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An optimised quadrupole mass spectrometer with a dual filter analyser for in-field chemical sniffing of volatile organic compounds

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We report a novel portable 17 kg system based on a quadrupole mass spectrometer (QMS) with an electronic power consumption of 24 W. The system can be used for the in-field identification of gases and volatile/semivolatile organic compounds (VOCs/SVOCs). The mass analyser is a custom-made quadrupole mass filter with a Brubaker pre-filter that gives a mass range of m/z 1–500. It is an upgrade of the previous m/z 1–200 range triple filter analyser system. Analyser design was optimized using 3D numerical simulations as a performance trade-off between single and triple filter designs while maintaining high sensitivity and ease of integration. This also required enhanced design of the electronic control unit (ECU) compared to the previous triple filter ECU designs with lower power consumption, size, weight and cost of the overall system. Another major ECU improvement includes high stability of DC voltage control and ultra-low RF drift, which is important for in-field applications that require stable mass peaks for reliable quantitative analysis and continuous monitoring. Experimental results are presented for the perfluorotri-butylamine (PFTBA) calibrant and acetone to assess the functionality of the instrument. Performance comparison between the dual and triple filter quadrupole analysers has also been done. Mass spectra are given for methyl benzoate (cocaine simulant), piperidine (phencyclidine simulant), cyclohexanone (C4 simulant) and 2-nitrotoluene (TNT simulant) to assess potential capability for the identification of threat compounds. All spectral results show good correlation with the NIST library mass spectra with unit resolution obtained for spectral peaks within a m/z 1–400 mass range.

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Introduction

The development of portable mass spectrometers (MSs) has greatly advanced in the last 15 years using linear quadrupole, ion trap and time-of-flight (TOF) mass analysers.¹ Portable quadrupole systems have been built using single filter^{2–4} and triple filter⁵ analysers with mass ranges from m/z 1–200 to m/z 15–515 and weights between 16.3 and 23 kg. Ion trap geometries in portable systems are cylindrical,^{6,7} four-parallel-disk,⁸ linear,^{9–11} rectilinear,^{12–14} toroidal^{15,16} and trap array.^{17,18} Mass ranges of mobile ion trap instruments start from m/z 30–300 to m/z 50–1500 with system weights between 1.5 and 25 kg. Portable TOF systems are still under development with some having mass ranges of m/z 1–1000 and weights from 15 to 35 kg.^{19–21} Sampling types vary for different systems and include direct leak, membrane inlet, thermal desorption, pre-

concentrator, GC fused silica capillary column, solid phase microextraction (SPME), swab sampling and atmospheric pressure interface (API) for ambient ionization. In general, physically smaller MS devices have limited performance (*i.e.*, sensitivity and resolution), while high performance instruments are too bulky for field use. Therefore, a trade-off between portable MS size and performance is needed for sufficiently reliable and accurate in-field chemical analyses.

The main requirements for the implementation of a commercial portable MS are performance, measurement accuracy and robustness including size, weight, power consumption and cost. The most important performance parameters for in-field applications are satisfactory resolution (typically unit), limit of detection (ppb or less), sufficiently high mass range (at least m/z 200) and fast analysis time (within minutes). The key parameters for measurement accuracy are reliability, repeatability and reproducibility of the results. A demand for robustness depends on target applications and can be from low to high levels in which different types of ion sources and vacuum systems must be used. All of the above requirements are driven by the designs of ion sources, mass analysers, voltage control methods and electronic control units (ECUs),

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which are crucial components for MS functionality and capability.

In this paper, we focus on the optimization of a portable MS system through the enhancement of a mass analyser and MS electronic control unit (ECU). The advantages of using a dual filter analyser instead of a single filter analyser are shown through 3D simulations of ion motion where greater ion stability and focus are seen when a pre-filter is used. The dual filter quadrupole was manufactured using high precision CNC machining with low tolerances for rod alignment and surface finish. It was assembled on a flange with a custom-made electron impact ion source and a commercial electron multiplier detector (Photonis Channeltron® 4769). Our previous triple filter ECU⁵ has been completely redesigned to drive a dual filter quadrupole and it was miniaturized to have four times lower weight, and less than half size and power consumption. In this way, the cost of the ECU has been significantly reduced. The resonant RF circuit has also been redesigned to enable ultra-low RF drift, purity and efficiency which are essential for stable and reliable analysis. The entire system was assembled in a Peli™ 1600 protector case²² to be fully functional for mass analysis using a direct leak, fused silica capillary and membrane inlet.

The following sections give specification details on the dual filter analyser, miniaturized ECU and experimental setup. Mass spectral results are also included to show MS functionality and capability for the detection of simulants of threat compounds. Discussion is made regarding the further reduction of size, weight, power consumption and cost of the overall instrument as well as improvement of resolution, scan speed and robustness.

Methods

The effect of adding a pre-filter to the main filter of a QMS was originally studied by Brubaker as a delayed DC ramp on the

QMS.²³ This was done in order to improve QMS sensitivity and resolution. The Brubaker pre-filter (or Brubaker lens) had the same RF voltage applied as the main filter, but without the DC ramp. This reduced ion losses as they pass through RF/DC fringing fields of the main filter. Numerical simulations have also been done by Gibson *et al.* for different pre-filter lengths, and gaps between the pre-filter and main filter to assess ion transmission and sensitivity.²⁴ It has been found that pre-filter length should be at least $6r_0$ for maximal ion transmission where r_0 is the radius of the inscribed circle inside the quadrupole rods. The maximum gap between the pre-filter and the main filter was found to be $1.2r_0$ before fringing fields start having a significant effect on ion transmission.

Our dual filter quadrupole with circular rods was simulated using the CPO3D software before completion of the fabrication design. CPO uses the boundary-element method which has been proven to be more accurate for modelling ion trajectories in mass analysers than more common finite element and finite difference methods.²⁵ Such modelling was done to further examine fringing field effects and stability of the ion motion when a pre-filter is used. An electron impact (EI) ion source was included in the model using an optimised einzel lens system for ion injection into the analyser.²⁶ A pre-filter of length $8r_0$ was selected in the design to provide high ion transmission. The gap between the pre-filter and the main filter was chosen to be $0.2r_0$ due to the minimal effect of the fringing fields and to maintain compactness of the analyser. Fig. 1a and b show an example of ion beam from the EI source passing through the optimised einzel lens system into the single and dual filter analyser, respectively. The beam is for m/z 304, a characteristic mass fragment of cocaine. Average simulated axial kinetic energies of the ions were respectively 3.5 eV after exiting the source lens system, 3 eV upon passing through the pre-filter and 8 eV after passing through the main filter. As can be seen from Fig. 1a and b, m/z 304 ion trajec-

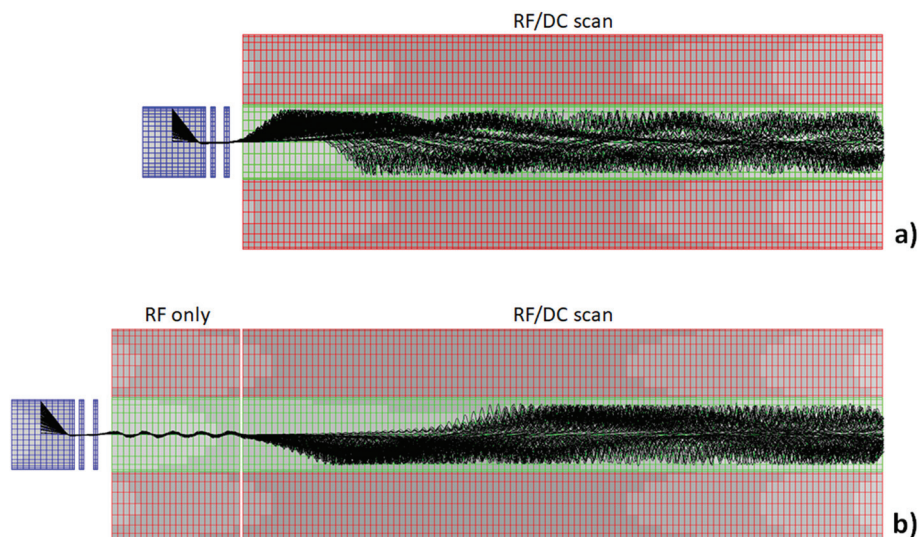


Fig. 1 Simulated ion beam in the CPO3D program showing trajectories for cocaine m/z 304 ions within (a) single filter and (b) dual filter quadrupole analysers. Initial ion energies are at 3 eV.

tories within the main filter are more stable when the pre-filter is used since it gives prolonged ion focus before analysis. Simulation results with this setting showed that two times more ions pass through the main filter when the pre-filter was used.

Experimental

QMS

The dual filter quadrupole analyser was fabricated using CNC machining. The rods were made from stainless steel (grade 304L) and mounted within a ceramics holder made from high purity alumina (Al_2O_3). The holder provides high precision electrode alignment with less than 5 μm tolerance. This is important for QMS operation since imperfect construction could greatly affect its performance.²⁷ Fig. 2 shows the assembly of the dual filter quadrupole. The diameter of the rods is 6.35 mm with r_0 of 2.76 mm. The lengths of the pre-filter and the main filter are 22 and 110 mm, respectively. The gap between the pre-filter and main filter rods is less than 0.5 mm. The analyser was mounted on a custom CF40 vacuum flange and fully shielded together with an electron multiplier detector (Photonis Channeltron® 4769) and an in-house made electron impact (EI) ion source. The EI source is an open-type with a thoria coated filament. It consists of an electron repeller, ion cage and three einzel lenses for ion extraction, focus and deceleration.

ECU

The electronic control unit (ECU) was supplied by Q Technologies Ltd to drive the dual filter quadrupole analyser with sufficient voltage support for m/z 1–500 mass range and above. It requires 24 V to ± 15 V to operate and consumes 24 W of power at maximum. The ECU consists of four main printed circuit boards (PCBs) which include:

(1) power supply board: generates system supplies to all QMS components, controls switching of ion source filaments including degas mode, and supplies DC voltages to ion source lenses and quadrupole rods within ± 180 V range.

(2) RF control board: provides control to the RF drive board and operates independently of the processor board. (3) RF drive board: uses power circuits to drive RF voltage across the QMS rods within ± 1600 V peak-to-peak voltage range and



Fig. 2 Optimized dual filter quadrupole analyser assembly with circular rods manufactured using CNC machining and integrated in the portable MS system. $r_0 = 2.76$ mm, rod diameter 6.35 mm, pre-filter length 22 mm, and main filter length 110 mm.

1.4–1.6 MHz frequency range with auto-tuning. (4) Processor board: contains an electrometer, real time clock and event counter.

Apart from PCBs, the ECU also contains some key control modules such as ion source electron emission (up to 20 A output), multiplier voltage (up to -3 kV supply), analogue electrometer (100 M Ω to 100 G Ω resistor range) and Ethernet. The pre-filter is driven from the ECU without any electronic components located inside the vacuum (*e.g.* resistors and capacitors). The ECU has 3 kV capacitively coupled drive with a DC bias of 0 V to provide RF only voltage to the pre-filter rods. It weighs 1 kg and its dimensions are 14 \times 11 \times 9 cm.

System assembly

The whole QMS system was assembled in an off-the-shelf Peli™ case with external dimensions of 61.6 \times 49.3 \times 22 cm as shown in Fig. 3. The main system parts include a custom-made vacuum chamber with the QMS mounted inside, ECU, vacuum system, pressure gauge, display unit, vacuum valves (electronic and manual) and 24 V DC power supply for powering all electronic components. The vacuum system consists of a Pfeiffer MVP 015-4 DC diaphragm pump with 0.75 m³ h⁻¹ pumping speed and a HiPace 80 turbomolecular pump with 67 L s⁻¹ pumping speed for N₂. The pressure gauge is Pfeiffer

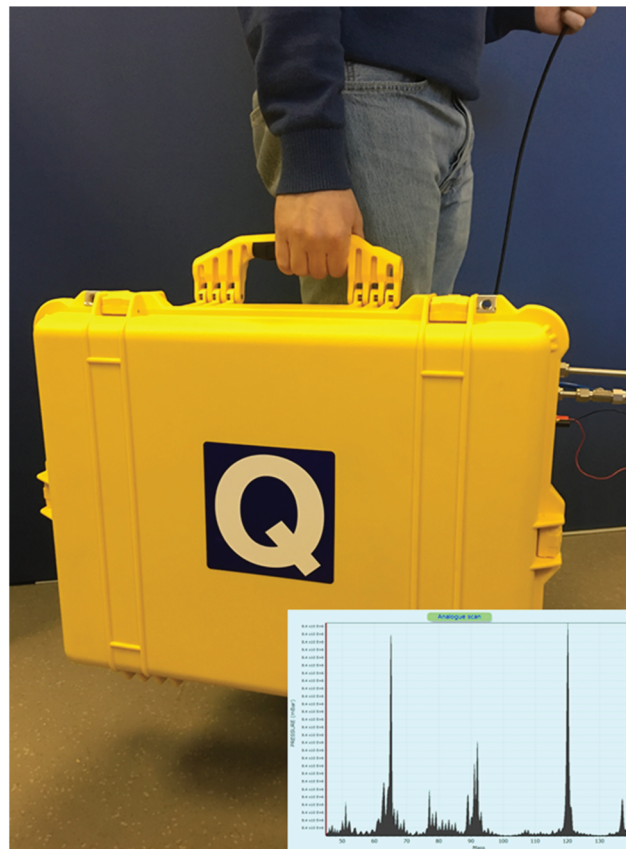


Fig. 3 A man-portable case with an optimized quadrupole mass spectrometer system with a dual filter analyser assembled inside.

PKR 361 cold cathode Pirani with a pressure range down to 10^{-9} Torr.

Sample inlets

The system contains fused silica capillary and membrane inlets that allow near real-time monitoring. The fused silica capillary inlet contains a circulation pump and a heater unit up to 110 °C for sensitivity enhancement. It offers a response time of 500 ms, low ppm detection limit for most gaseous samples and high ppb for some species. The membrane inlet consists of a PDMS sheet of 0.12 mm thickness and 32 mm² area mounted inside Swagelok vacuum fitting union as described by Giannoukos *et al.*²⁸ The thin membranes when heated at 70 °C have a response time of 1 s for trichloroethene and few seconds for other hydrocarbons.²⁹ The limit of detection for VOCs for the dual filter quadrupole system is in a low ppb range, while low ppt can be achieved using cryotrap enrichment.³⁰

Chemicals

Most chemicals used in experiments with the portable MS system were obtained from Sigma Aldrich Co. LLC., UK. These are: PFTBA, acetone ($\geq 99.9\%$), piperidine (99%), cyclohexanone ($\geq 99\%$) and 2-nitrotoluene ($\geq 99\%$). Methyl benzoate (99%) was obtained from Fisher Scientific Ltd, UK. All purchased chemicals were in the liquid phase.

Results and discussion

MS functionality and capability of the assembled portable system were verified for different substances. Samples were injected with a high precision micro-pipette (Brand GmbH, Germany) into a 1.1 L narrow-neck glass flask (Sigma Aldrich Co. LLC., UK) covered with parafilm and left for 3 hours to reach equilibrium at room temperature (25 °C). Gaseous standards of PFTBA, methyl benzoate, piperidine, cyclohexanone and 2-nitrotoluene were prepared at 1 ppm concentration each, while acetone was prepared at 100, 200, 300 and 500 ppb. All the samples were tested using a membrane inlet and ionized with a hot filament EI source at 70 eV. The filament current was 1.9 A with an electron emission current of 1.6 mA. Ion cage and extraction lens were held at 5 V, ion focusing lens at -98 V and deceleration lens at 0 V. The pre-filter and main filter were driven at 1.6 MHz for all mass analysis experiments. Operational pressure in the vacuum chamber was 1×10^{-6} Torr.

The demonstration of MS functionality and m/z 500 mass range was done for PFTBA. Fig. 4a shows the mass spectrum of PFTBA obtained from the dual filter analyser system with mass scanning done from m/z 50 to 550. Fig. 4b shows the centroided mass spectrum of PFTBA from the NIST library. The most visible mass peaks at m/z 69, 100, 131, 219, 264, 414 and 502 from the dual filter quadrupole show good correlation in intensities with spectral peaks from the NIST library. Unit resolution was attainable up to m/z 400, while m/z 414 and 502

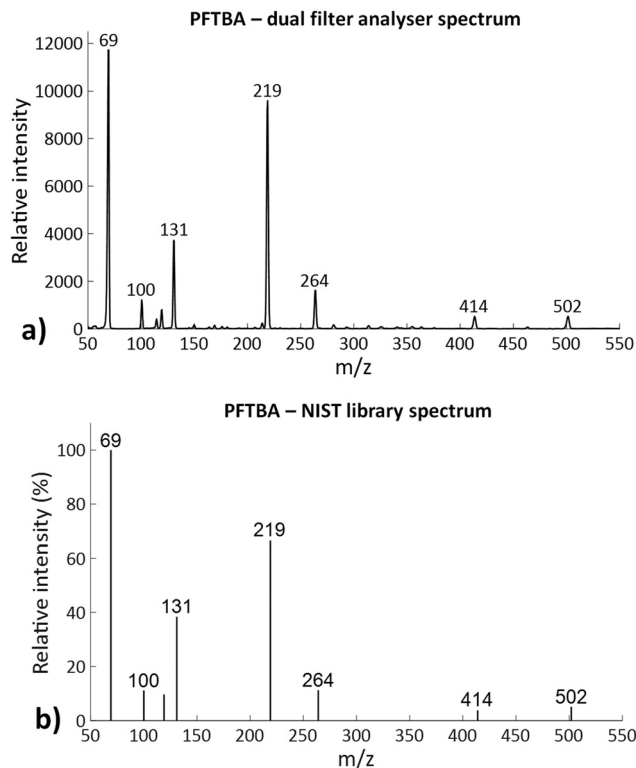


Fig. 4 (a) Profile mass spectrum for 1 ppm of PFTBA from m/z 50 to 550 obtained from the portable quadrupole mass spectrometer with a dual filter mass spectrum of PFTBA from the NIST library.

peaks were 1.2 and 1.4 Da wide, respectively. This can be further improved by increasing the capacity of the ECU to drive the instrument at higher RF frequencies. Another MS functionality test is done for the m/z 58 fragment of acetone by performing calibration to assess linearity. Fig. 5 shows the calibration curve with good linearity for acetone m/z 58 from 100 to 500 ppb concentrations. The calibration system that was used is a dynamic vapor generator that can create gas pulses of

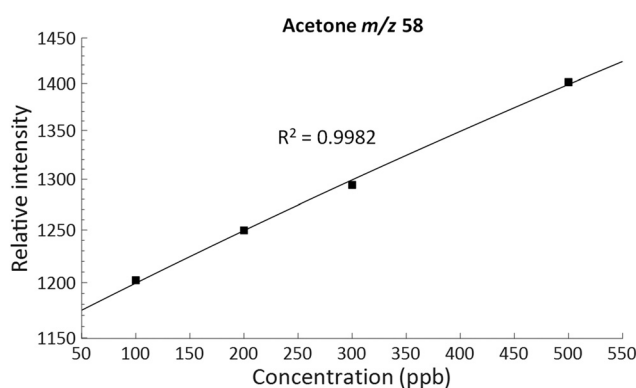


Fig. 5 The calibration curve for the acetone mass fragment m/z 58 obtained from the portable quadrupole mass spectrometer with a dual filter analyser.

single or multi-component mixtures at standard concentrations. The method is described by Giannoukos *et al.*³¹ The limit of detection (LOD) was estimated for the m/z 58 acetone fragment from the 100 ppb mass spectrum by observing the S/N ratio. It has been found that the LOD of 3.3 ppb can be achieved without any heating of the membrane or analyte enrichment. As a summary, a performance comparison between the previous triple filter⁵ and the new dual filter quadrupole (analyser + ECU) is given in Table 1. As can be seen, the triple filter gives higher sensitivity, while the dual filter analyser has lower weight, size, power consumption, faster scan speed and higher mass range.

Fig. 6a–d show mass spectra that demonstrate MS capability for the identification of simulants of threat compounds in security and forensic applications. Due to unavailability and licensing requirements for testing real drugs and explosives,

simulants were used for the tests. The spectra are given for methyl benzoate (cocaine simulant), piperidine (phencyclidine simulant), cyclohexanone (C4 simulant) and 2-nitrotoluene (TNT simulant). As can be seen, all characteristic mass fragments are visible for all the four substances and show good agreement with the corresponding fragments from the NIST library. The mass scanning rate was set to fast mode at 250 Da s^{-1} . This is important for the security industry for fast in-field screening of drugs, explosives and chemical warfare agents as well as for food and flavour industries for fast screening of VOCs and other organic compounds during process control monitoring.

Further optimization of the existing dual filter quadrupole analyser system can be achieved by improving the following parameters:

(a) size – the system can be fully integrated in a custom-made case, which could reduce the overall size by a further 30% from the existing off-the-shelf Peli™ case.

(b) Weight and robustness – using non-evaporable getters (NEG) and sputter ion pumps, the vacuum system weight can be reduced by a further 4 kg. Getter vacuum systems are also more robust than systems with turbomolecular pumps where there is a risk of damage to blades and bearings if the system is moved or shaken during operation. An NEG vacuum system is already being successfully used in a commercial portable HAPSITE® ER GC/MS system from Inficon.²

(c) Power consumption – replacing the hot filament on the EI source with a low-power glow discharge cell³² will reduce the ECU power consumption by 10 W.

Table 1 Performance comparison between the triple and the dual filter analyser systems

Performance parameters	Triple filter (analyser + ECU)	Dual filter (analyser + ECU)
Volume	4568 cm ³	1548.5 cm ³
Weight	5.1 kg	1.8 kg
Power	55 W	24 W
Mass range	m/z 1–200	m/z 1–500
Sensitivity	1×10^{-4} A mbar ⁻¹	3×10^{-4} A mbar ⁻¹
Resolution	Unit (m/z 1–200)	Unit (m/z 1–400)
Scan rate	50 Da s^{-1}	250 Da s^{-1}

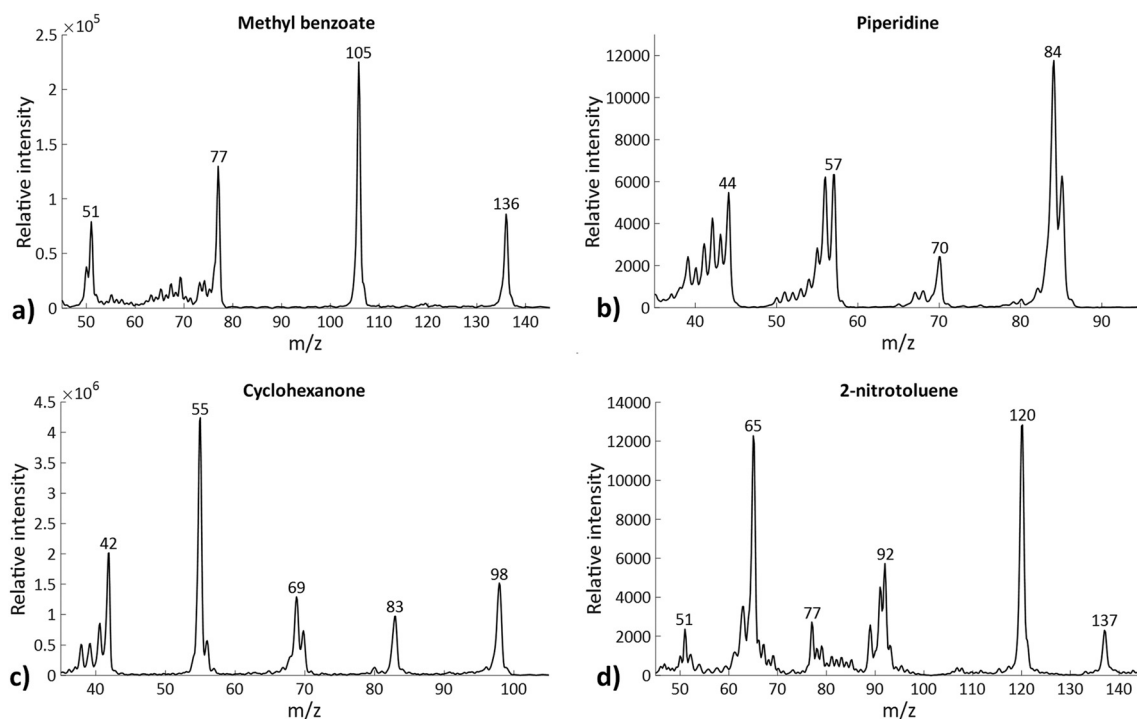


Fig. 6 Target mass spectra from the portable quadrupole mass spectrometer with a dual filter analyser for 1 ppm of (a) methyl benzoate, (b) piperidine, (c) cyclohexanone and (d) 2-nitrotoluene.

(d) Cost – using a digital light processing (DLP) technique for 3D printing of mass analysers³³ and the Metalise™ polymer coating process,³⁴ the cost of the mass analyser can be reduced by a factor of 40 compared to high precision CNC manufacturing. The DLP technique can be particularly useful for dual and triple filter analysers since gaps between individual filters would be blank polymer regions that can be precisely defined with the Metalise™ coating method.

(e) Resolution – by increasing the frequency range on the RF drive board to 2 MHz and above and applying an axial magnetic field,³⁵ unit resolution can be achieved for masses above m/z 400 up to m/z 550.

(f) Scan speed – by increasing the number of bits on an analogue-to-digital converter (ADC), using a high-speed amplifier and programming the gain on the electrometer, a mass scan speed can be increased to at least 1000 Da s⁻¹.

Conclusions

A portable MS system based on a pre-filtered quadrupole mass filter has been optimized by enhancement of the mass analyser using numerical modelling and through the redesign of control electronics. The system was implemented and tested for MS functionality and capability. Clear advantages of using a dual filter quadrupole analyser for performance and integration of the instrument were shown. A mass range of m/z 500 has been demonstrated using the PFTBA calibrant with unit resolution achievable up to m/z 400. Calibration of the instrument has been assessed for acetone mass fragment m/z 58 giving a good linearity and low ppb LOD without membrane heating or analyte enrichment. MS capability for security applications is shown for the identification of simulants of cocaine, phencyclidine, C4 and TNT. Improvements that are made to the MS ECU provide lower size, weight and cost of the instrument, higher mass range, better stability of mass peaks, and faster scan speed compared to our previous triple filter electrode set and electronics. In practice, dual and triple filters are much easier to tune and calibrate than single filter analysers particularly at high mass ranges. They also offer better stability of mass peaks.

Conflicts of interest

There are no conflicts to declare.

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