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Miniature Mass Spectrometer Systems Based on a Microengineered Quadrupole Filter

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Two miniature mass spectrometer systems based on a microengineered quadrupole mass filter have been developed. One of the instruments has a footprint of 27 cm × 20 cm and is intended for laboratory use when space is at a premium. The other is portable and intended for use in the field. It is battery powered, weighs 14.9 kg, and is housed in a rugged case. This is the first example of a portable mass spectrometer incorporating an analyzer fabricated using microelectromechanical systems (MEMS) techniques. The starting material for construction of the filters is a bonded silicon on insulator substrate, which is selectively etched using batch processing techniques to form coupling optics and springs that accurately hold 0.5 mm diameter stainless steel rods in the required geometry. Assembled filters measure 35 mm × 6 mm × 1.5 mm and are mounted, together with an ion source and channeltron detector, in small, interchangeable cartridges, which plug into a 220 cm^3 vacuum chamber. Recovery from accidental contamination or when servicing is required can be achieved within 5−10 min, as the cartridge is easily exchanged with a spare. A potential application to environmental monitoring has been investigated. The headspace above water spiked with dibutyl mercaptan was sampled with a solid phase microextraction (SPME) fiber, which was then injected directly into the vacuum chamber of the mass spectrometer. Using this method, the limit of detection was found to be approximately 5 ppm for a 15 s sampling period.

In common with many analytical instruments, there has been significant progress in the miniaturization of mass spectrometers over the past decade. There is a demand for small, low-cost versions of mass spectrometers that have typically been bulky, expensive, and confined to the laboratory. Applications include environmental monitoring, space exploration, online process monitoring, and the detection of drugs, explosives, and chemical weapons. Many types of miniature mass analyzer have been reported, including cylindrical,[1−4] toroidal,[5] Paul,[6] and rectilinear ion traps,[7−9] quadrupole[10−17] and crossed-field filters,[18−20] time-of-flight analyzers,[21−24] and magnetic sector instruments.[25−27] A number of miniature analyzers have been integrated into portable mass spectrometer systems suitable for the applications identified above.[21,22,27−31] Instruments based on a time-of-flight analyzer (the MS-200 from Kore Technology, Ely, Cambridgeshire, U.K.), a

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(1) Kornienko, O.; Reilly, P. T. A.; Whitten, W. B.; Ramsey, J. M. *Rapid Commun. Mass Spectrom.* **1999**, *13*, 50–53.

(2) Blain, M. G.; Riter, L. S.; Cruz, D.; Austin, D. E.; Wu, G. X.; Plass, W. R.; Cooks, R. G. *Int. J. Mass Spectrom.* **2004**, *236*, 91–104.

(3) Badman, E. R.; Johnson, R. C.; Plass, W. R.; Cooks, R. G. *Anal. Chem.* **1998**, *70*, 4896–4091.

(4) Chaudhary, A.; van Amerom, F. H. W.; Short, R. T.; Bhansali, S. *Int. J. Mass Spectrom.* **2006**, *251*, 32–39.

(5) Lammert, S. A.; Rockwood, A. A.; Wang, M.; Lee, M. L.; Lee, E. D.; Tolley, S. E.; Oliphant, J. R.; Jones, J. L.; Waite, R. W. *J. Am. Soc. Mass Spectrom.* **2006**, *17*, 916–922.

(6) Orient, O. J.; Chutjian, A. *Rev. Sci. Instrum.* **2003**, *74*, 2936–2938.

(7) Ouyang, Z.; Wu, G.; Song, Y.; Li, H.; Plass, W. R.; Cooks, R. G. *Anal. Chem.* **2004**, *76*, 4595–4605.

(8) Fico, M.; Yu, M.; Ouyang, Z.; Cooks, R. G.; Chappell, W. J. *Anal. Chem.* **2007**, *79*, 8076–8082.

(9) Li, X.; Jiang, G.; Luo, G.; Xu, F.; Wang, Y.; Ding, L.; Ding, C.-F. *Anal. Chem.* **2009**, *81*, 4840–4846.

(10) Wiberg, D.; Myung, N. V.; Eyre, B.; Shcheglov, K.; Orient, O.; Moore, E.; Munz, P. *SPIE Proc.* **2003**, *4878*, 8–13.

(11) Holkeboer, D. H.; Karandy, T. L.; Currier, F. C.; Frees, L. C.; Ellefson, R. E. *J. Vac. Sci. Technol., A* **1998**, *16*, 1157–1162.

(12) Ferran, R. J.; Boumsellek, S. *J. Vac. Sci. Technol., A* **1996**, *14*, 1258–1265.

(13) Velasquez-Garcia, L. F.; Akinwande, A. I. *Proceedings of Transducers and Eurosensors*, Lyon, France, June 10−14, 2007; pp 2315−2320.

(14) Taylor, S.; Tindall, R.; Syms, R. R. A. *J. Vac. Sci. Technol.* **2001**, *B19*, 557–562.

(15) Orient, O. J.; Chutjian, A.; Garkanian, V. *Rev. Sci. Instrum.* **1997**, *68*, 1393–1397.

(16) Wright, S.; Syms, R. R. A.; O'Prey, S.; Hong, G.; Holmes, A. S. *J. Am. Soc. Mass Spectrom.* **2009**, *20*, 146–147.

(17) Geear, M.; Syms, R. R. A.; Wright, S.; Holmes, A. S. *J. Microelectromech. Syst.* **2005**, *14*, 1156–1166.

(18) Diaz, J. A.; Vargas, A. E. M.; Diaz, F. C.; Squire, J. P.; Jacobsen, V.; McCaskill, G.; Rohrs, H.; Chatawal, R. *Trends Anal. Chem.* **2002**, *21*, 515–525.

(19) Freidhoff, C. B.; Young, R. M.; Sriram, S.; Braggins, T. T.; O'Keefe, T. W.; Adam, J. D.; Nathanson, H. C.; Syms, R. R. A.; Tate, T. J.; Ahmad, M. M.; Taylor, S.; Tunstall, J. *J. Vac. Sci. Technol., A* **1999**, *17*, 2300–2307.

(20) Sillon, N.; Baptist, R. *Sens. Actuators, B* **2002**, *83*, 129–137.

(21) Ecelberger, S. A.; Cornish, T. J.; Collins, B. F.; Lewis, D. L.; Bryden, W. A. *Johns Hopkins APL Tech. Dig.* **2004**, *25*, 14–19.

(22) White, A. J.; Blamire, M. G.; Corlett, C. A.; Griffiths, B. W.; Martin, D. M.; Spencer, S. B.; Mullock, S. J. *Rev. Sci. Instrum.* **1998**, *69*, 565–571.

(23) Syage, J. A.; Nies, B. J.; Evans, M. D.; Hanold, K. A. *J. Am. Soc. Mass Spectrom.* **2001**, *12*, 648–655.

(24) Yoon, H. J.; Kim, J. H.; Choi, E. S.; Yang, S. S.; Jung, K. W. *Sens. Actuators, A* **2002**, *97-8*, 441–447.

(25) Sinha, M. P.; Tomassian, A. D. *Rev. Sci. Instrum.* **1991**, *62*, 2618–2620.

(26) Sinha, M. P.; Wadsworth, M. *Rev. Sci. Instrum.* **2005**, *76*, 025103.

(27) Kogan, V. T.; Pavlov, A. K.; Chichagov, Y. V.; Tuboltsev, Y. V.; Gladkov, G. Y.; Kazanskii, A. D.; Nikolaev, V. A.; Pavlichkova, R. *Field Anal. Chem. Tech.* **1997**, *1*, 331–342.

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cylindrical ion trap (the Minotaur series from Griffin Analytical Technologies, West Lafayette, Indiana), a toroidal ion trap (the Guardion-7 from Torion Technologies American Fork, Utah), a magnetic sector (the Ion-Camera from OI Analytical, College Station, Texas), and a quadrupole filter (the Hapsite from Inficon, Syracuse, New York) are commercially available.

The smallest portable systems reported to date are based on the various types of ion trap. While the degree of miniaturization attempted is relatively modest, the concomitant reduction in size of the vacuum chamber and the rf power supplies, together with the availability of small pumps, has resulted in systems that are very much smaller than conventional laboratory instruments.[30,31] Although Paul and toroidal traps have been miniaturized, the geometries are relatively complex and the machining tolerances are known to be critical.[5,6] However, it has been shown that much simpler trap geometries can be optimized to give approximately correct fields.[7] This has been the approach pursued by Cooks and co-workers at Purdue University. Their early instruments were based on cylindrical traps,[32] while rectilinear traps were employed in later systems,[30] as these offer greater sensitivity and are more easily miniaturized.[8]

While conventional methods of fabricating small stainless steel and ceramic components have been used successfully to produce most of the miniature mass analyzers listed above, the techniques and materials that have emerged from the field of microelectromechanical systems (MEMS) offer an increasingly attractive route to smaller, low-cost instruments. MEMS technology is a generic description of devices incorporating integrated components with a characteristic dimension of less than 1 mm. These are typically fabricated by repetitive use of planar processes such as photolithography, material deposition, and etching,[33] which allow high-aspect ratio and movable microstructures to be formed. While MEMS devices can include components made from a variety of materials including plastics, metals, and various dielectrics, the substrate is often silicon,[34] since many of these processes originated in the silicon integrated circuit industry. However, the methods have since diverged considerably, and new processes specific to MEMS have been developed. Older silicon-based methods include bulk crystal-plane etching[35] and surface micromachining.[36] More recent techniques include fusion bonding[37] and deep reactive ion etching[38] of multilayer materials in high-density plasmas. Nonsilicon methods include the LIGA process,[39] which is used to form deep structures with near vertical sidewalls by electroplating metals in molds created by synchrotron exposure of the resist.

These methods have been used to produce mass analyzers with submillimeter dimensions. Surface micromachining has been employed to fabricate Wien[19] and traveling wave[40,41] filters, as well as a time-of-flight analyzer.[24] Deep reactive ion etching of silicon has been used to form quadrupole filters,[13,16,17] as has crystal plane etching.[14] Arrays of ion traps with micrometer dimensions have been formed using synchrotron exposure[1] and by surface micromachining of tungsten,[2] while very small, hyperbolic quadrupole arrays have been formed by the LIGA technique.[10] The performance achieved by many of these analyzers has been limited. Indeed, some have not yet yielded mass spectra.

Other MEMS mass spectrometer components, including coupling lenses,[42] hot-cathode[43] and cold-cathode[44,45] electron sources, plasma[40,41] and electrospray[46−48] ion sources, detector[49] and Faraday collector[50] arrays, electron multipliers[51,52] and vacuum gauges,[53−56] have been demonstrated. Some progress has also been made with MEMS vacuum pumps, and scroll,[10,57] thermal transpiration[58−60] and sputter ion[61] pumps have all been the subjects of investigation. There have been some attempts to integrate two or more system components. A monolithic time-of-flight mass spectrometer incorporating a thermionic ion source has been fabricated.[24] The filter and ion source were shown to function individually, but a mass spectrum from the components working in combination was not reported. More recently, spectra

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(28) Contreras, J. A.; Murray, J. A.; Tolley, S. E.; Oliphant, J. L.; Tolley, H. D.; Lammert, S. A.; Lee, E. D.; Later, D. W.; Lee, M. L. *J. Am. Soc. Mass Spectrom.* **2008**, *19*, 1425–1434.

(29) Yang, M.; Kim, T.-Y.; Hwang, H.-C.; Yi, S.-K.; Kim, D.-H. *J. Am. Soc. Mass Spectrom.* **2008**, *19*, 1442–1448.

(30) Gao, L.; Song, Q.; Patterson, G. E.; Cooks, R. G.; Ouyang, Z. *Anal. Chem.* **2006**, *78*, 5994–6002.

(31) Gao, L.; Sugiarto, A.; Harper, J. D.; Cooks, R. G.; Ouyang, Z. *Anal. Chem.* **2008**, *80*, 7198–7205.

(32) Patterson, G. E.; Guymon, A. J.; Riter, L. S.; Everly, M.; Griep-Raming, J.; Laughlin, B. C.; Ouyang, Z.; Cooks, R. G. *Anal. Chem.* **2002**, *74*, 6145–6153.

(33) Madou, M. J. *Fundamentals of Microfabrication*; CRC Press: Boca Raton, FL, 1997.

(34) Petersen, K. E. *Proc. IEEE* **1982**, *70*, 420–457.

(35) Kovacs, G. T. A.; Maluf, N. I.; Petersen, K. E. *Proc. IEEE* **1998**, *86*, 1536–1551.

(36) Bustillo, J. M.; Howe, R. T.; Muller, R. S. *Proc. IEEE* **1998**, *86*, 1552–1573.

(37) Barth, P. W. *Sens. Actuators, A* **1990**, *21*−*23*, 919–926.

(38) Hynes, A. M.; Ashraf, H.; Bhardwaj, J. K.; Hopkins, J.; Johnston, I.; Shepherd, J. N. *Sens. Actuators* **1999**, *74*, 13–17.

(39) Guckel, H. *Proc. IEEE* **1998**, *86*, 1586–1593.

(40) Siebert, P.; Petzold, G.; Hellenbart, A.; Müller, J. *Appl. Phys.A* **1998**, *67*, 155–160.

(41) Hauschild, J.-P.; Wapelhorst, E.; Müller, J. *Int. J. Mass Spectrom.* **2007**, *264*, 53–60.

(42) Syms, R. R. A.; Michelutti, L.; Ahmad, M. M. *Sens. Actuators, A* **2003**, *107*, 285–295.

(43) Yoon, H. J.; Kim, J. H.; Park, T. G.; Yang, S. S.; Jung, K. W. *Proc. SPIE* **2001**, *4408*, 360–367.

(44) Kornienko, O.; Reilly, P. T. A.; Whitten, W. B.; Ramsey, J. M. *Anal. Chem.* **2000**, *72*, 559–562.

(45) Cruz, D.; Chang, J. P.; Blain, M. G. *Appl. Phys. Lett.* **2005**, *86*, 153502.

(46) Syms, R. R. A.; Zou, H.; Bardwell, M.; Schwab, M.-A. *J. Micromech. Microeng.* **2007**, *17*, 1567.

(47) Licklider, L.; Wang, X. Q.; Desai, A.; Tai, Y. C.; Lee, T. D. *Anal. Chem.* **2000**, *15*, 367–375.

(48) Schultz, G. A.; Corso, T. N.; Prosser, S. J.; Zhang, S. *Anal. Chem.* **2000**, *72*, 4058–4063.

(49) Birkinshaw, K. *Int. J. Mass Spectrom.* **2002**, *215*, 195–209.

(50) Scheidemann, A. A.; Darling, R. B.; Schumacher, F. J.; Isakharov, A. *J. Vac. Sci. Technol., A* **2002**, *20*, 597–604.

(51) Beetz, C. P.; Boerstler, R.; Steinbeck, J.; Lemieux, B.; Winn, D. R. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2000**, *442*, 443–451.

(52) Tremsin, A. S.; Vallerga, J. V.; Siegmund, O. H. W.; Beetz, C. P.; Boerstler, R. W. *Proceedings of SPIE*, Waikoloa, Hawaii, August 22, 2002; Vol. 215, p 4854.

(53) van Herwaarden, A. W.; Sarro, P. M. *Sens. Actuators* **1985**, *8*, 187–196.

(54) Shie, J. S.; Chou, B. C. S.; Chen, Y. M. *J. Vac. Sci. Technol., A* **1995**, *13*, 2972–2979.

(55) Miyashita, H.; Esashi, M. *J. Vac. Sci. Technol., B* **2000**, *18*, 2692–2697.

(56) Wilfert, S.; Edelmann, C. *J. Vac. Sci. Technol., A* **2004**, *22*, 309–320.

(57) Moore, E. J.; Munitz, E. P.; Erye, F.; Myung, N.; Orient, O.; Shcheglov, K.; Wiberg, D. *Rarified Gas Dyn.* **2003**, *663*, 1033–1040.

(58) Young, R. M. *J. Vac. Sci. Technol., B* **1999**, *17*, 280–287.

(59) Vargo, S. E.; Muntz, E. P. *Rarified Gas Dyn.* **2001**, *585*, 502–509.

(60) McNamara, S.; Gianchandani, Y. B. *Proc. Transducers '03*, Boston, MA, June 8−12, 2003.

(61) Wright, S. A.; Gianchandani, Y. B. *Proc. MEMS '06*, Istanbul, Turkey, January 22−26, 2006; pp 754−757.

of simple gas mixtures in the range 10−80 Da have been recorded using a plasma ion source, energy filter, traveling wave mass analyzer, and detector integrated on a single chip.[41]

In the present article, we describe the development of two hybrid instruments based on a miniature mass filter fabricated using MEMS techniques. Most of the other system components are small but conventional in their design and construction. The benefit of this philosophy is that the ease of manufacture, small volume, and low drive voltages associated with such a mass filter can be exploited, while the development burden is minimized. We have previously described the design, fabrication, and performance of a promising miniature quadrupole filter with an inscribed radius, r_0, of only 220 μm.[16,17] Using a laboratory test system, a mass range of 0−400 Da, and an ultimate resolution of $M/\Delta M = 200$ (full width at half-maximum, fwhm) at $m/z = 219$ were demonstrated.

One of the instruments (ChemPack) is battery powered and housed in a rugged box. It is intended for use in the field, for applications such as identification of chemical spills or illicit substances, and trace detection. The other (ChemCube) is mains (outlet) powered and intended for laboratory use when space is at a premium and convenience is more important than achieving the sensitivity and resolution of conventional high end instruments. At present, neither instrument incorporates a gas chromatograph (GC). Consequently, applications are currently restricted to pure compounds, simple matrices, or situations in which selectivity can be achieved by the sample collection method. A number of microengineered GC columns have been reported,[62,63] and those developed by SLS Microtechnology (Hamburg, Germany) and C2V (Enschede, The Netherlands) are commercially available. It is anticipated that a suitable GC could be integrated with minimal impact on the size of the instruments.

The overall size and weight of a miniature mass spectrometer depends crucially on the choice of pumps and the desired method of sample introduction. Capillary and membrane inlets can be tailored to give a flow rate consistent with a particular pumping speed and have been successfully used for continuous atmospheric monitoring.[22,64,65] Similarly, the duty cycle of a pulsed inlet can be adjusted to match the pumping speed, a mode of operation suited to the cyclic nature of ion trap operation.[29,31] The pumps selected for the systems described in this article are not the smallest available but have a relatively high pumping speed. Although this results in size and weight penalties, the advantage is greater flexibility with respect to sample introduction. Most importantly, the systems can tolerate direct injection through a septum inlet or, potentially, from the gas flow from a miniature GC.

An inconvenience of conventional quadrupole mass spectrometers is that the mass filter itself is generally a costly component that must be kept in pristine condition. Maintenance requires disassembly and skilled servicing, during which time the instrument is unavailable. However, a benefit of MEMS technology exploited in our systems is that the filter is much less precious and potentially even disposable. The ion source, mass filter, and channeltron detector are integrated into a small cartridge which simply plugs into an electrical connector in the vacuum chamber. Replacing a faulty or dirty cartridge with a fresh spare is an unskilled task that takes no more than 5 min. Several replacement cartridges can reasonably be kept to hand or in stock. The minimal effort required to recover from a fault with the filter or accidental contamination is a clear advantage over conventional instruments, especially in the field.

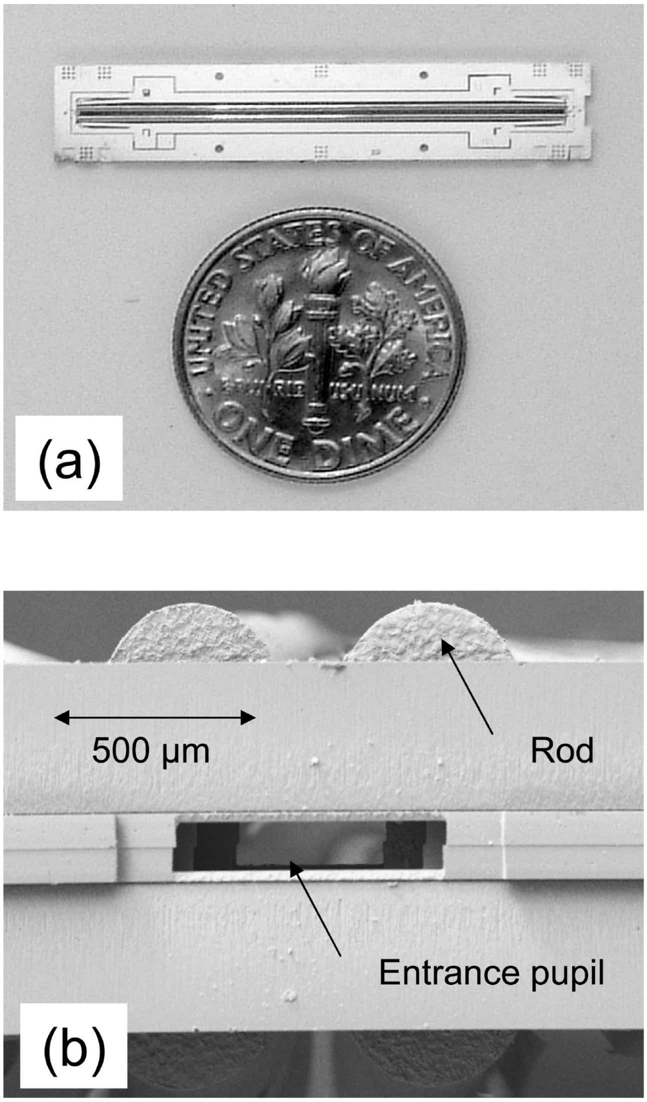

Figure 1. (a) Photograph of a completed microengineered quadrupole mass filter and (b) scanning electron microscope image of the input.

In the following sections, we first briefly outline the design of the mass filter and the steps involved in its construction. A much more detailed account can be found elsewhere.[16,17] The mass spectrometer cartridge and the two fully integrated systems alluded to above are then described. Initial results are also presented which demonstrate the performance of the instruments and a potential application to environmental monitoring.

Quadrupole Filter Fabrication. A completed quadrupole mass filter is shown in Figure 1. The silicon structure has an overall size of 32 mm × 6 mm × 1 mm and accommodates stainless

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(62) Eiceman, G. A.; Gardea-Torresdey, J.; Dorman, F.; Overton, E.; Bhushan, A.; Dharmasena, H. P. *Anal. Chem.* **2006**, *78*, 3985.

(63) Dorman, F. L.; Overton, E. B.; Whiting, J. J.; Cochran, J. W.; Gardea-Torresdey, J. *Anal. Chem.* **2008**, *80*, 4487–4497.

(64) Janfelt, C.; Graesboll, R.; Lauritsen, F. R. *Int. J. Mass Spectrom.* **2008**, *276*, 17–23.

(65) Keil, A.; Talaty, N.; Janfelt, C.; Noll, R. J.; Gao, L.; Ouyang, Z.; Cooks, R. G. *Anal. Chem.* **2007**, *79*, 7734–7739.

steel rods measuring 508 ± 5 μm in diameter and 30.650 ± 0.075 mm in length. Very thin horizontal and vertical alignment features accurately define the positions of the rods at their ends. They are positioned such that the inscribed radius of the quadrupole is 220 μm. Leaf springs firmly hold the rods in position by pushing them against the vertical alignment features. Ions enter and exit the filter through a series of lenses and tunnels etched into the silicon frame.

Each filter consists of two identical die, which are placed back-to-back and bonded together to form a single, monolithic structure. The dies are made by deep reactive etching (DRIE) of bonded silicon on insulator (BSOI), a substrate consisting of two layers of silicon separated by a thin layer of insulating oxide. To accommodate the rods in the correct geometry, the so-called handle and device silicon layers are required to be 400 and 80 μm thick, respectively. The springs and vertical alignment features are etched into the thick handle layer whereas the electrical connections, horizontal alignment features, and ion optics are etched into the thinner device layer.

All processing steps are based on wafer-scale techniques using industry-standard equipment. Photolithographic patterning is used to define the desired features in a layer of spin-coated photoresist. The excess silicon is then selectively removed at high rates by DRIE. Both silicon layers can be processed independently to form separate sets of near vertical structures. The etching stops accurately on the oxide, which can be left in place to provide electrical isolation between handle and device layers or selectively removed to allow motion of the springs. A total of four masks are required to define all the features in the two silicon layers. After being etched, the wafer is thermally oxidized and then sputter coated with gold. Each BSOI wafer is 100 mm in diameter and can accommodate 24 dies. The yield is typically 80−100%. Defective dies are identified either by visual inspection or during electrical characterization on a probe station and discarded before final assembly. Each complete filter is bonded to a printed circuit board (PCB). Wire bonds are made between the filter and bond pads on the PCB, which are routed to a pair of inline connectors.

Mass Spectrometer Cartridge. The images in Figure 2 show how the mass spectrometer cartridge evolved from an early prototype to a more rugged and ergonomic design. In Figure 2a, the electron impact ionization source can be seen to the right of the image. It consists of three rectangular aperture plates and a box-shaped shield, which conceals a cage and a tungsten filament. The two screws holding the shield in place also provide electrical connections for the filament legs, which are supported by the same screws from the rear of the cartridge base plate. Two banks of push fit electrical connectors support the quadrupole filter, which is enclosed within a two part shield. The cartridge base plate is sandwiched between the two halves of the connectors. This arrangement holds the filter in place while also allowing it to be easily removed. A channeltron detector (Detector Technologies Inc.) is housed in the angled stainless steel structure to the left of the image. The nine pin D-type plug at the base of the cartridge pushes into a mating D-type socket welded into the base of the vacuum chamber, which provides the necessary electrical connections and mechanical support. Many ion source and cartridge base plates were laser cut from large sheets and folded, where necessary, using jigs. Although this prototype worked well, the design is unsatisfactory in that assembly, especially soldering and spot-welding of the electrical connections, is labor-intensive. In addition, replacement of a blown filament is difficult and time-consuming.

Figure 2b shows an exploded view of a more advanced version. The concept is similar, but the assembly techniques and general arrangement have been refined to improve manufacturability and ergonomics. A cavity beneath the filter accommodates the channeltron, and all the wiring has been replaced by push fit connections to a base PCB. The quadrupole filter is covered by a folded stainless steel shield and securely screwed down to four posts. In common with the earlier prototype, the ion source is based on rectangular aperture plates. However, the use of push-fit spade connectors allows this to be easily installed and replaced as a complete unit. The filament is spot-welded to two tantalum posts that are mechanically supported and electrically isolated by a glass bead. This easily replaced assembly, which is similar in design to an automotive fuse, is held by two clips on the base PCB and is therefore structurally independent of the cartridge. The signal and noise levels are very similar to those of the earlier version in Figure 2a. However, the overwhelming advantage of the more advanced design is its modular construction, which is much better suited to volume production and more readily serviced.

System Architecture. Figure 3 shows ChemCube, the compact laboratory instrument. The system is enclosed in an injection molded plastic case that measures 27 cm × 27 cm × 20 cm. The total weight is 9 kg. An internal steel chassis supports the vacuum and electrical components. The mass spectrometer cartridge can be easily accessed through a spring-loaded flap, which exposes the vacuum chamber when in the open position. At the rear there is a ventilation grill and sockets for USB connection and mains (outlet) power.

Also shown in Figure 3 is ChemPack, the compact laboratory instrument. The system is housed in a more robust, waterproof ABS case measuring 19 cm × 40 cm × 33 cm. The total weight is 14.9 kg (including batteries). To protect the system during operation and transit, the internal chassis is mounted on shock absorbers. During operation, the lid must be left in the open position as the heat generated by the pumps and electronics is dissipated by a fan. Electrical power is taken from 4 V, 7 A h prismatic lithium-ion batteries arranged as two 28 V stacks and mounted as shown in Figure 3. The average power consumption is 45 W, of which 30 W is attributable to the pumps. The battery lifetime depends on how the system is used but is typically 7−9 h. ChemPack is much more robust than ChemCube. ChemPack systems have produced mass spectra in field trials within minutes of startup after long haul journeys without secondary packaging.

Apart from differences in circuit board layout, the system components for both instruments are mostly identical. The vacuum chamber has a cylindrical cross-section and measures 75 mm in diameter by 50 mm deep. As well as the D-type electrical feed-through that connects the mass spectrometer cartridge with the circuit board beneath, the chamber has a high voltage feed-through for the multiplying detector supply and ports for pumping and a vacuum gauge. A sample introduction port is provided on the chamber lid, which can be fitted with either a septum inlet (VICI Valco Instruments Co. Inc.) for direct injection or a leak

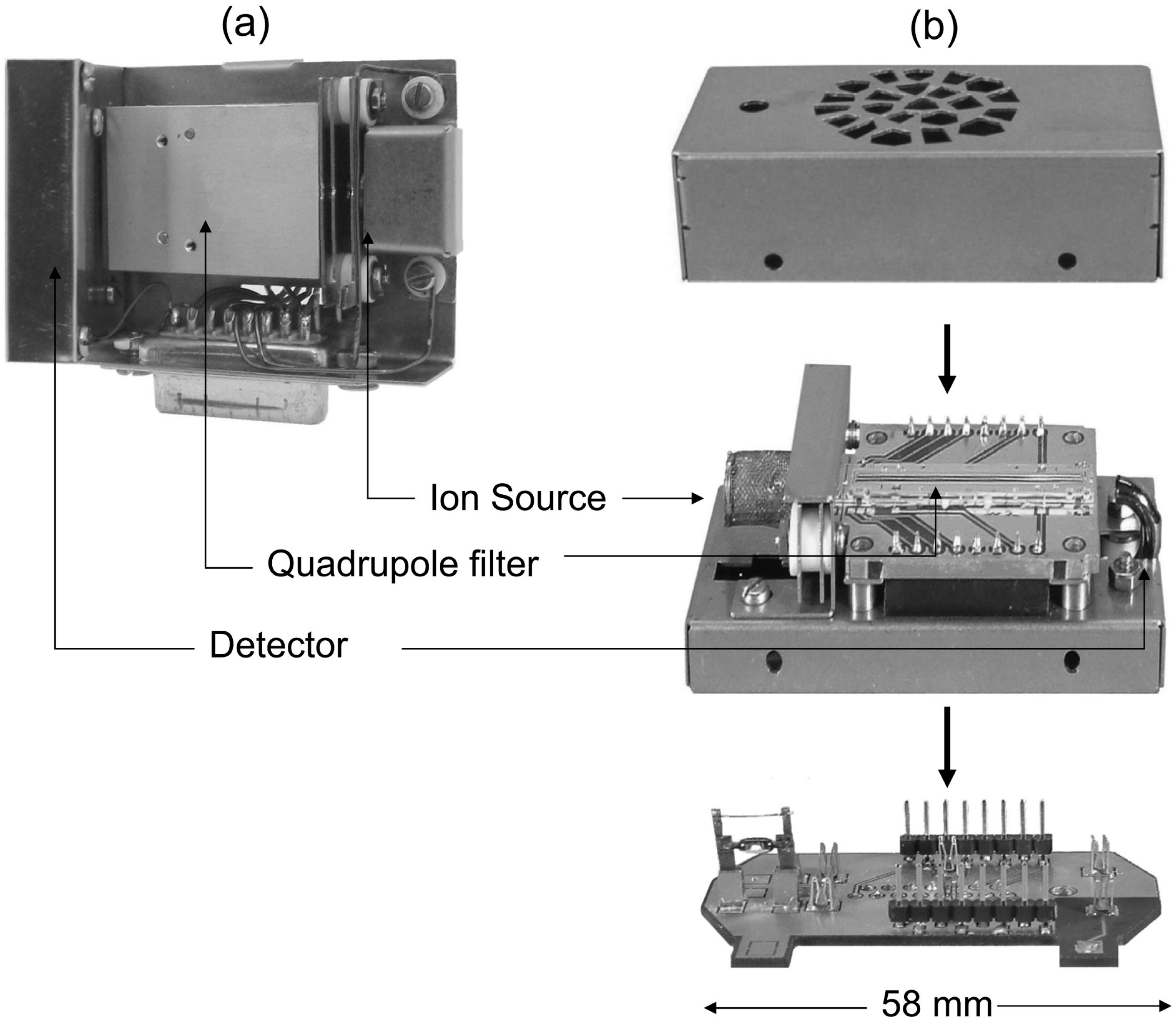

Figure 2. (a) Early prototype of the interchangeable mass spectrometer cartridge, consisting of an ion source, a microengineered quadrupole mass filter, and a channeltron detector. (b) A more advanced cartridge designed for simplified production. All the electrical connections are made with push fit connectors. The filament is supported by two spade connectors, which are pushed into spring clips on the base PCB.

valve for continuous sampling. Internal heaters can be used to heat the inlet liner up to a maximum temperature of 370 °C. The chamber is pumped using a 10 L s^{-1} turbo-molecular pump (Pfeiffer Vacuum TPD 011) backed by a two-stage diaphragm pump (KNF Neuberger N84.4ANDC). A commercially available MEMS component, a MicroPirani (MKS Instruments) thermal conductivity gauge, is used to monitor the vacuum level. Pump down typically takes approximately 5−10 min. The base pressure achieved is less than or equal to 1×10^{-5} Torr, which is the lowest pressure that can be measured by the gauge.

The motherboard contains a RISC core running at 48 MHz equipped with 256 kB flash program ROM, 8 kB flash data ROM and 10 kB static RAM. Data is stored externally in 1 MB RAM. The dc voltages needed for operation of the ion source, ion optics, detector, and quadrupole are produced using 16 bit D-to-A converters, while the rf waveform (up to 100 V p−p at approximately 6 MHz) is generated using a digitally controlled frequency source and an rf power amplifier. Pulses from the detector are processed by a threshold discriminator in a shielded enclosure and then counted.

While all the low level tasks are handled by the on-board processor, a graphical user interface running on an external PC provides user control and postprocessing. Communication to the host PC occurs via a USB 1.1 interface. Standard setup functions include automatic tuning to the quadrupole filter resonance by minimization of the drive current and mass scale calibration based on user selection of known masses. Mass spectra can be stored after each scan or averaged (continuous or boxcar). There is also provision for total and selected (up to five channels) ion counting. The maximum scan speed and minimum mass increment are currently limited by software to 1 ms per data point and 0.1 amu, respectively. However, the rf drive is capable of being scanned at the faster rates that would be appropriate if the instrument was coupled to a GC.

Performance. All of the data described below was obtained with a ChemPack system during trials. Identical resolution and

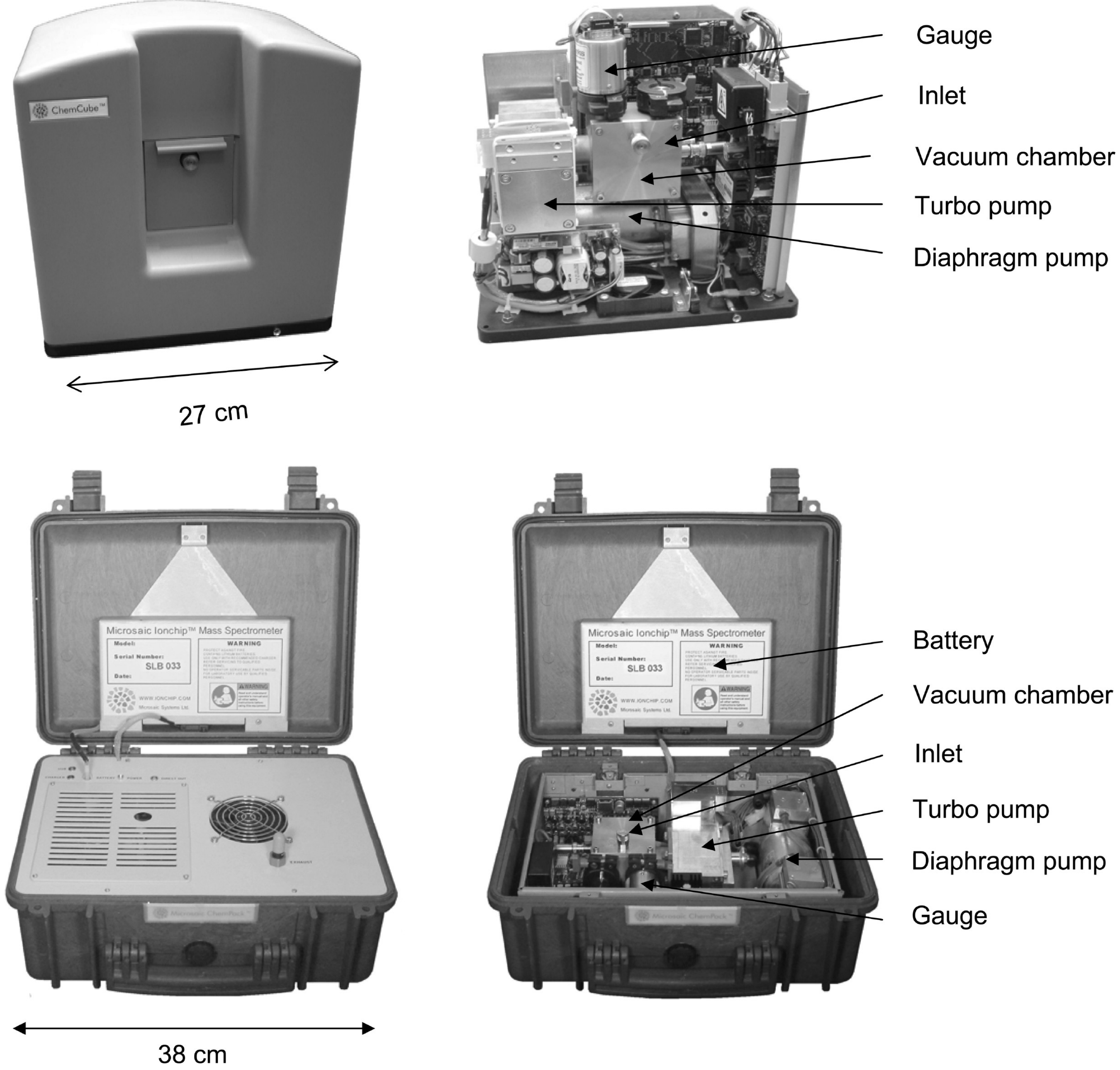

Figure 3. Images of ChemCube (top) and ChemPack (bottom) mass spectrometers. ChemCube is intended for laboratory use when space is at a premium, while ChemPack is a portable instrument intended for use in the field.

sensitivity can be achieved with ChemCube, which is constructed from essentially the same system components. A mass spectrometer cartridge of the type shown in Figure 2a was used. Figure 4a shows a mass spectrum of perfluorotributylamine (PFTBA) acquired over a period of 40 s. For the purposes of this test, the septum inlet was removed and replaced with a leak valve connected to a sample vial containing the PFTBA. The partial pressure of PFTBA was set at 1×10^{-5} Torr. The peak height distribution is very similar to that of the National Institute of Standards and Technology (NIST) library spectrum, which is also shown for comparison. Other types of mass spectrometer operating with electron impact ionization sources, particularly ion traps, produce spectra that are often quite different. For example, in the case of PFTBA, the prominent peak at $m/z = 219$ is often small or absent in spectra from ion traps.[32] Similar discrepancies have been observed for a number of common organic compounds.[66]

The sensitivity of the instruments was investigated by sampling the headspace above aqueous solutions of butyl mercaptan and toluene using solid phase microextraction (SPME). SPME is a means of preconcentration and sample introduction that is ideally suited to the systems described here. Butyl mercaptan and toluene are examples of compounds that are monitored in wastewater from petrochemical plants. Solutions with butyl mercaptan concentrations of 1, 10, and 100 ppm were prepared by sequential dilution and stored in partially filled vials sealed with rubber septa. A solution of 100 ppm toluene in water was also prepared and stored in the same manner. The SPME fiber (Supelco Stableflex PDMS-

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(66) Sokol, E.; Edwards, K. E.; Qian, K.; Cooks, R. G. *Analyst* **2008**, *133*, 1064–71.

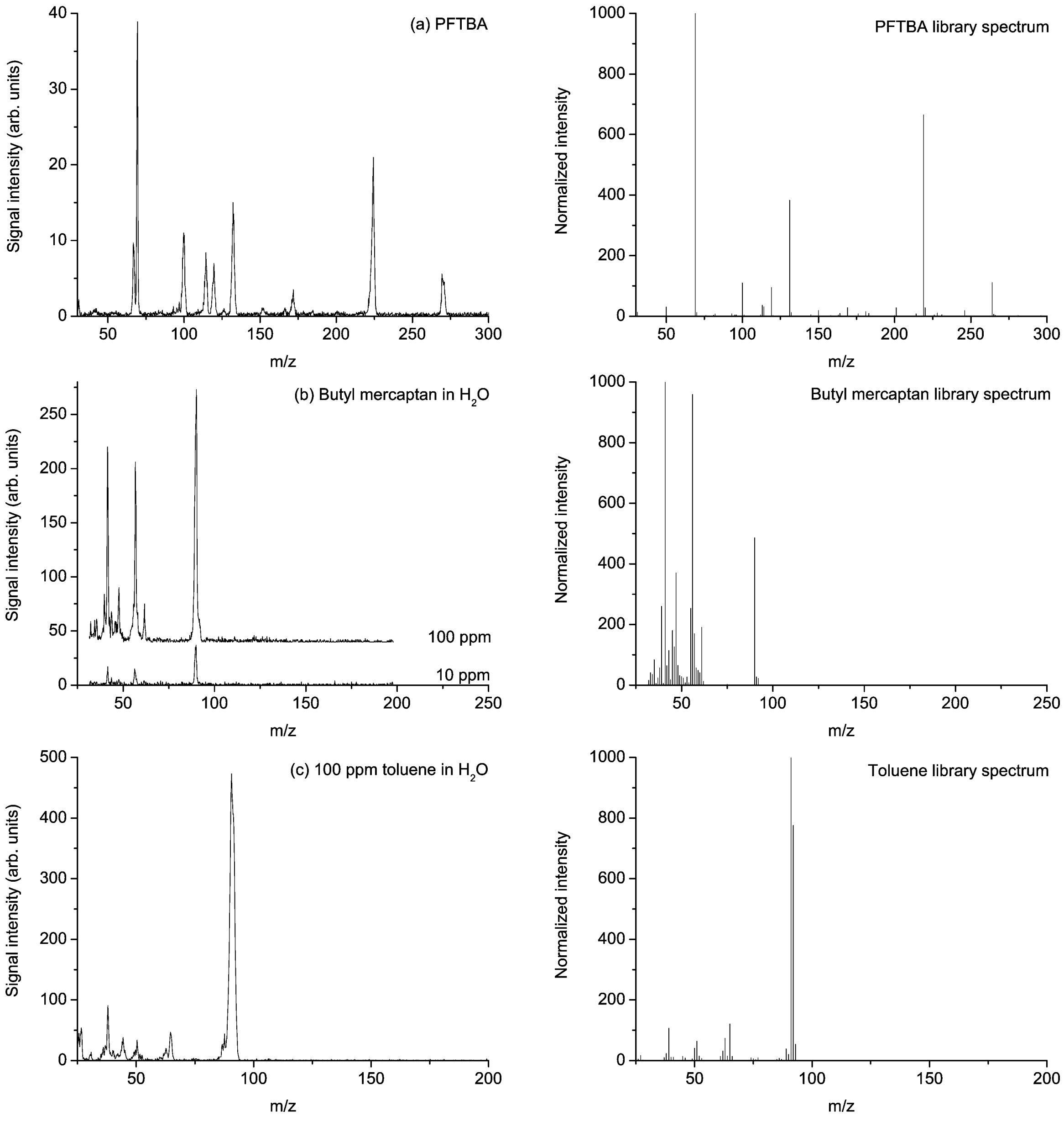

Figure 4. (a) Mass spectrum of PFTBA, which was introduced through a leak valve attached to the inlet fitting. (b) Mass spectra of butyl mercaptan. The samples were collected by SPME from the headspace above aqueous solutions and injected directly into the vacuum chamber through a septum inlet. (c) Mass spectrum of toluene, also collected by SPME from the headspace above an aqueous solution. All data were obtained using a ChemPack system during trials.

DVB) was exposed to the headspace for 15 s and then immediately injected into the mass spectrometer. The pressure increased briefly to approximately 1×10^{-3} Torr as a result of the small slug of air introduced as the needle pierced the septum, the water absorbed on the fiber, and the analyte extracted from the headspace. The inlet liner was at ambient temperature throughout these experiments as the analytes are relatively volatile. Both analytes could be detected during the first three scans after injection (each scan is approximately 3 s), with 75% of the total signal appearing in the first scan. Parts b and c of Figure 4 show the first full scan after injection for 100 and 10 ppm butyl mercaptan and 100 ppm toluene. The initial slug of air introduced with the needle pumped away quickly, and consequently the pressure during the first full scan had dropped to approximately 5×10^{-4} Torr. Again, the peak height distributions are in good agreement with the NIST library spectra. Only very small peaks were observed after sampling the 1 ppm butyl mercaptan solution. The $m/z = 90$ peak has a signal-to-noise ratio of approximately 2:1, whereas it is 20:1 for the 10 ppm solution. Hence, we conservatively place the detection limit at 5 ppm.

Previous tests[16,17] in a laboratory test system have shown that at U/V values close to the point of extinction, unit resolution (measured at fwhm) can be achieved at $m/z = 219$. The resolution at $m/z = 219$ in Figure 4a is approximately half this value. In part, this is because a lower U/V value was used in order to increase transmission at the expense of resolution (so that a full spectrum with a good signal-to-noise ratio could be acquired in a reasonable time). However, the achievable resolution is also degraded by the inevitable compromises that must be made with respect to mechanical and electrical stability when transitioning from a laboratory test system to a fully integrated, miniature instrument.

For example, vibration due to the pumps is much more significant in the integrated systems. Further system developments are likely to resolve these issues.

In parts b and c of Figure 4, the peak widths are also somewhat wider than can be achieved at ultimate resolution in a laboratory test system. Peaks separated by two mass units are well resolved in both cases. However, the $m/z = 91$ and 92 peaks are not resolved in the spectrum of toluene. The molecular ion peak in the butyl mercaptan spectrum has a width (fwhm) of 1.3 mass units, whereas baseline separation of the krypton isotope peaks has previously been reported.[16] When the amount of analyte desorbed from the fiber was particularly high, for example, after sampling the headspace above neat volatile organic compounds, the resolution was further compromised by the high pressure during analysis. In such cases, better resolution was observed after the initial pressure burst in the second and third scans.

CONCLUSIONS

Two miniature mass spectrometer systems based on a MEMS quadrupole mass filter have been demonstrated. Headspace samples were collected using a SPME fiber and injected directly into the vacuum chamber. The minimum concentration of butyl mercaptan dissolved in water that could be detected after sampling for 15 s was found to be approximately 5 ppm. The resolution, demonstrated is somewhat less than the intrinsic capabilities of the mass filter because of the need to increase transmission at the expense of resolution and compromises associated with transitioning from a laboratory test system to a fully integrated instrument, but is nevertheless comparable with other miniature mass spectrometers.

Clearly, performance could be enhanced in many applications using a preseparation device such as a gas chromatograph. Similarly, development of a direct insertion probe would allow analysis of powder samples with low vapor pressures. There are also opportunities for further integration, for example, by fabricating additional system components such as the pressure gauge, ion source, and detector using MEMS technology.

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