysprosium/terbium that can be collected and transported to collaborating medical research institutes. It is highly desirable to first of all know how much contaminants can be expected and secondly also to optimize the target and ion-source such that dysprosium/terbium production is maximized. A typical optimization procedure is shown in Fig. 4.3. The A=149 beam cocktail was sufficiently separated with the MR-ToF MS and a gate was set for each ion to be able to monitor its count rate. Subsequently, target ion source parameters (I-VII) were varied to optimize the ratio of Dy/Tb to contaminating ions which are listed in Tab. 4.3. The collected isotopes were then used in different studies in nuclear medicine [Mül16; Mül14].

![Graph](image)

**Figure 4.7:** Typical time-of-flight spectrum of mass A=149 delivered from ISOLDE and analyzed with the MR-ToF MS.

**Figure 4.8:** Count rate as a function of the observation time for the different species that are delivered by ISOLDE on mass A=149 during the optimization of the ion-source parameters to increase the production of $^{149}$Dy with respect to the accompanying ions.
5 Conclusion and Outlook

The MR-ToF MS at ISOLTRAP has manifested itself as widely used tool in nuclear research. The applications range from nuclear structure, as shown in the present work in performing the first mass measurements of $^{53,54}$Ca to establish the $N = 32$ sub-shell closer for the calcium isotopic chain, to identifying beam constituents for target and ion source optimization. An additional example, which has not been further discussed in the present work, but which became a regular application is the field of in-source laser spectroscopy where the MR-ToF mass spectrometer serves as an almost background-free, highly selective, single-ion counting detector [Cub18a; Cub18b; Mar18].

Figure 5.1 summarizes the measurements that were performed at ISOLTRAP during the time from 2010 to 2018. A total of 477 different isotopes were investigated.

To increase the performance of the MR-ToF device, a voltage stabilization system has been developed and implemented which, in combination with the newly introduced in-trap lift cleaning technique, will allow a more reliable use of the device for beam cleaning but also for precision mass measurements. This will pave the way to measure even more exotic isotopes in yet uncharted regions of the charts of nuclides. It is planned to stabilize also other power supplies with the same or a similar technique to further increase the performance in terms of mass resolving power and stability during extended measurement campaigns.
6 Bibliography

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7 Cummulative thesis articles

7.1 Author contributions

Article I: Masses of exotic calcium isotopes pin down nuclear forces

Article II: Towards ultrahigh-resolution multi-reflection time-of-flight mass spectrometry at ISOLTRAP

Article III: Mass-selective ion ejection from multi-reflection time-of-flight devices via a pulsed in-trap lift

Article IV: Improved stability of multi-reflection time-of-flight mass spectrometers through passive and active voltage stabilization

Confirmed:
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Masses of exotic calcium isotopes pin down nuclear forces

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The properties of exotic nuclei on the verge of existence play a fundamental part in our understanding of nuclear interactions1. Exceedingly neutron-rich nuclei become sensitive to new aspects of nuclear forces2. Calcium, with its doubly magic isotopes 40Ca and 48Ca, is an ideal test for nuclear shell evolution, from the valley of stability to the limits of existence. With a closed proton shell, the calcium isotopes mark the frontier for calculations with three-nucleon forces, which are similar for the excitation spectra at atomic number Z = 20 (refs 3, 5). These predictions withstand a recent challenge from direct Penning-trap mass measurements of 47Ca and 49Ca at TITAN/TRIUMF3, which have established a substantial change from the previous mass evaluation and leave completely open how nuclear masses evolve past 52Ca. This region is also very exciting because of evidence of a new magic neutron number N = 32 from nuclear spectroscopy3–5, with a high 2+ excitation energy in 50Ca (refs 19, 20). These results are accompanied by successful theoretical studies based on phenomenological shell-model interactions6,7, which are similar for the excitation spectra at N = 32 but disagree markedly in their predictions for 53Ca and further away from stability.

Here we present the first mass measurements of the exotic calcium isotopes 53Ca and 54Ca. These provide key masses for all theoretical models, and unambiguously establish a strong shell closure, in excellent agreement with our theoretical calculations. These results increase our understanding of neutron-rich matter and pin down the subtle components of nuclear forces that are at the forefront of theoretical developments constrained by quantum chromodynamics6.

Exotic nuclei with extreme neutron-to-proton asymmetries exhibit shell structures generated by unexpected orderings of shell occupancies. Their description poses enormous challenges, because most theoretical models have been developed for nuclei at the valley of stability. It is thus an open question how well they can predict new magic numbers emerging far from stability9–11. This is closely linked to our understanding of the different components of the strong force between neutrons and protons, such as the spin–orbit or tensor interactions, which modify the gaps between single-particle orbits12, and of three-body forces, which are pivotal in calculations of extreme neutron-rich systems based on nuclear forces13–15. The resulting magic numbers, as well as the strength of the corresponding shell closures, are critical for global predictions of the nuclear landscape16, and thus for the successful modelling of matter in astrophysical environments.

Three-body forces arise naturally in chiral effective field theory17, which provides a systematic basis for nuclear forces connected via the spin operator. These are constrained by the properties of light nuclei3H and 4He only, so that all heavier elements are predictions in chiral effective field theory. The present frontier of three-nucleon forces is located in the calcium isotopes, where the structural evolution is dominated by valence neutrons due to the closed proton shell at atomic number Z = 20 (refs 3, 5). These predictions withstand a recent challenge from direct Penning-trap mass measurements of 47Ca and 49Ca at TITAN/TRIUMF3, which have established a substantial change from the previous mass evaluation and leave completely open how nuclear masses evolve past 52Ca. This region is also very exciting because of evidence of a new magic neutron number N = 32 from nuclear spectroscopy3–5, with a high 2+ excitation energy in 50Ca (refs 19, 20). These results are accompanied by successful theoretical studies based on phenomenological shell-model interactions6,7, which are similar for the excitation spectra at N = 32 but disagree markedly in their predictions for 53Ca and further away from stability.

Here we present the first mass measurements of the exotic calcium isotopes 53Ca and 54Ca. These provide key masses for all theoretical models, and unambiguously establish a strong shell closure, in excellent agreement with the predictions including three-nucleon forces. The mass of a nucleus provides direct access to the binding energy, the net result of all interactions between nucleons. Penning traps have proven to be the method of choice when it comes to high-precision mass determination of exotic nuclei16–18. The mass m of an ion of interest with charge q stored in a magnetic field B is determined by comparing its cyclotron frequency νc = qB/(2mπ) to that of a well-known reference ion, νc,Ref. The frequency ratio rνc = νc/νc,Ref yields the mass ratio directly and thus the atomic mass of the isotope.

We have made a critical step towards determining the pivotal calcium masses by introducing a new method of precision mass spectrometry for short-lived isotopes. The developments and measurements were performed with ISOLTRAP19, a high-resolution Penning-trap mass spectrometer at the ISOLDE/CERN facility. This method was used to confirm and even improve the accuracy of the recent mass measurements.
of $^{51}$Ca and $^{52}$Ca (ref. 4). To advance past $^{52}$Ca, we added a multi-reflection time-of-flight mass spectrometer/separator$^{26}$ (MR-TOF MS, see Fig. 1) to the three other ion traps that constitute ISOLTRAP, namely a linear Paul trap and two Penning traps (the latter are not shown in Fig. 1). In the MR-TOF MS, flight paths of several kilometres are folded into table-top dimensions. This device provides not only a mass-resolving power of more than $10^6$, but also a mass uncertainty in the sub-parts-per-million (sub-p.p.m.) range. As typical flight times are about 10 ms, nuclides with half-lives of the same order are accessible. Likewise, nuclei with a lower production rate can be accessed, pushing the limits currently set by Penning-trap mass spectrometry to isotopes farther away from stability.

The neutron-rich calcium isotopes were produced at the online isotope separator ISOLDE in proton-induced fission reactions of a uranium carbide target at 1.4 GeV proton energy. The nuclides of interest were ionized by a highly selective, three-step laser-excitation scheme$^{27}$. The ions were accelerated and transported to the ISOLTRAP set-up via ISOLDE’s high-resolution separator as an essentially continuous 30 keV beam. They were captured and cooled in the radio-frequency quadrupole (RFQ) buncher and forwarded to the MR-TOF MS as bunches of about 60 ns duration. In the case of $^{53}$Ca and $^{54}$Ca, the MR-TOF MS was operated as an isobar separator, delivering the purified bunches to the Penning traps, where the mass measurements were performed by determining the cyclotron-frequency ratios as described above. Nevertheless, for $^{53}$Ca and $^{54}$Ca the Penning-trap mass measurements were not possible because of the low production rates and copious isobaric contamination. For example, only a few $^{54}$Ca ions per minute were detected behind the MR-TOF system, accompanied by several thousand contaminating $^{54}$Cr ions. The rate of delivery of $^{54}$Ca$^+$ to the Penning traps was considerably reduced owing to the lower transport efficiency and the decay losses caused by the required extra ion trapping time.

Thus for $^{53}$Ca and $^{54}$Ca the MR-TOF device itself was employed as a mass spectrometer, where the time of flight $t$ of an ion is related to the mass-over-charge ratio $m/q$ by $t = \frac{a}{m/q} + \beta$. Measuring the time of flight of two well-known reference ions, here $^{39}$K and $^{53/54}$Cr (see Fig. 2), determines the experimental parameters $a$ and $\beta$. With this calibration the mass $m$ of the ions of interest, $^{53}$Ca and $^{54}$Ca, results directly from their time of flight. This relation can be expressed by $m = \frac{1}{\beta} - \frac{\alpha}{a}$ and $\beta = \frac{1}{\alpha} - \frac{\alpha}{a}$, where $\alpha$ is the sum of the square roots of the masses of the two reference ions. $C_{\text{TITAN}} = \frac{1}{\sqrt{t_1^2 + t_2^2}}$ comprises all measured time-of-flight values $t_1$ and $t_2$ of the ion of interest and the reference ions, respectively. Thus, it relates the mass $m$ of the ion of interest to the reference-ion masses $m_{1/2}$ and allows re-evaluation of the data if the value of the reference masses changes.

Our application of the MR-TOF MS method is the first for rare isotope beams. Figure 2a shows a typical time-of-flight spectrum of the mass-53 ions, which resulted from the addition of 47,000 single-shot spectra (experimental cycles) taken over a period of about 3.5 h. The typical timescale for an ‘experimental cycle’, that is, the time from proton impact, after which we collect an ion ensemble, until its ejection from the offline ion source. At bottom is the same spectrum compressed to a plot with colour-coded ion counts. Two-dimensional colour-coded intensity plot of time-of-flight spectra of $A = 54$ nuclides. The number of ion counts (colour coded, key at right) is shown as a function of time of flight on the abscissa and as a function of the measurement time (spectrum number) on the ordinate. Intensity plots are shown for different experimental conditions (with laser ionization on and protons on target, unless indicated otherwise).

![Figure 2](image_url)

### Table 1: Results of the calcium mass measurements

<table>
<thead>
<tr>
<th>Isotope</th>
<th>$T_{1/2}$ (s)</th>
<th>Meas. type</th>
<th>Ref. nuclide(s)</th>
<th>$t_{\text{ref}}$ (s)</th>
<th>$C_{\text{INT}}$</th>
<th>Mass excess (keV/u)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{51}$Ca</td>
<td>10.0(8)</td>
<td>ICR</td>
<td>$^{39}$K</td>
<td>1.3079136760(144)</td>
<td>NA</td>
<td>$-36332.07(0.58)$</td>
</tr>
<tr>
<td>$^{52}$Ca</td>
<td>4.6(3)</td>
<td>ICR</td>
<td>$^{39}$K</td>
<td>1.3366358720(184)</td>
<td>NA</td>
<td>$-34266.02(0.71)$</td>
</tr>
<tr>
<td>$^{53}$Ca</td>
<td>461(90) ms</td>
<td>MR-TOF</td>
<td>$^{39}$K, $^{35}$Cr</td>
<td>NA</td>
<td>0.501632110(785)</td>
<td>$-34271.7(10.2)$</td>
</tr>
<tr>
<td>$^{54}$Ca</td>
<td>94(6) ms</td>
<td>MR-TOF</td>
<td>$^{39}$K, $^{35}$Cr</td>
<td>NA</td>
<td>0.50187613(309)</td>
<td>$-29387.8(43.3)$</td>
</tr>
</tbody>
</table>

$T_{1/2}$, half-life$^{28}$; measurement (mass.) type (ICR, ion cyclotron resonance; MR-TOF, multi-reflection time-of-flight mass spectrometry); reference (ref.) nuclide(s) used for the calibration; $t_{\text{ref}}$, experimental frequency ratio; $C_{\text{INT}}$, TOF constant; mass excess, $M_{\text{excess}} = M(\text{AT}) - A(m)$, where $M$ is the atomic mass, $A$ is the atomic number and $u$ is the unified atomic mass unit. For comparison, the TITAN$^{29}$ values are also listed. The mass values of the reference nuclides are $m(A,K) = 38963706.4864(49)$ u, $m(\text{ICR}) = 51940503.26(83)$ u, $m(\text{MR-TOF}) = 52940648.17(62)$ u, $m(\text{ICR}) = 53938879.18(61)$ u (ref. 28), NA, not applicable.

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during spectra 5 to 11, which resulted in the disappearance of the ion counts in question. This unambiguously identified these ions as $^{52}\text{Ca}$. Figure 2b corresponds to about 90 min of data-taking. MR-TOF MS spectra of $^{53}\text{Ca}$ and $^{54}\text{Ca}$ were taken in total for 12.6 h and 18.2 h, respectively. Figure 2b corresponds to about 90 min of data-taking. MR-TOF MS spectrum of $^{53}\text{Ca}$ and $^{54}\text{Ca}$ were taken in total for 12.6 h and 18.2 h, respectively.

Our results ($r_{\text{CC}}$ and $C_{\text{TOF}}$) for the exotic calcium isotopes investigated ($^{52}\text{Ca}$ and $^{53,54}\text{Ca}$, respectively) are summarized in Table 1, including the resulting mass excesses. The ISOLTRAP values of $^{51}\text{Ca}$ and $^{52}\text{Ca}$ determined with the Penning trap agree well with the recent measurements by TITAN. The uncertainties were reduced by factors of 40 and 80, respectively, owing to longer excitation times (600 ms in the case of ISOLTRAP as compared to 80 ms in the case of TITAN), higher cyclotron frequencies and higher calcium ion yields. The masses of $^{53,54}\text{Ca}$ determined by the MR-TOF MS have been experimentally addressed for the first time. As a consistency check, the $^{53}\text{Ca}$ mass was also measured by the new MR-TOF method, and the mass excess is in full agreement with both Penning-trap results (Table 1). Furthermore, a second cross-check measurement in the vicinity of the newly measured masses was performed. The mass excess of the stable isotope $^{58}\text{Fe}$ was determined with the stable reference isotopes $^{56}\text{Ni}$ and $^{85}\text{Rb}$. The measurement resulted in a mass excess of $-62.168.0(47.0)\text{keV}/c^2$, with a measurement uncertainty given in parentheses. A deviation of $13.5\text{keV}/c^2$ from the literature value is acceptable within the standard uncertainty uncertainty. The uncertainties in the MR-TOF method quoted in Table 1 for $^{53}\text{Ca}$ and $^{54}\text{Ca}$ apply to both $^{53}\text{Ca}$ and $^{54}\text{Fe}$, respectively. The deviations from the Penning-trap measurement and the literature value, respectively, are taken as estimates of the relative systematic uncertainty, which lies in the low $10^{-7}$ range. Additional cross-check measurements to determine the systematic uncertainty have been performed over a wide mass range and will be detailed elsewhere. The precision and fast measurement cycle of the MR-TOF method makes this a promising approach for the mass spectrometry of isotopes with lower yield and shorter half-life than currently accessible.

The binding energies encode information about the ordering of shell occupation, and thus are essential in the quest for shell closures in exotic regions of the nuclear chart. Our high-precision data can be used to provide a critical benchmark for the behaviour far from stability, namely, the two-neutron separation energy $S_{2n}$ is a function of proton number $N$, which is the two-neutron separation energy $S_{2n} = B(ZN) - B(ZN - 2)$, where $B(ZN)$ is the binding energy (defined as positive) of a nucleus with $Z$ protons and $N$ neutrons. The $S_{2n}$ values are a preferred probe of the evolution of nuclear structure with neutron number, and can be used to challenge model predictions, as shown in Fig. 3. The pronounced decrease in $S_{2n}$ revealed by the new $^{53}\text{Ca}$ and $^{54}\text{Ca}$ ISOLTRAP masses is similar to the decrease beyond the doubly magic $^{48}\text{Ca}$. In general, correlations induced by deformation could also cause such a reduction in $S_{2n}$, but in the calcium isotopes studied here deformation is expected to have no role. Therefore, our new data unambiguously establish a prominent shell closure at $N = 32$. The strength of this shell closure can be evaluated from the two-neutron shell gap, that is, the two-neutron separation energy difference $S_{2n}(ZN) - S_{2n}(ZN - 2)$. Figure 3c shows a two-neutron shell gap for $^{52}\text{Ca}$ of almost $4\text{MeV}$, where the rise towards $^{52}\text{Ca}$ at $N = 32$ is as steep as that towards $^{48}\text{Ca}$ at $N = 28$. The peaks at $N = 2$ in Fig. 3c are due to the additional correlation energy for symmetric $N = Z$ nuclei, known as Wigner energy.

Calcium marks the heaviest chain of isotopes studied with three-nucleon forces based on chiral effective field theory. Figure 3a shows the predictions of our microscopic calculations with three-nucleon forces (that is, ‘$NN + 3N$’) using many-body perturbation theory...
(MBPT) for the valence-neutron interactions\cite{3,4}, it also shows predictions of large-scale coupled-cluster ("CC") calculations including the continuum and three-nucleon forces as density-dependent two-body interactions\cite{5}. Confronted with the $S_{nn}$ values obtained from the new masses of $^{53}$Ca and $^{54}$Ca, we find an excellent agreement with the predictions. We have also calculated perturbatively the effect of residual three-valence-neutron forces. This provides only a very small repulsive contribution, lowering $S_{nn}$ by about 50 keV to 250 keV from $^{53}$Ca to $^{54}$Ca in the MBPT framework. The agreement of the NN+3N calculations with the new ISOLTRAP masses is remarkable, because their parameters are fitted only to the properties of few-nucleon systems while their level of accuracy here is similar to the phenomenological shell-model interactions KB3G\cite{29} and GXPF1A\cite{27}, which are adjusted to the medium-mass region. The CC calculations predict $N=29$ shell gap very close to our measurements; however, the oscillations in $S_{nn}$ for odd neutron numbers on either side of the shell closure disagree with experiment.

In Fig. 3b we compare the new ISOLTRAP masses to state-of-the-art nuclear density-functional-theory (DFT) predictions\cite{15,29}, which have recently provided global predictions for nuclear driplines\cite{30}. (The dripline marks the limit of existence where nuclei cease to be bound.) This shows that modern DFT calculations can reproduce the masses of $^{52-54}$Ca. In particular, the UNEDf0 and SV-min functionals are in very good agreement. However, the DFT calculations predict an almost linear progression of the two-neutron separation energy that does not lead to the experimentally observed decrease in $S_{nn}$ at $^{48}$Ca and at $^{52}$Ca, established by the new masses of $^{53}$Ca and $^{54}$Ca. In the NN+3N calculations, the neutron dripline is obtained at $^{52}$Ca, but owing to the very flat behaviour of the binding energies past $^{60}$Ca (refs 3, 5, 15, 29), the limit of calcium isotopes is very difficult to predict theoretically. In addition, the effects of the continuum, not included in the MBPT calculations, will be decisive for nuclei close to the dripline\cite{29}.

Note that the calcium isotopes studied here are still well bound, with 4.2 MeV separation energy in $^{54}$Ca, so that the effects of the continuum on the ground-state energies are small (of the order of 100 keV), comparable to the small effects of residual three-nucleon forces.

The present results based on precision mass measurements with a multi-reflection time-of-flight method reinforce the suggestion that pronounced structural effects are important in exotic nuclei and that shell effects do not smear out far from stability. Our results provide useful information for all theoretical models, and they show that a description of extreme neutron-rich nuclei can be closely connected to a deeper understanding of nuclear forces. Chiral effective field theory provides this connection and an exciting framework for exploring neutron-rich nuclei. The measurements of the $^{53}$Ca and $^{54}$Ca isotopes, accessed in this work, present anchor points to pin down nuclear forces. Finally, we note that the advantages of the MR-TOF method as compared to Penning-trap mass spectrometry will also be important for new experimental facilities, which will provide even more exotic ion beams. The present and future developments of low-energy beams at facilities for the study of exotic nuclides such as ARIEL, CARIBU, FAIR, FRIB, HE-ISOLDE, RIBF and SPIRAL 2 will considerably extend the available range of rare isotopes towards the nuclear driplines. The minute production rates of isotopes with half-lives in the millisecond range and substantial isobaric contamination pose experimental challenges that are barely met by Penning traps now, but can be overcome with the MR-TOF method.
Towards ultrahigh-resolution multi-reflection time-of-flight mass spectrometry at ISOLTRAP

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Abstract
The mass resolving power of the multi-reflection time-of-flight mass spectrometer of ISOLTRAP was studied by monitoring $^{39}$K⁺ signals. A drift tube at the center of the MR-ToF MS allows decreasing or increasing the kinetic energy of the ion bunch, by switching its potential when the ions are traversing it. This offers the possibility of capturing and ejecting ion bunches by controlling a single voltage by the so-called in-trap lift technique. It also allows changing the energy of the trapped ions inside the MR-ToF MS, offering a way to optimize the resolving power of the device. For a fixed number of 2000 laps corresponding to a total ion flight time of about 30 ms, data was accumulated for 100 experimental cycles, adding to a duration of 10 s for each spectrum. Without any subsequent corrections for broadening effects, mass resolving powers in excess of 300 000 (FWHM) were obtained.

Keywords: multiple-reflection time-of-flight mass spectrometer, ion purification, mass resolving power, mass spectrometry, nuclear physics, isobar separator

1. Introduction
During the last couple of years, ISOLTRAP’s [1, 2] multi-reflection time-of-flight (MR-ToF) device [3–7] has established itself as an essential component for on-line precision mass spectrometry (MS). In particular, it has been applied as a beam purifier for the subsequent Penning-trap mass measurement of $^{82}$Zn [8] and as a mass spectrometer of its own for the mass determination of $^{53,54}$Ca [9] and $^{52,53}$K [10], which previously had been inaccessible for mass spectrometry. In addition, it was used for target and ion source development at ISOLDE/CERN [11] as well as for studying the hyperfine structure of radioactive isotopes [12].

A technique which distinguishes ISOLTRAP’s MR-ToF MS from similar devices is the ion injection and ejection by use of an in-trap lift electrode, as described in detail in the next section. Apart from offering a convenient way of capturing an ion bunch, it allows to optimize the mass resolving power for any number of revolutions by simply varying its potential, which effectively changes the mean kinetic energy of the ions inside the MR-ToF MS [4]. We report on the result of such an optimization for the particular case of $^{39}$K⁺ and flight times of about 30 ms corresponding to 2000 laps.

2. Multi-reflection time-of-flight mass spectrometry and the in-trap lift technique
In time-of-flight mass spectrometry, ions start from a potential $U_0$ in an ideally very small region of an ion source and fly towards a detector via a path s of potential $U(s)$. At coordinates along the flight path they have a velocity...
\[ v_i = \sqrt{q/m_i \cdot 2(U_0 - U(s))} \]

which depends on their mass-to-charge ratio \( m_i/q_i \), where the index indicates the ion species. Assuming that all ions have the same flight path, the flight time of an ion species is

\[ t_i = \sqrt{2m_i/q_i \cdot a + b} \]

where \( a \) is a device-specific parameter and \( b \) an offset originating from possibly different timing delays of the apparatus (ideally zero). In general, ions do not have the same flight path because they do not start at the same position. The arrival times in a ToF mass spectrometer depend on their initial positions \( \theta_0 \) and also of their velocities \( v_0 \) in the source region, \( t_i(\theta_0, v_0) \).

The aim of most ToF mass spectrometers is to minimize the difference in time of flight due to these distributions. A commonly used performance criterion is the mass resolving power \( R = \frac{m}{\Delta m} = \frac{L}{\Delta t} \) where \( \Delta m \) and \( \Delta t \) are the width of a mass signal or time-of-flight signal in the spectrum, respectively. To achieve a high mass resolving power, a long flight time or a narrow ion-flight-time distribution at the detector has to be achieved.

In general, there are practical limitations to the minimal bunch width as well as to the length of the drift section. To overcome the latter, Wollnik and Przewloka suggested in the early 1990s to increase the effective drift length by reflecting the ions back and forth between ion-optical mirrors [13], see figure 1. The resulting ‘multi-reflection time-of-flight mass spectrometers’ can store ions on stable trajectories, while losses are mostly determined by ion-neutral collisions, i.e. only depend on the residual gas pressure. This opens the possibility to extend the flight time \( t \) to tens of milliseconds and beyond. For typical bunch widths \( \Delta t \) of tens of nanoseconds, mass resolving powers of above \( R = 100,000 \) have been achieved, increasing the performance of ToF devices by several orders of magnitude while keeping the apparatus compact. Over the years, this scheme has been further developed in particular by Wollnik et al. [14, 15] and Ventchikov et al [16, 17]. The MR-ToF method found applications in nuclear physics, and such devices are developed or used not only at ISOLTRAP but also in Gießen, Germany [18, 19], at RIKEN, Japan [20, 21], at the Oak Ridge National Laboratory, USA [22] as well as at the Argonne National Laboratory, USA [23], at TRIUMF in Vancouver, Canada [24], and at the RAON facility in South Korea [25]. MR-ToF devices are also planned at IGISOL in Finland, at GANIL in France, at the University of Notre Dame, USA and in Lanzhou in China. Besides this usage in nuclear physics the MR-ToF technique found interest in analytical chemistry [26–29] and recently even in space science [30]. We note that similar two-mirror systems are used also as ion-storage devices for the investigation of properties of trapped particles, e.g., in atomic cluster research [31, 32].

In order to store ions between the two electrostatic mirrors of the MR-ToF analyser, their energies need to be below the potential barriers created by the mirrors. The immediate idea for axial injection and ejection is to lower the mirror potentials during the ion passage. However, in general, it involves the switching of several mirror electrodes on each side. In addition, switching voltages introduces perturbations of the potentials, which may deteriorate the performance of the MR-ToF device. Thus, alternatively, the in-trap lift method uses a single voltage, which is switched to ground during injection and storage and to the original potential for ejection, thus minimizing perturbations.

The principle of the in-trap lift technique is detailed in figure 1. Ion bunches coming either directly from an ion source or, as in the case of ISOLTRAP, from an RFQ ion trap [33] are injected axially from the left at kinetic energy high enough to overcome the potentials of the entrance-mirror electrodes (figure 1(a)). The ions then enter a drift tube at a given potential \( U_{\text{lift}} \) and are decelerated. During their passage through the drift tube, its potential is switched to the ground potential (figure 1(b)), so that the total energy (potential plus kinetic) of the ions is no longer enough to overcome the potential barriers of the ion mirrors (figure 1(c)). To rapidly change the potential of the in-trap lift electrode, a solid-state MOSFET switch (Behlke HTS 61-03-GSM) was used, which allows changing the potential within a couple of 10 nanoseconds. This time is small compared to the flight time of the ions across the switched electrode allowing to capture and eject the ion bunches while they are close to the center. Therefore the ions are not disturbed by the switching process, which could have a negative effect on the resolving power of the device. In analogy, for ion ejection the drift-tube potential is raised back up again during the ion passage (figure 1(d)). This procedure on the one hand simplifies the operation since only one voltage has to be switched and it furthermore decouples the kinetic energies of the ions in MR-ToF MS from the ones required in the adjacent beam lines.

However, the most important advantage of the in-trap lift technique is that it opens the possibility to maximize the mass resolving power for any number of laps and to react on slight changes of the mirror potentials that shift the time-of-flight focus position. By adjusting the kinetic energy of the ions in the moment they enter the device, one can literally ‘navigate’ the energy distribution of the ions on the time-of-flight-energy/dispersion curve. It therefore changes the time-of-flight dispersion per revolution to compensate the dispersion obtained in the flight path outside the MR-ToF device to...
achieve an overall isochronous flight path. In the following it is shown for a particular case how the resolving power of the MR-ToF MS can be maximized with the in-trap lift technique.

3. Optimization of the MR-ToF MS resolving power by variation of the in-trap lift potential

As outlined above, the mass resolving power of a mass spectrometer is defined as $R = \frac{m}{\Delta m}$ where $m$ is the mass of the ion and $\Delta m$ is the width of the peak at a certain height, e.g. the full-width-at-half-maximum (FWHM), as used in the following. For time-of-flight spectrometers one finds that $R_{\text{FWHM}} = \frac{m}{\Delta m} = \frac{1}{2\Delta t}$ where $t$ is the total flight time and $\Delta t$ is the FWHM time spread of the ion peak. Figure 2(a) shows the measured resolving power as a function of the in-trap lift voltage $R_{\text{FWHM}}(U_{\text{lift}})$ at 2000 laps for $^{39}\text{K}^+$ ions from ISOLTRAP’s reference ion source [1]. For every point of figure 2(a) the data of 100 experimental cycles, each of about 100 milliseconds total length (with 70 ms for ion accumulation and bunching in the RFQ ion trap and 30 ms total flight time in the MR-ToF MS), were accumulated to one time-of-flight spectrum. Resolving powers above 300,000 were found for a 6 V range of in-trap lift voltages $U_{\text{lift}}$ around 1096 V, where the ions had storage energies of about 2104 eV.

As an example, figure 2(b) shows the $^{39}\text{K}^+$ signal of theToF spectrum that corresponds to the data point marked in red in figure 2(a). In total, it contains 753 ion counts from 100 cycles during about 10 s. These raw data without any corrections were fitted with a Gaussian (red) and with an exponential-Gaussian hybrid function [34] (blue), which was recently proposed for MR-ToF spectra by Schury et al [21]. The initial shape and width of the injected ion pulse depends on the ejection field strength of the extraction pulse of the RFQ cooler and buncher, which was modified from its first design, to accommodate for the need of a small initial time-of-flight distribution, for details see [6]. A further reduction of the ion initial time-of-flight spread would enable reaching the maximum resolving power in less flight time. However, higher RFQ ejection field strength also increases the energy distribution, which may lead to a lower maximum in mass resolving power. The transmission through the device in the present case where the ions travel 2000 laps through the apparatus had previously been determined to be around 50% [6].

4. Summary and outlook

Repeatedly, a mass resolving power in excess of 300,000 has been demonstrated for ISOLTRAP’s MR-ToF MS by varying the potential of the in-trap lift electrode. The measurements are part of a more extensive study using both stable potassium and caesium ions where several lap numbers, up to the present 2000, have been investigated. The data are currently under evaluation [35]. The studies presented have been performed with only a few counts per cycle, i.e. there were only a few ions simultaneously stored in the MR-ToF device. In general, however, there may be significantly more ions which, in addition, are not all of the same ion species. In such cases the mutual interaction between the simultaneously stored ions is non-negligible and will influence the achievable resolving power. In extreme cases peak coalescence is observed [7]. Further measurements are currently performed to investigate these phenomena [36].
Acknowledgments

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7.4 Mass-selective ion ejection from multi-reflection
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Mass-selective ion ejection from multi-reflection time-of-flight devices via a pulsed in-trap lift

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1. Introduction

Mass spectrometry in nuclear research [1–3] is hampered when contaminant ions are simultaneously delivered from the sources of the exotic nuclides of interest. As the contaminants are often isobars of the nuclides of interest, high mass resolving powers are needed. In addition, the ions of interest are mostly the very exotic and short-lived ones and their production yields can be as low as only a few ions per second, while at the same time the unwanted ion species – often long-lived or even stable nuclides – have a much higher abundance.

For many experiments these conditions lead to unpredictable high systematic shifts due to Coulomb interactions between the ions which can even make the measurements impossible [4]. Therefore, an efficient preparation of pure samples is extremely important.

This situation is encountered in precision Penning-trap mass spectrometry of radioactive species where relative uncertainties on the order of $\Delta m/m = 10^{-8}$ or even better have been achieved. It allows to determine nuclear binding energies and thus to investigate various fundamental questions of, e.g., nuclear structure or nucleosynthesis [2]. If, however, the Penning traps are loaded not only with the ions of interest but also with additional contaminating species, this can lead to hardly controllable relative mass shifts on the order of $10^{-6}$ and more [4,5]. As the nuclear binding energies result from small differences between nuclear masses, their values suffer heavily from such mass shifts. Thus, it is of utmost importance to exclude sample contamination in these kinds of investigations.

Already 25 years ago, multi-reflection time-of-flight (MR-ToF) mass spectrometry has been introduced [6]. Recently, these ideas have been realized at the ISOLTRAP setup at ISOLDE/CERN [7], expanding the knowledge in nuclear structure and nuclear astrophysics by use of an MR-ToF device as a mass separator followed by Penning-trap mass spectrometry [8–10] as well as by making use of itself as a mass spectrometer [10–12]. Furthermore, it has proven very versatile as a high-resolution mass analyzer for target and ion-source developments [13], in-source ionization spectroscopy [14], and half-life measurements [15]. Furthermore, other facilities in the field of nuclear physics are using or planning to use an MR-ToF MS; see [16] and the references therein.
In the following, we focus on the mass separation which is not only necessary for subsequent precision mass spectrometry by Penning traps but also for further investigations, such as nuclear decay studies [17].

Until recently, for the selection of separated isobaric ion species, MR-ToF devices have been combined with subsequent ion gates, most notably the Bradbury–Nielsen gate (BNG) [18–20]. In contrast, a new selection method is presented that does not rely on any such additional external device but makes use of an internal component of ISOLTRAP’s MR-ToF section itself, namely its drift-tube electrode between the ion-optical mirrors. This electrode has been introduced as an “in-trap potential lift” to capture and eject ions [21]. The new selection method is based on the timing of the ejection pulse of this electrode to selectively address only the ions of interest. This technique has already been applied in several on-line experiments, e.g. during the studies reported in [10].

The next section gives a brief overview of the ISOLTRAP setup including its MR-ToF mass spectrometer/separator (MS), Section 3 reviews the in-trap lift technique and its performance for mass spectrometry. This is followed by the introduction and characterization of the new in-trap lift based selection method in Section 4. Finally, in Section 5 several examples of on-line applications illustrate its usefulness for the investigation of short-lived nuclides.

2. The ISOLTRAP experiment at ISOLDE/CERN

In the late 1980s precision mass spectrometry of short-lived nuclides was revolutionized with the installation of ISOLTRAP at the ISOLDE facility at CERN/Geneva, the first on-line Penning-trap system for this purpose [22–24]. Overviews of the ISOLTRAP setup and of its developments over the years can be found in Bollen et al. [25], Mukherjee et al. [26] and Kreim et al. [27]. Today, it comprises four ion-trapping components as schematically presented in Fig. 1.

(1) A linear radio-frequency quadrupole (RFQ) ion trap [28] for cooling and bunching the quasi-continuous ISOLDE ion beam of up to 60 keV. The ions are ejected in 3.2-keV pulses to the ISOLTRAP components downstream.

(2) The MR-ToF mass analyzer for mass measurements and beam purification as described in detail in the next section.

(3) The so-called preparation Penning trap [29,30] were mass-selective buffer-gas centering [31] is applied to prepare the ions for mass measurement in the precision Penning trap. This method is used to center and cool the ions of interest and, if necessary, to further purify them from contaminations with mass resolving powers on the order of $R = 1 \cdot 10^5$ within a few 100 ms [32]. Additionally, the preparation trap has been used to access nuclides that are not or only barely produced directly in the ISOLDE target, by use of in-trap decays, i.e. capturing the recoiling daughter nuclides from the corresponding beta-decaying precursor nuclides [33].

(4) The precision Penning trap for mass measurements of high accuracy. This is achieved by determination of the cyclotron frequency $\nu_C = qB/(2\pi m)$ of the ion of interest in a homogenous magnetic field $B$ and comparing it to the cyclotron frequency of a reference ion with well-known mass. These measurements are based on the time-of-flight ion-cyclotron resonance (ToF-ICR) technique [29,34,35] with single rf-pulse-type or Ramsey-type excitation patterns [36]. Excitation times of the ion motion from a few tens of milliseconds [9,37] up to several seconds have been applied, the latter resulting in resolving powers of well over $R = 10^6$ [38] and relative statistical uncertainties down to $\delta m/m = 10^{-8}$ [39]. Recently, the phase-imaging ion-cyclotron resonance (PI-ICR) method [40,41] has been implemented by which even higher resolving powers and lower mass uncertainties can be obtained. Furthermore, the precision Penning trap has provided isomerically pure ion bunches to a decay-station extension which can be mounted downstream as the last component of the setup [42,43].

The present study is focused on the MR-ToF mass analyzer. The insets of Fig. 1 show a cut view of a simplified CAD model of the

![Fig. 1. Schematic overview of the ISOLTRAP setup. For more details, see text. Lower inset: The MR-ToF device composed of the electrostatic mirror electrodes and the in-trap lift. An ion bunch containing different ion species is injected and captured between the mirror electrodes. With increasing storage time the different ions separate. Upper inset: Time-of-flight spectrum of A/z = 57 isobars after 1000 revolutions in the MR-ToF MS. A total of 30773 ion counts were accumulated in 2706 experimental cycles.](image-url)
device, in particular its electrostatic mirrors and the in-trap lift electrode, along with a typical ion spectrum, in this case of several isotopic species of mass number over charge state of $A/z = 57$, including signals from several doubly charged $A = 114$ ions. The next section describes ISOLTRAP’s MR-ToF device in more detail, focusing on its in-trap lift component, which is essential for the new ion-separation technique described in Section 4, along with a summary of the current status of its performance.

3. The MR-ToF in-trap lift technique for ion capturing and ToF focusing

The MR-ToF device is a low-energy electrostatic time-of-flight mass spectrometer, i.e. ions in the $z$ keV energy range, where $z$ is the charge state of the ions, fly from a source to a detector and their flight time $t$ is precisely measured. The flight time depends on the mass-to-charge ratio $t_i \propto \sqrt{m_i/q_i}$ of the ions and on the initial conditions which have a non-zero position and momentum distribution. This initial phase-space spread leads to a time spread $\Delta t$ of the arrival times. By carefully designing and tuning the spectrometer, one can reduce this spread to a minimum, or in other words, increase the mass resolving power $R = m/\Delta m = t/\Delta t$.

To reach higher mass resolving powers one can increase the flight times $t$. This can be achieved by either reducing the kinetic energy or increasing the length of the flight path of the ions. The former often also increases the relative energy distribution and, thus, the time spread, and is therefore limited. The latter increases the dimensions of the time-of-flight setup considerably. This is where the multi-reflection method comes into play: On their way from source to detector, ions are trapped between two electrostatic ion-optical mirrors which leads to folded ion paths that can sum up to several thousand times the length of the physical device, which is usually the order of a meter, see [16] and the references therein for more information about different MR-ToF systems. The electric potential as a function of position between the two ion mirrors is plotted in Fig. 2 for the different states of the MR-ToF lift.

Compared to a single path spectrometer, this MR-ToF method increases the resolving power by several orders of magnitude. It is given as:

$$ R = \frac{m}{\Delta m} = \frac{t}{\Delta t} \approx \frac{1}{2} \frac{t_{\text{transfer}} + nT}{\sqrt{\Delta t_i^2 + \left(\Delta E - nT \frac{\Delta E}{\Delta t_i} \right)^2 + (\Delta m + n \Delta T)^2}}. $$

(1)

Here, $T$ is the revolution period inside the MR-ToF device, $n$ is the number of revolutions and $t_{\text{transfer}}$ the flight time from the ion source to detector without capturing the ions in the MR-ToF MS, i.e. “single path” time from source to detector without reflection between the ion mirrors. The total time-of-flight spread $\Delta t$ consists of several contributions: $\Delta t_0$ is the thermal time spread originating from the turnaround time of the ions in the ion source and defines the lower limit of the total time spread, $\Delta t_2$ is the time spread with respect to kinetic energy gained on the “single path”, $\Delta \delta T/\delta E$ the ToF energy dispersion coefficient, $\Delta \delta T$ the relative kinetic energy spread, and $\Delta T_0$ and $\Delta T_2$ higher order aberrations accumulated outside and inside the MR-ToF MS, respectively.

The point in the flight path and, thus, in the case of an MR-ToF device, the number of revolutions after which the time-of-flight focus occurs, depends on the energy-dependent bunch spread outside the device $\Delta E$, the ToF energy dispersion coefficient, $\Delta \delta T/\delta E$ and the relative kinetic energy spread $\Delta \delta T$. The maximum mass resolving power after a given number of revolutions $n$ can be optimized by tuning $\Delta \delta T/\delta E$, either by adjusting the mirror-potential distribution or the mean kinetic energy of the ions. The latter can be realized by use of a pulsed drift tube i.e. the in-trap lift electrode. In this so called time-of-flight focus, the difference term in the denominator in Eq. (1) becomes minimal and, therefore, the bunch width $\Delta$ is minimized. This leaves only the thermal and higher order aberration dependent time deviations contributing to the total time spread. The interested reader can find a schematic plot of the relative revolution time difference $\Delta t$ as a function of the relative kinetic energy difference $\Delta E$ as Fig. 3 of Ref. [20]. The experimental representation of the same plot is presented as Fig. 3a of Ref. [4] in which the ion flight times are plotted for different potentials of the in-trap lift electrode.

Ion bunches coming either directly from an ion source or, as at ISOLTRAP, from an RFQ trap and are injected into the MR-ToF MS at a kinetic energy high enough to overcome the electric potentials of the entrance mirror electrodes. The ions enter the in-trap lift electrode on a potential $U_{\text{trap}}$ which is chosen in a way that the ions are decelerated to the kinetic energy $E_{\text{trap}} = q \cdot U_{\text{trap}} = q \cdot (U_{\text{source}} - U_{\text{trap}})$ when they enter the tube. During their passage, the in-trap lift potential is switched to a lower value, e.g. ground potential, such that they cannot overcome the mirror potentials any longer. For ion ejection the lift potential is raised back up again during the ion passage. Further details of this technique are given in Ref. [21].

This procedure has several advantages with respect to the more common method where capture and release of the ions is performed by reducing the mirror potentials: The resolving power

![Fig. 2. Electric potential distribution along the axis of the MR-ToF MS during storage (red) and capture/release (black dashed) with an in-trap lift potential of $U_{\text{trap}} = 1070$V. The drawing also indicates the length and positions of the mirror electrodes, the focusing lens and the in-trap lift electrode (grey boxes at the bottom).](image-url)
of an MR-ToF MS is very sensitive to mirror-voltage fluctuations. Therefore, a dynamical change of the mirror potentials during ion trapping should be avoided, which would require a voltage stabilization time on the order of a microsecond that is so far not achievable for commercial high-voltage-power supplies. In contrast, the in-trap lift can be switched to ground potential via a low impedance which eliminates any voltage variations on this electrode. The mirror voltages stay active and unchanged. In addition, as already mentioned above, with the in-trap-lift voltage, i.e. one single parameter, the time-focus position can be tuned to be at the position of the ion detector or an ion gate for mass measurements or separation, respectively.

This is demonstrated in Fig. 3 where the mass resolving power $R$ of ISOLTRAP’s MR-ToF MS is plotted as a function of the in-trap lift potential $U_{\text{lift}}$ for several revolution numbers. The measurements have been performed with $^{39}\text{K}$ and $^{133}\text{Cs}$ ions supplied by ISOLTRAP’s offline ion source via the RFQ trap mentioned above. For any number of revolutions two local maxima of $R$ are found. These are due to two different regions in which the ToF energy dispersion coefficient fulfills the condition to minimize the difference term in the denominator in Eq. (1). Fig. 4a shows both the maximum resolving powers achieved as a function of the number of revolutions as well as the corresponding lift voltages. Fig. 4b shows the relation between $R$ and $U_{\text{lift}}$ for this particular experiment.

In the case of ISOLTRAP’s MR-ToF device, mass resolving powers of up to $R_{\text{FWHM}} = 3 \times 10^4$ have been achieved [16]. In the next section the selection of a specific ion species, in particular by the new ion-separation technique, will be discussed.

4. Mass selection by in-trap lift switching

Instead of a detector an ion gate can be placed at the time-focal point (or rather the lift voltage can be tuned to place the time-focal point at the position of the ion gate). Thus, specific ion species of interest can be selected as the ion bunches of the different species pass the ion gate at different times. As already pointed out a Bradbury-Nielsen gate (BNG) is often used for this purpose as this device produces a well-defined, spatially limited deflection region, allowing to manipulate nearby ion bunches independently. A BNG consists of two sets of thin, parallel metal wires arranged in a plane, which are on the same electric potentials when the gate is “open” but on alternating polarity when it is “closed”. In the latter case the passing ions are deflected and thus removed from the beam axis. The time resolution of this device is typically in the order of just a few 10 ns. However, the ions’ energy, spatial and angle distributions in conjunction with the small deflection angles achievable at high kinetic energies can limit the suppression of the unwanted ions. In the following, the new method it is presented which is based on the selective ejection of the ions of interest while the unwanted are blocked by the potential barrier of the mirrors. This technique makes use of only the in-trap lift, i.e. it is not based on a further device such as an ion-gate or deflector.

The ion injection into the MR-ToF device is performed as described in the previous section, i.e. initially the in-trap lift is on a high potential during the injection period $t_\text{inj}$, see Fig. 5. When the ions are within the in-trap electrode ($t_b$), it is switched to the storage potential (ground) for the duration $t_b$. The moment $t_{\text{center}}$ marks the point in time at which the ions have spent a certain number of full revolutions between the mirrors, i.e. are flying in the direction of the detector and are at the center of the lift electrode. For simplicity, we assume in the following that there are only two ion species one of which is to be selected.

The time of ejection $t_b$ can be shifted to only eject one or the other ion species. If the lift is operated early (“early switching”) such that only the first, i.e. leading, ion bunch has entered the lift when its potential is increased, only the first bunch will gain enough energy to leave the MR-ToF mass analyzer, while the second bunch is reflected (or lost as the trapping conditions may no longer be fulfilled). Similarly, if the lift is operated late (“late switching”) ions that are in front have already left the lift and are not ejected towards the detector as the second, i.e. the trailing, bunch, see Fig. 5b. The ions that are cut off by early and late switching have either a somewhat higher or lower mass-of-charge ratio $m/q$, respectively, or may have larger $m/q$ differences such that one species has already overlapped the other during the storage time. Fig. 6 gives an experimental example of the latter to demonstrate the principle of lift separation with a color-coded time-of-flight plot where the ToF spectra (flight time from application of ejection pulse to ion-arrival time at the detector, $x$-axis) are shown as a function of the ejection-pulse timing ($y$-axis): Ions of the two stable rubidium isotopes were injected and stored for about 7 ms. The $^{85}\text{Rb}^+$ ions had performed 343 revolutions while the heavier $^{87}\text{Rb}^+$ ions were 4 revolutions behind. Depending on when the lift was activated, either early or late, only the corresponding isotope in the lift during the switching made its way to the detector.

In more detail, the time difference between the two ion species’ centroid positions was about 400 ns at the position of the detector, with $^{87}\text{Rb}^+$ being first (at about 7631.8 µs) and $^{85}\text{Rb}^+$ appearing later (at about 7632.2 µs) although it has to be added that in this particular case the ions were actually about 180 ns further away from each other at the time of the lift switching. From about $t_b - t_{\text{center}} = -3.6$ to $-3.35$ µs the $^{87}\text{Rb}$ peak is significantly disturbed by the switching of the lift voltages but from $t_b - t_{\text{center}} = -3.35$ to $-3.15$ µs onwards the $^{87}\text{Rb}$ ions are ejected towards the detec-
tor undisturbed until also the $^{85}\text{Rb}$ ions start entering the drift tube (t$_b$-t$_{center}$ = −3.15 to −2.8 µs). Both ion species are ejected towards the detector undisturbed for times t$_b$-t$_{center}$ = −2.8 to about 2.8 µs. If t$_b$ is further delayed with respect to t$_{center}$, the leading ion bunch begins to enter the fringe field towards the mirror electrodes and thus gains not the full energy and is thus not properly ejected (t$_b$-t$_{center}$ = 2.9–3.25 µs). The $^{87}\text{Rb}$ ion bunch is spread over several microseconds until no $^{87}\text{Rb}$ ions reach the detector any longer and only the $^{85}\text{Rb}$ ion bunch remains undisturbed (t$_b$-t$_{center}$ = 3.25–3.45 µs). Delaying t$_b$ even more also leads to the $^{85}\text{Rb}$ ion bunch being improperly ejected and subsequently lost (t$_b$-t$_{center}$ = 3.45–3.70 µs). Time-of-flight spectra for the different cases are presented as insets in Fig. 5. Corresponding to (from top to bottom) t$_b$-t$_{center}$ = 3.33 µs (late switching), t$_b$-t$_{center}$ = 0 µs (no selection) and t$_b$-t$_{center}$ = −3.22 µs (early switching).

To determine the suppression that is possible with the technique, data was taken for about 20 min accumulating 20,000 experimental cycles, using a t$_b$-t$_{center}$ = 3.33 µs to only transmit $^{85}\text{Rb}^+$ to the detector. In that time about 250,000 $^{85}\text{Rb}$ ions were detected but no $^{87}\text{Rb}^+$ implying about 100,000 $^{87}\text{Rb}$ ions (assuming the natural abundance ratio, which was validated for the data taken at the time t$_{center}$) were suppressed by the late switching of the in-trap lift.

Early or late switching are sufficient for the selection of a species out of an arbitrary ensemble, as long as it is the first or the last entering the lift, respectively. For the selection of an ion species that is sandwiched between two others, both the activation t$_a$ as well as the deactivation time t$_d$ of the lift are important (Fig. 7a). By late switching the earlier ions are cut off and, in addition, by carefully choosing the duration t$_c$, also later ions can be removed from the ejected bunch (Fig. 7b).

This is experimentally demonstrated in Fig. 8 were for different activation durations t$_c$ of 1000 ns, 500 ns, 400 ns and 250 ns the time t$_b$ was varied. Below a t$_c$ of about 500 ns either one or the other ion bunch is ejected (or none, but never both). t$_c$, can be chosen as short as 250 ns for selected ion ejection. At such ejection-pulse length, however, the ion cloud of interest itself is disturbed significantly as evident from the ToF distribution (Fig. 8d). This could, in principle, influence the subsequent Penning trap measurements. However, the timing for capturing of the ions and the deceleration elements to reduce the ions kinetic energy can be adapted to the new ion-bunch characteristics. Similarly, subsequent decay experiments are not influenced significantly but rather profit from the higher level of sample purity. The maximum number of counts for each ion peak is for all chosen ejection windows t$_c$, the same which means that all ions can be transmitted. Only for t$_c$ = 250 ns the number of counts is reduced by about 10%.

The smaller the time window t$_c$, the closer two ion species can be to still selectively transfer only one of the two ion bunches.

The effective resolving power for separation that can be achieved presently with the method is given by the width (t$_b$-t$_{center}$) of the disturbed ion peaks in Fig. 8 which is around 200 ns. This value is on the one hand given by the flight time through the fringe-field region formed by the in-trap lift electrode and the adjacent electrode, which is determined by their distance and electrode diameters, and on the other hand by the rise and fall times of the high voltage switch. For the case of ions with mass to charge ratio $\lambda$z = 39 after 2000 revolutions (around 30 ms total flight time) in the MR-ToF MS, an expected resolving power for separation of 75,000 should be achievable with this method.

### 5. Online applications of mass-selective ion ejection

The following measurements illustrate the benefit of the new ion selection method: Section 5.1 highlights the “late switching” technique by removing ions of an isobaric molecular sideband for subsequent precision Penning-trap mass measurements of $^{156}\text{Dy}$, and in Section 5.2 the selection of $^{61}\text{Cr}$ ions ($t_{1/2}$ = 243 ms) from...
close-lying lighter and heavier isobars with the refined late switching technique is presented. Finally, in the example of Section 5.3, combinations of ion species were selected and forwarded to the Penning traps to test the implementation of the new PI-ICR technique [40,41] at the ISOLTRAP setup.

5.1. Purification of $^{156}$Dy$^+$ from isobaric molecular sidebands

Prior to the 2014 on-line measurement campaign, data was taken to re-commission the ISOLTRAP setup after extensive maintenance work performed during the long shut-down period of the CERN accelerators in 2013/2014. A time-of-flight spectrum of $A/Z = 156$ nuclei from that time is shown in Fig. 5a, in which 4000 experimental cycles are accumulated. The lighter oxides $^{140}$Ce$^+$ and $^{140}$Nd$^+$, surface ionized in the ISOLDE target unit, were removed with the help of the in-trap lift by use of the late switching method as described above. This left only the $^{156}$Dy$^+$ ions in the spectrum which were ionized with a Resonance Ionization Laser Ion Source (RILIS) scheme [44]. The mass resolving power ($R = \Delta m/m$) of the time of flight spectrum was 90,000, and the time-of-flight difference between the molecular double-peak that was removed and the ions of interest was about 2 $\mu$s which is well above the necessary separation time of 200 ns as shown above. Thus, the ToF difference was sufficient to selectively address only the wanted ions for ejection from the MR-ToF MS. The purified $^{156}$Dy$^+$ ion bunches were

![Diagram of timing and ion switching](image)

**Fig. 7.** a) Timing diagram of the refined late switching of the in-trap lift electrode between the two potentials and b) the position of three ions in the MR ToF MS at the moment $t_b$ and $t_c$. Only the second ion is transmitted. For more details, see text.

![Diagram of color-coded plots](image)

**Fig. 6.** Color-coded plot of time-of-flight spectra of $^{87}$Rb$^+$ (339 revolutions) and $^{85}$Rb$^+$ (343 revolutions) for different switching times $t_0$ of the in-trap lift voltage with respect to the time $t_{\text{center}}$ (see text). The insets show the time-of-flight spectra for late (top, only $^{85}$Rb$^+$ signal), center (both species) and early (bottom, only $^{87}$Rb$^+$) switching of the potential lift. For each spectrum, the data of 20 experimental cycles was accumulated.

![Diagram of color-coded plots](image)

**Fig. 8.** Color-coded plots of time-of-flight spectra (x-axis) of $^{87}$Rb$^+$ (339 revolutions) and $^{85}$Rb$^+$ (343 revolutions) for different switching times $t_0$ of the in-trap lift voltage with respect to the time $t_{\text{center}}$. Beginning from the top with $t_\ell = 1 \mu$s the parameter is varied down to $t_\ell = 0.25 \mu$s. The total number of counts for $^{85}$Rb$^+$ and $^{87}$Rb$^+$ in each spectrum is displayed on the right side. For each spectrum, the data of 200 experimental cycles was accumulated.
forwarded to the Penning-trap setup, where two ToF-ICR measurements could be performed. An ion accumulation time in the RFQ of only 300 μs was used to avoid space-charge effects and thus shifts of the flight times of the ion species [45]. The average count rate of \(^{156}\text{Dy}^+\) was only 0.2 ions per experimental cycle. Thus, the preparation Penning-trap stacking technique was employed [46] to reduce the time needed to perform the ToF-ICR measurement by an order of magnitude. One of the ToF-ICR resonances is shown in Fig. 9b where each color coded square represents how many ions were counted at the indicated arrival time and excitation frequency. This representation of the resonance shows that at the center of the resonance all ions have been excited, as evident from their ToF times from Penning trap to detector of well below 500 μs. This means that the cleaning process was successful and no unwanted ions were forwarded to the precision Penning trap. The ratio of the cyclotron frequencies of \(^{133}\text{Cs}^+\) to \(^{156}\text{Dy}^+\) \((r = V_{\text{Cs}}/V_{\text{Dy}})\) was determined to be 1.173197792(41) which results in a mass excess of \(^{156}\text{Dy}^+\) of ~70525.4(5.1) keV. The atomic mass of \(^{133}\text{Cs}\) that was used is \(m_{\text{133Cs}} = 132905451.961(9)\) μs and was taken from the Atomic-Mass Evaluation [47]. The measured mass excess agrees well with the value reported in the literature [48] and adopted in the AME2012.

5.2. Purification of \(^{61}\text{Cr}^+\) from multiple isobaric contaminations

Another case in which isobar separation and subsequent cleaning was necessary was encountered at \(A/2 = 61\) where \(^{61}\text{Cr}^+\) as the ion of interest was sandwiched between the highly abundant molecules \(^{45}\text{Sc}^{16}\text{O}^+\) and \(^{42}\text{Ca}^{19}\text{F}^+\) and the less abundant, doubly charged \(A = 122\) ions, as evident after 1000 revolutions in the MR-ToF MS, see Fig. 10a. All ion species but the chromium were surface ionized as an inevitable result of the necessarily high temperatures of the ISOLDE target and transfer line. \(^{61}\text{Cr}^+\) was ionized by use of the RILIS at ISOLDE [49]. To separate the \(^{61}\text{Cr}^+\) component from the \(^{42}\text{Ca}^{19}\text{F}^+\) ions, a mass resolving power of about \(R = 30,000\) is needed. In Fig. 10b time-of-flight spectra of successive measurement cycles are shown, i.e. as in Fig. 6 and 8 horizontal slices represent individual spectra. Within the data-acquisition duration for these spectra \(t_d = t_{1000}\) \((t_{1000}\) being the time needed for \(^{61}\text{Cr}^+\) to travel 1000 revolutions in the MR-ToF MS) \(t_c\) were progressively adjusted to 2.3 μs and 0.65 μs, respectively. This led to ejection and detection of only \(^{61}\text{Cr}^+\) which was then sent to the precision Penning trap for the ToF-ICR mass measurement. The mass data collected along the chromium isotopic chain \((A = 52–63)\) will be presented elsewhere [50].
5.3. Test-sample preparation for setup development and commissioning

The last example shows how either $^{152}\text{Dy}^+$ (RILIS ionized) or combinations of ionic molecular isobars $^{130}\text{Ce}^{16}\text{O}^+$, $^{136}\text{Pr}^{16}\text{O}^+$, and $^{136}\text{Nd}^{16}\text{O}^+$ (surface ionized) can be separated. The time-of-flight spectrum of the beam after 1000 revolutions in the MR-ToF MS is shown in Fig. 11a. In Fig. 11b five different regions can be identified for different combination of ion-species selection. In the following $\tau_{1000}$ refers to the time that is needed for centering $^{152}\text{Dy}^+$ in the in-trap lift after 1000 revolutions. In case of region (i) ($\tau_s - \tau_{1000}$ = 0 μs and $\tau_c$ = 100 μs) all ions were transferred, in region (ii) ($\tau_s - \tau_{1000}$ = 4.3 μs and $\tau_c$ = 3 μs) only $^{152}\text{Dy}^+$, region (iii) ($\tau_s - \tau_{1000}$ = 2.0 μs and $\tau_c$ = 2 μs) the oxides of $^{130}\text{Ce}^+$, $^{136}\text{Pr}^+$ and $^{136}\text{Nd}^+$, region (iv) ($\tau_s - \tau_{1000}$ = 2 μs and $\tau_c$ = 1 μs) only $^{136}\text{Ce}^+$ and finally in region (v) ($\tau_s - \tau_{1000}$ = 2.7 μs and $\tau_c$ = 1.5 μs) $^{136}\text{Pr}^+$ and $^{136}\text{Nd}^+$ oxides were transferred to the detector. The different combinations of ions were subsequently used to test the new PI-ICR technique at the ISOLTRAP setup, to be published elsewhere.

6. Conclusion and outlook

The in-trap lift technique offers not only an easy and convenient way to inject and eject ions into/from the MR-ToF mass analyzer and to adjust the position of the time focus on a detector, but can also be used to selectively eject specific ion bunches after their spatial separation due to the mass-dependent ion velocities. Thus, mass selection is achieved with no additional device. This new method allows to separately eject species as close as 0.2 μs to another species and at the same time reaches a high level of suppression of the unwanted ion species.

The technique has been successfully demonstrated and applied in various offline and online measurements. Actually, it is currently the standard mode of ion selection of the MR-ToF component of ISOLTRAP. The method can be extended to improve mass measurements using species with large mass differences and would thus, for a given number of revolutions, not be ejected simultaneously. However, for accurate time-of-flight mass measurements, the ions must travel the same path and therefore the same number of revolutions. A selective ejection, while keeping the other ions still trapped in the device and ejecting them later, i.e. after they have reached the same number of revolutions, would allow using even ions further apart in mass as reference ions. This can be achieved by waiting until the ions which are not to be ejected are in the mirror electrodes, or by dividing the in-trap lift electrode into shorter pieces and using just such a small section for selective ejection.

Also, once the ion species are separated unwanted ions could be selectively ejected via voltage switching of the in-trap lift, thus leaving the ions of interest further trapped and no longer subjected to, e.g. unwanted space-charge phenomena.

The selectivity of the method can be further increased if the MR-ToF MS is tuned (using the in-trap lift) such that time focal point is not on the detector but in region of the fringe field which is used for the selection.

Finally, as for the ion injection into the MR-ToF device, it should be noted, that also the end of the timing of the lift activation for ion capture, i.e. the end of activation $\tau_s$ and its length $\tau_c$ (and, thus, also the time of the beginning of this pulse) can be chosen according to the purpose of the succeeding measurement. These timings can be adjusted to only capture ions of a certain mass range, provided they come from a pulsed source and have undergone a flight-time dispersion, as in the case of ISOLTRAP’s RFQ cooler and buncher. This can be particularly useful when, e.g., molecular ions are either formed or broken up in the RFQ’s high-pressure buffer-gas environment, or when the ions of interest come with heavier and/or lighter contaminant ion species from ISOLDE.

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References

Improved stability of multi-reflection time-of-flight mass spectrometers through passive and active voltage stabilization

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Abstract

Multi-reflection time-of-flight (MR-ToF) spectrometers are devices in which ions are reflected between two electrostatic mirrors to prolong their flight path. The performance of the apparatus relies on the stability of the voltages that are used to define the mirror potentials. Especially the voltage of the mirror electrodes at the point where the ions reverse the direction of their axial motion needs to be stable in order to minimize fluctuations of their total flight time. Here we present a method to increase the short- and long-term stability of suitable voltage supplies for enhanced performance of the spectrometer.

Keywords: Voltage stabilization, Multi-reflection time-of-flight mass spectrometry, MR-ToF MS, short-lived nuclides, ISOLTRAP

1. Introduction

Recently, multi-reflection time-of-flight mass spectrometers (MR-ToF MS) gained high attention as these table top devices allowed the extension of the flight path of the ions to reach mass resolving powers \( R = \frac{m}{\Delta m} \) on the order of \( 10^5 \) in only a few milliseconds [1–5]. This makes the devices suitable for various studies in molecular physics [6–8], cluster physics [9–12] and nuclear physics [13–15].

At the ISOLTRAP experiment [16, 17], located at the ISOLDE facility at CERN [18], the MR-ToF device has been used to determine the masses of short-lived as well as stable ion-beam constituents with high precision for many physics topics, such as nuclear structure [13, 19–22], nuclear astrophysics [23, 24], and to support high precision measurements of decay energies for neutrino physics [25]. In addition to mass spectrometry, the MR-ToF MS also provided purified samples for decay spectroscopy [26, 27] and, in combination with the Resonant Ionization Laser Ion Source (RILIS) of ISOLDE [28], assisted measurements of nuclear moments and charge radii with background suppression [29–32]. The fast-identification capabilities also make the MR-ToF device a very attractive tool for target and ion-source optimization and ion-yield determination [33]. Improvements of the performance and the reliability of the spectrometer will have direct implications to many experimental set-ups exploiting MR-ToF devices. In this paper we demonstrate a method to increase the MR-ToF MS performance with respect to the stability of the mass resolving power by employing passive and active voltage stabilization.

2. Experimental setup and procedure

The measurements were performed with a part of the ISOLTRAP setup which has been described in Refs. [1, 2] and is shown in Fig. 1. The RFQ cooler and buncher [34] is used to capture, cool and bunch the continuous ion beam from the offline alkali ion source which delivers singly charged stable rubidium and cesium isotopes. The ions are subsequently captured into and later ejected from the MR-ToF device by use of the in-trap lift technique [1, 35]. Once extracted from the MR-ToF apparatus, they are detected by employing a
MagneTOF secondary electron multiplier ion detector\textsuperscript{1} and a multichannel scaler\textsuperscript{2}.

The voltages for the mirror electrodes of the MR-ToF device range from about \( -4 \) kV to about 4 kV and are supplied by an EHS 8240x voltage module\textsuperscript{3}. It is specified to have voltage ripples of less then 5 mV for frequencies higher then 10Hz and a temperature coefficient of 10 ppm/K. The output of the power supply can be set with a resolution of 8 mV.

Since the stability of the total time of flight depends on the stability of the voltages applied to the mirror electrodes (see Fig. 9 in Wolf et al. \cite{36}), it is of utmost importance to find voltage sources stable enough or, alternatively, to stabilize a given voltage source adequately.

The stability of the power supplies connected to the ion optics of the components in front and behind the MR-ToF device (buncher ejection optics, MR-ToF injection and ejection optics) are influencing the stability of the ion time of flight as well but much less significantly compared to the mirror electrode 5. For this electrode’s voltage Fig. 2 shows a strong correlation with the ToF of \(^{85}\text{Rb}\) ions after 1000 revolutions in the MR-ToF MS. This suggests that it has the most significant impact on the observed ToF fluctuations, as already suggested in \cite{36}: The voltage of mirror electrode 5 determines the voltage gradient at the point where the ions reverse their axial motion, i.e. the ions turn around and are reflected towards the opposite mirror stack. Thus they are most sensitive to slight changes of this electrodes electrical potential.

Figure 2 also shows the temperature in the laboratory as a function of time. No correlation is visible. For longer time scales, temperature changes are likely to have an influence on the device (the power supplies and the mechanical setup) but the involved time constants may be large so that a delayed reaction seems to manifest itself only later.

To improve the short- and long-term voltage stability, a passive electric low-pass filter together with an active software-based\textsuperscript{4} proportional-integral (PI) regulation was implemented. The principle is shown in the schematic drawing of Fig. 3.

For the precise measurement of the voltage on mirror electrode 5, a high precision 8.5 digit multimeter\textsuperscript{5} is used in combination with a precision high voltage divider\textsuperscript{6}, which reduces the input voltage by a factor 1000 with a total impedance of 50 M\(\Omega\). The internal resistor chain has a temperature coefficient of less then 5 ppm/K but to avoid any drifts due to the changes of the environment temperature, the divider box was temperature stabilized to about \( \pm 5 \) mK by use of a Peltier element.

\textsuperscript{1}DM291, ETP, Ermington, Australia
\textsuperscript{2}MCS6, Fast ComTec, München, Germany
\textsuperscript{3}ISEG, Dresden, Germany
\textsuperscript{4}LabVIEW, National Instruments, Austin, USA
\textsuperscript{5}Keithley 2002, Keithley Instruments, Solon, USA
\textsuperscript{6}KV-30A, Ohm-Labs, Pittsburg, USA
which was PI-regulated as well. The multimeter was
used in the 20 V range where it can measure with a res-
olution of 1 µV in 20 ms.

For the low-pass filter, a resistance of $R = 1 \, \text{M} \Omega$ and
a capacitor of $C = 40 \, \text{µF}$ were used. That results in a
time constant of $\tau = R \cdot C = 40 \, \text{s}$ and a cut-off fre-
quency as low as $f_c = 1/(2\pi\tau) \approx 4 \, \text{mHz}$. The low-pass
filter thus suppresses mid- and high- frequency fluctu-
ations which is important since one revolution of ions
with mass $A = 85$ in the MR-ToF device takes about
22.2 µs. On this time scale we cannot correct the fluctu-
ations with the PI-regulation since we cannot measure
the voltage fast enough with the necessary precision.

For 1000 revolutions in the device the rubidium ions
need about 22.2 ms. Fluctuations on this time scale can
be corrected with the PI-regulation.

Employing low-pass filters with large time constants to
stabilize the potential of electrodes is in many appli-
cations impractical since it makes the optimization or
scanning of the potential in-feasible. In this contexts
the PI-regulation offers a simple solution in which the
desired voltage can be reached much faster.

3. Results and Discussion

The improvement of the voltage stability of the MR-
ToF MS impacts both the resolving power of the appar-
atatus and the accuracy of mass measurements, especially
when the reference ToF values (used for calibration) are
not recorded in the same spectrum as the ions of interest,
i.e. when the references are not isobaric contaminants
of the latter. In this section, both aspects of this develop-
ment will be discussed.

3.1. Enhancement of resolving power

For the first tests of the voltage stabilization, the dif-
derence in adding the low-pass filter to the circuit was
determined while utilizing the PI-regulation to suppress
deeper fluctuations. To this end, the voltage of the in-
trap lift was varied to determine the time focal point of
the ion distribution at the position of the ion detector.
This corresponds to the maximal mass resolving power
attainable for a given number of revolutions, in this case
1000 revolutions in MR-ToF MS, see Fig. 3 in Wolf
et al. [2]. The result is presented in Fig. 4. The meas-
urements were performed with $^{85}\text{Rb}$ and for each spec-
trum, 300 experimental cycles, corresponding to about
500 ions, were accumulated.

By employing the low-pass filter and thus attenuat-
ing voltage fluctuations, a 30 % higher mass resolving
power could be reached. The mass resolving power was
determined for each voltage step by fitting a Gaussian
profile to the time-of-flight distribution. The relevant
parameters of the fit used to describe the mass resolv-
ing power as a function of the in-trap lift voltage (again
described by a Gaussian) can be found in Tab. 1. The
slightly shift of 2.90(63) V between the optimal in-trap
lift voltage is probably due to a slight shift of the high-
voltage (HV) power supplies of the HV-platform of the
buncher, i.e. the slightly different initial ion energy be-
tween the measurement series.

![Figure 4: Mass resolving power for different in-trap lift voltages with and without the low-pass filter and an activated PI-regulation. For details see text.](image)

<table>
<thead>
<tr>
<th>no low-pass</th>
<th>with low-pass</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Centroid</strong></td>
<td>1071.90(35) V</td>
</tr>
<tr>
<td><strong>Width</strong></td>
<td>33.41(97) V</td>
</tr>
<tr>
<td><strong>$R_{\text{max}}$</strong></td>
<td>111.1(4.2)k</td>
</tr>
</tbody>
</table>

Table 1: Parameters of the Gaussian fits of Fig. 4.

Similar measurements as the one shown in Fig. 2
were performed to determine the fluctuations with and
without low-pass filter, with and without activated PI-
regulation. Figure 5 shows a measurement for 1 h us-
ing $^{85}\text{Rb}$ ions after 1500 revolutions in the MR-ToF MS
with the low-pass filter but without PI-regulation.

One can see that compared to Fig. 2 the short-term
fluctuations are reduced but there are still drifts. The
correlation to the mirror electrode 5 voltage is still ap-
parent. If the PI-regulation is added, see Fig. 6, again
for a 1h measurement of $^{85}\text{Rb}$ ions after 1500 revolu-
ions in the MR-ToF MS with about 150-200 ions from
50 experimental cycles, the long-term drifts are reduced
as well.

Now that the main source of the fluctuations is elimi-
nated, the next to leading order fluctuation becomes ap-
parent in the ToF, see Fig. 7. The figure includes the
change of the temperature in the laboratory but obviously, there is no correlation with the remaining voltage fluctuations. Most probably, those originate from the voltage source connected to the neighboring mirror electrodes which are supplied by another channel of an EHS 8240x module.

The relative stability for the different scenarios is summarized in Tab. 2. An improvement of about a factor of 4 has been achieved.

To further characterize the improvement, the Allan deviation [37] for the data presented in Fig. 2, 5 and 6 was determined (Fig. 8). The Allan deviation is a two-sample deviation formed by the average of the squared differences between successive values of a repeatedly measured quantity taken over sampling periods from the measuring interval up to half the maximum measurement time [38, 39]. In comparison with the commonly used standard deviation, the Allan deviation is based on measurement to measurement deviation rather than on individual measurement to mean measurement deviation.

The difference compared to using no low-pass and no PI-regulations is clearly visible. The black curve in the left plot of Fig. 8, where the Allan deviation of the voltage measurements are shown, shows a behavior that is compatible with white phase noise \( \sigma(\tau) \propto \tau^{-1} \) for \( \tau \geq 1 \) s.

This performance improvement of the MR-ToF device can be translated to how long it is able to sustain a certain mass resolving power. This is particularly important when for extended times a purification of the ion distribution shall be applied after the time-of-flight separation, e.g. when delivering a isotopically or isobarically clean beam to a subsequent apparatus for further investigation. To illustrate this, the data presented in Fig. 5 and 6 was used and single time-of-flight spectra were added iteratively. After each addition, the mass resolving power of the resulting ion peak was determined as plotted in Fig. 9. Note that the number of revolutions was chosen to be 1500 which translated to an increased mass resolving power compared to data used in Fig. 4 were the ions traveled for only 1000 revolutions in the MR-ToF device.

Note that the number of revolutions was chosen to be 1500 which translated to an increased mass resolving power compared to data used in Fig. 4.

Table 2: Relative stability of the voltage and the ToF for the measurements presented in this manuscript. The values are representing the standard deviation of the measurement series divided by its mean.

<table>
<thead>
<tr>
<th></th>
<th>no filter, no PI</th>
<th>filter, no PI</th>
<th>filter and PI</th>
</tr>
</thead>
<tbody>
<tr>
<td>ToF drift</td>
<td>1.5 ppm</td>
<td>1.1 ppm</td>
<td>0.35 ppm</td>
</tr>
<tr>
<td>voltage drift</td>
<td>2 ppm</td>
<td>1.8 ppm</td>
<td>0.53 ppm</td>
</tr>
</tbody>
</table>
The time-of-flight/mass relation of the apparatus is generally of the form:

\[ t = a \sqrt{m_i} + b, \]  
(1)

where \( m_i \) is the ion mass and \( a \) and \( b \) are device parameters, of which \( a \) depends also on the number of revolutions at which the measurement is performed and \( b \) incorporates mass-independent offsets, such as electronics or switching delays.

For a mass determination one thus performs three ToF measurements, one for the ion of interest, \( t_x \), and two other for ion species of well-known mass, \( t_{1,2} \). From this, the unknown (ionic) mass \( m_{ix} \) is determined as [13]:

\[ m_{ix}^{1/2} = C_{TOF} \Delta_{Ref} + \frac{1}{2} \Sigma_{Ref}, \]  
(2)

where \( \Delta_{Ref} = m_{ix}^{1/2} - m_{i1,2}^{1/2} \), \( \Sigma_{Ref} = m_{i1}^{1/2} + m_{i2}^{1/2} \) and \( C_{TOF} \) is the so-called TOF constant:

\[ C_{TOF} = \frac{2t_x - t_1 - t_2}{2(t_1 - t_2)}. \]  
(3)

Drifts in any parameter affecting the ion ToF induce a drift of the value of \( a \) between the moments at which \( t_1, t_2 \) and \( t_x \) are measured, which leads to mass-measurement errors. At ISOLTRAP, the leading-order effects originate from the drifts of the MR-ToF MS voltages outlined so far and from the periodic effect of the RF field of the cooler-buncher, which produces a variation of the ion ToF with the phase of the RF field at the moment of ejection as displayed in Fig. 10.

The improvement with PI-regulation on the overall stability translates to a constant overall time-of-flight of the ions in the device. That implies that a high mass-resolving power of \( 2.5 \times 10^5 \) can be maintained for more than one hour (red curve in Fig. 9). When the PI-regulation was off (blue curve in Fig. 9) the mass-resolving power fluctuated and dropped significantly (by about 50 %) in the last 20 minutes of this measurement.

### 3.2. Enhancement of mass-measurement accuracy

Mass measurements with the MR-ToF MS of ISOLTRAP have been reported already in a number of publications [13, 22, 24, 25, 40].
To circumvent these problems, in all reported ISOLTRAP measurements at least one of the two references was an isobar of the ion of interest, belonging to the sameToF spectrum. This measurement approach has two advantages: first, the isobaric reference will be measured at the same time as the ion of interest and hence not be affected by a systematic drift of $a$; second, it will be very close in mass to the ion of interest and hence carry most of the weight of the two references, minimizing the impact of any possible voltage drift before the measurement of the second reference is performed.

Nevertheless, this approach also has a series of shortcomings. First of all, the reliance on isobaric contaminants as references goes against the goal of target-ion-source and mass-spectrometer developments which is to provide pure beams of radioactive isotopes. Second, of all, isobaric contaminants can’t often be unambiguously identified, case in which the approach is to determine their mass first using Penning-trap mass spectrometry, before passing to the MR-ToF mass measurement, which wastes precious on-line measurement time. Finally, even when present in the spectrum and identified, the isobaric contaminants are most of the time much more abundant than the ion of interest and require limiting artificially the ion rate through of the MR-ToF MS in order to avoid saturation effects of the detector and the data acquisition or Coulomb effects.

All these aspects make the use of well-known, off-line references highly desirable on the long term. This, however, makes the voltage stability of the MR-ToF MS a critical aspect which directly impacts its accuracy. Consequently, a study of the accuracy of MR-ToF MS measurements when using only off-line references was performed, in connection to the reported improvement of voltage stability.

Such a accuracy measurement is performed in a cycle of three subsequentToF recordings, one for each reference species and, in between, one for the ion of interest. In this study, the mass of $^{87}\text{Rb}$ was measured with $^{85}\text{Rb}$ and $^{133}\text{Cs}$ as references and then compared to the literature value. All masses where taken from the AME2016 [41].

In order to minimize the impact of the RF field of the cooler-buncher on the ToF of the ions, the buncher was operated in phase-locked mode. This means that the RF generator is triggered, with fixed initial phase, and is stopped close to the moment of ion ejection. This ensures that between different ion bunches of the same mass, the ToF shift due to the RF phase has the same magnitude and the same direction, which solves the issue of ToF stability. However for ions of very different mass, because of different transport times in the buncher extraction section, the shift can have different magnitude and even sign. This latter aspect poses a serious issue for mass measurements.

In order to solve this latter problem one exploits the fact that the stopping of the RF field is not instantaneous, due to the energy stored in the RF system, electrodes and resonance circuits. The electric field amplitude decreases exponentially with a time constant of $\tau = 8.7\,\mu s$. In order to minimize the effect of the RF field on the ion ToF, the RF field is thus switched off before the extraction of the ions. The exact time difference between the end of the RF gate and ion extraction is optimized to be as large as possible, without sacrificing ion count rate [42].

The timing pattern is schematically displayed in Fig. 11.

![Figure 11: Schematic of the timing pattern of the ion preparation in the ISOLTRAP buncher and amplitude of the RF field during the ion extraction. During the decrease of the RF amplitude, the ion cloud expands.](image)

The weaker electric RF field at the moment of ion extraction leads to a strong reduction of the ToF dependence on the RF phase as can be seen in Fig. 12. Finally, in order to average out any remaining effect, during each ToF measurement the buncher holding time is scanned in steps of 25 ns over an integer number of RF periods (in our case, the frequency was 1.405 MHz). This effectively translates to a scan of the last RF phase seen by the ions at extraction, as the initial phase is fixed. This alone would not have been a sufficient remedy without optimizing the RF stopping time, because the RF field produces an out-of-phase oscillation of both ion ToF and count rate, which when averaged over many phases leads to a ToF bias with respect to the correct value (as shown in [42]).

With this preparation of the RFQ cooler-buncher, the accuracy of MR-ToF mass measurements was tested with the PI loop off and on. The results of many consecutive measurements performed without the PI regulation are presented in Fig. 13 as difference between the determined mass of $^{87}\text{Rb}$ and the AME2016 value.
The ToF measurement for each ion species takes about a minute before changing ion species (which with a moderate ion rate corresponds to about 250-350 recorded ions per peak) in an automated sequence which ensures reproducibility.

One notices first of all that the experimental results scatter around their mean with a standard deviation of about 70 keV, which is significantly larger than the individual statistical uncertainties, as illustrated by the Birge ratio [43] of 2.70. Second, the mean of all results is only about 7 keV away from the AME value. This means that in an on-line experiment a result of very good accuracy can be achieved if enough measurements are performed in order to average all voltage fluctuations. If, however, only a single, or a limited number of measurements can be performed, the systematic uncertainty is given by the standard deviation of the distribution in Fig. 13, so about 70 keV in the case of no PI regulation.

Figure 14 depicts a series of mass measurements performed for the exact same conditions as for Fig. 13, but with the PI regulation on. As the ion ToF is more stable with the activated PI loop, the standard deviation of the scattering around the AME mass value is reduced from 70.3 keV to 40.3 keV. One notices that the average of all results differs from the AME value by about the same amount of ≈7 keV, which suggests that this error originates from other sources than the voltage drifts of the MR-ToF MS. The systematic uncertainty of a single measurement, however, is reduced by almost a factor 2. The reduced Birge ratio of only 1.6 shows that, combining the PI regulation with very short measurements, which reduce the available time for voltage fluctuations (significantly below a minute) and increase the statistical uncertainty, would lead to experimental results scattering with the normal, statistical standard deviation.

4. Summary and Outlook

We have shown that we can stabilize a voltage supply to a level of 0.5 ppm by use of a low-pass filter and a software-based PI controller. This method was applied to the voltage of the most crucial element in an MR-ToF device, the mirror electrode which defines the turn-around point of the ion bunch. Significant improvements in terms of short- and long-term stability were observed which leads to a more stable total flight time of the ions in the MR-ToF device and thus to a mass resolving power which is stable even on time scales of hours. This is particularly useful when a subsequent purification of the ion bunch (using the in-trap lift [1] or a Bradbury Nielsen beam gate [36, 44]) is intended for extended time durations. Also the precision of mass measurements using reference species that are non iso-
baric with respect to the ion of interest is enhanced. It is planned to add a PI-regulation of the voltage which is responsible for the next to leading order fluctuations, in our case the one of the neighbouring electrode.

5. Acknowledgement

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8 Publications and conference contributions

Peer-reviewed publications

1. **Lifting of the trapping potential during ion storage for multi-anion production in a Penning trap**
   F. Martinez, S. Bandelow, C. Breitenfeldt, G. Marx, L. Schweikhard, F. Wienholtz and F. Ziegler

2. **Buffer-gas-free mass-selective ion centering in Penning traps by simultaneous dipolar excitation of magnetron motion and quadrupolar excitation for interconversion between magnetron and cyclotron motion**
   M. Rosenbusch, K. Blaum, Ch. Borgmann, S. Kreim, M. Kretzschmar, D. Lunney, L. Schweikhard, F. Wienholtz and R. N. Wolf

3. **On-line separation of short-lived nuclei by a multi-reflection time-of-flight device**

4. **Recent exploits of the ISOLTRAP mass spectrometer**

5. **New developments of the in-source spectroscopy method at RILIS/ISOLDE**
6. **Collective degrees of freedom of neutron-rich A≈100 nuclei and the first mass measurement of the short-lived nuclide $^{100}$Rb**


7. **Appearance size of poly-anionic aluminum clusters, $\text{Al}_n^{z-}$, $z=2-5$**

F. Martinez, S. Bandelow, C. Breitenfeldt, G. Marx, L. Schweikhard, F. Wienholtz and F. Ziegler


8. **Mass spectrometry and decay spectroscopy of isomers across the Z=82 shell closure**


9. **Masses of exotic calcium isotopes pin down nuclear forces**


*Nature* 498, 346 (2013), DOI: 10.1038/nature12226

10. **Plumbing Neutron Stars to New Depths with the Binding Energy of the Exotic Nuclide $^{82}$Zn**

11. ISOLTRAP’s multi-reflection time-of-flight mass separator/spectrometer
DOI: 10.1016/j.ijms.2013.03.020

12. Isobar separation and precision mass spectrometry of short-lived nuclides with a multi-reflection time-of-flight analyzer
L. Schweikhard, M. Rosenbusch, F. Wienholtz and R. Wolf
DOI: 10.22323/1.194.0011

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14. Competition between pairing correlations and deformation from the odd-even mass staggering of francium and radium isotopes
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DOI: 10.1103/PhysRevC.90.024301

15. Upgrades at ClusterTrap and latest results
F. Martinez, S. Bandelow, Ch. Breitenfeldt, G. Marx, L. Schweikhard, A. Vass and F. Wienholtz
DOI: 10.1016/j.ijms.2013.12.018

16. Ion bunch stacking in a Penning trap after purification in an electrostatic mirror trap
DOI: 10.1007/s00340-013-5702-0

17. Probing the N=32 Shell Closure below the Magic Proton Number Z=20: Mass Measurements of the Exotic Isotopes $^{52,53}$K

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8 Publications and conference contributions


18. Precision mass measurements of $^{129-131}$Cd and their impact on stellar nucleosynthesis via the rapid neutron capture process


19. Delayed bunching for multi-reflection time-of-flight mass separation


20. Towards ultrahigh-resolution multi-reflection time-of-flight mass spectrometry at ISOLTRAP
F. Wienholtz, D. Atanasov, S. Kreim, V. Manea, M. Rosenbusch, L. Schweikhard, A. Welker and R. N. Wolf

Physica Scripta T166, 014068 (2015), DOI: 10.1088/0031-8949/2015/T166/014068

21. Background-free beta-decay half-life measurements by in-trap decay and high-resolution MR-ToF mass analysis
R.N. Wolf, D. Atanasov, K. Blaum, S. Kreim, D. Lunney, V. Manea, M. Rosenbusch, L. Schweikhard, A. Welker, F. Wienholtz and K. Zuber


22. Precision mass measurements of cesium isotopes—new entries in the ISOLTRAP chronicles


23. New laser polarization line at the ISOLDE facility
M. Kowalska, P. Aschenbrenner, M. Baranowski, M. L. Bissell, W. Gins, R. D. Harding, H. Heylen, G. Neyens, S. Pallada, N. Severijns, Ph. Velten, M. Walczak,
24. Penning-trap mass spectrometry and mean-field study of nuclear shape coexistence in the neutron-deficient lead region

25. Nuclear deformation in the $A \approx 100$ region: Comparison between new masses and mean-field predictions

26. Spectroscopy of the long-lived excited state in the neutron-deficient nuclides $^{195,197,199}$Po by precision mass measurements

27. Precision electron-capture energy in $^{202}$Pb and its relevance for neutrino mass determination

28. Binding Energy of $^{78}$Cu: Probing the Structure of the Doubly Magic $^{78}$Ni from Only One Proton Away
29. **Mass-selective ion ejection from multi-reflection time-of-flight devices via a pulsed in-trap lift**

E. Wienholtz, S. Kreim, M. Rosenbusch, L. Schweikhard and R.N. Wolf


DOI: 10.1016/j.ijms.2017.07.016

30. **Charge radii and electromagnetic moments of $^{195-211}$At**


*Phys. Rev. C* 97, 054327 (2018),

DOI: 10.1103/PhysRevC.97.054327

31. **Change in structure between the $I=1/2$ states in $^{181}$Tl and $^{177,179}$Au**


*Physics Letters B* 786, 355-363 (2018),

DOI: 10.1016/j.physletb.2018.10.005

32. **Precision Mass Measurements of $^{58-63}$Cr: Nuclear Collectivity Towards the $N=40$ Island of Inversion**


*Phys. Rev. Lett.* 120, 232501 (2018),

DOI: 10.1103/PhysRevLett.120.232501
33. **Characterization of the shape-staggering effect in mercury nuclei**
Nature Physics 14, 1163-1167 (2018), DOI: 10.1038/s41567-018-0292-8

34. **Improved stability of multi-reflection time-of-flight mass spectrometers through passive and active voltage stabilization**

35. **First steps in the development of the Multi Ion Reflection Apparatus for Collinear Laser Spectroscopy**

36. **Simulations of a proof-of-principle experiment for collinear laser spectroscopy within a multi-reflection time-of-flight device**

37. **Inverse odd-even staggering in nuclear charge radii and possible octupole collectivity in $^{217,218,219}$At revealed by in-source laser spectroscopy**
8 Publications and conference contributions

Wakabayashi, K. D. A. Wendt, F. Wienholtz, B. W. Whitmore, G. L. Wilson, R. N. Wolf and K. Zuber

DOI: 10.1103/PhysRevC.99.054317

38. A new beamline for laser spin-polarization at ISOLDE
DOI: 10.1016/j.nima.2019.01.082

39. Charge radii and electromagnetic moments of $^{195−211}$At
DOI: 10.1103/PhysRevC.99.044306

40. Radioactive boron beams produced by isotope online mass separation at CERN-ISOLDE
DOI: 10.1140/epja/i2019-12719-1

41. Direct decay-energy measurement as a route to the neutrino mass

Hyperfine Interact. 240, 61 (2019),
DOI: 10.1007/s10751-019-1601-z

42. Evaluation of high-precision atomic masses of $A \approx 50−80$ and rare-earth nuclides measured with ISOLTRAP
DOI: 10.1140/epja/i2019-12775-5
Mass measurements of neutron-rich isotopes near $N = 20$ by in-trap decay with the ISOLTRAP spectrometer


Miscellaneous, non-reviewed publications

- **Multi-Reflection Time-of-Flight Mass Separation and Spectrometry**
  S. Kreim, F. Wienholtz, and R. N. Wolf
  Nuclear Physics News 24, 20-23 (2014), DOI: 10.1080/10619127.2014.910430

Conference contributions


- **Neutron-rich Ca isotopes studied with the online mass spectrometer ISOLTRAP. Invited talk.** NUSTAR week, Helsinki, Finland, Oct. 07, 2013.

- **Neutron-rich Ca isotopes studied with a multi-reflection time-of-flight mass spectrometer. Invited talk.** EMMI Physics Days, GSI, Darmstadt, Germany, Sep. 18, 2013.
8 Publications and conference contributions

- **Precision Measurements with the Multi-Reflection Time-of-Flight Mass Spectrometer of ISOLTRAP at ISOLDE/CERN. Invited talk.** DPG spring meeting (AMOP), Berlin, Germany, Mar. 17, 2014.


- **The multi-reflection time-of-flight mass spectrometer of ISOLTRAP at ISOLDE/CERN. Invited talk.** 9th International Conference on Nuclear Physics at Storage Rings (STORI'14), Sankt Goar, Germany, Sep. 29, 2014.


- **Applications of ISOLTRAP’s multi-reflection time-of-flight mass spectrometer. Invited talk.** DPG spring meeting (AMOP), Hannover, Germany, Mar. 01, 2016.

- **Precision mass measurements and more at ISOLTRAP. Invited talk.** DPG spring meeting (Hadronic and nuclear physics), Darmstadt, Germany, Mar. 16, 2016.

- **Dedicated laser-polarization setup at ISOLDE. Contributed talk.** Application of lasers and storage devices in atomic nuclei research, Poznan, Poland, May 18, 2016.


- **ISOLTRAP’s toolbox for nuclear physics and recent results. Invited seminar.** IKS Leuven, Belgium, Jan. 01, 2017.

• Recent applications of ISOLTRAP’s multi-reflection time-of-flight mass separator/spectrometer (MR-ToF MS) and the development of a dedicated ISOLDE MR-ToF MS. **Contributed talk.** Capture Gamma-Ray Spectroscopy and Related Topics (CGS16), Shanghai, China, Sep. 12, 2017.

• Recent applications and results obtained with of ISOLTRAP’s multi-reflection time-of-flight mass separator/spectrometer (MR-ToF MS) and the adjunct Penning traps. **Invited talk.** 10th International Conference on Nuclear Physics at Storage Rings (STORI’17), Kanazawa, Japan, Nov. 13, 2017.

• Recent applications of ISOLTRAP’s multi-reflection time-of-flight mass separator/spectrometer (MR-ToF MS) and the development of a dedicated ISOLDE MR-ToF. **Invited talk.** 9th Topical Workshop on Modern Aspects in Nuclear Structure, Bormio, Italy, Feb. 22, 2018.


• Recent applications of the online mass spectrometer ISOLTRAP@ISOLDE,CERN. **Invited seminar.** University of Greifswald, Germany, Jul. 10, 2018.

• Lessons learned from the success of ISOLTRAP’s MR-ToF for a future general-purpose device. **Poster.** International Conference on Electromagnetic Isotope Separators and Related Topics (EMIS), Geneva, Switzerland, Sep. 16, 2018.

• Lessons learned from the success of ISOLTRAP’s MR-TOF and a possible future 30-kV ISOLDE device. **Invited seminar.** University of Jyväskylä, Finnlnd, Oct. 7, 2018.


• **MR-ToF MS assistance in recent studies of the hyperfine structure of $^{41}$Hg, $A \geq 177$, medical radionuclides and, last but not least, precision mass spectrometry.** **Colloquium.** University of Greifswald, Germany, Jan. 31, 2019.