Quadrupole ion traps and trap arrays: geometry, material, scale, performance

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Quadrupole ion traps are reviewed, emphasizing recent developments, especially the investigation of new geometries, guided by multiple particle simulations such as the ITSIM program. These geometries include linear ion traps (LITs) and the simplified rectilinear ion trap (RIT). Various methods of fabrication are described, including the use of rapid prototyping apparatus (RPA), in which 3D objects are generated through point-by-point laser polymerization. Fabrication in silicon using multilayer semiconductor fabrication techniques has been used to construct arrays of micro-traps. The performance of instruments containing individual traps as well as arrays of traps of various sizes and geometries is reviewed. Two types of array are differentiated. In the first type, trap arrays constitute fully multiplexed mass spectrometers in which multiple samples are examined using multiple sources, analyzers and detectors, to achieve high throughput analysis. In the second, an array of individual traps acts collectively as a composite trap to increase trapping capacity and performance for a single sample. Much progress has been made in building miniaturized mass spectrometers; a specific example is a 10 kg hand-held tandem mass spectrometer based on the RIT mass analyzer. The performance of this instrument in air and water analysis, using membrane sampling, is described.

Keywords: miniature instrument, fieldable mass spectrometer, multiplexed mass spectrometer, portable instrument, trace analysis, ion motion, simulations

Introduction

As chemical analysis outside the laboratory has become more important, so has the need to miniaturize analytical instruments, including the mass spectrometer. Among the various types of mass analyzers, the quadrupole ion trap is probably best suited to miniaturization. The reasons for this are (i) **pressure tolerance**: ion traps can be operated at higher pressures than other mass spectrometers and, as their size is reduced, the shorter ion paths result in fewer collisions, thereby requiring even less pumping and (ii) **lower voltage/power**: reducing trap size can be achieved while maintaining constant field strength even while using lower voltages and, hence, smaller and lighter rf power supplies. In spite of the advantages of these small analyzers, difficulties arise, principally (i) **fabrication precision**: greater absolute precision is required to build smaller traps and (ii) **lower trapping capacity**. This is an inevitable result of using smaller analyzers but it can be offset by using arrays of smaller traps.

The development of miniature ion trap mass spectrometers is traced in Table 1. The major instrumentation developments in ion traps since the early demonstrations of mass analysis capabilities, the introduction of the tandem mass spectrometry (MS/MS) experiment and the mass-selective instability scan, have dealt with alternative trap geometries. Reduction in trap size calls for simplifications in geometry and also for alternative methods of fabrication, provided that these can meet the necessary precision requirements. The simple cylindrical ion trap[1] (CIT, Figure 1) is easy to fabricate and is especially easy to make in planar arrays of identical units. The recognition that linear ion traps (LITs, or 2D traps) have (i) much greater efficiency for trapping externally generated ions and (ii) much greater ion trapping capacities than quadrupole ion traps [QITs (3D traps)] of the same volume[2–4] has led to widespread use of these devices in laboratory-scale mass spectrometers. These same advantages can be made available in miniature fieldable instruments by simplification of the ion trap geometry. This is achieved in the rectilinear ion trap (RIT),[4] a six-element device that bears the same formal relationship to the LIT that the CIT does to the QIT. (Figure 1) An alternative and elegant high ion capacity

DOI: 10.1255/ejms.832 ISSN 1469-0667

Table 1. Time line for miniature ion traps.

Contributor	Contribution	Time
Paul & Dehmelt	Concept & demonstration of ion traps as mass analyzers	1950s
Todd & March	Ion traps as ion/molecule reactors	1970s
Stafford	Mass selective instability scan	1984
Cooks & Todd	MS/MS using ion traps	1987
Hemberger	¼ size Paul trap	1991
Cooks *et al.*	Mass Range extension by moving working point	1991
Franzen	Higher order field components; resonant ejection	1992–96
Cooks *et al.*	Ion Trap arrays	2002
Patterson *et al.*	Miniature ion trap mass spectrometer	2002
Blain; Ramsey	Micro ion traps arrays	2002–06
Ouyang, Cooks	Rectilinear ion trap (RIT)	2004
Ouyang *et al.*	Handheld ion trap mass spectrometer	2006
Lammert *et al.*	Miniature toroidal ion trap	2006

geometry also used in a miniature mass spectrometer is the toroidal trap,[5] although ion injection and ejection is not as simple. Table 2 lists geometries used in both miniature and laboratory scale mass spectrometers.

Adequate performance from the simplified CIT[1] and RIT[4] ion traps requires that critical dimensions relating to spacing and size of the electrodes (rings in the CIT, planar plates in the RIT) be used. This task is best accomplished in a systematic fashion with the aid of simulations of mass spectra. A simulation program, such as ITSIM created in our laboratory, should calculate the motions of the collection of ions in a trap, allowing the user to specify exact details of electrode geometry and exact operating conditions, including pressure. For the simulation of ion motion inside an electrode assembly, a 3D mechanical model was first generated using a computer-aided design (CAD) drawing program such as ProEngineering, Inventor, AutoCAD or Solid Works. The mechanical model was then imported into a 3D field solver, such as COMSOL (Comsol Inc.) or HFSS (Ansoft Inc.), to solve the electric field inside the structure. The calculated

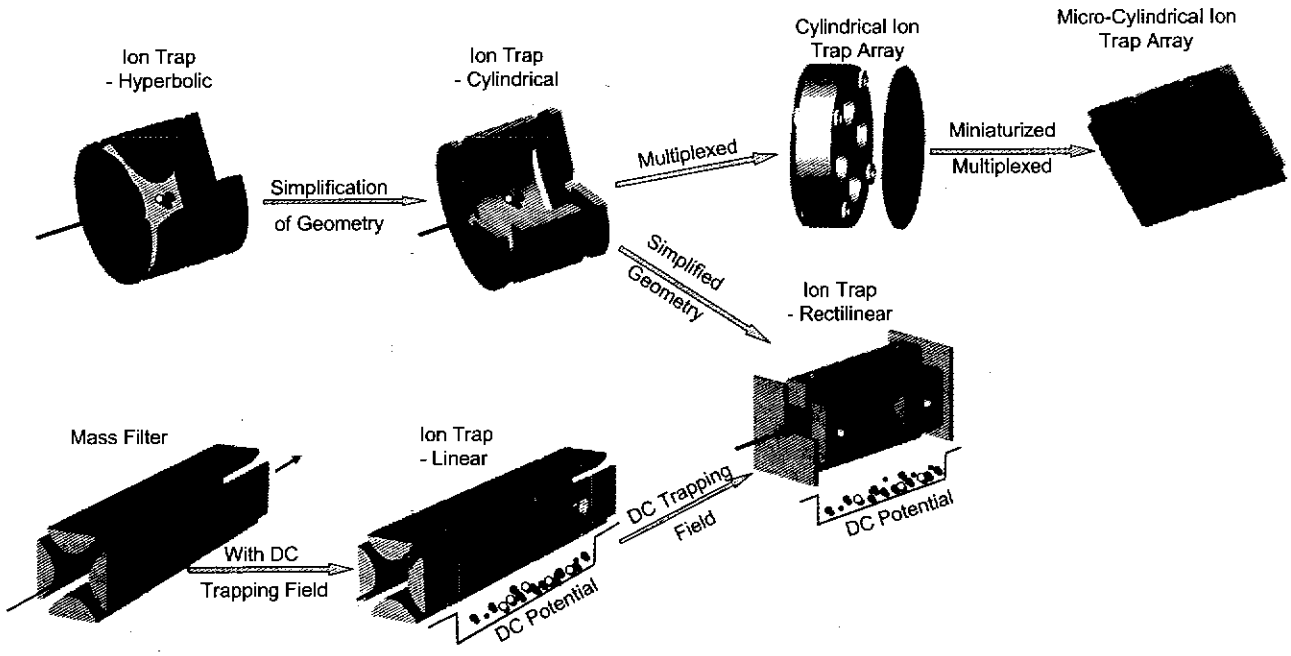

Figure 1. Relationship between 2D- and 3D ion trap geometries and the simplified CIT and RIT forms used in miniature mass spectrometers.

Table 2. Ion trap geometries.

Geometry	Developer	Time	Feature
Quadrupole ion trap[6]	W. Paul	1953	3D, hyperbolic electrodes
Cylindrical ion trap[1]	Langmuir	1961	3D, cylindrical electrode
Toroidal ion trap[7]	Oak Ridge	2001	Toroidal, hyperbolic electrodes
Linear ion trap[2,8]	Thermo Electron	1995/2002	2D, hyperbolic electrodes, orthogonal ejection
Linear ion trap[3]	Sciex	2002	2D, round electrodes, axial ejection
Rectilinear ion trap[4]	Purdue University	2004	2D, rectilinear electrodes, orthogonal ejection

field was then imported into ITSIM. The processes used in ion manipulation are followed in the simulation. Ion trajectories are calculated by solving the classical equation of motion using Runge–Kutta integration methods. Ion–neutral collisions and ion–ion space charge effects can be considered. Simulated ion trajectories and ion spatial distributions, as well as mass spectra, can be displayed and exported.

Alternatives to ITSIM,[9] including the more widely used SIMION program,can be used to simulate mass spectra. The advantages of ITSIM are that it is designed for ion traps and considers collisions stochastically, including the possibility of accounting for inelastic as well as elastic collisions.[10] Both approaches simulate ion transport through ion optical systems. In the future, ITSIM will cover higher pressure regimes in which flow forces are not negligible compared to electrical forces. The **simulation-before-fabrication approach** involves a cycle of simulations: geometry → field → ion motion → simulated mass spectrum → modified geometry → modified field → modified ion motion → modified simulated mass spectrum, etc. which is run until performance is optimized. Simulations not only help optimize the design but provide information on dimensional sensitivity and failure mechanisms.

In launching a program of miniaturization of quadrupole ion traps, two contrasting approaches are possible, conveniently termed the **top-down approach** and the **bottom-up approach**. The top-down approach starts with an existing lab-scale instrument and reduces the size of the mass analyzer and vacuum pumping system, which allows reduction in the size of the electronics and in power consumption. This, in turn, allows reduction in the size and weight of the instrument as well as operation under battery power, permitting the development of hand-held devices. This top-down approach has been employed in this laboratory in a program that started in 1998 and is continuing. The effort has led to a series of miniature instruments, mini 5, mini 7 and mini 10, amongst them, of successively smaller size but not greatly reduced performance. Significantly, reduction in size of the mass analyzer, while the starting point for these developments, has turned out not to be the main power/size/weight limiting factor. Currently the 10 kg mini 10[11] uses an analyzer with a 10×8 mm cross-section, not that much smaller than the standard $r_0 = 10$ mm "full-sized" mass analyzers used in benchtop systems. The performance of this mini mass spectrometer is summarized below. Note that the systematic process of miniaturization is not completed with this system and that further top-down miniaturization to perhaps a 3 kg total system size can be expected in future.

The alternative **bottom-up approach** starts with a micro-scale ion trap and develops a mass spectrometer around this element. Because it uses a microtrap, ion trapping capacity is greatly reduced and must be increased by utilizing an array of identical traps. Considerable work has been done on using arrays of small traps by the Sandia/Purdue[12] and UNC/IBM[13] teams. Standard silicon micro-electronic fabrication methods were used and this major task has been the focus of these efforts. Arrays of cylindrical ion traps have been built but these efforts are still in the early stages, so testing has been done in much larger instruments meaning that the total package size is still larger than that resulting from the top-down approach. In addition, issues with the performance of micro-trap arrays remains limited.

Ion trap arrays in the bottom-up approach

Blain *et al.*[12] have used a tungsten/silicon based micro-fabrication technique to create arrays of micro-cylindrical ion traps on the 1, 2, 5 and 10 micron scales for the individual trap radii. These arrays are several cm^2 in area and consist of 10^6 individual elements in the smallest (1 μm) scale. Simulations[12] indicate several remarkable properties of the smallest traps: (i) strong space charge effects in the 1 μm devices result in spontaneous ion ejection until just one ion remains in each trap, (ii) the devices could be operated at atmospheric pressure because of the short mean-free paths involved and (iii) the total number of trapped ions is greater than that in a full-size conventional trap. However, there are significant problems (i) the geometry includes sloping cylinder sides and surface roughness, (ii) the trap capacitance is ~500 pF which requires a high RF driving power and (iii) conventional electron multiplier detection cannot be used, so detection must rely on electronic amplification or image current measurement.

Ramsey and co-workers[13] have fabricated arrays of 256 and 2304 cylindrical ion traps on the 20 μm scale using

phosphorus-doped polysilicon and silicon dioxide. These trap arrays were tested at a pressure of 10^{-4} torr, using an RF of 100 MHz. Spectra of xenon ions were obtained at a resolution (FWHM) of ~5 units. In a related development typical of other efforts, Syms *et al.* of Imperial College, London and Microsaics Systems, reported the microelectromechanical systems (MEMS)-based fabrication of a quadruopole mass filter with rods of 500 micron diameter and 30 mm in length. The device shows reasonable performance (mass range 400, unit resolution at 219) although the total instrument body is roughly shoebox sized and weighs 10 kg.[14]

It is also worth explicitly mentioning other complementary methods used to fabricate small ion traps, which can be divided into two categories: conventional machining techniques and selective metallization of insulators (Table 3). The latter category includes methodologies which rely on well established fabrication techniques to create the insulating skeleton paired with novel metallization processes to form the electrodes. One of the inherent problems with selective metallization procedures of insulators is uniform distribution of the metallic coating within the formed structure; many of the problems with mini-traps are believed to have been the result of charge build-up on insulating surfaces.

Ion trap arrays in multiplexed mass spectrometers

The arrays of ion traps used in the bottom-up approach function collectively, increasing ion trapping capacity and decreasing power requirements, but not otherwise influencing the data taken. Arrays of ion traps, often smaller than full-sized, are also used in multiplexed experiments. In the best-known of these experiments, multiple samples are examined in parallel using multiple sources, mass analyzers and detectors, but sharing the vacuum system and some components of the electronics. These arrayed instruments allow high throughput to be carried out on a set of samples; or they can be used to record different types of mass spectra on a sample that is split prior to analysis, thereby increasing the rate of acquisition of complementary information. An example of the latter is the simultaneous recording of positive and negative ion spectra using electron ionization (EI) and chemical ionization (CI) on the same sample.[19]

Miniature mass spectrometers from the top-down approach

Construction of mini 10

Rectilinear ion traps (RITs)[4] are used as mass analyzers in hand-held mass spectrometers to retain adequate sensitivity and to provide high selectivity via MS^n capabilities. The dimensions of the current mini 10 shoebox-size, hand-held mass spectrometers[11] are 34 cm in length, 21 cm in width and 19 cm in height. The total weight, including vacuum system and batteries, is just under 10 kg. The mass analyzer is fabricated in metal. The RF circuit, using air cooling and a compact coil, provides sufficient RF amplitude for the desired mass range given the chosen size analyzer (usually a few mm in critical dimensions and a few cm in length). Small turbo pumps allow the device to be operated while in motion and oil-free, two-stage diaphragm pumps serve as rough pumps. Power is provided by rechargeable metal hydride batteries. A glow discharge cell has been developed as a pressure tolerant low power (0.4 W) electron source for EI and CI. Control electronics with networking capabilities have been developed. Air samples of small volume can be examined directly; alternatively, a short preconcentration period using a semi-permeable membrane can be used for water or air analysis, while solid sorbents allow preconcentration of components of air samples. The instrument can be continuously operated in the field in the active analysis mode for more than 40 min using three 7.2 V battery packs.

Performance of mini 10

Water and gas samples containing various organic compounds, including methyl salicylate, naphthalene, triacetone triperoxide (TATP) and para-nitrotoluene, have been analyzed in the MS and product ion MS/MS modes. A mass/charge range of *m/z* 30 to *m/z* 500 has been achieved with unit resolution over much of the range. Detection limits of 1 ppb have been obtained for both methyl salicylate in air and naphthalene in a water/methanol solution using non-heated membrane tubing. The solid explosive TATP can be detected in 1 ng (absolute) amounts. Collision induced dissociation is achieved using SWIFT waveforms for isolation and a resonant AC signal for mass-selective excitation. The handheld instrument can communicate with remote computers via wired or wireless networks. A network sensing

Table 3. Miniature ion trap fabrication techniques.

Fabrication methodology	Size scale	Time	Featured example
Conventional machining	1 mm	Days	Patterson *et al.*[15], Ramsey *et al.*[16]
LIGA	100 s μm	Months	Blain *et al.*[12]
LTCC	0.5 mm	Weeks	Short *et al.*[17]
Extrusion	1 mm	Weeks	Cooks and Ouyang, unpublished
Stereolithography	100 s μm	Days	Chappell *et al.*[18]

system has also been developed to acquire the data from multiple handheld mass spectrometers to perform compound recognition and sound alarms automatically when targeted chemicals are observed in monitored samples

Lessons and prospects

The development of mini mass spectrometers at Purdue University has served as a mechanism for driving experiments in entrepreneurship and commercialization. The low-cost methodologies used have helped launch several companies under the Indiana Instrumentation Institute, the most successful of which is Griffin Analytical Technologies, Inc. Much has been learned about driving a project through the lab prototype stage and into the engineering prototype stage, through development of a prototyping facility in Purdue's interdisciplinary Discovery Park. The mini 10 was developed during 2005 and 2006 in this non-commercial facility by a group of professional engineers, graduate students in engineering and graduate students in analytical chemistry. Such a diverse team is a model for future work at the interface between analytical instrumentation and engineering.

For the next generation of hand-held instruments, micro turbo pumps with a weight of 500 g will be used. MS^n will be performed without using SWIFT and other functions will also be simplified to reduce the electronics needed. Various methods of intelligent power control will be used to extend greatly the instrument operation time on battery power. The size and power consumption of the next generation of hand-held instruments are both estimated to be half of the current values.

Acknowledgement

This work was supported by HSARPA (HSHQPA-05-9-0033) and NSF (05-289-486ECS). Contributions from the Indiana 21st Century Fund, and the Purdue Research Foundation TRASK fund are gratefully acknowledged. The collaboration of Dennis Barket and Garth Patterson at Griffin Analytical Technologies is much appreciated.

References

1. J.M. Wells, E.R. Badman and R.G. Cooks, "A Quadrupole Ion Trap with Cylindrical Geometry Operated in the Mass-Selective Instability Mode", *Anal. Chem.* **70,** 438–444 (1998). doi: 10.1021/ac971198h
2. J.C. Schwartz, M.W. Senko and J.E.P. Syka, "A Two-Dimensional Quadrupole Ion Trap Mass Spectrometer", *J. Am. Soc. Mass Spectrom.* **13,** 659–669 (2002). doi: 10.1016/S1044-0305(02)00384-7
3. J.M. Hager, "A New Linear Ion Trap Mass Spectrometer", *Rapid Commun. Mass Spectrom.* **16,** 512–526 (2002). doi: 10.1002/rcm.607
4. Z. Ouyang, G. Wu, Y. Song, H. Li, W.R. Plass and R.G. Cooks, "Rectilinear Ion Trap: Concepts, Calculations, and Analytical Performance of a New Mass Analyzer", *Anal. Chem.* **76,** 4595–4605 (2004). doi: 10.1021/ac049420n
5. S.A. Lammert, A.A. Rockwood, M. Wang, M.L. Lee, E.D. Lee, S.E. Tolley, J.R. Oliphant, J.L. Jones and R.W. Waite, "Miniature Toroidal Radio Frequency Ion Trap Mass Analyzer", *J. Am. Soc. Mass Spectrom.* **17,** 916–922 (2006). doi: 10.1016/j.jasms.2006.02.009
6. W. Paul and H. Steinwedel, "A New Mass Spectrometer without a Magnetic Field", *Z. Naturforsch.* **8a,** 448 (1953).
7. S.A. Lammert, W.R. Plass, C.V. Thompson and M.B. Wise, "Design, Optimization and Initial Performance of a Toroidal Rf Ion Trap Mass Spectrometer", *Int. J. Mass Spectrom.* **212,** 25–40 (2001). doi: 10.1016/S1387-3806(01)00507-3
8. M.E.S. Bier and E.P. John, "Ion Trap Mass Spectrometer System and Method", *US patent 5,420,425.* (1995).
9. H.A. Bui and R.G. Cooks, "Windows Version of the Ion Trap Simulation Program ITSIM: A Powerful Heuristic and Predictive Tool in Ion Trap Mass Spectrometry", *J. Mass Spectrom.* **33,** 297–304 (1998). doi: 10.1002/(SICI)1096-9888(199804)33:4<297::AID-JMS665>3.0.CO;2-V
10. W.R. Plass and R.G. Cooks, "A Model for Energy Transfer in Inelastic Molecular Collisions Applicable at Steady State or Non-Steady State and for an Arbitrary Distribution of Collision Energies", *J. Am. Chem. Soc. Mass Spectrom.* **14,** 1348–1359 (2003). doi: 10.1016/j.jasms.2003.08.012
11. L. Gao, Q. Song, G.E. Patterson, R.G. Cooks and Z. Ouyang, "Handheld Rectilinear Ion Trap Mass Spectrometer", *Anal. Chem.* **78,** 5994–6002 (2006). doi: 10.1021/ac061144k
12. M.G. Blain, L.S. Riter, D. Cruz, D.E. Austin, G. Wu, W.R. Plass and R.G. Cooks, "Towards the Hand-Held Mass Spectrometer: Design Considerations, Simulation, and Fabrication of Micrometer-Scaled Cylindrical Ion Traps", *Int. J. Mass Spectrom.* **236,** 91–104 (2004). doi: 10.1016/j.ijms.2004.06.011
13. S. Pau, C.S. Pai, Y.L. Low, J. Moxom, P.T.A. Reilly, W.B. Whitten and J.M. Ramsey, "Microfabricated Quadrupole Ion Trap for Mass Spectrometer Applications", *Phys. Rev. Lett.* **96,** 120801 (2006). doi: 10.1103/PhysRevLett.96.120801
14. M. Gear, R. Syms, S. Wright and A. Holmes, "Monolithic MEMS Quadrupole Mass Spectrometers by Deep Silicon Etching", *J. Microelectromech. Syst.* **14,** 1156–1166 (2005). doi: 10.1109/JMEMS.2005.851799
15. L. Riter, Y. Peng, R. Noll, G. Patterson, T. Aggerholm and R. Cooks, "Analytical Performance of a Miniature Cylindrical Ion Trap Mass Spectrometer", *Anal. Chem.* **74,** 6154–6162 (2002). doi: 10.1021/ac0204956
16. J. Moxom, P. Reilly, W. Whitten and J. Ramsey, "Analysis of Volatile Organic Compounds in Air with a Micro Ion Trap Mass Analyzer", *Anal. Chem.* **75,** 3739–3743 (2003). doi: 10.1021/ac034043k

17. A. Chaudhary, F.H.W. van Amerom, R.T. Short and S. Bhansali, "Fabrication and Testing of a Miniature Cylindrical Ion Trap Mass Spectrometer Constructed from Low Temperature Co-Fired Ceramics", *Int. J. Mass Spectrom.* **251,** 32–39 (2006). doi: 10.1016/j.ijms.2005.12.013
18. M. Yu, M. Fico, S. Kothari, Z. Ouyang and W.J. Chappell, "Polymer-Based Ion Trap Chemical Sensor", *IEEE Sens. J.* **6,** 1429–1434 (2006).
19. A.M. Tabert, A.S. Misharin and R.G. Cooks, "Performance of a Multiplexed Chemical Ionization Miniature Cylindrical Ion Trap Array Mass Spectrometer", *Analyst* **129,** 323–330 (2004). doi: 10.1039/b314178k

Received: 2 December 2006
Revised 29 December 2006
Accepted: 29 December 2006
Publication: 9 January 2007