

Inductively coupled plasma mass spectrometry, coincidence laser spectroscopy (ICP-MS-CLS), simulation of the transmission efficiency of a 3D quadrupole ion trap for cooling energetic ions from the ICP prior to optical detection

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A fundamental requirement of ICP-MS-CLS is a post mass separation ion beam with an energy spread of less than ~ 0.2 eV to enable efficient pumping of fluorescent lines with a narrow band ($\Delta\nu \sim 100$ kHz) laser for the optical detection step. The role of a 3D quadrupole ion trap for ion beam cooling, as an accessory for a new generation of ICP-MS-CLS (inductively coupled plasma mass spectrometry, coincidence laser spectroscopy) (B. L. Sharp, P. S. Goodall, L. M. Ignjatović and H. Teng, *J. Anal. At. Spectrom.*, 2007, **22**, 1447) instrument, was investigated by means of numerical simulation. Whereas in-trap ion cooling is well established, it was found that extraction of cooled ions from the trap introduced additional broadening and a loss of transmission efficiency. Modelling was based on a beam of 20 eV mean energy with a spread of 3 eV which represents a worst case scenario for the ions derived from an ICP source. The efficiency of the cooling process (trapping + extraction), as well as the energy distributions of ions exiting the trap, were calculated and compared for several methods of extraction. Trapping efficiencies of $\sim 25\%$ were obtained at buffer gas pressures up to 10 mTorr. The addition of virtual reflectrons to the trap resulted in an improvement in the energy distribution of the trapped ions by lowering the wings of the distribution, but did not significantly improve the efficiency. Zero field, rf field only, quadrupolar field and homogeneous field ion extraction were investigated to recover ions from the trap, and of these quadrupolar extraction was best. However, extraction efficiency and ion energy distribution were inversely related so that quadrupolar extraction at $U_q = 10$ V yielded an exit ion energy distribution of 0.5 eV half width, compared with a trapped width of 0.03 eV, but with only 10% transmission efficiency. Thus, it was demonstrated that a 3D trap can be used to cool energetic ions for post-trap mass or spectroscopic examination, but the low efficiency makes it unsuitable for use with ICP-MS-CLS.

1. Introduction

Recently, Sharp *et al.*¹ have investigated the possibility of improving the performance of ICP-MS for rare abundance isotopes by use of coincidence laser spectroscopy (CLS) for ion detection. Essentially this ICP-MS-CLS technique employs laser-induced ionic fluorescence as a highly specific ion detector to remove spectral interferences and increase the abundance sensitivity. They found that ICP-MS-CLS could potentially provide significant gains in performance, making it a competitor for techniques such as AMS or RIMS, but that there was a need to reduce the ion energy spread to maximise the laser pumping efficiency. The kinetic energy spread (~ 3 eV) of ions extracted from the ICP through the differentially pumped interface is such that ions are Doppler shifted over a significant optical bandwidth (a few 10s of MHz) thereby reducing the pumping efficiency of the narrow band cw laser source ($\Delta\nu \sim 100$ kHz). Means must

therefore be found to reduce the energy spread to ≤ 0.2 eV so that the laser power is coupled efficiently into the peak of the absorption profile. Working on similar problems Nieminen *et al.*² obtained good results for energy narrowing using a linear ion trap with axial field obtaining 60% transmission, but for ions having a 1 eV energy spread.

The aim of this work was to investigate the possibility of using a 3D quadrupole ion trap (QIT) for ion cooling in ICP-MS-CLS. The QIT has been used in conjunction with the ICP previously,^{3–9} but as a collision-reaction cell or mass spectrometer, not specifically as an ion cooler. Ion traps have been in general use for nearly half a century^{10,11} and have found applications in many fields of physics and chemistry, for example in mass spectrometry, quantum computing *etc.* The principles of the QIT are well known and have been described in numerous review papers (see for example ref. 12). Further, in-trap optical spectroscopy on cooled ions is a well established technique (see for example ref. 13) and therefore the QIT was an obvious choice for cooling low flux ions prior to detecting them by laser coincidence spectroscopy. Unlike conventional in-trap spectroscopy however, coincidence spectroscopy requires the cooled ions to be extracted from the trap prior to acceleration and excitation, and to our knowledge the efficiency and consequences of this process for ion

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energy distribution have not been investigated. Therefore, different ways for the extraction of cooled ions from the trap were investigated and only the basic features of the relevant QIT are described (see Section 2) as required to delineate the problem. Section 3 contains the details of the simulation including a description of the ion beam (representative of that derived from an ICP) entering the trap, *i.e.* its mean energy and energy spread. The process of ion injection is described, as well as the conditions in the QIT. All the parameters that remained fixed during the simulation are also introduced in this section. The results and discussion are presented in Section 4.

2. The QIT as an ion cooler for ICP-MS-CLS – theoretical background

The QIT, as shown in Fig. 1, consists of three electrodes: a circular ring electrode and two end-cap electrodes enclosing a volume in which ions can be trapped. Both end caps have a small central aperture through which ions enter or leave the trap. All three electrodes have hyperbolic surfaces. The distance from the centre of the trap to the ring electrode is r_0 and to each of the end-caps is z_0 . For a pure quadrupolar field to be established the following condition has to be satisfied

$$r_0^2 = 2z_0^2 \quad (1)$$

The electromagnetic field inside an ion trap is given by

$$\Phi(x, y, z) = \frac{\Phi_0}{r_0^2} (x^2 + y^2 - 2z^2) \quad (2)$$

which is created by applying the potential

$$\Phi_0 = U + V \cos(\Omega t + \theta) \quad (3)$$

to the ring electrode while the end-caps are grounded. Here, U is a d.c. potential and V an RF potential with angular frequency Ω and phase angle θ (note θ here refers to single ions entering the trap, the assembly of ions in the beam from the ICP would be evenly distributed with respect to θ). The trapping efficiencies of ions injected into the ion trap are strongly dependent on the value of θ . This is one of the principal problems in coupling an ICP source to the trap in that ions from the source have random phase with respect to the field in the trap.

The movement of an ion with mass m and charge Z in such a potential is described by well known equations:

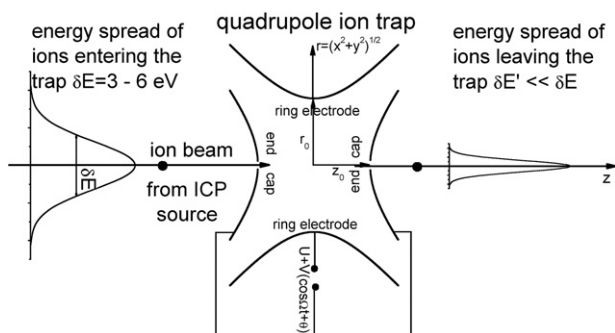


Fig. 1 QIT conditions for the simulation.

$$m \frac{d^2x}{dt^2} = -\frac{2Z}{r_0^2} [U + V \cos(\Omega t + \theta)]x \quad (4)$$

$$m \frac{d^2y}{dt^2} = -\frac{2Z}{r_0^2} [U + V \cos(\Omega t + \theta)]y \quad (5)$$

$$m \frac{d^2z}{dt^2} = \frac{4Z}{r_0^2} [U + V \cos(\Omega t + \theta)]z \quad (6)$$

where x , y and z denote the ion coordinates with respect to the reference frame in the centre of the QIT (see Fig. 1). Introducing a new variable $\xi = (\Omega t + \theta)/2$ these equations can be re-written as:

$$\frac{d^2u}{d\xi^2} + (a - 2q \cos 2\xi)u = 0, \quad u = x; y; z \quad (7)$$

which is known as the Mathieu equation. When $u = z$, the parameters a and q are given by:

$$a_z = \frac{-8ZU}{mr_0^2\Omega^2}, \quad q_z = \frac{4ZV}{mr_0^2\Omega^2} \quad (8)$$

while in the case of $u = x, y$ they are given by $a_x = a_y = -a_z/2$ and $q_x = q_y = -q_z/2$. It is well known that for certain values of parameters a_z and q_z , an ion of a particular m/z ratio moves along a stable orbit. These “stable” values of a_z and q_z compose a compact region in the (a_z, q_z) plane.¹² These equations apply when the motion of the ion is governed by the RF field only, so space charge effects are not taken into account. ICP-MS-CLS is an ultra trace technique and the trap is placed post mass separation so this simplification is justified here.

In this work eqn (7) was solved numerically, by means of Numerov’s method.¹⁴ The calculation was carefully tested and, under all the conditions considered, it exactly reproduced the results obtained by the ITSIM version 5.0 programme.¹⁵

Operation of a QIT requires the presence of a buffer gas, the main purpose of which is to cool the trapped ions. The ion mean free path between two collisions with the atoms of the buffer gas is given by

$$\lambda = \frac{kT}{\sigma p} \quad (9)$$

where σ denotes the cross-section for elastic scattering of the ion with an atom of buffer gas, p and T are the pressure and temperature of buffer gas, and k the Boltzmann constant.

In order to serve as an ion beam cooler for ICP-MS-CLS the QIT has to work in two regimes, as shown in Fig. 2. During the “trapping” regime, which lasts the time t_t , the ions inside the QIT are governed only by the radio-frequency (RF) field. They lose energy through collisions with atoms of buffer gas, so that the “cooled” ion cloud concentrates near the centre of the trap. In the “extraction” regime, which lasts the time t_e , the electromagnetic field inside the trap is adjusted, to eject ions out of it.

There are 4 ways of extracting ions from the trap:

(a) By applying a high RF voltage, which is the usual way to extract ions in QIT mass spectrometry.

(b) By allowing ions to drift out of the trap under zero field conditions, potentially assisted by exiting buffer gas.

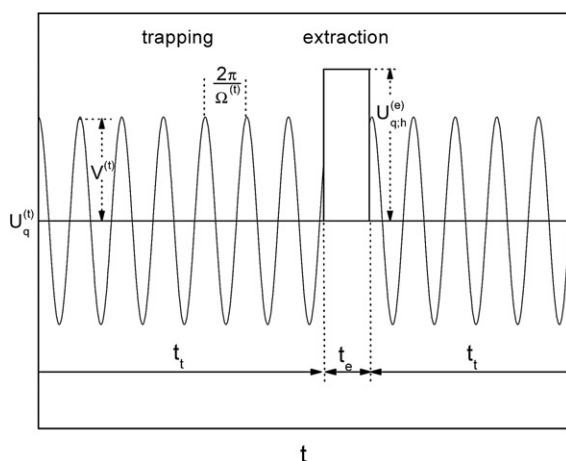


Fig. 2 Two regimes of QIT operation: (t) – trapping regime with $\Omega^{(t)} > 0$, $V^{(t)} > 0$, $U_q^{(t)} \geq 0$, and (e) – extraction regime $\Omega^{(e)} = 0$, $V^{(e)} = 0$, $U_q^{(e)} \geq 0$, $U_h^{(e)} \geq 0$. U_q is the d.c. voltage applied to the ring electrode (quadrupolar field) and U_h the d.c. voltage applied to the end caps (homogeneous field).

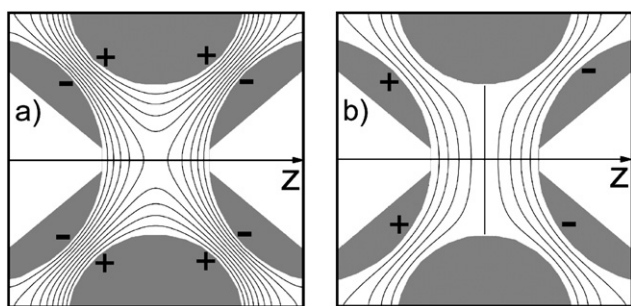


Fig. 3 Electrostatic potential inside the trap during “extraction”; mode: (a) quadrupolar field; (b) “homogeneous” field. The figures were drawn by SIMION 6.0.¹⁶

(c) By applying a d.c. voltage U_q to the ring, and end-cap electrodes. The field inside the trap is quadrupolar, see Fig. 3a (drawn in SIMION),¹⁶ but a constant one, so that the ion motion is described by eqn (4)–(6) with $U \neq 0$ and $V = 0$. The established field moves the ions toward both end caps (see Fig. 3a).

(d) By applying a d.c. voltage U_h to the end-caps, keeping the ring electrode grounded. Such a field moves the ions toward the aperture at the right end-cap (see Fig. 3b). Bearing in mind that the electric field applied for ion extraction is relatively weak, it can be treated as homogeneous near the z -axis. Using this approximation, the ion motion is described by the equations:

$$m \frac{d^2x}{dt^2} = m \frac{d^2y}{dt^2} = 0; \quad m \frac{d^2z}{dt^2} = \frac{ZU_h}{2z_0} \quad (10)$$

3. Simulation of ion beam cooling

The investigation presented here consists of optimizing the operational parameters of the QIT so that it can serve as an ion beam cooler for ICP-MS-CLS. The principal difference from normal trapping/cooling experiments is that the ions have to be extracted from the trap for subsequent acceleration and CLS detection. A commonly used trap geometry has the dimensions

$r_0 = 1$ cm and $z_0 = 0.7071$ cm, which exactly satisfy eqn (1). Because of this, just these values have been used in these calculations. The buffer gas employed was helium (He).

Keeping in mind that the purpose of this work was to investigate the possibility of using a 3D trap for cooling ions for CLS detection, and to limit the computational effort, specific conditions were chosen that are representative of those that might be found in ICP experiments. Thus an unspecified ion with mass $m = 100$ amu and charge $Z = 1$ was chosen as the test analyte. The mean ion energy in the beam was $E = 20$ eV (a range from 8–25 eV might be typical, so this was at the upper and least favourable end) with an energy spread of $\delta E = 3$ eV. The energy (velocity) of ions which entered the trap in the simulation was determined randomly, but in such a way that the chosen distribution was conserved (see Fig. 1 and 4).

The time of appearance of an ion in the trap entrance was determined randomly, in agreement with the beam intensity. The ions entered the trap through the aperture with diameter $D = 1.2$ mm, this means that every ion appeared at a randomly determined point $(x, y, -z_0)$, where the coordinates x and y satisfied the condition $\sqrt{x^2 + y^2} < D/2$. Finally, the direction of the ion velocity at that point was also randomly chosen among all directions from a cone whose axis of symmetry was parallel to the z -axis and the angle at the cone’s top was $\pi/6$.

It has already been mentioned that the ions, when they enter the trap, suffer collisions with atoms of the buffer gas and become “cooled”. Thus, modelling of the collision process was an important part of the simulation.

Between two consecutive collisions the ion moves along the trajectory $\vec{r}(t)$ which represents a solution of eqn (4)–(6) or (10). As was stated, these equations can be solved numerically; thus: knowing the ion’s position and velocity in two moments of time, t and $t - \Delta t$, the new position and velocity at time $t + \Delta t$ was calculated by means of Numerov’s method. It is clear that the time interval Δt , called the “step”, has to be much smaller than the period of RF field oscillations. Keeping in mind that the frequency of RF field used here is $f = 1$ MHz, the step was set at $\Delta t = 10^{-9}$ s.

Ion collisions with buffer gas atoms were modelled in a standard way:¹⁷ knowing the ion’s position $\vec{r}(t)$ and velocity $\vec{v}(t)$, the collision factor (CF) was determined from

$$CF = 1 - e^{-\frac{v\Delta t}{\lambda}} \quad (11)$$

After that, the velocity-dependent CF was compared with a random number between zero and one; when the random

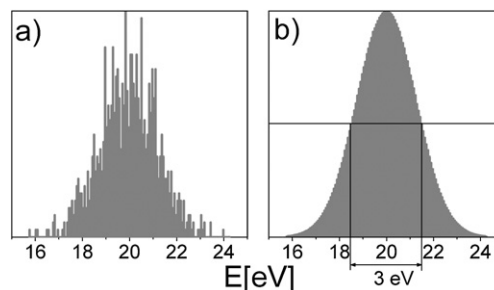


Fig. 4 The distribution of randomly determined input ion energies: (a) 10^3 ions; (b) 10^7 ions.

number was greater than CF, a collision occurred. The velocity of a particular buffer gas atom, \vec{v}_b , was randomly selected from the Maxwellian distribution which corresponded to a gas temperature $T = 300$ K. After that, the colliding analyte ion's velocity was adjusted in accordance with the formula:¹⁸

$$\vec{v}' = \frac{m_b v_r \vec{n}}{m + m_b} + \frac{m \vec{v} + m_b \vec{v}_b}{m + m_b} \quad (12)$$

where \vec{v}' and \vec{v} are the ion's velocities after and before collision, m and m_b are the masses of the ion and buffer gas atom, respectively. $v_r = |\vec{v} - \vec{v}_b|$ denotes the relative velocity of the ion and buffer gas atom, while \vec{n} is the unit-vector of the ion's direction after the collision. It was chosen randomly from among all possible directions.

The collisions were treated here in the frame of the hard sphere collision model, with the cross section $\sigma = 50 \text{ \AA}^2$ (set as default in ITSIM 5.0).¹⁵

4. Results and discussion

This work addressed two main questions: is it possible to achieve significant narrowing of the input ion beam and maintain that during extraction of ions from the QIT and, what is the efficiency of the whole process, *i.e.* what is the ratio of the number of trapped and extracted ions to the number of ions that entered the ion trap?

Ion trapping

The first step was determination of the best conditions for ion trapping. An important consideration, as already mentioned, is that the success of ion trapping strongly depends on the phase of the RF field θ relative to ion injection. A consequence is that an ion can enter the trap only if it appears at the trap entrance during short "time windows" and this significantly decreases the trapping efficiency from a continuous source, such as the ICP. However, once an ion finds itself inside the trap, then its destiny is determined, to a great extent, by the frequency and voltage of the RF field and the buffer gas pressure.

Fig. 5 shows the trapping efficiency as a function of RF field voltage and pressure. Obviously, the trapping efficiency is the

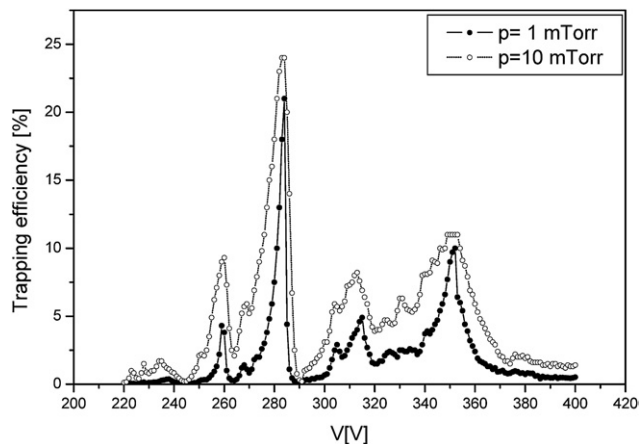


Fig. 5 The trapping efficiency of a 3D QIT as a function of RF field voltage and the buffer gas pressure.

upper limit of the efficiency for the combined process of (trapping + extraction). As can be seen from Fig. 5, the trapping efficiency strongly depends on the RF voltage and reached its highest value (for the $m/z = 100$ ion) at $V = 284$ V; this value was therefore used in all further work. Also, as expected, the trapping efficiency increases with pressure, because collisional "cooling" becomes more efficient. Apparently, further increase in pressure would improve the results presented, but at the cost of a loss of efficiency during the extraction cycle. Here, higher pressure causes lowering of the extraction efficiency and a broadening of the extracted ion energy spread.

Given that ICP-MS-CLS is ultimately an ultra trace technique, a 25% trapping efficiency is not fit for purpose. The random phase of the input ions is a major factor in this loss of efficiency, but one that is not readily overcome.

Ion extraction

Using the RF drive voltage. Extraction by raising the RF voltage, was found to be unsuitable for use with ICP-MS-CLS. The pressure in the trap was 1 mTorr and RF field voltage was raised to a high value of 1500 V to encourage complete extraction. The edge of the stability region for the ion occurs at $q_z = 0.908$ which is reached at ~ 928 volts and so all the ions should be ejected. As can be seen in Fig. 6, the ion energy distribution of the extracted ions was much worse than the distribution of "cooled" ions in the QIT ($T \approx 300$ K, $\Delta E \sim 0.03$ eV) and even much worse than that of the input ions from the ICP source

Zero field extraction. Before considering ion extraction by means of constant fields, the special case in which the electromagnetic field is completely switched off during the extraction time was considered. This means that the cooled ions leave the trap by drifting towards the exit aperture. As can be seen in Fig. 7, a significant part of the ions which are transmitted from the trap have energies distributed within 0.18 eV which is the desired result, however, the overall efficiency of such a regime, as expected, was found to be low approximately 6%. This might be increased by directing the buffer gas flow through the exit orifice,

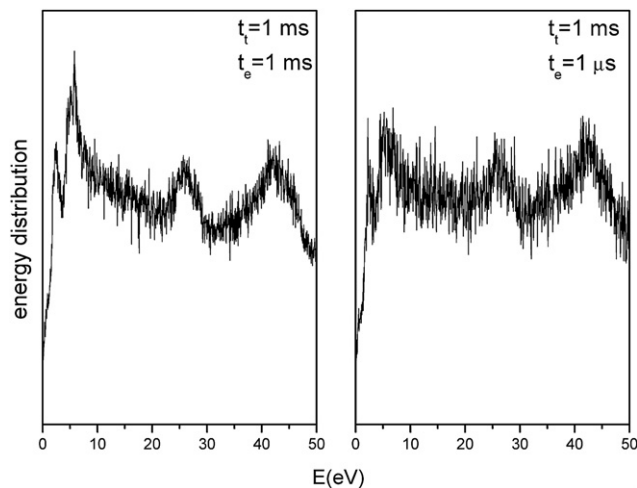


Fig. 6 Energy distribution of ions extracted from the trap by RF voltage $V = 1500$ V.

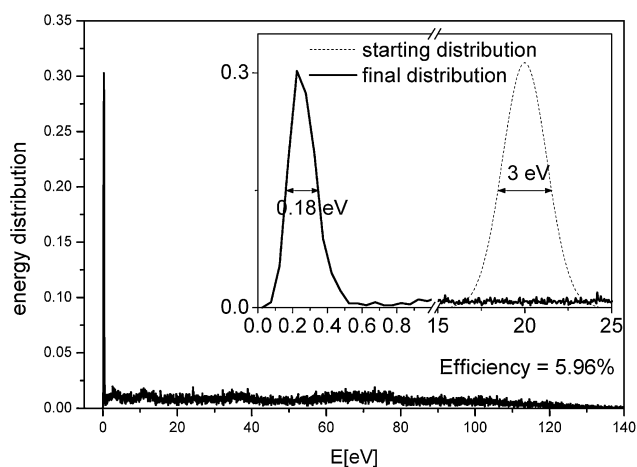


Fig. 7 Energy distribution of the ions exiting the trap by drifting towards the exit aperture. The parameters of the trap regime considered: $f^{(0)} = \Omega^{(0)}/2\pi = 1$ MHz, $V^{(0)} = 284$ V, $U_q^{(0)} = 0$, $p = 1$ mTorr, $t_t = 1$ ms, and $t_e = 50$ μ s. The efficiency was 5.96%.

but this was not investigated as part of this simulation because it requires additional design work on the trap environment and calculation of neutral gas flow fields.

Constant field extraction – quadrupolar and homogeneous fields.

Figs. 8–10 show the energy distributions of ions extracted from the QIT by quadrupolar (q) (see Fig. 3a) and “homogenous” (h) (see Fig. 3b) fields produced by applied voltages of 10, 20 and 50 V respectively. First of all, they clearly demonstrate that the extracted ion energy distribution is very dependent on the applied d.c. potential. As expected, the efficiency of the entire process increases with increasing extraction voltage, but the energy spread also increases: for $U_q^{(e)} = U_h^{(e)} = 10$ V, $\delta E \sim 0.5$ eV; for $U_q^{(e)} = U_h^{(e)} = 20$ V, $\delta E \sim 1$ eV and for $U_q^{(e)} = U_h^{(e)} = 50$ V, $\delta E \sim 2$ eV. Extraction by means of the quadrupolar field (thick line) was more successful than extraction by a “homogenous” field (thin line). It yielded a slightly higher efficiency together with

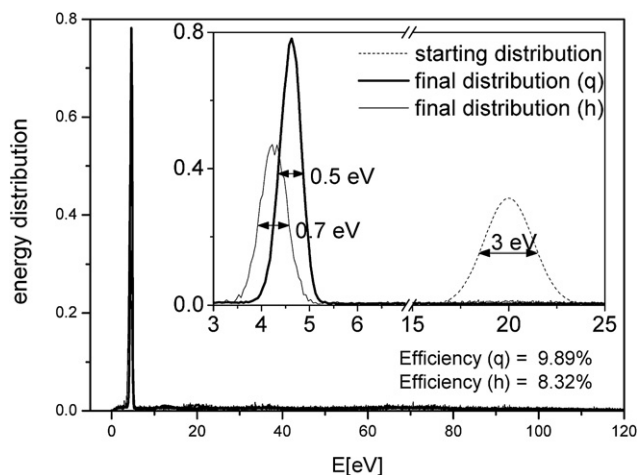


Fig. 8 Energy distribution of ions extracted from the trap with quadrupolar (q) $U_q^{(e)} = 10$ V and homogeneous (h) fields $U_h^{(e)} = 10$ V. The parameters of the trap regime are the same as in Fig. 7.

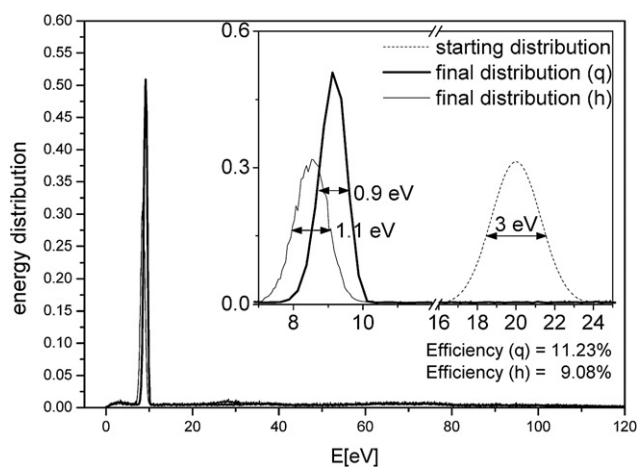


Fig. 9 Energy distribution of ions extracted from the trap with quadrupolar (q) $U_q^{(e)} = 20$ V and homogeneous (h) fields $U_h^{(e)} = 20$ V. The parameters of the trap regime are the same as in Fig. 7.

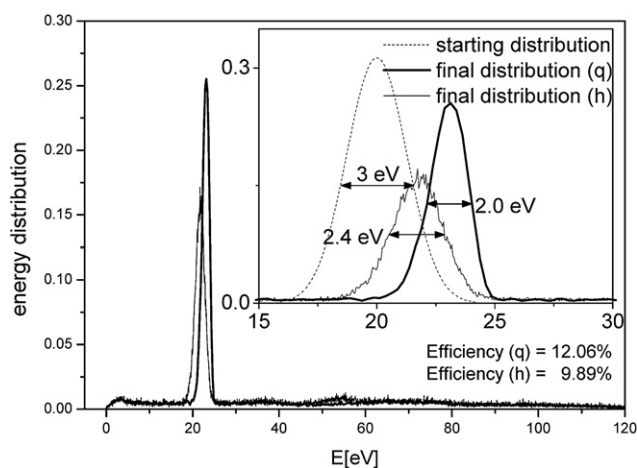


Fig. 10 Energy distribution of ions extracted from the trap with quadrupolar (q) $U_q^{(e)} = 50$ V and homogeneous (h) fields $U_h^{(e)} = 50$ V. The parameters of the trap regime are the same as in Fig. 7.

a narrower energy distribution, but still outside the requirements of ICP-MS-CLS.

Addition of reflectrons. Interestingly, it was noted that all the ion energy distributions had long, low intensity wings which suggested the presence of very energetic ions. These derive from ions that pass straight through the trap (the source was left “ON” during t_e to approximate real conditions with a continuous source such as the ICP), and are not cooled during t_t . To solve this problem, lines of code were included in the simulation that mimic the effect of reflectrons being added to the entrance and exit apertures such that the exit reflectron would be on during trapping and the entrance reflectron would be on during extraction. Reflectrons are well known devices used in TOF-MS systems.

This innovation solved the problem of ions passing straight through the trap and produced a narrowly distributed population of ions. This is demonstrated in Fig. 11 where it can be seen that the entire ion population is localised around well

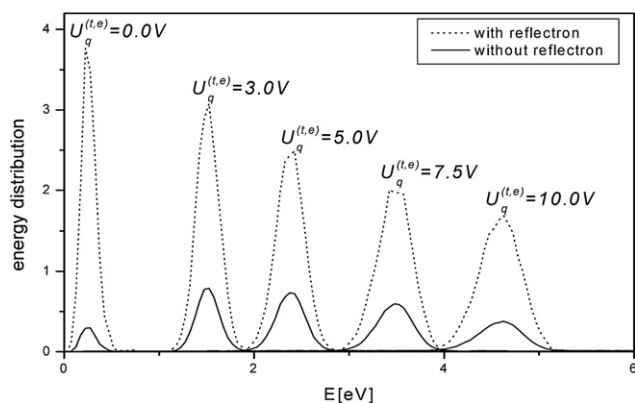


Fig. 11 Effect of introducing reflectrons to the entrance and exit apertures. The results in this figure are obtained under different conditions to those in Fig. 8–10. Namely, the d.c. quadrupolar voltage is turned on in both trapping and extraction regime, i.e. $U_q^{(t)} = U_q^{(e)}$. The transition to the extraction regime, and *vice versa*, is realized only by switching off/on the RF voltage.

Table 1 Efficiency and ion energy spread for ions extracted with a quadrupolar field from a QIT fitted with reflectrons. Fig. 1

U_q/V	Efficiency [%]	Energy Half Width/eV
0.00	6.21	0.18
3.00	8.07	0.30
5.00	8.93	0.35
7.50	9.32	0.44
10.00	10.51	0.53

defined and narrow energy regions with low wing contributions that are conserved upon extraction. However, there was little effect on the efficiency (a marginal improvement of <10%) because this was determined largely by the initial trapping efficiency, which depends strongly on the phase of the field as the ion enters the trap, and by ions missing the aperture and striking the walls during extraction. The data are summarised in Table 1.

The observation that it is difficult to conserve the cooled ion energy distribution during extraction and that the ion energy spread was strongly related to extraction voltage for all field configurations tested was not entirely expected. However, there are several factors that the model takes into account that explain this outcome. Firstly, the trapped ions have different directions when the extraction field is switched on and so some velocities will be additive and others subtractive, although this effect should be small because the ions should be thermalized at this point ($\Delta E \sim 0.3\text{eV}$). Similarly, they have differing start positions so that the effective field varies for each ion. Finally, energetic collisions occurring with the buffer gas may also be responsible for re-partitioning energy into the observed distribution.

Conclusions

The modeling has shown that the QIT in the form described here is not suitable for ion cooling for ICP-MS-CLS.

Ion cooling within the QIT (based on a standard small format commercial trap) is straightforward, as widely reported in the literature. The aim of this simulation however was to examine

whether these cooled ions could be extracted, whilst conserving the cooled energy distribution, for subsequent co-linear laser spectroscopy. This is certainly possible, but only with low overall efficiency (<10%). Four means of extraction were investigated using zero field, RF field only, quadrupolar field and homogeneous field. Of these, the standard RF field method produced a broadening of the ICP source energy distribution and the best results were obtained with a quadrupolar field.

It was found that the extracted ion energy distributions exhibited extended wings which were attributed to energetic ions passing straight through the trap during trapping and extraction. An innovation was the addition of virtual reflectrons to the QIT to block input ions during trapping and extraction and these produced a significant improvement in the extracted energy distribution, but did not significantly improve efficiency. The poor efficiency reflects the well known difficulty of coupling a continuous ion source, such as the ICP, with a phase sensitive trapping device. A second loss process occurs during the extraction process due to ions missing the exit aperture.

A practical device for ICP-MS-CLS application would require a transmission efficiency of >75% and conservation of the in-trap energy distribution shown in Fig. 7. To ascertain whether this might be attainable requires considerably more computational effort, perhaps within the context of a self-optimising design. Parameters to be further investigated would be: trap pressure, use of other gases, or trap geometry/size. Alternatively a linear trap, derivative of those used in collision/reaction cell ICP-MS instruments or as described previously,² might be considered.

The major limitations of ICP-MS and ICP-MS-CLS in their current state of development relate to the interface, where most of the sample ions are lost and broadening of the ion energy distribution occurs. Thus, current work is focussed on this area, which may ultimately be more productive than attempting to correct the problems created downstream.

Acknowledgements

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