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**MASS MEASUREMENTS OF VERY HIGH ACCURACY
BY TOF-ICR OF IONS INJECTED INTO A PENNING TRAP*
(IS130)**

St. Becker¹, G. Bollen², F. Kern¹, H.-J. Kluge¹, R.B. Moore^{2,3},
G. Savard¹, L. Schweikhard¹, H. Stolzenberg¹,
and the ISOLDE Collaboration

¹ Institut für Physik, Universität Mainz, Mainz, Fed. Rep. Germany

² CERN, Geneva, Switzerland

³ Foster Radiation Laboratory, McGill University, Montreal, Canada

Abstract

The possibility of absolute mass measurements using time-of-flight (TOF) detection of ICR on ions injected into a Penning trap has been demonstrated. Resolving powers of 2 million have been achieved, with accuracies of about 0.5 ppm. Absolute accuracy is obtained by direct observation of the sum frequency of the cyclotron and the magnetron motions through the use of an azimuthal quadrupole rf field to transform initial magnetron motion into cyclotron motion. Imperfection of the Penning trap leading to systematic errors are discussed. The system was designed specifically to measure the masses of radionuclides produced at the on-line isotope separator ISOLDE. With further developments this system will provide mass measurements of 0.1 ppm accuracy on nuclei which are available in quantities such that on the average one will survive nuclear decay for the duration of the measurement cycle.

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INTRODUCTION

Since the invention of the Omegatron [1] by Sommer, Thomas and Hipple in 1951 to determine e/m by Ion Cyclotron Resonance (ICR), and the application of the Fourier Transform (FT) technique to such a device by Comisarow and Marshall [2] in the mid-1970's, the technique of ion cyclotron resonance (ICR) in a Penning trap has become extensively used in mass spectroscopy [3]. Mass resolving powers of over 10^6 for each mass in a single collection of ions with a wide mass range have been routinely achieved in a wide variety of applications, particularly in organic chemistry.

There is a need for such high-resolution mass discrimination in nuclear physics. The sequence of events in nuclear decay processes, or in nuclear synthesis in stars, is extremely sensitive to small differences in the nuclear binding energies which show as small mass differences in the radionuclides. The extremely high resolution and the associated high precision with which ion cyclotron frequencies can be observed in a Penning trap make this technique very attractive for nuclear mass determinations.

The application of the standard FT-ICR technique to nuclear mass determinations is not trivial. This is partly because of the number of ions required in the trap to create an observable signal. Radionuclides of particular interest for mass measurement are generally available at very low production rates and often have half-lives that prohibit their assembly into one large collection in an electromagnetic trap. Furthermore, this means that usually they must be transferred into the trap as ions from some efficient outside source. Finally, an even more stringent requirement is the accuracy of the measurements. In many of the cases of interest in nuclear physics, accurate absolute mass determinations are needed and the standard FT-ICR techniques do not give sufficient accuracy. Typical absolute accuracies from FT-ICR are 70 ppm [4]. Accuracies of 1 ppm have been achieved [5] with the simultaneous availability in the trap of two calibrant masses with masses very near that of an unknown. Mass determinations in nuclear physics are desired to an absolute accuracy of well below 1 ppm and to 1 part in 10^9 in special cases such as the ^3He -Tritium mass difference.

The high precision to which modern Penning trap parameters can be established and the high stability of the devices should make them useful for high-accuracy measurements. Van Dyck, Schwinberg and Dehmelt [6] have dramatically demonstrated the possibilities by their work on a single electron in a Penning trap (which they have christened "Geonium"). The accuracy of their measurement of the magnetic moment of the electron, 4 parts in 10^{12} , is about 900 times better than previous measurements by other techniques. Wineland et al [7] have suggested that mass measurements using ICR in Penning traps should be possible to accuracies approaching 1 part in 10^{13} .

The inaccuracies in FT-ICR mass spectroscopy are primarily due to uncertainties concerning the electric field experienced by the ions in the trap. The effect of the electric field on the motion of charged particles in a Penning trap was published in the seminal paper [1]. A summary of the important effects for pure cylindrical quadrupole electric fields is given in the next section. In simple terms, the radially repulsive electric field experienced by an ion cancels some of the Lorentz force due to the magnetic field. The

actual cyclotron frequency of the ion (commonly denoted as ω_+) is therefore reduced from the cyclotron frequency ω_c that the ions would have if there were no electric field; i.e. $(q/m)B$. In the literature on FT-ICR it is often not clear that the authors realize this to be the case even though, in a typical Penning trap used for FT-ICR, the difference will be about 0.5%. Accurate mass determination using the cyclotron frequency requires taking this electric field effect into account.

In principle, for a precisely constructed trap, the effect of the applied electric field on the cyclotron frequency can be calculated. In an alternative approach, Wang and Marshall [8] have shown that it is possible to reduce the electric field effect by a factor of 100 using end screening in a cubical trap. However, there will remain a considerable uncertainty associated with the electric field from the space charge of the ions confined in the trap. This electric field depends on the shape and density of the confined ion cloud [4]. In the original paper on ICR cells [1] it was acknowledged that space charge electric fields present a "different but related" effect to that of the applied trapping voltage. (It is different in that it is not fixed by the geometry and by the externally applied fields of the trap but depends on the distribution of the various ion components in the ion cloud in the trap, the properties of which are very difficult to determine or to control. It is related in that the space charge effect does also depend on the strength of the applied electric field.) Nevertheless, for a given cloud there will be a very definite precise frequency to a given coherent cyclotron motion for each of the ion species in the cloud and these precisely defined frequencies can be highly resolved [9] and measured by the Fourier transform technique. However, the relationship of these frequencies to the individual masses of the ions is very difficult to establish. Thus high-precision frequency determinations are obtained, but not necessarily high-accuracy mass measurements. The key to the success with Geonium, and to the high accuracy suggested in [7], is the use of a single charged particle with its motion cooled so as to be very near the center of a precisely constructed trap. This reduces all space charge effects and minimizes the uncertainties of the effect of the applied electric and magnetic fields.

The need for reducing the number of ions in a trap to improve accuracy and the fact that, in many cases for radionuclides, not many are indeed available, leads to the consideration of a scheme for detecting ion cyclotron resonance by observing ejected ions. Since destructive detection is quite feasible for even a single ion, such a scheme would make it possible to attain the goal of observing the cyclotron resonance with only a single ion in the trap at any one time. Of course, to observe the full resonance and determine the frequency of the cyclotron motion, the observation has to be repeated many times at different driving frequencies scanning the cyclotron resonance. Such a measurement will generally take as many ions in total as that required in the one bunch for an FT-ICR observation. However, they do not have to be assembled as a bunch and this can be very important for radionuclides of short half-lives and low production rates.

We have developed a system at ISOLDE [10,11] to prove the feasibility of measuring the masses of radionuclide ions injected into a Penning trap from an outside source and using ICR detection by ion ejection from the trap. A schematic of the system is shown in Fig. 1.

The principle on which the system is based is that published by Gräff, Kalinowsky, and Traut [12]. This is that a change in the motion of a charged particle resulting in a change in its magnetic potential energy can be detected by observing a change in the kinetic energy of the particle when it is ejected from the magnetic field. This idea was first published by Bloch [13] in a proposal of a scheme for a determination of the g-factor of an electron. In the case of the increased magnetic potential of an ion due to an enhanced cyclotron motion, the resulting increase in the kinetic energy of an ejected ion can be observed in the time-of-flight (TOF) of the ion from the trap to a detector. As a representative example, a singly charged ion of mass 100 with a cyclotron radius of 1 mm in a magnetic field of 6 Teslas will have, after it is ejected into a magnetic field which is negligible, an axial kinetic energy of about 17 eV due to its original magnetic potential.

In Ref. [12] it was shown that it was possible to induce cyclotron motion in such a system by a resonance effect at the unperturbed cyclotron frequency ω_c . This frequency for both protons and electrons in a field of about 6 Teslas was used to determine the proton to electron mass ratio to an accuracy of 0.05 ppm. It was this success that inspired the construction of the system installed at ISOLDE. In 1986 the in-flight capture of alkali ions was reported[14] followed in 1987 by the first report on absolute mass measurements of radioactive strontium and rubidium isotopes[15,16,17] and in 1988 by measurements of radioactive cesium isotopes, including ^{122}Cs [16,17,18]. This paper presents the basic principles of the technique and the performance that has been achieved with the system. It also presents some of the design features which we have included as a further development.

THEORY

The dynamics of ions in an ideal Penning trap are well known. They are most thoroughly presented in the review article by Brown and Gabrielse [19]. We will summarize the important points here.

The cylindrical quadrupole electric field used in a Penning trap has the form

$$E_r = \frac{a}{2} r ; \quad E_z = -a z \quad . \quad (1)$$

Such a field is produced by electrodes which are infinite hyperboloids of revolution following the equation

$$\frac{r^2}{r_0^2} - \frac{z^2}{z_0^2} = -1 \quad (2a)$$

$$\frac{r^2}{r_0^2} - \frac{z^2}{z_0^2} = +1 \quad (2b)$$

where equations 2a and 2b are for the end electrodes and the ring electrode respectively, $r_0 (= \sqrt{2}z_0)$ is the inner radius of the ring electrode and $2z_0$ is the distance between the endcaps. With a voltage V (positive for the containment of positive ions) applied to the end electrodes relative to the ring, the coefficient a in (1) then becomes

$$a = \frac{V}{z_0^2} \quad . \quad (3)$$

This electric field has three effects on ion motion in a Penning trap formed from such electrodes. It not only provides the restoring force on the charge particle that confines the axial motion to oscillations at ω_z , it also modifies the cyclotron frequency as already mentioned above and, in addition, introduces a third type of motion; a slow "magnetron" precession. In the pure cylindrical quadrupole field, these three motions are completely independent oscillations with the following angular frequency relationships

$$\omega_{\pm} = \frac{\omega_c}{2} \pm \sqrt{\left(\frac{\omega_c}{2}\right)^2 - \frac{\omega_z^2}{2}} \quad (4)$$

where $\omega_c = (q/m)B$ is the unperturbed cyclotron frequency, $\omega_{\pm}$ is the reduced cyclotron frequency, ω_z is the magnetron frequency and the axial angular oscillation frequency is given by

$$\omega_z^2 = \frac{q}{m} a \quad . \quad (5)$$

In standard ICR in Penning traps it is the reduced cyclotron frequency $\nu_+ = \omega_+/2\pi$ that is observed, this motion having been induced by a dipole rf field applied for a specific period. The energy gain from such a field at a frequency near that of the cyclotron motion and applied at a constant amplitude for a time T_{rf} is given by the Fourier transform

$$I(\omega_d) \propto \frac{\sin^2\left(\frac{\omega_d - \omega_+}{2} T_{rf}\right)}{\left(\frac{\omega_d - \omega_+}{2} T_{rf}\right)^2} \quad (6)$$

This response function is shown in Fig. 2. Defining the resolving power R as the center frequency ν_+ divided by the FWHM of this function (in Hz) gives

$$R \approx 1.1 \nu_+ T_{rf} \quad (7)$$

However, as shown above, the frequency of this motion will be strongly dependent on the electric field parameters of the trap and, if there is more than one ion involved, on the space charge field of the ion bunch. Thus, in the case of ω_+ excitation, a high-resolving power does not necessarily give a high absolute accuracy since these fields effects have to be taken into account.

As stated above, the measurement reported in Ref. [12] was made by observing a "resonance" at ω_c . How the ω_c frequency is related to the actual motions in an ideal Penning trap is well known. The relationship between these three fundamental frequencies of ion motion in a Penning trap are more clearly seen by noting that

$$\begin{aligned} \omega_+ + \omega_- &= \omega_c \quad , \\ \omega_+ \omega_- &= \frac{\omega_z^2}{2} \quad , \end{aligned} \quad (8)$$

or that

$$\omega_+^2 + \omega_-^2 + \omega_z^2 = \omega_c^2 \quad (9)$$

Thus, in an ideal Penning trap, the sum frequency $\omega_+ + \omega_-$ is exactly the unperturbed cyclotron frequency ω_c . A direct observation of this frequency therefore eliminates the electric field effects without having to know what they are.

Schweikhard et al [20,21] have shown that a direct observation of the sum frequency $\nu_+ + \nu_-$ is possible in FT-ICR with a quadrupole configuration for the detection electrodes. Mechanisms by which an applied field of this frequency in a Penning trap can have a "resonance" effect on the cyclotron motion are therefore of considerable interest.

The electrode geometry originally used by Gräff et al [12] was a standard configuration used for inducing cyclotron motion; a simple splitting of the ring electrode to produce a predominantly dipole field. It was recognized by the original developers that the required coupling of the cyclotron and magnetron motion to give a response of the system at $\omega_+ + \omega_-$ can not be through this dipole field; that it must arise from some higher order coupling terms [22]. This is because the cyclotron and magnetron motions, as mentioned above, form completely independent degrees of freedom and an applied dipole field (uniform electric field in a given direction) couples independently to the components of these two motions in the field direction.

To our knowledge there has been no discussion in the literature on the actual nature of the higher order coupling terms that can result in a response of the system at $\omega_+ + \omega_-$. Recently, a more thorough examination of the effects of multipole fields [23] has shown that the "resonance" effect at $\omega_+ + \omega_-$ is caused by an azimuthal quadrupole component in the applied field, most easily achieved by splitting the ring electrode into quadrants and applying potentials as shown in Fig. 3. Such a field, which introduces a coupling of the x and y motions, will couple the x component of the magnetron motion to the y component of the cyclotron motion (and vice-versa). Thus the previously independent motions are now coupled, the strength of the coupling constant being proportional to the strength of the applied quadrupole field.^(a)

Just as a weak coupling of two pendula will produce eigenfrequencies which are perturbed from the independent values, the coupling introduced by an azimuthal quadrupole electric field will perturb the eigenfrequencies of the previously independent cyclotron and magnetron motions. Also, as in the coupled pendula, an initial condition made up of only one of the motions (say the magnetron) can be decomposed into two equal amplitude eigensolutions which have a beat frequency equal to the frequency difference. The magnetron motion will therefore transform into a cyclotron motion and back, just as a motion of only one of a coupled pendula will transform to the other and back. An important point coming from the work of Ref. [23] is that the cyclotron-magnetron motion coupling through the azimuthal quadrupole field results in perturbations of the eigenfrequencies which are equal but of opposite sign for the two motions. The sum frequency therefore is unaffected.

The beat frequency between the magnetron and cyclotron motions coupled through an applied azimuthal quadrupole electric field will be proportional to the coupling constant, which in turn, is proportional to the quadrupole voltage applied to the split ring.

(a) Of course, the radial electric field of the trapping axial quadrupole potential also introduces a coupling of the magnetron and the cyclotron motion. However, the coupling due to this field produces a "resonance" effect at the difference frequency $\omega_+ - \omega_-$. This can be seen to be reasonable since the radial oscillation frequency in combined cyclotron and magnetron motion is $\omega_+ - \omega_-$ and it is this oscillation which couples to a purely radial electric field. This has been made use of in the so-called parametric-mode excitation [24,25]. In the frame of reference of a radial vector rotating at ω_- an azimuthal quadrupole field rotates backwards twice in one revolution of the vector and so such an applied field is seen to present a frequency of $\omega_+ + \omega_-$.

This phenomenon is easily seen in computer simulations of ion motion in a uniform magnetic field with such an applied electric field (Fig. 4).

In Ref. [23] it is shown that the beat period T for an rf quadrupole voltage amplitude V_0 applied as shown in Fig. 3 to a trap with a pure axial quadrupole geometry will be given by

$$T \approx 1.2 \frac{\pi}{V_0} Br_0^2 \quad (10)$$

Thus, if an ion in a Penning trap has practically only magnetron motion before the rf field is applied, then that motion will be completely converted to cyclotron motion in a time which is half the value in (10). For a conversion time of 1 s in a trap with $r_0 = 1$ cm in a field of 6 T, the required voltage is about 1.2 mV. This compares with voltages of the order of 100 mV apparently used in Ref. 12 and of about 50 mV for the ISOLDE apparatus when using a dipole configuration for the ring electrode. When using a quadrupole excitation in the ISOLDE apparatus, we have found that only about 0.7 mV is required for an equivalent enhancement of the cyclotron motion. It is easy to believe that the excitation of the cyclotron motion in the dipole configuration is due to a quadrupole component arising from mechanical and electrical asymmetries.

The use of this quadrupole "resonance" in a practical measurement will involve setting the rf amplitude at the value required for a desired conversion time at "resonance" and scanning the drive frequency through $\omega_+ + \omega_-$ for observable effects on the ion energy or magnetic moment. At frequencies deviating from $\omega_+ + \omega_-$, the driving field will not have time to complete the motion transform before it moves out of the proper phase relationship for achieving this transform. Thus a high field strength which completes this transform in a shorter time will allow a broader range of frequencies to satisfactorily complete the transform. For complete transformation of the magnetron motion to cyclotron motion, the frequency width of the response of the system is therefore inversely proportional to the time required for this transform. Calculations of the response for off-resonance driving fields have been reported in [23], the results being summarized in Fig. 5.

It is seen that the FWHM of the response function for field strengths near a_{max} (the quadrupole field strength that will completely transform magnetron motion to cyclotron motion in T_{rf}) is about $1/T_{rf}$. Defining the resolving power in the same way as for the case of dipole cyclotron excitation gives

$$R \approx v_c T_{rf} \quad (11)$$

where v_c is the unperturbed cyclotron frequency in Hz. It is seen that this resolving power is about the same as that for the direct dipole excitation of the cyclotron motion.

It is interesting to consider the possibilities of higher even-order azimuthal multipoles. From symmetry considerations the $\omega_+ + \omega_-$ frequency should appear for any even $2m$ multipole ($m \geq 2$, even), the frequency at which it appears being $(m/2)(\omega_+ + \omega_-)$. The octapole ($m = 4$) excitation would be obtained by a ring split into octants. The multipoles with $m/2$ having an odd value are especially interesting since they will arise for a ring split into quadrants.

These higher frequency versions of $\omega_+ + \omega_-$ could be of particular use in ICR-ion ejection schemes in cases where the observation of the ion motion must be carried out as quickly as possible, such as for the observation of short-lived radioactive ions. The resolving power of the system, for a given time of application of the driving field, will be proportional to $m/2$.

We have not attempted to determine the degree to which the ion motions can be influenced by these higher order multipoles. As to what may be expected, it can be noted that the electric field strength for an m^{th} order multipole near the center of the trap will vary as the $(m-1)^{\text{th}}$ power of the radius. Thus the use of higher azimuthal multipoles will require the application of higher voltages.

In any case, the accuracy of a mass measurement of an ion based on an observation of its $\omega_+ + \omega_-$ will depend on how well this frequency can be related to the q/m of the ion and this, of course, depends on how closely the trap resembles the ideal Penning trap discussed above. The trap used in the ISOLDE system (with $r_0 = 8$ mm and $r_0^2 = 2z_0^2$) has 2 mm diameter holes in the end electrodes for the injection and extraction of the ions. Also, the hyperboloidal electrodes are, of course, truncated and the ring electrode slit to form quadrants. As well, the diamagnetism of the material forming the trap can distort the magnetic field and there can be possible axial asymmetries and misalignments of the electric and magnetic trapping fields.

The effects of trap imperfections on the sum frequency $\omega_+ + \omega_-$ have been investigated in detail in [23]. Applying the results of that work to the ISOLDE mass measuring system, it has been found that the most significant imperfections, by far, are the axial octupole and dodecapole components of the electric trapping field, caused by the holes in the endcaps. For ion motions ($m=100$ amu) confined to a diameter of 2 mm and an axial extent of 4 mm in the measuring trap used in that system, these can contribute frequency shifts in $\omega_+ + \omega_-$, away from ω_c , of up to 20 ppm. The effect of magnetic inhomogeneity caused by the diamagnetism of the trap material is estimated to be a shift of about 0.6 ppm for the same extent of motion and the effects of misalignment and axial asymmetries in the trapping fields is estimated to be less than 0.1 ppm for mass comparisons over an interval of 10 amu.

It is also shown in [23] that the octupole component causes a shift of the sum frequency $\omega_+ + \omega_-$ which depends only on the radial extent of the motion but that the dodecapole component causes a dependence on both the radial and the axial extent. The forms of the dependencies are

Octupole;

$$\Delta(\omega_+ + \omega_-) = \frac{3}{4} \frac{C_4}{z_0^2} \frac{\omega_z^2}{(\omega_+ - \omega_-)} (\rho_-^2 - \rho_+^2)$$

Dodecapole;

$$\Delta(\omega_+ + \omega_-) = \frac{15}{8} \frac{C_6}{z_0^4} \frac{\omega_z^2}{(\omega_+ - \omega_-)} [3z^2(\rho_-^2 - \rho_+^2) + (\rho_+^4 - \rho_-^4)] \quad (12)$$

In these equations, ρ_+ , ρ_- and z refer to the radii of the cyclotron motion and magnetron motion and the amplitude of the axial motion respectively and C_4 and C_6 are dimensionless representations of the octupole and dodecapole imperfections. Specifically, they are related to the potential imperfection ϕ_l expressed in the Legendre polynomials $P_l(\cos \theta)$;

$$\phi_l = a_l r^l P_l(\cos \theta) \quad (13)$$

through the equation

$$a_l = \frac{V_0}{2z_0^l} C_l \quad (14)$$

where V_0 is the voltage applied to the end electrodes relative to the ring, θ is the angle with the z axis and l is equal to 4 and 6 for the octupole and dodecapole components respectively .

In passing, it is noted that the octupole component arises from both the main electrode truncation and the entry and exit holes. The dodecapole component comes almost completely from the holes (which bring in all l even order components).

Equations (12) show the importance of keeping the cyclotron and magnetron motions under control, particularly if there is a significant amplitude of z motion. If the strength of the rf quadrupole field and the time of its application is precisely that required to complete a transform of the magnetron motion to cyclotron motion, and the initial motion is completely magnetron, then the symmetry of the equations show that the frequency shifts during the transformation of ρ_- to ρ_+ will average to zero. The effects of both the octupole and the dodecapole components on the observed "resonance" frequency will then be annulled.

Of course, in such a situation the applied frequency, ω_c , is only equal to $\omega_+ + \omega_-$ at the instant when ρ_+ equals ρ_- . The applied field is therefore generally "off-resonance" from $\omega_+ + \omega_-$ and more applied power will be necessary to complete the transform in a specified time then is calculated from (10). Also, it is to be expected that the energy absorption curves shown in Fig. 5 will be skewed. Numerically integrating the equations of motion, taking into account this variation in $\omega_+ + \omega_-$ during the transformation, gives the result shown in Fig. 6. It is seen that if the applied field is too strong the ions will be spending a larger fraction of the time of the transformation in a condition where $\rho_+ > \rho_-$ and the resonance will be shifted positively (as it is in the solid curve in Fig. 6). On the other hand, if it is not strong enough to complete the transformation, the "resonance" will be shifted negatively.

Thus, by maintaining the rf quadrupole field strength for exactly the time required to complete a transformation of magnetron motion to cyclotron motion for an ion with its motion centered on the average for the ion collection in the trap, the observed resonance will be at ω_c . This condition can be set up experimentally by maximizing the effect on the TOF of the extracted ions. The effect of a spread of axial motion amplitudes and of finite initial cyclotron motion will then only be to broaden this resonance.

THE SYSTEM PERFORMANCE

Details of the mass measuring system are given in Ref. [14]. As already referenced, [15-18] present first results for the masses of some radionuclei. Here we present details of the performance of the system.

The response of the system to a dipole excitation at ω_+ is shown in Fig. 7. Here the shape of the Fourier transform of a constant amplitude frequency burst shown in Fig. 2 is manifested. The central peak is clipped because of the limited aperture of the exit hole for the ions, the time-of-flight observations in the peak being due to a few stray ions that have managed to escape. It may also be noted that the time of application of the rf field so as to have the resolution Fourier-limited was only 90 ms, giving a resolving power of about 10^5 .

Typical resonance effects at $\omega_+ + \omega_-$ are shown in Fig. 8. The curve in Fig. 8b is for an applied field which is about 10% greater than that in Fig. 8a. Both curves were obtained with rf field durations of 900 ms. Comparison with Fig. 6, where the lines under the peaks conform to the positions of the minima in the upper curve of Fig. 8, shows clearly the effect of the imperfections of the trapping electric field.

In Fig. 9a is shown the effect of varying the strength of the applied field on the TOF of the extracted ions. It is seen that there is a field strength which gives a maximum effect. This, of course, is the field strength that will just cause a complete conversion of magnetron motion into cyclotron motion. The shaded curve shown is an estimation of the time of flight effect which would have a maximum at the same position as the data, based on numerical integration of the equations of motion including the estimated C_4 and C_6 electric field components of the trap.

Fig 9b shows the frequency shifts of the resonance due to trap imperfection for these same field strengths. The shaded curve is again a calculation based on the estimated C_4 and C_6 electric field components of the trap. The zero for the frequency scale is the resonance frequency at the field strength which gave a maximum TOF effect for the calculated curve in Fig 9a. The agreement between the observed and the calculated frequency shifts indicates the validity of the theoretical model of the ion motion and that the significant trap imperfections are the octapole and the dodecapole electric field components.

Fig. 10 shows the best resonance that has been obtained using ions that have been injected into the measuring trap after collection following surface ionization on the stopping foil in the collecting Penning trap (Fig. 1). These ions are believed to have an axial energy spread approaching 1 eV. The duration of application of the rf field was 1.8 s. It is seen that the resolving power of the system is about 1.1×10^6 while the Fourier-limit would be about 1.2×10^6 . The effects of trap imperfections on the ion motions are therefore just noticeable at these resolving powers.

A feature which has been recently added to the system described in [14] is the possibility of buffer gas cooling in the collecting trap [24]. This is used to reduce the phase space of the ion collection before delivery to the measuring trap. Not only does

this increase the efficiency by about a factor of from 10 to 100 but it also allows the placement of the ion bunch in a smaller region near the center of the trap so as to have less effect from the field imperfections. Fig. 11 shows a recent resonance that has been achieved using this system. The duration of application of the rf field in this case was 3.6 s. It is seen that the resolving power of the system is about 2.3×10^6 while the Fourier-limit would be about 2.5×10^6 . The effects of trap imperfections on the ion motions are now just noticeable at about twice the resolving power of before.

By increasing the duration of application of the rf field (and, of course, decreasing its intensity) it would, in principle, be possible to increase the resolving power to the limit imposed by the trap imperfections. It would appear from the above figures that this limit would be about 3×10^6 . It is perhaps worth noting that the effect of the trap imperfections, as exhibited by equations (12), is to introduce a fractional error which is proportional to $(\omega_z/\omega_c)^2$. For given electric and magnetic fields it can be seen from (3) and (5) that $(\omega_z/\omega_c)^2$ is proportional to the mass. Thus the quality of the system as a mass measuring instrument can be related to the effect of the trap imperfections on the observation of the mass of the proton. The resolving power times A thus becomes a "figure of merit" for the system. Such a figure of merit for our system would be about 4×10^8 .

Of course, when dealing with short-lived radionuclides many of the ions in the measuring trap may not survive the full conversion time necessary for the ultimate resolving power. However, the ions that decay with such short half-lives will typically receive kinetic energies of several hundred eV from the decay and so will be lost from the useful volume of the trap and not provide a TOF signal. Those that do not decay will have gone through the full magnetron-cyclotron motion conversion and hence be resolved at the full resolving power. The number of ions initially loaded into the trap will have to be sufficient to make up for the decay loss, but the resolution of the system will not be affected.

If the half-life is so short, or the production rate so limited, that the decay of the ions in the trap for the full conversion time cannot be tolerated, then the cycle time for the measurement will have to be decreased and the resultant decrease in the Fourier-limit of the resolving power must be accepted. An example would be the case of ^{11}Li which has a half-life of about 10 ms and is available at a rate of about 1000/s at ISOLDE. For a factor of 30 loss in the quantity of ions in the trap, the measurement cycle would have to be shortened to about 50 ms, yielding a resolving power (for the same trap parameters as for ^{133}Cs) of about 4×10^5 .

While high resolution is important in distinguishing between two closely adjacent masses, as pointed out in the introduction it does not automatically lead to high accuracy. Accuracy will depend ultimately on systematic errors that occur in the comparison of the resonant frequency for an unknown mass with that for a reference mass. Analysis of the results available to the present indicate that an accuracy of about 0.5 ppm has been achieved but that accuracies of better than 0.1 ppm should be possible once the systematic effects have been evaluated.

A final point concerning the performance of the system is the effect of contaminant ions of a different mass than that which is to be measured. As pointed out in Ref. [4], ions of a different species will have a much greater space-charge effect on the cyclotron frequency of an individual ion than will other ions of the same species. This effect is seen in the left-hand diagram of Fig. 12 where the resonance at $\nu_+ + \nu_-$ for ^{85}Rb is seen to be about 10-Hz wide, a broadening that is due to the presence of about 30% of ^{87}Rb in the natural abundance ratio for these stable isotopes. We have been able to clear the unwanted contaminant ions from the operating central region of the trap by directly exciting their cyclotron motion using a dipole rf field. The resultant improvement of the resolving power by a factor of about 10 is easily seen.

FURTHER DEVELOPMENTS

As shown in the previous chapter, the high resolving power of the present set-up and analysis of the effects leading to systematic errors in the mass determinations have allowed mass determinations with accuracies in the sub-ppm range. From this work we have established the features which we think are required to achieve accuracies better than 0.1 ppm. These are listed below.

1. The Penning trap must be as large as possible and cause as little distortion of the magnetic field as possible.
2. The geometrical symmetry of the electrode configuration should be preserved to better than 1% of z_0 or about 0.1-mm for a practical design.
3. There must be as good a correction as possible of the octupole and dodecapole components of the trapping electric field. The octupole component can be cancelled by a pair of secondary ring electrodes between the main ring electrode and the end electrodes. The dodecapole cancellation requires a separate pair of rings, which are most effectively placed at the entrance and exit holes of the end electrodes (i.e. near the source of the imperfection).
4. It must be possible to accurately align the system for the injection of the ions into the Penning trap with a precisely controlled phase space volume. The axial dimensions of this volume are controlled by the amplitude and timing of the retardation voltage. The radial motion is controlled by the alignment of the ion path with the magnetic field lines of the solenoid.

With these points in mind, a new Penning trap and injection system has been designed and constructed. A cross-sectional view of the trap is shown in Fig. 13.

A further development will be a more effective scheme for collecting the radioactive ions of ISOLDE for delivery to the mass measuring system. This scheme is based on the work published in [25] on the collection of ions in a Paul type radiofrequency quadrupole (RFQ) trap. This trap is to collect the ions directly from the ISOLDE beam at a point about 5-m from the present collecting Penning trap. At the end of a collection period, the RFQ trap is brought to ground potential and the collected ions ejected and transferred to the set-up shown in Fig. 1. Such a procedure will enable high efficiency collection of any ion species delivered by ISOLDE.

CONCLUSIONS

High resolution and high absolute accuracy mass measurements have been demonstrated as being possible for radionuclides injected from an outside source into a Penning trap. The TOF-ICR technique has been shown to give accuracies in the sub-ppm range with only a few ions in the trap at any one time. The motion of the ions in the trap is well understood, as is the interaction of the ions with an applied rf field. This has allowed the design of a system which should give accuracies below 0.1 ppm.

The apparatus described is designed specifically for absolute mass measurements of radioisotopes. A mass accuracy of 0.1 ppm corresponds to an accuracy in the binding energy of about 10-keV for a medium mass nucleus ($A = 100$) and of 1-keV for light nuclei ($A = 10$). This is well beyond that available from any other direct mass-measuring technique and approaches that which is available from the best indirect techniques such as the measurement of beta-decay end-point energies (which suffers from requiring a detailed knowledge of the nuclear decay scheme to determine the ground state masses) and observation of production reaction kinematics (which is applicable only if there is an available projectile-target pair which leads directly to the desired nucleus). Furthermore, with sacrifice in resolving power (but not necessarily a proportionate sacrifice in accuracy) the system is useful for studying even the shortest-lived radionuclides produced and mass separated at ISOLDE (i.e. with half-lives of about 10-ms).

The high resolving powers achieved also allows, for the first time in mass spectrometry, the discrimination of isomers from the ground state. Evidence for such a possibility has already been found in the case of the ^{122}Cs isotope [16,17,18].

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FIGURE CAPTIONS

Fig. 1 The mass measuring system at ISOLDE. Radioactive ion beams from the ISOLDE-2 mass separator are implanted on a foil which, after a collection interval, is turned and heated so as to evaporate and surface-ionize the collected atoms into the collection Penning trap. The collected ions are then transported as a pulse to the mass-measuring Penning trap. After cyclotron motion has been induced in the ions they are ejected, again as a sharp pulse, to the time-of-flight detector. The signal of cyclotron motion is a decrease in the time-of-flight of the ions from the trap to the detector.

Fig. 2 The response of a system with a natural oscillation frequency when driven for a time T at a frequency which deviates from the natural frequency. To have the same graph applicable to all driving times, the frequency deviation is expressed in units of $1/T$.

Fig. 3. A circuit connected to a ring electrode split into quadrants to induce an azimuthal quadrupole field.

Fig. 4. The result of the numerical integration of the equations of motion for a particle in a Penning trap with an applied azimuthal quadrupole electric field of frequency equal to the sum of the cyclotron and magnetron frequencies. The center of the trap is indicated by a cross. The initial motion was chosen to be completely magnetron and the quadrupole field strength was chosen to cause a transition to completely cyclotron motion in about 60 cyclotron orbits. Frame 1 shows the first 32 orbits whereupon the cyclotron and the magnetron radius have become equal. Here, as in frame 4, the trace for an undisturbed magnetron orbit is shown for reference. Frame 2 shows the orbits leading to completely cyclotron motion while 3 and 4 show the progression back to completely magnetron motion.

Fig. 5. The solid curves show the orbital energy at the end of application of various rf azimuthal quadrupole field strengths for a specific time. (The dashed curves show the maximum energy that was achieved during this period.) The quadrupole field strength which would completely transform the initial magnetron motion into cyclotron motion when applied in resonance to $\omega_+ + \omega_-$ during this period is denoted by a_{max} . When the strength is twice this value, it is seen that the cyclotron energy returns to zero at the resonant frequency.

Fig. 6. The solid curve shows orbital energy at the end of application of an rf quadrupole field strength for a specific time of a strength 1.4 times that which would have completely converted an initial magnetron motion into a cyclotron motion with the octupole and the dodecapole components determined to be in the ISOLDE measuring Penning trap. The dashed curve shows the maximum energy achieved during the conversion cycle. It is seen that this peaks at zero frequency shift.

Fig. 7. A Fourier-limited ω_+ resonance of ^{133}Cs ions in the Penning trap using dipole excitation. The duration of the rf field was 90-ms. It is seen that the deviations of the sideband peaks from the central frequency are roughly proportional to $\pm \frac{3}{2\pi}, \pm \frac{5}{2\pi}, \dots$

Fig. 8. Variation of the TOF with frequency of an applied rf field at frequencies near $\omega_+ + \omega_-$ for ^{133}Cs ions in the Penning trap. The duration of application of the rf field was 900-ms in all cases. In (a) the strength of the rf field was about 1.4 times that appropriate for a full conversion in 900-ms and in (b) it was 1.6 times that value.

Fig. 9. Variation, with applied field strength, of the TOF (a) and of the resonance frequency (b) at resonance on $\omega_+ + \omega_-$ for ^{133}Cs ions in the Penning trap. The duration of application of the rf field was 900-ms in all cases. The zero for the frequency scale in (b) is at the frequency which gave the maximum TOF effect, in this case 685100.36 Hz. The shaded curves are from estimates of the time of flight effect which would have a maximum at the same position as the data as shown in (a) and based on numerical integration of the equations of motion including the estimated C_4 and C_6 electric field components of the trap.

Fig. 10. The best resonance obtained on ^{133}Cs ions at $\omega_+ + \omega_-$ using the ions from the collection trap without cooling. The resonance frequency was 685100.2-Hz with a FWHM of 0.6-Hz. The duration of the rf field was 1.8-s.

Fig. 11. A recent resonance obtained on ^{133}Cs ions at $\omega_+ + \omega_-$ with cooling of the ions in the collection trap before delivery to the measuring trap. The resonance frequency was 685075.6-Hz with a FWHM of 0.3-Hz. The duration of the rf field was 3.6-s. The FWHM is calculated for a gaussian fitted to the central peak. The broader background under this peak is probably due to ions which have not been cooled to the same degree as those contributing to the peak.

Fig. 12 Resonances showing the effect of ion contamination in the measuring trap. On the left are shown the broadened resonances obtained with rubidium ions of the natural abundance ratios of $^{85,87}\text{Rb}$. For the figure on the right, the ^{85}Rb ions were excited to a larger cyclotron radius by dipole excitation before application of the rf field at ω_c . As a result, there is no ^{87}Rb signal and the ^{85}Rb signal becomes much narrower. The frequency scales are broken in the middle of each figure so as to incorporate the data for both isotopes.

Fig. 13 Cross-sectional view of the new Penning trap to be installed in the ISOLDE mass measuring system.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

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Fig. 8

Fig. 9

Fig. 10

Fig. 11

Fig. 12

Fig. 13