Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
International Journal of Mass Spectrometry 255–256 (2006) 1–10
International Journal of Mass Spectrometry
www.elsevier.com/locate/ijms

Instrumentation and methods for ion and reaction monitoring using a non-scanning rectilinear ion trap

Chao Zhang, Huanwen Chen, Andrew J. Guymon, Guangxiang Wu,
R. Graham Cooks**, Zheng Ouyang*

Department of Chemistry, Purdue University, West Lafayette, IN 47907, USA

Received 31 May 2005; received in revised form 5 October 2005; accepted 12 October 2005

To Diethard Bohme in celebration of the quality and range of mass spectrometry that his York laboratory has produced over several decades.

Abstract

A method of single ion or single reaction monitoring which avoids high RF voltage scanning is identified and implemented in an ion trap mass spectrometer. A rectilinear ion trap (RIT) mass spectrometer was constructed and characterized and used to develop a simple method of monitoring targeted compounds without using RF voltage scanning. The ions were first isolated, and then ejected axially from the aperture in one of the *z*-electrodes for detection. Various ion monitoring modes, including selected ion monitoring (SIM), multiple ion monitoring (MIM), and selected reaction monitoring (SRM), are demonstrated using RF/DC isolation or waveform isolation in combination with the axial DC pulses to eject and detect ions of particular mass/charge ratios.

Keywords: Miniature mass spectrometer; Rectilinear ion trap; Axial ejection; In situ analysis; Quadrupole ion trap

1. Introduction

As an analytical method and technology, mass spectrometry has unique capabilities for detecting a wide variety of chemical species at low concentrations [1,2]. However, the use of mass spectrometers for in situ analysis applications has been limited due to the size and power consumption of lab-scale instruments. Efforts put into the miniaturization of mass analyzers and entire mass spectrometers [3,4] have resulted in significant reduction in the instrument size, weight, and power consumption [5–16]. Some portable instruments, such as an ion trap mass spectrometer weighting 17 kg with 135 W power consumption, have been developed with the full functionality of the corresponding lab-scale instruments [17–19]. However, it is highly desirable to further decrease the size and the power consumption of mass spectrometers so they can be deployed for in situ applications, such as industrial process monitoring, environmental pollutant monitoring, chemical and biological warfare agent detection, process monitoring, industrial hygiene, extra-terrestrial exploration, etc. This goal will require another round of overall reduction of every part of the instrument, including the RF amplifier and scan circuits, data acquisition, monitoring and display system, and vacuum system, which inevitably will compromise the performance of the instrument. However, in many in situ applications, chemical analysis can be carried out using specific modes of mass spectrometric analysis and an instrument with the full functionality of lab instruments is not necessary. For instance, monitoring the concentrations of targeted compounds by using selected ion monitoring (SIM) or selected reaction monitoring (SRM) without the need to acquire full mass spectra would be a valuable capability. It is possible to use a much simplified mass spectrometer with limited functionality to achieve these useful goals.

In the development of portable ion trap instruments, it is challenging to develop a compact RF system with a high quality factor *Q* (the ratio of the center frequency to the bandwidth) and simultaneously achieve a highly linear RF scan. The high *Q* is required for a compact RF system to allow high RF voltages with low power consumption to achieve the required mass range, while the high stability of the RF voltage even during a fast scan is essential for adequate mass resolution. The construction of an

---

* Corresponding author. Tel.: +1 765 496 1539; fax: +1 765 494 9421.
** Corresponding author. Tel.: +1 765 494 5262; fax: +1 765 494 9421.
E-mail addresses: cooks@purdue.edu (R.G. Cooks), ouyang@purdue.edu (Z. Ouyang).

1387-3806/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2005.10.013

ion trap mass spectrometer would be much simplified if these two requirements did not have to be met. One reported solution for a non-RF scanning instrument is to use an array of mass analyzers of different size to monitor ions of different mass-to-charge ratios. This has been done using a cylindrical ion trap (CIT) array operated at constant RF and DC voltage [20]. The ions were simultaneously isolated and trapped in each CIT by RF/DC isolation based on the mass-to-charge ratio preset by the CIT size, RF frequency, RF voltage and DC voltage; the isolated ions could then be pulsed out sequentially from each trap for detection. A related approach is employed here but it uses a single trap, in this case a rectilinear ion trap (RIT), an ion trap with simplified geometry and improved trapping capacity [21]. The RIT allows manipulation of the ions in the same way as in a Paul ion trap [22]. In this paper, we discuss the concept of using an RIT for mass analysis at constant RF, describe the instrumentation, and demonstrate the concept with preliminary experimental results.

2. Concept

These experiments employed an RIT with the configuration shown in Fig. 1. An RF signal is applied to the *y*-electrode pair to form an RF trapping field in the *xy*-plane. The DC voltages (DC 1 and DC 3) are applied to the *z*-electrode pair and the trapping float DC voltage is applied to both the *x*- and *y*-electrodes to form a DC potential well that confines the ions in the *z*-direction. In normal mass analysis using the mass selective instability scan, the ions are generated inside of the RIT or injected into the RIT, trapped by the RF and DC fields, cooled by collision with background gas molecules, and finally ejected by scanning the RF amplitude, which leads to ion ejection through the slits in the *x*-electrodes in order of their mass-to-charge ratios. Given the similarity of the RIT to a linear quadrupole mass filter, the trapped ions can also be ejected along the *z*-axis if the voltage applied to one of the *z*-electrodes is dropped so that the DC trapping potential well in the *z*-direction is appropriately reduced. The combination of this axial ejection mode with mass selective isolation of the trapped ions allows the RIT to be used for mass selective ion monitoring. Compared to the mass-filtering mode of a quadrupole mass filter, the ions are trapped in the RIT before they are ejected, and the pressure at which the RIT can be operated is one or two orders of magnitude higher than that typically used for a mass filter, which is important for the development of miniature instruments. A disadvantage of the experiment is that, as in the case of the quadrupole mass filter, ions have to be re-created for each measurement.

The mass selective isolation of the trapped ions in an RIT is demonstrated with both RF/DC isolation and waveform isolation. In the RF/DC isolation mode, the RF voltage and its trapping float DC voltage are adjusted to achieve a condition where the working point of the ions of interest falls near the apex of the stability diagram. To implement the waveform isolation mode, a stored waveform inverse Fourier transform (SWIFT) with a notch at the frequency of interest is used for ion isolation [23]. Multiple SWIFT waveforms with different notches can be used to isolate ions of different mass-to-charge ratios while still operating at a fixed RF voltage, although the isolation efficiency is expected to vary with mass-to-charge ratio due to the difference in the pseudopotential well depth as a function of the

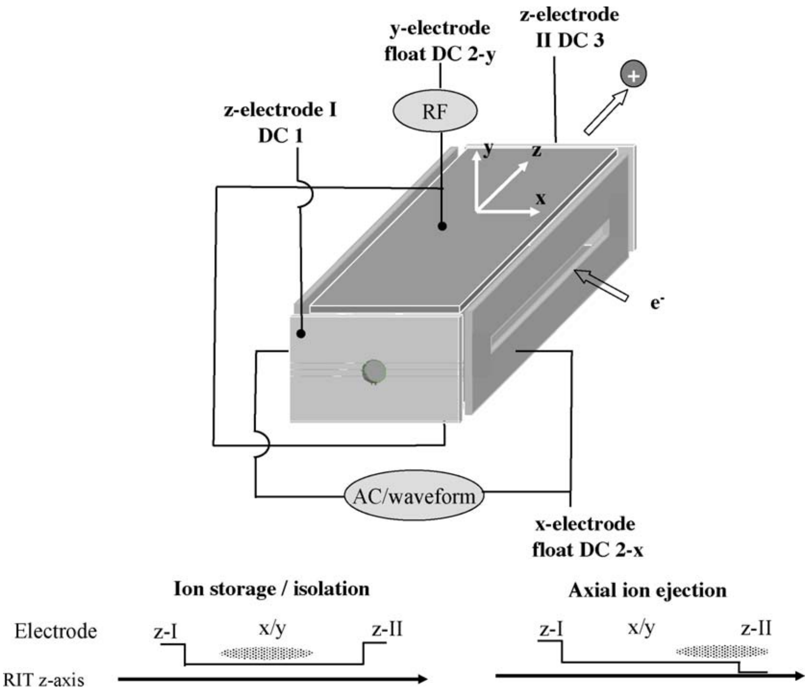

Fig. 1. Configuration of rectilinear ion trap mass spectrometer and the applied control signals. A trapping field in the *xy*-plane is formed by applying an RF signal to the *y*-electrode pair. Confinement of ions in the *z*-direction is achieved by applying DC voltages to the *z*-electrodes and the trapping float DC voltages to both the *x*- and *y*-electrodes. Ion isolation and activation are achieved by applying an AC signal to the *x*-electrode pair. The trapped ions can be ejected from the RIT along the *z*-axis if the voltage applied on *z*-electrode II (DC 3) is dropped to appropriately reduce the potential well in the *z*-direction.

Mathieu parameter q. When performing such multiple notched SWIFT waveforms, the primary ions must be regenerated prior to the application of the second and subsequent SWIFT waveforms. This is because of the DC pulse out method which is non-mass selective; hence, only a single notch can be used in a SWIFT waveform.

3. Instrumentation

The experiment of monitoring targeted compounds using a fixed RF voltage was performed using the newly developed RIT mass spectrometer. The configuration of the major components are shown in Fig. 2 and detailed as follows.

3.1. Vacuum manifold

A four-way reducing cross (MDC, Hayward, CA) with two NW 25 ports and two NW 50 ports was used as the vacuum manifold to house the filament, RIT mass analyzer, and the detectors. A Pfeiffer TPD 011 turbo pump (Pfeiffer Vacuum, Inc., Nashua, NH) with a pumping speed of 10 L/s backed by a KNF 813.4 diaphragm pump (KNF Neuberger, Inc., Trenton, NJ) constituted the pumping system. Vapors of samples were leaked into the manifold using a variable leak valve (Granville-Phillips, Series 203, Helix Technology, Longmont, CO). The pressure inside the manifold was monitored by a Leybold Combivac CM31 (Leybold Vacuum Products, Inc., Export, PA) ionization gauge and typically it was 4.0×10^{-6} Torr for background and 1.0×10^{-5} Torr with sample present. Air was used as buffer gas at an indicated pressure of 7.0×10^{-5} Torr.

3.2. RIT mass analyzer

The RIT electrodes used in this work were machined from 304-stainless steel and assembled as shown in the expanded view included in Fig. 2. The x-electrode took an “L” shape with a y-electrode fixed onto it by epoxy (EPO-TEK 353ND, Epoxy Technology, Billerica, MA), with a quartz plate (1.6 mm thick) in between as an insulator. The slits in the x-electrode allowed the entrance and exit of electrons and ions, respectively. The two x-electrodes were assembled by two polycarbonate holders with a thin Teflon film between them for electrical isolation. The dimensions of the RIT are the result of separate optimization studies [21]. The lengths of both the x- and y-pairs of electrodes are 50.0 mm and the half distance between each pair is 5.0 mm for the x-electrode and 3.8 mm for the y-electrode, respectively. The slits are in the center of the x-electrodes and are 40.0 mm long and 1.0 mm wide. The inter-electrode distance between the x- and y-electrodes is 1.6 mm. Two flat z-electrodes with center holes 3.0 mm in diameter are installed orthogonal to the z-axis, 1.5 mm from the ends of the x- and y-electrodes.

3.3. Ion source

Internal electron ionization was used to generate ions inside the RIT. A commercially available FF700 filament (Scientific Instrument Services, Inc., Ringoes, NY) was mounted on a NW 25 flange and located parallel to the slit in one of the x-electrodes to introduce the electrons into the trap. A thin stainless steel plate with a center slit 8.0 mm in length and 1.0 mm in width was used between the filament and the RIT to gate the electron beam. The

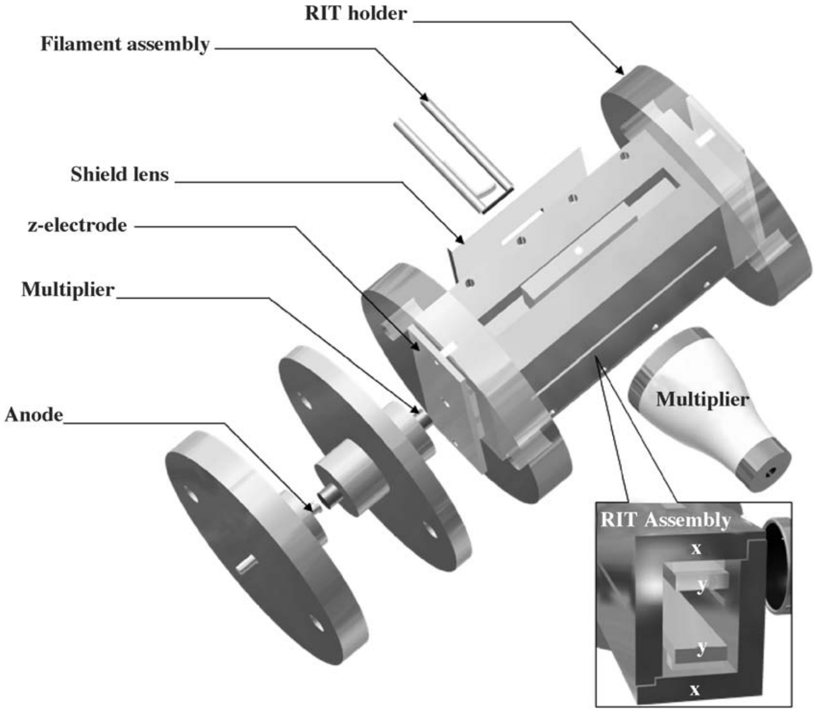

Fig. 2. Configuration of the major components of the newly developed RIT mass spectrometer described in this paper.

filament control circuit was built using a current power supply (model VI-J1R-EX, Vicor Co., Andover MA). Typically, a −20 V DC bias was applied to the filament, and an emission current of 20 μA was used.

3.4. RF signal configuration

The RIT was operated in the monopolar RF mode, such that the RF signal was applied only to the *y*-electrode pair. An RF signal with amplitude of 2.25 V (voltages reported as 0-peak in this paper) and frequency of 846 kHz was amplified by a custom-made RF amplifier, and then fed into a compact custom-made RF transformer that consists of one input and two output coils, in which the primary coil has 3 turns and the secondary coils have 50 turns each. The amplified RF signal was applied to the *y*-electrodes to form a trapping field in the *xy*-plane. AC signals were fed through another custom-made transformer to produce dipolar signals with 180° phase difference that were applied to the *x*-electrodes to facilitate efficient ion isolation and resonance excitation during the collision-induced dissociation (CID) period.

3.5. Detection system and data acquisition

A miniature electron multiplier (3.0 mm in diameter and 26.0 mm in length, Model xp-2609, Detector Technology, Inc., Palmer, MA) was used to detect ions ejected from the RIT along the *z*-axis. A piece of 12 mm × 12 mm square mesh was installed between the multiplier and *z*-electrode to minimize the image current induced by the change in the voltage applied to the *z*-electrode. To compare ion monitoring performance using the axial and radial (through the *x*-electrode slits) ion ejection modes, a second channeltron electron multiplier (model 7505, K and M Electronics, Inc., West Springfield, MA) mounted on a NW 25 flange facing the ion exit slit of the RIT *x*-electrode.

The Argos quadrupole instrument controller (Griffin Analytical Technologies, Inc., West Lafayette, IN) was used to provide waveform-generating functions and to provide timing control. The Griffin scan editor software provides three user interfaces, viz., segment editor, real-time scan viewer, and data analyzer, which can be used for programming the scan configuration, controlling the timing sequence, and for data acquisition as well as off-line data analysis.

3.6. Sample preparation and introduction

All chemicals were obtained from Sigma–Aldrich (Milwaukee, WI) and were introduced as headspace vapors at ambient temperature from the neat liquids using a variable leak valve. Gas-phase standards of methyl salicylate were prepared by serial dilution from a saturated headspace sample of methyl salicylate. A sample of approximately 10 μL of methyl salicylate was introduce into a sealed 10 L gas bag (BOC Gases, Murray Hill, NJ) and filled with 10 L nitrogen using a mass flow controller (model HFC-302, Teledyne-Hastings Instruments, Hampton, VA). The sample bag was maintained at 25 °C for 1 h to allow liquid-vapor equilibrium to be reached. A series of gas-phase standards were prepared by taking a portion of this gas mixture using a gas-tight syringe fitted with a shutoff valve (sample lock series, Hamilton, Reno, NV).

4. Results and discussion

4.1. Characterization of the instrument for ion monitoring using RF scanning

Before this instrument could be used to demonstrate mass selective ion monitoring without RF voltage scanning, the normal RF-ramp mass selective instability scan mode was used to obtain information on performance as well as for mass calibration and characterization of the ion trap stability region. This information was essential for setting the conditions for ion monitoring using the non-scanning ion isolation methodology.

Perfluorotributylamine (PFTBA), a typical compound employed for mass calibration, was introduced into the manifold as a vapor and a mass spectrum covering the mass/charge range of 108–500 Th (Thomson, Th = Dalton/Charge) was recorded using an RF scan with boundary ejection, as shown in Fig. 3. An upper limit of mass/charge range of 500 Th [24] was measured for this RIT instrument using these operating conditions with the low-mass cutoff (LMCO) set at 108 Th. Data showing the RF voltage versus mass-to-charge ratio calibration based on the PFTBA spectrum are shown in the inset of Fig. 3. The RF voltage corresponding to ions of specific *m*/*z* values specific can easily be selected from this calibration curve.

The stability diagram for the RIT analyzer with $x_0 = 5.0$ mm, $y_0 = 3.8$ mm has been mapped using the ITMS instrument by following the procedure reported earlier using the fragment ions of 105 Th of acetophenone [21,25]. The information obtained from the stability diagram was used to guide RF/DC isolation experiments in the ion monitoring mode. The working point for ions of interest was moved to near the upper apex of the stability diagram by appropriately adjusting the corresponding RF voltage and applying a negative DC bias. For ions of any given *m*/*z* value, the corresponding RF amplitude and DC bias required can be easily calculated by rearranging the expressions for the Mathieu parameters to give the following equations:

$$V_{\mathrm{RF}} = \frac{qmx_0^2\Omega^2}{4eA_2} \tag{1}$$

$$U_{\mathrm{DC}} = \frac{-amx_0^2\Omega}{8eA_2} \tag{2}$$

where a and q are the Mathieu parameters obtained from the mapped stability diagram, A_2 the quadrupole coefficient in the multipole expansion expression of the electric potential, V_{RF} and U_{DC} the amplitudes of the RF signal and the DC bias applied to the *y*-electrodes, respectively, x_0 the center to *x*-electrode distance, and Ω is the radial frequency of the applied RF. Using the measured boundary voltages for the 105 Th ion, the stability diagram for any ion (m) with a specific mass-to-charge ratio can

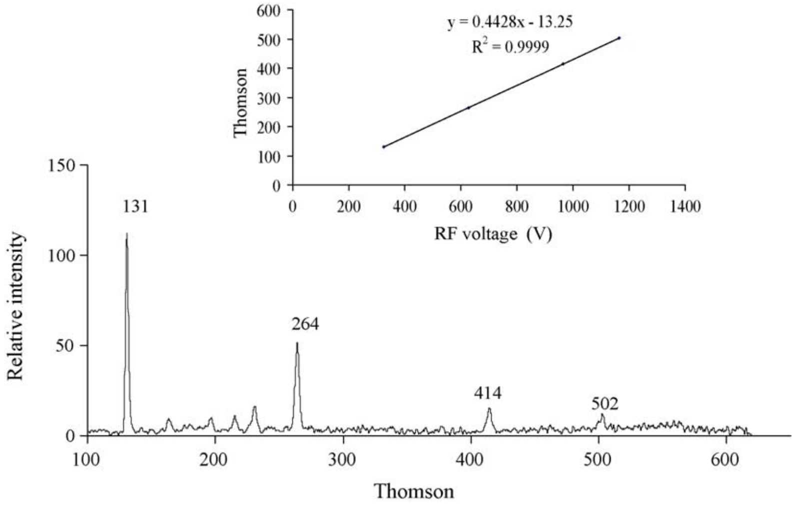

Fig. 3. PFTBA mass spectrum in the higher mass range recorded with RF scanning and boundary ejection with the low-mass cutoff set at 108 Th. The inset shows RF voltage vs. Thomson calibration data based on the PFTBA spectrum.

be calculated from:

$$V_m = \frac{V_{105} \times m}{105} \tag{3}$$

$$U_m = \frac{U_{105} \times m}{105} \tag{4}$$

An example of RF/DC isolation of the ion 152 Th from methyl salicylate followed by axial DC pulse will be described in the following section.

4.2. Non-RF scanning selected ion monitoring

Selected ion monitoring without RF voltage scanning was performed by mass selective RF/DC isolation of the trapped ions and then axial ejection for detection. The stability diagram (upper portion) expressed as a function of RF amplitude (V) and DC bias (U) measured for 152 Th from Eqs. (3) and (4) is shown in Fig. 4. It can be seen that by adjusting the RF amplitude to 260 V and the RF float DC voltage to −32 V, the working point of ions of 152 Th is moved to near the apex for isolation. The scan function shown in Fig. 5 allows the selection and ejection of ions of a particular m/z value; the most important feature is that RF amplitude is kept constant at 260 V. To implement this experiment for 152 Th, the z-electrode voltages were set to 100 V and the RF float DC voltages for both the x- and y-electrodes were set to 30 V during the trapping period; then the RF float DC applied to the y-electrode was decreased to −2 V for 10 ms to generate a DC voltage difference of 32 V between the x- and y-RF DC floats, which allowed the isolation of 152 Th with a mass window of 4 Th. The potential on the z-II electrode (viz., the ion exit z-electrode) was dropped to −100 V for 30 ms to completely eject the isolated 152 Th ions and to drive them along the z-axis and into the multiplier for detection.

A sample of methyl salicylate prepared as indicated in the sample preparation section was introduced though a leak valve and the molecular radical cation 152 Th was monitored. The signal recorded at the detection limit of 40 ppb (by volume in nitrogen) was recorded (Fig. 6A). The background intensity was also recorded (Fig. 6B) by monitoring a mass region 4 Th wide and centered at 160 Th, a region that did not include analyte ions. The intensity of the ions at 152 Th (Fig. 6C) is reported as the difference between the integrated areas of peaks in Fig. 6A and B. The intensity as a function of sample concentration is used for quantitative analysis. The calibration curve for methyl salicylate detection is shown in Fig. 7 with the intensities reported as the difference between the integrated areas of the peaks for sample and background.

4.3. Non-RF scanning multiple ion monitoring

An alternative to the use of RF/DC for ion isolation is to apply a SWIFT waveform which contains a notch corresponding to the secular frequency of the ion to be isolated. The combination of

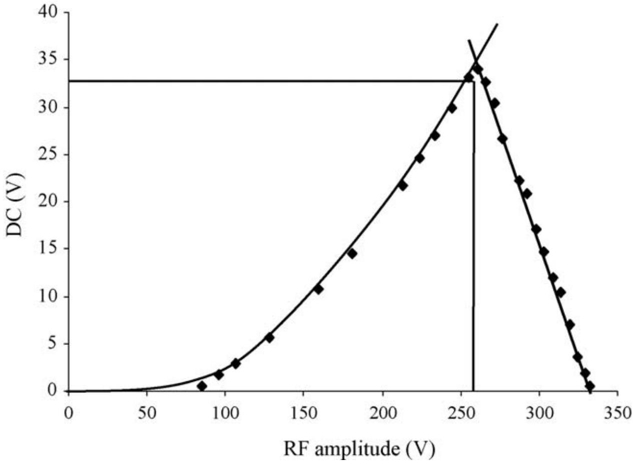

Fig. 4. Stability diagram (upper portion) for 152 Th of methyl salicylate as a function of RF amplitude (V) and DC bias (U) for an RIT with $x_0 = 5$ mm, $y_0 = 3.8$ mm, and $z_0 = 50$ mm. The RF/DC isolation for 152 Th was performed at the point ($V = 260$ V, $U = 32$ V) near the upper apex of the stability diagram.

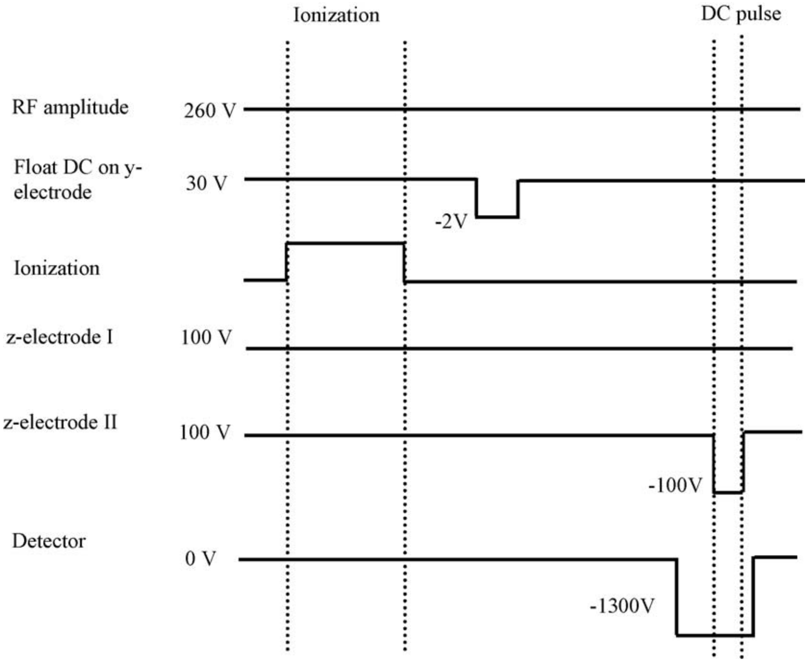

Fig. 5. Scan diagram for selective ion monitoring configuration of 152 Th of methyl salicylate using RF/DC isolation with an axial DC pulse without using RF scanning and monitoring. The working point of the ions of 152 Th to be isolated was moved near the apex of the stability region by setting the RF amplitude at 260 V and the DC bias at −32 V. The selected ions were trapped in the *z*-direction since the DC voltages applied to both *z*-electrodes I and II were set at 100 V; they were ejected along the *z*-axis and into the multiplier for detection when the potential on the *z*-II electrode was dropped to −100 V for 30 ms.

SWIFT isolation of selected ions with a subsequent axial DC pulse provides a second method of measuring the intensities of selected ions without using an RF scan. Waveform isolation can be applied to isolate ions at an RF voltage much lower than that required for RF/DC isolation, as long as the trapping potential well is deep enough to perform the waveform isolation. Another significant advantage of waveform isolation is that ions with different mass-to-charge ratios can be isolated at a fixed RF voltage using waveforms with different frequency notches. Fig. 8 shows the scan function for a multiple ion monitoring (MIM) experiment that uses a set of ionization, waveform isolation, and axial DC pulse ejection components. For each of the targeted ions, the primary ions were first generated followed by their isolation using a SWIFT waveform and detected using an axial DC pulse. Different SWIFT waveforms were applied for different targeted ions.

The multiple ion monitoring mode is demonstrated using dimethyl methylphosphonate (DMMP), a nerve agent simulant,

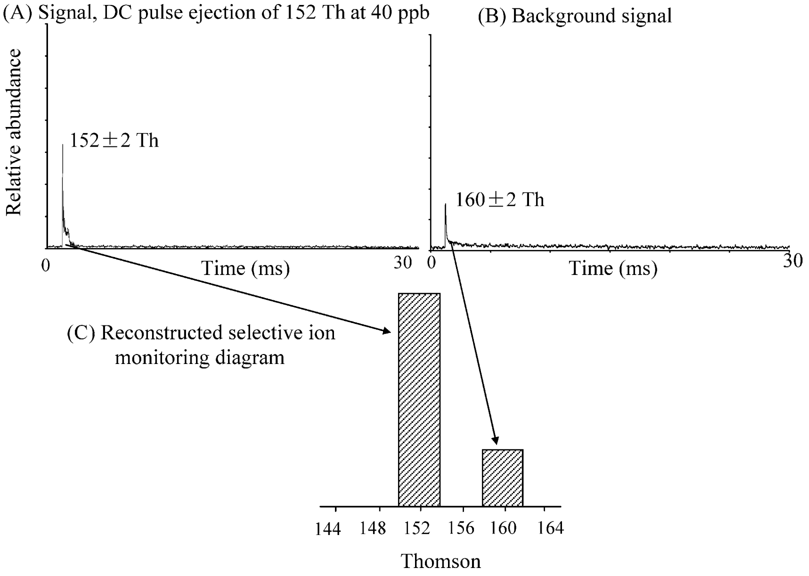

Fig. 6. Selected ion monitoring data for 152 Th of methyl salicylate recorded without using RF scanning. (A) Peak intensity of ions 152 Th at 40 ppb (by volume in nitrogen) as a function of pulse time, the isolation window is ca. 4 Th. (B) Background intensity recorded by monitoring a mass region 4 Th wide and centered at 160 Th. (C) The intensity of ions 152 Th, reported as the difference between the integrated areas of peaks.

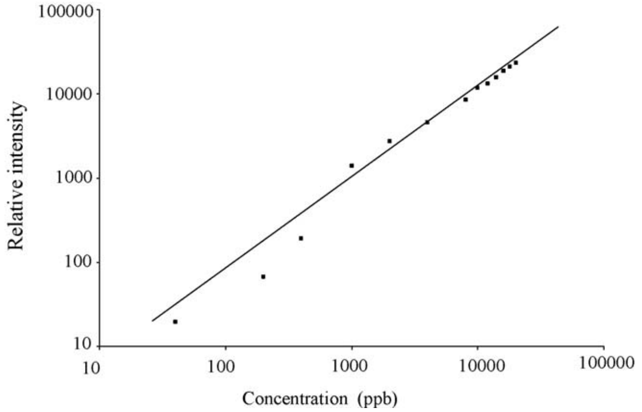

Fig. 7. Calibration curve monitoring for vapor-phase methyl salicylate, 152 Th, over the concentration range 40 ppb to 20 ppm using RF/DC isolation followed by axial DC pulse detection in the selected ion monitoring mode (SIM) without using RF scanning.

as shown in Fig. 9. The MIM experiments employed headspace sampling of the saturated vapor of DMMP (0.962 Torr at 25 °C) introduced into the manifold using a leak valve. The LMCO was set at 70 Th. Four cycles of ionization/SWIFT waveform isolation/axial DC pulse were used to monitor separately the molecular ion 124 Th and its fragment ions 109, 94, and 79 Th. Four different SWIFT waveforms were used (124 Th: 0.75 V, 140–147 kHz notch, 4 ms; 109 Th: 0.7 V, 163–169 kHz notch, 4 ms; 94 Th: 0.75 V, 202–213 kHz notch, 4 ms; 79 Th: 0.85 V, 238–253 kHz notch, 4 ms). The frequency notch for each ion corresponds to an isolation window with a width of ca. 4 Th. The DC pulse conditions were the same as that used for RF/DC isolation axial DC pulse mode. As was the case for the SIM experiments, the intensities in the MIM experiments in Fig. 9 are also reported as the difference between the integrated areas of the peaks for sample and background. The peak intensities for these four ions monitored were measured based on the DC pulse signals (Fig. 9A) and the MIM data were reconstructed based on the measured relative intensities shown in Fig. 9B. This multiple ion monitoring mode is useful for simultaneously monitoring different targeted compounds or a targeted compound with a known fragmentation pattern or for monitoring an analyte in the presence of an internal standard for quantitation.

4.4. Non-RF scanning selected reaction monitoring

Selected ion monitoring is simple and rapidly performed in in-field chemical analysis when using a miniature mass spectrometer. However, if the miniature mass spectrometer has poor mass resolution, this selected ion monitoring mode may suffer from the relatively poor selectivity for particular components in a mixture of compounds more than one of which gives ions having the same or very similar mass-to-charge values. An example is given in Fig. 10. For the SRM experiments, headspace sampling of saturated vapor of a mixture of methyl salicylate (0.0343 Torr at 25 °C) and benzyl acetate (0.177 Torr at 25 °C) with a leak valve was used to introduce this mixture into the manifold. The vapor of a mixture of benzyl acetate and methyl salicylate was introduced into the manifold, ionized, and the resulting ions were analyzed using the RIT mass spectrometer. Using selected ion monitoring, either by an RF scanning (Fig. 10A) or by the non-RF scanning method described above (Fig. 10B and C), the abundances of the molecular ions 150 Th (benzyl acetate) and 152 Th (methyl salicylate) were not distin-

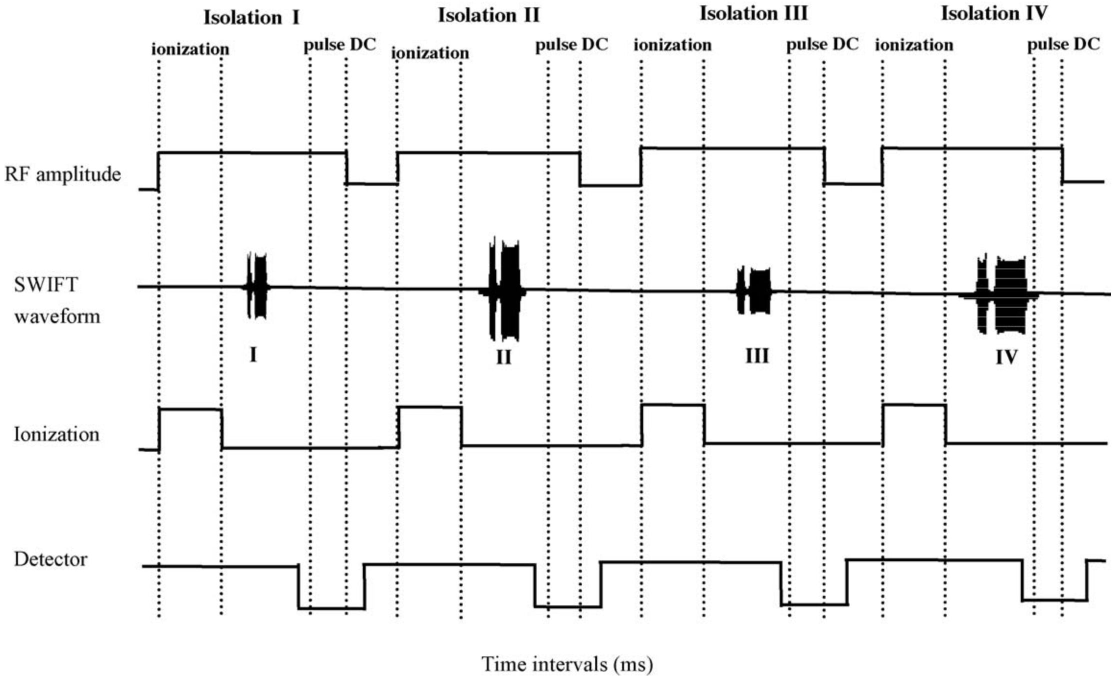

Fig. 8. Scan function for multiple ion monitoring without using RF scanning. The scan sequence for monitoring each specific ion includes ionization, SWIFT waveform isolation and axial DC pulse steps. Multiple sequences can be applied in consecutively but with different frequency notches for each SWIFT waveform for MIM experiments.

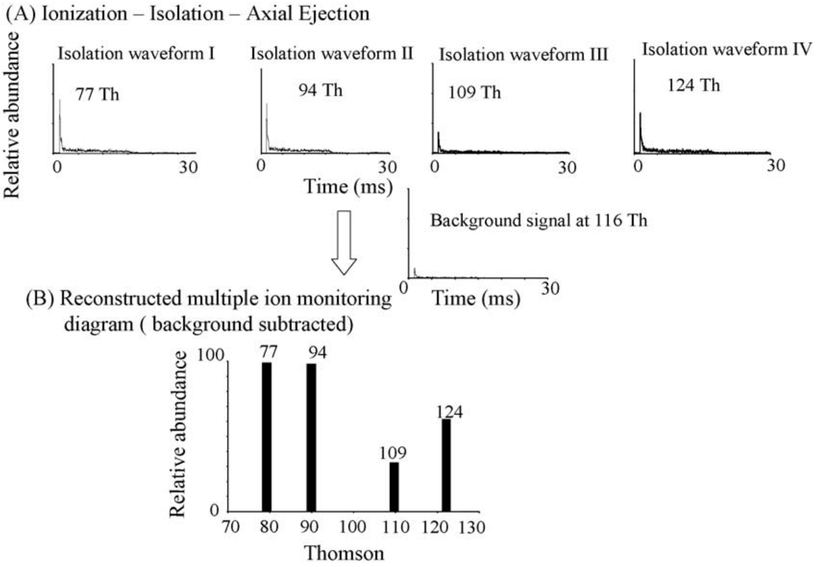

Fig. 9. Multiple ion monitoring of dimethyl methylphosphonate (DMMP) without using RF scanning. (A) Intensities when monitoring ions of 124, 109, 94, and 79 Th using the axial DC pulse method. The isolation window is ca. 4 Th. The axial DC pulse conditions were the same as those used for the SIM RF/DC isolation/pulse out mode. (B) Reconstructed data for multiple ion monitoring based on the measured intensity in (A).

guishable due to the limitation of the mass resolution. However, selected reaction monitoring based on tandem mass spectrometry could be utilized to monitor the intensities of these two compounds via measurements of the fragment ions generated from the same parent ions. This provides the additional selectivity needed in the measurement. The scan diagram used for performing SRM is shown in Fig. 11. The parent ions were first isolated with a SWIFT waveform using a frequency notch, and then subjected to waveform excitation. A targeted fragment ion could then be detected by applying a second isolation SWIFT waveform followed by the axial DC pulse for ion ejection and detection. At the fixed RF voltage corresponding to a LMCO of 70 Th, the parent ions of 150 Th from benzyl acetate and 152 Th from methyl salicylate were isolated from all other ions by a 4 ms SWIFT (amplitude 0.8 V, frequency notch 110–117 kHz) with an isolation window of ca. 6 Th. A 50 ms dipolar AC excitation waveform (amplitude 0.05 V, secular frequency 114 kHz) was then used to fragment the parent ions. The targeted fragment ions could subsequently be monitored using the SIM mode described above. A 4 ms isolation SWIFT waveform, 0.5 V

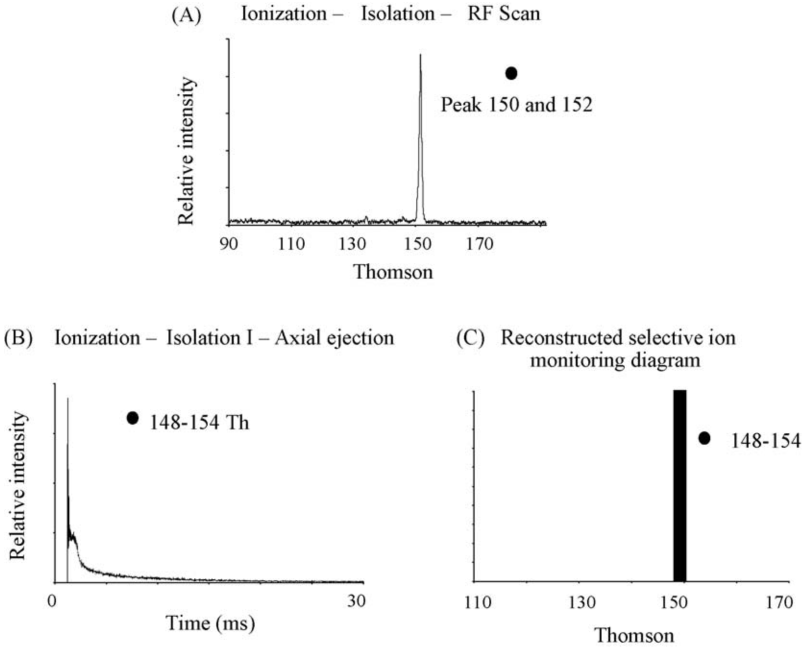

Fig. 10. Selected ion monitoring of the molecular ions 150 Th from benzyl acetate and 152 Th from methyl salicylate in the mixture, without using RF scanning. (A) Mass spectrum recorded using RF-ramp mass selective instability scan method. (B) Intensities monitored using axial DC pulse method with an isolation window of ca. 6 Th. (C) Reconstructed data for selected ion monitoring based on the measured intensity in (B).

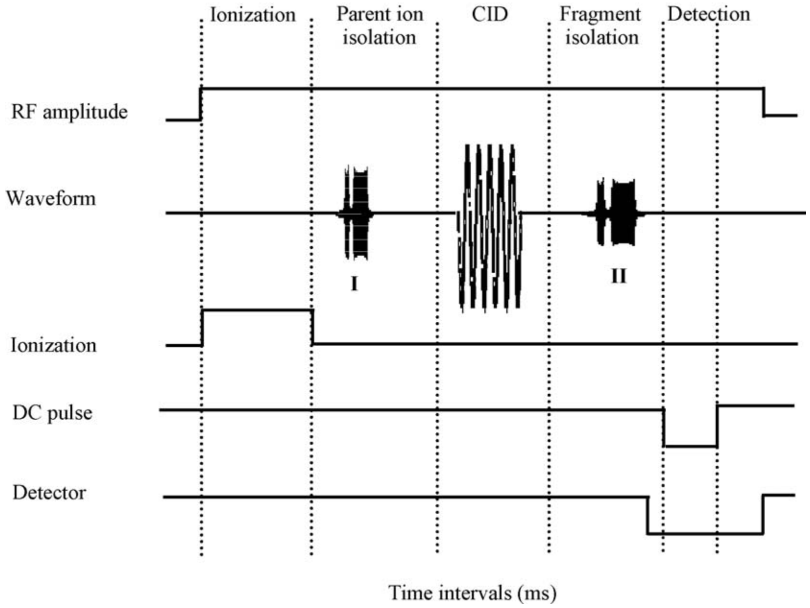

Fig. 11. Scan diagram for performing selected reaction monitoring (SRM) without using RF scanning. For each of the targeted fragment ions (108 or 120 Th), the parent ions covering the mass range of 148–154 Th were isolated using a SWIFT waveform with a corresponding frequency notch and then subjected to dipolar AC excitation. A targeted fragment ion was then detected by applying a second isolation SWIFT waveform followed by axial DC pulse.

amplitude and 162–170 kHz notch, was used for isolation of the fragment ions 108 Th from 150 Th and another 4 ms isolation waveform, 0.63 V amplitude and 145–153 kHz notch width was used to isolate the fragment ions 120 Th generated from 152 Th. The axial DC pulse conditions were the same as that used for RF/DC isolation/axial DC pulse mode. For comparison purposes, the CID mass spectrum using RF-ramp mass selective instability scan is shown in Fig. 12A. The detected signals using the non-RF scanning method for the fragment ions are shown in Fig. 12B. For each of targeted fragment ions (108 or 120 Th), a SWIFT waveform was applied to isolate the parent ions covering the mass range of 148–154 Th followed by the CID period. A second SWIFT waveform for the targeted fragment ion was then applied for their isolation and detection using an axial DC pulse. SRM data shown in Fig. 12C are reconstructed from the measured intensities difference between the sample and background. This experiment demonstrates a simple mass analysis mode for directly monitoring particular targeted compounds provided they have known fragmentation patterns.

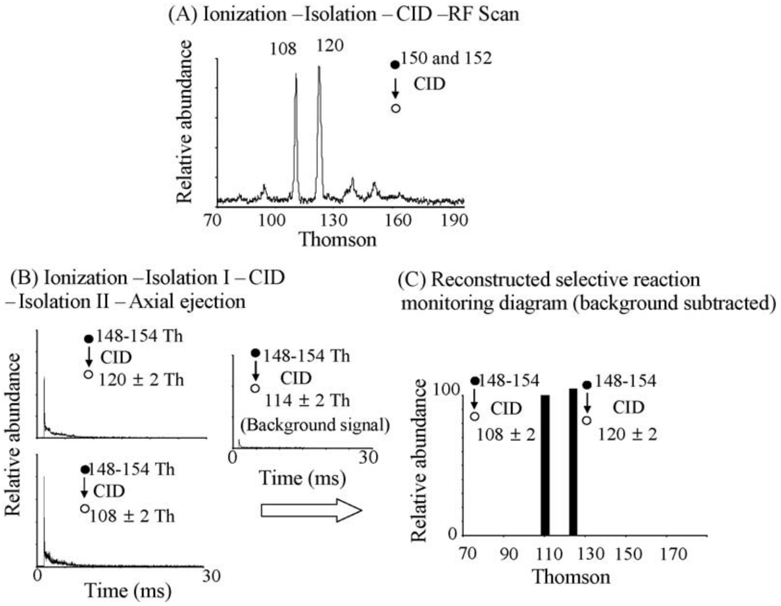

Fig. 12. Selected reaction monitoring of components of a mixture of benzyl acetate (MW 150) and methyl salicylate (MW 152) without using RF scanning. The reactions 150–108 Th for benzyl acetate and 152–120 Th for methyl salicylate were monitored. (A) CID mass spectrum of molecular ion of 152 and 150 Th from the mixture using RF-ramp mass selective instability scan with an isolation window of ca. 6 Th. (B) Intensities monitoring using axial DC pulse method (background intensities were subtracted). (C) Reconstructed data of SRM based on the measured intensities in (B).

5. Conclusions

Using a rectilinear ion trap, ion monitoring methods which do not require RF scanning have been developed. The configuration of the rectilinear ion trap allows experiments which combine ion isolation and subsequent ion ejection along the *z*-axis for detection. Without using an RF scan, selected ion monitoring is achieved. A series of selected ion monitoring events applied to different targeted ions provides an effective multiple ion monitoring method. Tandem mass spectrometry experiments carried out at a fixed RF voltage are possible by using AC excitation and dissociation of selective ions, allowing selected reaction monitoring. The limited resolution and necessity for multiple ionization events to record data in the form of multiple ion or multiple reaction monitoring experiments are offset by the simplicity and small size of the instrument.

Acknowledgements

This work was supported by a Purdue Research Foundation Trask award (P-02138) and by the Office of Naval Research (N00014-02-1-0834).

References

[1] S.A. Mcluckey, J.M. Wells, Chem. Rev. 101 (2001) 571.

[2] C.Y. Hao, R.E. March, Int. J. Mass Spectrom. 212 (2001) 337.

[3] M.G. Blain, L.S. Riter, D. Cruz, D.E. Austin, G.X. Wu, W.R. Plass, R.G. Cooks, Int. J. Mass Spectrom. 236 (2004) 91.

[4] E.R. Badman, R.G. Cooks, J. Mass Spectrom. 35 (2000) 659.

[5] C.R. Arkin, T.P. Griffin, A.K. Ottens, J.A. Diaz, D.W. Follistein, F.W. Adams, W.R. Helms, J. Am. Soc. Mass Spectrom. 13 (2002) 1004.

[6] V.D. Berkout, R.J. Cotter, D.P. Segers, J. Am. Soc. Mass Spectrom. 12 (2001) 641.

[7] R.J. Cotter, C. Fancher, T.J. Cornish, J. Mass Spectrom. 34 (1999) 1368.

[8] J.A. Diaz, C.F. Giese, W.R. Gentry, Field Anal. Chem. Technol. 5 (2001) 156.

[9] B.C. Laughlin, C.C. Mulligan, R.G. Cooks, Anal. Chem. 77 (2005) 2928.

[10] O.J. Orient, A. Chutjian, V. Garkanian, Rev. Sci. Instrum. 68 (1997) 1393.

[11] U. Rohner, J.A. Whitby, P. Wurz, Meas. Sci. Technol. 14 (2003) 2159.

[12] R.T. Short, D.P. Fries, S.K. Toler, C.E. Lembke, R.H. Byrne, Meas. Sci. Technol. 10 (1999) 1195.

[13] M.P. Sinha, M. Wadsworth, Rev. Sci. Instrum. 76 (2005) 025103.

[14] A.J. White, M.G. Blamire, C.A. Corlett, B.W. Griffiths, D.M. Martin, S.B. Spencer, S.J. Mullock, Rev. Sci. Instrum. 62 (1998) 565.

[15] C.R. Arkin, T.P. Griffin, J.A. Diaz, D.W. Follistein, C.H. Curley, D.P. Floyd, G.R. Naylor, W.D. Haskell, M. Blalock, F.W. Adams, Trends Anal. Chem. 23 (2004) 322.

[16] P.G. Hughes, O. Votava, M.B.A. West, F.T. Zhang, S.H. Kable, Anal. Chem. 77 (2005) 4448.

[17] L.S. Riter, E.C. Meurer, E.S. Handberg, B.C. Laughlin, H. Chen, G.E. Patterson, M.N. Eberlin, R.G. Cooks, Analyst 128 (2003) 1112.

[18] L.S. Riter, Y.A. Peng, R.J. Noll, G.E. Patterson, T. Aggerholm, R.G. Cooks, Anal. Chem. 74 (2002) 6154.

[19] G.E. Patterson, A.I. Guymon, L.S. Riter, M. Everly, J. Griep-Raming, B.C. Laughlin, O. Zheng, R.G. Cooks, Anal. Chem. 74 (2002) 6145.

[20] E.R. Badman, R.G. Cooks, Anal. Chem. 72 (2000) 5079.

[21] Z. Ouyang, G.X. Wu, Y.S. Song, H.Y. Li, W.R. Plass, R.G. Cooks, Anal. Chem. 76 (2004) 4595.

[22] Z. Ouyang, R.G. Cooks, US Patent 6,838,666 B2 (2005).

[23] S.H. Guan, A.G. Marshall, Anal. Chem. 65 (1993) 1288.

[24] R.G. Cooks, A.L. Rockwood, Rapid Commun. Mass Spectrom. 5 (1991) 93.

[25] G. Lawson, R.F. Bonner, J.F.J. Todd, Int. J. Mass Spectrom. Ion Process. 28 (1978) 141.