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Short communication

Performance of a low voltage ion trap

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ABSTRACT

Reduced power operation of a mass analyzer with minimum loss of spectral resolution and mass range is desirable in portable instruments. Miniaturizing quadrupole-based ion traps can be especially worthwhile since the RF amplitude necessary for mass analysis scales with the square of the analyzer dimensions. The performance of a miniature, stainless steel, rectilinear ion trap (RIT) with dimensions of 1.66 mm × 1.43 mm (x_0 and y_0 respectively) is characterized by sampling externally generated ions and performing mass analysis without benefit of differential pumping to simulate conditions in a miniature system. This system is capable of detecting analyte ions of up to m/z 1250 at operating voltages of 610 $V_{0\text{-p}}$ (drive frequency of 1.105 MHz), and with spectral resolution on the order of 2 Th (FWHM) across the entire mass range. The ability to acquire structural information through tandem MS is also demonstrated.

1. Introduction

Demand for in situ detection of specific compounds at the parts-per-billion (ppb) and parts-per-million (ppm) levels is one of the factors driving the development of portable mass spectrometers [1–5]. The ability to successfully miniaturize and/or simplify the geometry of instrument components, particularly the electronics, vacuum system, and mass analyzer [6,7] is the key to this development. Quadrupole ion trap mass analyzers are well suited for use in portable instruments due to their ability to operate at elevated pressures (10^{-2} to 10^{-3} Torr), relaxing the vacuum system requirements, and the ability to use a single mass analyzer for tandem MS experiments. Additionally, ion traps, especially those with electrodes of simple geometry such as the cylindrical ion trap [8] (CIT) and the rectilinear ion trap [7] (RIT), are more easily scaled to mini [9–11] and micro [12–15] dimensions than other mass analyzer types.

RITs are simplified linear ion trap mass analyzers consisting of planar electrodes, viz. two end caps, and pairs of Y-electrodes and X-electrodes, respectively. At the usual size scale the optimized, dimensions are 5 mm × 4 mm nominally (one-half the distance between opposing X and Y-electrodes) [7]. This device has been well characterized and utilized as the mass analyzer in portable instruments for in-field applications [16–19]. Since the operating voltage scales as the square of the dimensions of the trapping electrodes, and power scales to the square of the RF amplitude, greatly reduced power requirements needed for portable instruments can be achieved by size reduction [10].

RIT mass analyzers have previously been fabricated with nearly the same geometry as used in this work and they have given peak widths of approximately 1.5–2 Th (FWHM) [20,21]. However, these earlier experiments did not employ small total MS systems, and notably they did not suffer from the limited pumping capabilities characteristic of handheld MS systems. In this work a miniaturized, steel, RIT was characterized in a single stage manifold, without ion optics or specialized buffer gas, and under pressure conditions comparable to those of a portable mass spectrometer utilizing a discontinuous atmospheric pressure interface (DAPI) to sample externally generated ions [22–24]. The performance of a miniaturized, steel, RIT analyzer (1.66 mm × 1.43 mm for X_0 and Y_0 respectively; 1/3rd the scale of the usual RIT dimensions) operated at pressures expected for a portable instrument is characterized and evaluated in this study.

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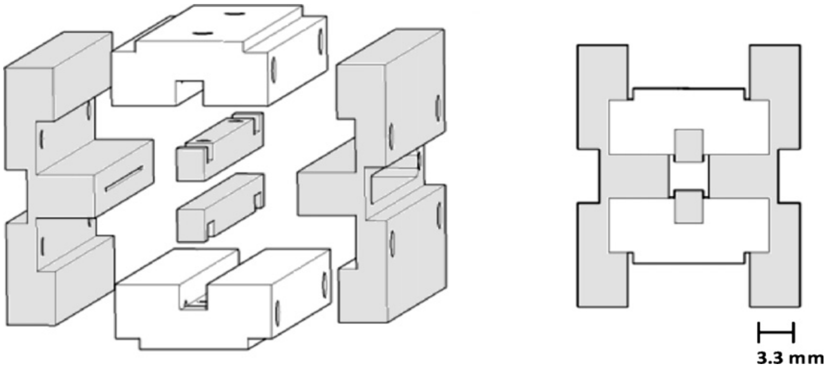

Fig. 1. Computer aided design (CAD) model of the miniature RIT trapping electrodes and ceramic spacers. The ceramic spacers (white) ensure proper alignment of the trapping electrodes (gray) and act as insulators.

2. Materials and methods

Machining of the electrodes (304 stainless steel) was executed using computer numerical control (CNC) followed by hand polishing of the inner electrode surfaces to a mirror finish. Precision cut Macor ceramic established the inter-electrode distances and formed the insulating spacers between adjacent electrodes (Fig. 1). Analyzer assembly was completed by hand. Upon final assembly the average gap spacing (distance between adjacent X and Y-electrodes) was 0.590 mm, and the trapping dimensions (distance between opposing X and Y-electrode pairs) were 1.66 mm and 1.43 mm respectively. These measurements were made using an optical microscope (SmartScope MVP 300, Optical Gauging Products, Inc.) and are accurate to ±1 μm. The length of the ion trap (*z*-dimension) and the dimensions of the ion ejection slits in the X-electrodes were measured to be 40 mm and 0.33 mm × 25 mm, respectively, as measured with a micrometer (Mitutoyo, CD-6 BS). As in all linear ion traps, the *z*-dimension of this device is critical to the ion trapping volume but does not impact the generation of a quadrupolar field in the *x*–*y* plane. A confining force is however, established in the *z*-dimension by applying a DC potential to the end cap electrodes.

Mass calibration and experimental determination of the upper limit of the m/z range was determined using polyethylene glycol (PEG) in methanol/water (1:1 by vol.) at concentrations ranging from 10 μM to 100 μM. The PEG mix was prepared from seven oligomers with average molecular weights ranging from approximately 100 to 600 (Sigma–Aldrich, Inc.) all used without further purification or modification. PEG was selected for its ability to produce singly charged, sodiated adducts in the presence of sodium salts. Ions generated by nano-ESI were pulsed into the vacuum manifold using a discontinuous atmospheric pressure interface (DAPI) [22–24]. This ion introduction interface is comprised of a controllable, short duration valve (ASCO Scientific, Florham Park, NJ) with a conductive rubber capillary as the seating material (Simolex Rubber Corp., Plymouth, MI). When the DAPI valve is open, gas phase neutrals and the ions generated in the ambient environment are passed to the low pressure (base pressure $\sim 10^{-4}$ to 10^{-6} Torr) vacuum manifold that contains the mass analyzer. Once the DAPI valve is closed, the introduced ions are trapped while neutral gas phase molecules are pumped away. This decreases the operating pressure of the ion trap, and allows the electron multiplier (Photonics, Magnum 5903) to be turned on. In the scan function implemented for these experiments (Fig. 2), the DAPI valve was opened to the atmosphere for 50 ms and then closed for the duration of the pump down and mass scan period, which was approximately 2000 ms. The stainless steel ion introduction capillary was aligned co-axially with the aperture in the ion trap front end cap and positioned such that there was a 1 mm gap between the two components. This allowed gating of the ions into the trap using the front end cap voltage and it avoided perturbation of the quadrupolar field by inserting the capillary directly between the X and Y electrodes.

A laboratory built system that utilized LCQ Duo (Thermo Fisher Scientific, San Jose, CA) electronics and LCQ Duo Tune 1.0 software/Ion Trap Control Language interface was used for electronic

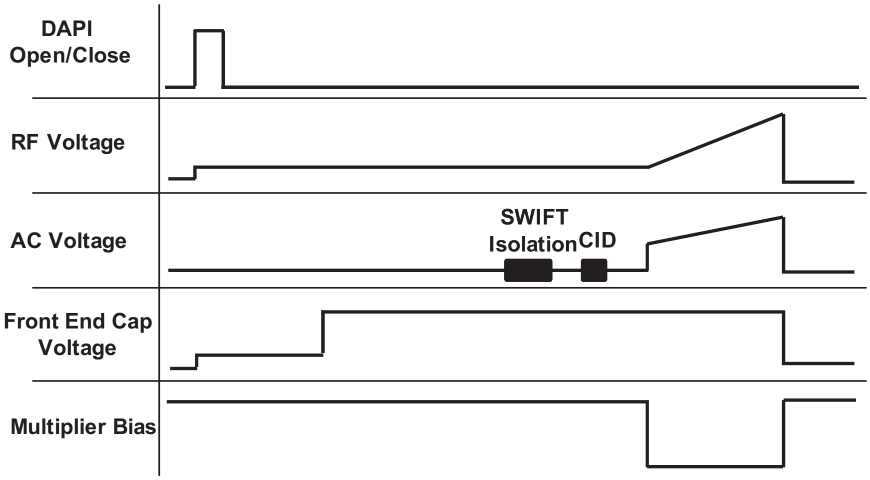

Fig. 2. Scan function used to operate the miniaturized RIT. During experiments in which no ion isolation or activation was conducted amplitudes and time segments for SWIFT and CID were set to zero.

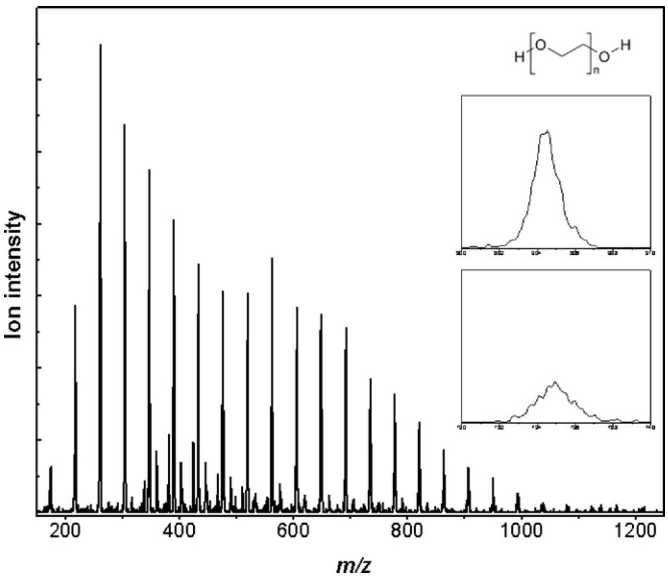

Fig. 3. Nano-electrospray ionization of PEG oligomers 2 Th (FWHM) at concentrations of 10–100 μM in 1×10^{-3} M NaOH. RF voltage amplitude scan from 68 $V_{0\text{-}p}$ to 610 $V_{0\text{-}p}$, using resonance ejection at 358 kHz with the AC amplitude ramped from 340 $mV_{p\text{-}p}$ to 1.1 $V_{p\text{-}p}$ throughout the analytical scan.

timing and control. The vacuum consisted of a TSQ7000 manifold with single stage pumping. A BocEdwards E2M30 (30 m^3/h) rotary vane pump at the front and a Pfeifer 260 turbo molecular pump (210 L/s) backed by a second BocEdwards E2M40 (40 m^3/h) was necessary to accommodate the large vacuum manifold. The performance was specifically de-tuned to achieve pressures in the ion trap similar to those given by miniature systems. After the DAPI valve was closed, ending the 50 ms ion sampling pulse, the front end cap was held at 1.8 V for 150 ms to allow the ions in the sample volume to transfer completely out of the 200 mm introduction capillary and into the ion trap. Next, the front end cap was raised to 15 V, and the rear end cap continued to be held at 25 V. Ions were allowed to cool for 500 ms while the manifold pressure dropped from its peak pressure of ~75 mTorr to ~15 mTorr, at which point the RF (drive frequency 1.105 MHz) amplitude was scanned from 68 $V_{0\text{-}p}$ to 610 $V_{0\text{-}p}$ at a rate of 833.3 Th/s, thus completing the analytical mass scan (Fig. 2). The scan rate in this work is slower than that used in typical operation of full size RITs (10,000 Th/s) and was done to maximize mass spectral resolution. Resonance ejection was implemented by applying a dipolar supplementary RF to the *x*-electrodes at a frequency of 358 kHz ($q_z = 0.77$) and its amplitude was ramped linearly from 340 $mV_{p\text{-}p}$ to 1.1 $V_{p\text{-}p}$ throughout the analytical scan.

3. Results and discussion

3.1. MS performance

The trapping voltage (depth of the effective potential well) for the miniature RIT was optimized by increasing the RF amplitude several volts at a time until the *m*/*z* distribution of the PEG sample was detected. A trapping voltage of 68 $V_{0\text{-}p}$ (low mass cutoff ~*m*/*z* 140) was determined experimentally to be the minimum voltage necessary to detect ions of up to *m*/*z* 1250. These ions covered the entire mass range and were separated by intervals of 44 Th (Fig. 3). The peak RF voltage necessary for completing an analytical scan over this mass range was 610 $V_{0\text{-}p}$ and spectral resolution was on the order of 2 Th FWHM at *m*/*z* 305, which increased with *m*/*z*.

By way of comparison the Mini 11, a portable mass spectrometer that uses a full size RIT, is limited by the available RF voltage (2250 $V_{0\text{-}p}$) to a maximum *m*/*z* of 700 when operated at ~1 MHz [25]. Under the operating conditions described in Section 2, the miniaturized RIT is capable of detecting *m*/*z* of 900 at 448 $V_{0\text{-}p}$. The two systems give comparable mass resolution. The miniaturized RIT mass analyzer, when tested on a laboratory scale instrument, exhibits the necessary performance characteristics in terms of resolution, mass range, and operating voltage. It therefore should be recognized that the operational parameters for an ion trap do not depend on whether it is installed in a laboratory scale or a miniaturized instrument making the prospect of using such a mass analyzer in a portable instrument highly attractive. To further support the feasibility of using a 1/3rd size RIT in a portable instrument the method of ion introduction in the present study is similar to that expected for a portable instrument also utilizing a DAPI source. It is anticipated that operational pressure for the laboratory scale and the portable instrument will be sufficiently similar to avoid a significant decrease in performance of the mass analyzer.

The DAPI source provides a method for sampling charged analytes at atmospheric pressure while satisfying the vacuum requirements of the mass spectrometer. We note, however, the somewhat inefficient use of the sample since the duty cycle (open time vs. overall cycle period) of the DAPI is just a few percent. Another drawback is that the mass analyzer is operated at pressures that are an order of magnitude or more above the optimal working pressure of 10^{-3} Torr. This together with mechanical imperfections contributes to peak broadening. The results obtained here are consistent with the performance anticipated for a device of this geometry, scale, and operation inside the pressure range achieved using a DAPI source.

3.2. Mass selective ion ejection

Frequencies which correlate with effective ion ejection were measured by applying supplementary, low amplitude AC to the X-electrodes during the ion trapping phase of the scan function. Ions of a selected *m*/*z* were resonantly excited and ejected from the ion trap by controlling the frequency, amplitude, and time of the applied AC. Typical time and amplitude values ranged from 50 to 100 ms and 100 to 200 $mV_{p\text{-}p}$.

An approximate determination of the ejection frequency for an ion of a particular *m*/*z* ratio can be made by monitoring the frequency at which the ion disappears from the mass spectrum (Figs. 4 and 5). Repeating this experiment for the most abundant ions in the sample, allows a plot of the ejection frequency versus *m*/*z* to be constructed. The results (Fig. 5) demonstrate that the ejection frequencies for a given *m*/*z* are in close agreement with the calculated secular frequency and follow the theoretical trend attributable to the inverse relationship between q_z and *m*/*z*.

3.3. Tandem MS performance

The protonated cocaine molecule, *m*/*z* 304, fragments to give *m*/*z* 182 by elimination of benzoic acid [26,27]. Also observable, although in lower abundance, is a competing fragmentation pathway in which benzaldehyde is lost from the protonated molecule, forming an ion of *m*/*z* 198. Conditions under which both fragmentation pathways are observed can be particularly useful for chemical profiling experiments used to identify pure compounds and/or compound metabolites using known fragmentations [28]. Cocaine was isolated through the application of a stored waveform inverse Fourier transform (SWIFT)[29] function for 450 ms, followed by activation at $q_z = 0.36$ (~147 kHz) for 30 ms at amplitudes of approximately 200 $mV_{p\text{-}p}$. DAPI, as previously described, allows introduction of both analyte ions and neutral molecules into

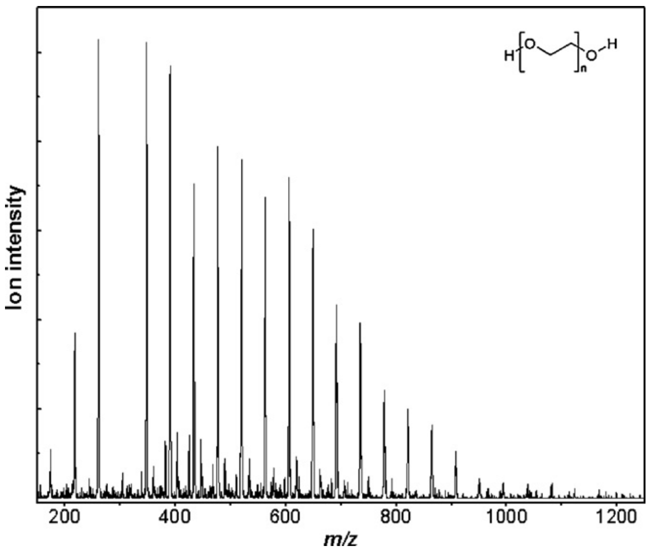

Fig. 4. Selective ejection of m/z 305 ($n = 6$) by application of dipolar supplementary AC excitation voltage applied to the X-electrodes; freq 142 kHz, 130 mV_{p-p}, 50 ms.

the vacuum manifold and consequently the mass analyzer. The manifold pressure for CID was optimized at 20 mTorr, where the neutral molecules introduced during the DAPI pulse serve as the buffer gas during these experiments.

To optimize MS/MS performance the AC amplitude was varied from 200 to 250 mV_{p-p} by increments of approximately 10 mV_{p-p} (Fig. 6). The maximum fragmentation efficiency was found to be 9.1% (Fig. 7). The mechanisms by which ions are activated in CID and by which they are resonantly ejected from the ion trap are similar. Excitation energy is supplied using a supplementary AC applied in resonance with the ion secular frequency. Considering that the pseudopotential well depth is proportional to the magnitude of the applied RF, the well for a miniaturized RIT is shallower than its full-size counterpart by approximately a factor of nine (due to the three-fold reduction in physical size). Under these conditions resonance ejection increasingly competes with activation and results in poor fragmentation efficiency. In this experiment over 90% of the precursor ions are lost prior to dissociation.

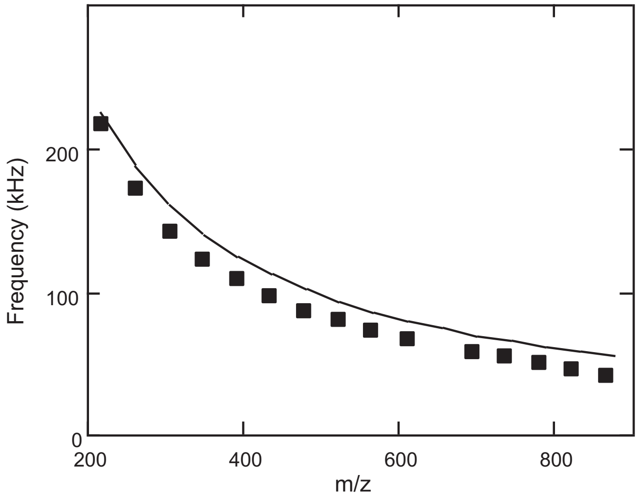

Fig. 5. Ion frequency map: solid line indicates the calculated secular ion frequencies. Points indicate frequencies determined experimentally through selective ion resonant ejection.

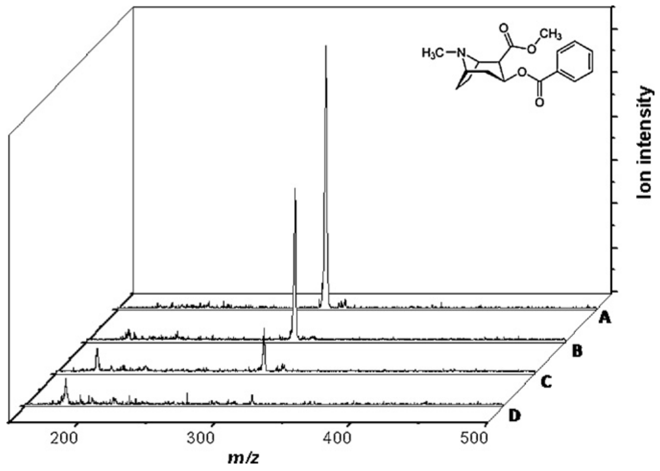

Fig. 6. Cocaine after (A) 200 mV_{p-p} activation, (B) 220 mV_{p-p} activation, (C) 230 mV_{p-p} activation, and (D) 250 mV_{p-p} activation. All activation experiments were initiated at a pressure of 20 mTorr and at 10 μg/ml concentration.

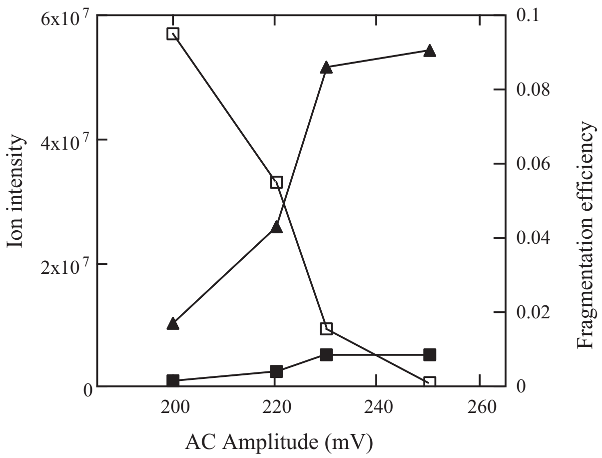

Fig. 7. (Left axis) Precursor m/z 304, □, and product ion 182, ■, intensity vs. AC amplitude; (right axis) fragmentation efficiency, ▲ (fragment ion intensity/total intensity).

4. Conclusions

The mass range, spectral quality, tandem MS capabilities, and operating voltages of a miniaturized RIT make it an attractive mass analyzer for use in portable mass spectrometers. It also serves as a method for evaluation of ion traps in other areas of research namely, even more miniaturized devices, traps made of electrodes fabricated using new technologies/materials, traps with novel electrode geometries, and ion trap arrays [9,21,30–32]. In addition, at this scale (and smaller) the RF amplitude necessary to complete mass analysis over a range of approximately 100–500 Th, suitable for the detection of most standard organic compounds, is within the range of commercially available operational amplifiers. A "direct drive" approach to RF control would offer the benefit of ion trap operation without the use of specially designed inductance coils, thus simplifying the design and construction of field portable mass spectrometers.

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References

[1] A. Keil, H. Hernandez-Soto, R.J. Noll, M. Fico, L. Gao, Z. Ouyang, R.G. Cooks, Monitoring of toxic compounds in air using a handheld rectilinear ion trap mass spectrometer, Analytical Chemistry 80 (2008) 734–741.

[2] C.C. Mulligan, D.R. Justes, R.J. Noll, N.L. Sanders, B.C. Laughlin, R.G. Cooks, Direct monitoring of toxic compounds in air using a portable mass spectrometer, Analyst 131 (2006) 556–567.

[3] L.S. Riter, Y. Peng, R.J. Noll, G.E. Patterson, T. Aggerholm, R.G. Cooks, Analytical performance of a miniature cylindrical ion trap mass spectrometer, Analytical Chemistry 74 (2002) 6154–6162.

[4] J.N. Smith, A. Keil, J. Likens, R.J. Noll, R.G. Cooks, Facility monitoring of toxic industrial compounds in air using an automated, fieldable, miniature mass spectrometer, Analyst 135 (2010) 994–1003.

[5] J.N. Smith, A.D. Keil, R.J. Noll, R.G. Cooks, Ion/molecule reactions for detecting ammonia using miniature cylindrical ion trap mass spectrometers, Analyst 136 (2011) 120–127.

[6] E.R. Badman, R. Graham Cooks, Miniature mass analyzers, Journal of Mass Spectrometry 35 (2000) 659–671.

[7] Z. Ouyang, G. Wu, Y. Song, H. Li, W.R. Plass, R.G. Cooks, Rectilinear ion trap: concepts, calculations, and analytical performance of a new mass analyzer, Analytical Chemistry 76 (2004) 4595–4605.

[8] R.F Bonner, J.E. Fulford, R.E. March, G.F. Hamilton, The cylindrical ion trap. Part I. General introduction, International Journal or Mass Spectrometry and Ion Physics 24 (1977) 255–269.

[9] D.E. Austin, Y. Peng, B.J. Hansen, I.W. Miller, A.L. Rockwood, A.R. Hawkins, S.E. Tolley, Novel ion traps using planar resistive electrodes: implications for miniaturized mass analyzers, Journal of the American Society for Mass Spectrometry 19 (2008) 1435–1441.

[10] G.E. Patterson, A.J. Guymon, L.S. Riter, M. Everly, J. Griep-Raming, B.C. Laughlin, Z. Ouyang, R.G. Cooks, Miniature cylindrical ion trap mass spectrometer, Analytical Chemistry 74 (2002) 6145–6153.

[11] Z. Zhu, C. Xiong, G. Xu, H. Liu, X. Zhou, R. Chen, W.-P. Peng, Z. Nie, Characterization of bioparticles using a miniature cylindrical ion trap mass spectrometer operated at rough vacuum, Analyst (2011).

[12] M.G. Blain, L.S. Riter, D. Cruz, D.E. Austin, G. Wu, W.R. Plass, R.G. Cooks, Towards the hand-held mass spectrometer: design considerations, simulation, and fabrication of micrometer-scaled cylindrical ion traps, International Journal of Mass Spectrometry 236 (2004) 91–104.

[13] A Chaudhary, F. van Amerom, R.T. Short, Development of microfabricated cylindrical ion trap mass spectrometer arrays, Journal of Microelectromechanical Systems 18 (2009) 442–448.

[14] D. Cruz, J.P. Chang, M. Fico, A.J. Guymon, D.E. Austin, M.G. Blain, Design, microfabrication, and analysis of micrometer-sized cylindrical ion trap arrays, Review of Scientific Instruments 78 (2007) 015107.

[15] J. Moxom, P.T.A. Reilly, W.B. Whitten, J.M. Ramsey, Analysis of volatile organic compounds in air with a micro ion trap mass analyzer, Analytical Chemistry 75 (2003) 3739–3743.

[16] G. Huang, W. Xu, M.A. Visbal-Onufrak, Z. Ouyang, R.G. Cooks, Direct analysis of melamine in complex matrices using a handheld mass spectrometer, Analyst 135 (2010) 705–711.

[17] A. Keil, N. Talaty, C. Janfelt, R.J. Noll, L. Gao, Z. Ouyang, R.G. Cooks, Ambient mass spectrometry with a handheld mass spectrometer at high pressure, Analytical Chemistry 79 (2007) 7734–7739.

[18] N.L. Sanders, E. Sokol, R.H. Perry, G.M. Huang, R.J. Noll, J.S. Duncan, R.G. Cooks, Hand-held mass spectrometer for environmentally relevant analytes using a variety of sampling and ionization methods, European Journal of Mass Spectrometry 16 (2010) 11–20.

[19] E. Sokol, K.E. Edwards, K. Qian, R.G. Cooks, Rapid hydrocarbon analysis using a miniature rectilinear ion trap mass spectrometer, Analyst 133 (2008) 1064–1071.

[20] M. Fico, J.D. Maas, S.A. Smith, A.B. Costa, Z. Ouyang, W.J. Chappell, R.G. Cooks, Circular arrays of polymer-based miniature rectilinear ion traps, Analyst 134 (2009) 1338–1347.

[21] M. Fico, M. Yu, Z. Ouyang, R.G. Cooks, W.J. Chappell, Miniaturization and geometry optimization of a polymer-based rectilinear ion trap, Analytical Chemistry 79 (2007) 8076–8082.

[22] L. Gao, R.G. Cooks, Z. Ouyang, Breaking the pumping speed barrier in mass spectrometry: discontinuous atmospheric pressure interface, Analytical Chemistry 80 (2008) 4026–4032.

[23] L. Gao, G. Li, Z. Nie, J. Duncan, Z. Ouyang, R.G. Cooks, Characterization of a discontinuous atmospheric pressure interface. Multiple ion introduction pulses for improved performance, International Journal of Mass Spectrometry 283 (2009) 30–34.

[24] W. Xu, N. Charipar, M.A. Kirleis, Y. Xia, Z. Ouyang, Study of discontinuous atmospheric pressure interfaces for mass spectrometry instrumentation development, Analytical Chemistry 82 (2010) 6584–6592.

[25] L. Gao, Q. Song, G.E. Patterson, R.G. Cooks, Z. Ouyang, Handheld rectilinear ion trap mass spectrometer, Analytical Chemistry 78 (2006) 5994–6002.

[26] P. Wang, M.G. Bartlett, Collision-induced dissociation mass spectra of cocaine, and its metabolites and pyrolysis products, Journal of Mass Spectrometry 33 (1998) 961–967.

[27] S.A. McLuckey, D.E. Goeringer, G.L. Glish, Collisional activation with random noise in ion trap mass-spectrometry, Analytical Chemistry 64 (1992) 1455–1460.

[28] R.W. Kondrat, G.A. McClusky, R.G. Cooks, Multiple reaction monitoring in mass spectrometry/mass spectrometry for direct analysis of complex mixtures, Analytical Chemistry 50 (1978) 2017–2021.

[29] S. Guan, A.G. Marshall, Stored waveform inverse Fourier transform (SWIFT) ion excitation in trapped-ion mass spectrometry: theory and applications, International Journal of Mass Spectrometry and Ion Processes 157–158 (1996) 5–37.

[30] A.T. Clare, L. Gao, B. Brkic, P.R. Chalker, S. Taylor, Linear ion trap fabricated using rapid manufacturing technology, Journal of the American Society for Mass Spectrometry 21 (2010) 317–322.

[31] J.D. Maas, P.I. Hendricks, O. Zheng, R.G. Cooks, W.J. Chappell, Miniature monolithic rectilinear ion trap arrays by stereolithography on printed circuit board, Journal of Microelectromechanical Systems 19 (2010) 951–960.

[32] M. Yang, T.-Y. Kim, H.-C. Hwang, S.-K. Yi, D.-H. Kim, Development of a palm portable mass spectrometer, Journal of the American Society for Mass Spectrometry 19 (2008) 1442–1448.