True Smart and Green City?
8th Conference of the
International Forum on Urbanism

Conference Proceedings Paper

Low-cost Multispecies Air Quality Sensor

Chunting Michelle Wang*, Benjamin David Esse, Nicola Carslaw and Alastair Lewis

University of York / Heslington, York, YO10 5DD, United Kingdom

* Author to whom correspondence should be addressed; E-Mail: michelle.wang@york.ac.uk;
Tel.: +44-1904-32-4754

Abstract: Field measurements of volatile organic compounds (VOCs) are important in a range of disciplines including air pollution science, medical diagnostics and security screening. There is an enduring need for a portable device that provides reliable compound-specific measurements, at mixing ratios in the part per billion and part per trillion range. Outdoor VOCs sources are primarily from traffic, and the information provided from such measurements could inform the public of the sources of emission and potentially affect their decisions and behaviour. Similarly, measurements of VOCs in indoor environments could increase awareness of emissions from building materials or the use of various consumer products and provide information on indoor ventilation. This work describes the development of a lab-on-a-chip (LOC) device for VOC measurements, a collaboration of multiple disciplines, involving research and development from a number of different fields in sciences and engineering. The objective is to develop a multispecies sensor for measuring VOCs in gas phase samples, through the deployment of thermal desorption methods in combination with a micro-fabricated gas chromatography – photoionization detection (GC-PID) device. Most of the work has been done in the evaluation of the PID detection means, which has shown to offer substantial potential for the development of a field portable air quality sensor. Initial tests on a Peltier device to control the temperature of a GC column have also been carried out. The use of such device removes the dependence on the bulky GC oven which has high power consumption, and allows the initial temperature of the column to be as low as 10°C, potentially enabling the analysis of VOCs without the need for cryogenic cooling. The final developed system will be validated using controlled experiments and against reference standards and measurement techniques, and applied in number of real-world monitoring investigations, including indoor atmospheres and air pollution studies.

---

1. Introduction

Volatile organic compounds (VOCs) are organic compounds with boiling points of less than or equal to 250 °C measured at a standard atmospheric pressure of 101.3 kPa [1]. These compounds can have both direct and indirect impacts on human health. VOCs are emitted from natural and anthropogenic (man-made) sources. Some natural sources of VOCs include vegetation, forest fires, and animals and these dominate the global budget of emissions. Although on a global scale VOC emissions are largely from natural sources, air quality problems in populated and industrialized areas are mainly a result of anthropogenic sources [2]. Some examples of anthropogenic VOCs include tobacco smoke, biomass burning from human activities i.e. to exploit land for agricultural activities or to rid of agricultural waste, the production, storage and use of fossil fuels, and the production and use of household chemicals such as cleaning agents, coatings and paints.

VOCs contribute to the production of ozone, a constituent of photochemical smog that causes adverse health problems and also, when degraded in air, to the formation of organic aerosols. Ozone is formed in the atmosphere via a photochemical process whereby VOCs react with hydroxyl radicals in the presence of sunlight forming short-lived peroxy radical species (RO_2). RO_2 can then react further rapidly converting NO to NO_2, perturbing the natural photostationary state. Photolysis of the NO_2 formed then induces additional ozone formation. Thus ground level ozone is as a secondary pollutant and a harmful photochemical oxidant which inhabits that troposphere and it is the main component of photochemical smog [3].

Ozone can be produced from hydrocarbons such as ethane, propane or from oxygenated compounds like formaldehyde and acetaldehyde. In indoor microenvironments and urban air, formaldehyde mixing ratios can vary from 1 to 100 ppb, while in remote clean oceanic areas formaldehyde is generally in the range 0.1 – 1.0 ppb [4]. Ethane and propane originate substantially from anthropogenic pollution sources and have relatively long lifetimes against photochemical destruction. Background tropospheric mixing ratios of ethane and propane are 0.3 – 2.5 ppbv and 0.01 – 1.0 ppbv respectively. In addition to the production of ozone, acetaldehyde is also a precursor to peroxyacetyl nitrate (PAN), a secondary pollutant found in photochemical smog. It is a lachrymator and causes eye irritation. It has been reported that mixing ratios of PAN in clean air are typically 2 – 100 pptv, whereas that of polluted air can be as high as 35 ppbv [5]. The rapid and sensitive measurements of VOCs in ambient and indoor environments are therefore of great utility to environmental toxicology and atmospheric chemistry.

For the field measurement of VOCs, there is a need for a portable device that provides reliable information on a range of different VOCs, since the impact on downstream effects such as ozone and aerosol formation and health toxicology are structure-specific. Bulk measurements (e.g. total carbon mass per unit volume) of VOCs do not provide sufficient detail on the precise VOC composition to be useful in most environmental and health applications. Any portable device should be robust, low-cost and have low-power demands, since many applications are likely to be off-grid. The development of a

Lab on a Chip (LOC) device requires a collaboration of multiple disciplines, involving research and development from different fields in sciences and engineering. This is necessary for the assembling and integration of the different components involved in a LOC to create a complete functional system.

1.1. Current measurement methods

There are numerous techniques and instruments used for the detection and measurement of VOCs, mostly based around gas chromatography and mass spectrometry. Some examples are summarised in Table 1, together with the respective trade-offs of each method for field analysis. In very general terms, the development of a VOC instrument starts with laboratory standard devices, such as GC and MS, with modifications and additions then made to accommodate a trace level gaseous sample matrix. The key front-end adaptation to all chromatography-based systems is the inclusion of a thermal pre-concentration step, which strips VOCs from litre volumes of air and introduces them to the GC column with a concentration factor of up to 1000. A consequence is that most instruments in the literature for VOC detection are essentially hybrid lab instruments, not devices intrinsically designed with size, power or weight as constraining factors.

Table 1. Current measurement methods for VOCs.

Current measurement methods and its characteristics	Pros	Cons
Thermal desorption - Gas Chromatography with Flame Ionisation Detectors (FID) o Most commonly used in laboratories for VOCs detection.	• Very sensitive and linear in response, and compound calibration can be based in part on a per carbon atom response function. • Good in serviced laboratories or for fixed site observatories. • Stable and reliable when operated autonomously.	• Not selective: The FID will respond to all organic compounds (except HCHO), so identification is based on retention times. Issues due to co-elutions; unable to identify unknown compounds. • Not typically portable due to of its size, mass. Requirement for hydrogen gas is a major constraint on portability.
Bulk Photo-Ionisation Detection (PID) o Utilises an ultraviolet (UV) light source to break down VOCs in the air into positive and negative ions. o Detection of the ions results in a current flow with a magnitude proportional to the concentration of VOCs present.	• Portable detector suitable for field applications because of its small size and no need for supply gases. • The trade-off between using the PID or the FID in detection of VOCs has been discussed [6]; the FID gave well-resolved peaks whereas peak tailing was an issue when the PID was used. However, the low-power demands of the PID and its portability were advantages that the FID would not be able to provide.	• Operated in isolation the PID is not selective: will respond to all organic compounds. • Each VOC has a different ionisation potential, which requires calibration.
Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) o Air is pumped through a drift tube reactor, and a fraction of the VOCs is ionized in PTR with hydronium ions [7]. o Soft ionization method; does not lead to fragmentation of the product ions.	• Allows numerous VOCs of atmospheric interest to be monitored with a high sensitivity (10 – 100 pptv) and rapid response time (1 – 10 sec). • Does not require any sample treatment such as drying or pre-concentration, and is thus well suited for oxygenated VOCs, which cannot be quantified from canister samples.	• Only determines the mass of product ions, which is not a unique indicator of the VOC identity. • Isomers cannot be distinguished, and the interpretation of mass spectra is further complicated by the formation of cluster ions and the fragmentation of product ions.

|		
o Reagent and product ions are measured by a quadrupole mass spectrometer; signal is proportional to the VOC mixing ratio.	• Provides a fast-response measurement of several key atmospheric VOCs, and complements the highly sensitive and chemically detailed snapshots obtained by GC techniques.	• Not easily portable for field measurements. • 200K – 400K USD hardware costs.
Thermal Desorption GC-MS o Sample collection using either packed adsorbent tubes of canisters. o Samples preconcentrated by thermal desorption. o Typically uses quadrupole MS detection, but also increasingly TOF is applied.	• Sensitive and accurate means of retrospective analysis of VOCs adsorbed in soil samples [8, 9], other solids [10, 11], liquids [12, 13] and gases [14 – 16]. • Sensitive and flexible, compound identifications available from mass spectra. • Capable of identifying unknown compounds in an air sample via MS libraries. • More sensitive from similar FID systems if operated in selected ion modes.	• Size and mass of the bench-top instrumentation render this method unsuitable for field analysis. • More challenging to calibrate and less stable when operated continuously. • Water can be a significant interference. • Higher cost, more complex and typically requires thermostated lab environment for optimal operation. • Several kilowatt power requirement.
Colorimetric ("Stain") tubes i.e. Draeger tubes o Tube readings in the form of colour changes and intensities.	• Inexpensive method of measuring classes of toxic gases and vapours.	• Tubes have to be continuously observed to ensure that there is no sudden complete discoloration. • Ultra-violet radiation may result in a change in the discoloration [17]. • Readings in the form of colour changes and intensities are subjected to human interpretation. • Not VOC specific.
Metal Oxide Semiconductor (MOS) sensors	• Compact and low cost sensors with high sensitivity and short response time.	• Also respond to inorganic gases [18]: problem when trying to measure trace or low concentrations of VOCs in the presence of gases such as NO, NO_2 or CO which are found in the surrounding air. • Not favourable in the field measurement of VOCs because of the lack of selectivity and control of the sensor response.

Given the limitations of current technologies for field analysis of VOCs, this work aims to address these issues and develop a portable sensor for the detection and analysis of VOCs, combining elements of thermal desorption, gas chromatography and PID, but in a device built bottom up, rather than from standard lab equipment.

2. Preliminary design of the GC – LOC

The simple design for a GC – LOC column arrangement is as shown in Figure 1. The device is etched in a planar form which facilitates heating of the GC – LOC with a Peltier thermoelectric device [19], rather than the much higher power of a standard turbulent fan oven. A secondary advantage of a Peltier controlled device is an ability to operate below ambient temperatures, something not achievable in a fan

oven without cryogenic cooling. The chip design is formatted to the same shape as existing Peltier devices commonly available at low cost. The design here uses two wafers, with etched channels on one side, bonded together to form a single chip. A number of different materials can be potentially used including glass, acrylic and PDMS. Prototyping using PDMS provides a quick and cost-efficient way of testing the feasibility of the GC – LOC design and is the initial route taken. The 45 x 45 mm chip will have an etch depth of a 150 µm semi-circle on one side. Etches will be spaced 100 µm apart and the capillary has a total length of about 4 m.

Figure 1. Preliminary design of GC – LOC on square-shaped chip.
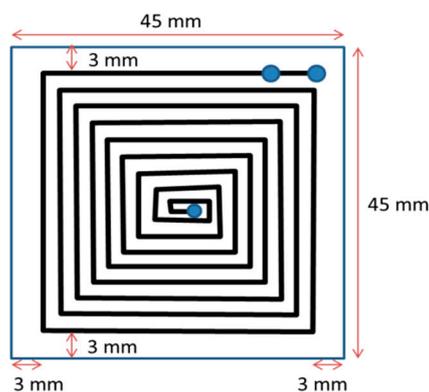

3. Heating of the column

One important factor for an effective GC separation is the uniform heating of the GC column and the ability to increase this temperature linearly to elute higher boiling compounds sequentially. The heating of GC columns by conventional means is primarily based on the turbulent fan oven, which is an excellent means to achieve even heating of the column. However the size of such ovens renders this a difficult technique to use in remote locations for field analysis in environmental research, and the power consumption is of the order 1.5 kW for a typical 10ºC min^{-1} heating rate. The fabrication of a GC – LOC described above allows a structural geometry that is much easier to heat using planar devices, such as a Peltier device which could be placed on the surface of the fabricated chip. In addition, the Peltier device allows the starting temperature to be below room temperature, allowing the improved separation of volatile VOCs without the need for cryogenic cooling, as used in standard GC ovens. To mimic the temperature control in existing GC ovens, it is essential that the temperature gradients and set points of the Peltier device can be manipulated to allow manual control of the device.

3.1. Temperature control of the peltier device

A program is designed using LABVIEW to control the temperature (set points and gradients) of a Peltier device. We have estimated that a functional working range of temperature should be from 10°C to 100°C, which broadly mimics in terms of peak capacities a standard separation of VOCs performed over 40-150°C. The Peltier device is used as both a heater and a cooler, with a switch over between cooling and heating achieved via a polarity reversal in the d.c. supply. The control software essentially mimics a standard GC bringing the temperature of the device to an initial value (10°C), holding it there, and then ramping the temperature at a given rate (10°C min^{-1}) until the final temperature is reached

(100°C) before cooling back down to 30°C. This is achieved through Proportional Integral Derivative control. Figure 2 shows the result of the one temperature cycle test. The program produces a desired set point temperature profile (blue graph) and adjusts the power supplied to the Peltier device to bring the temperature of the device (red graph) to this value. The Peltier device is fitted with a heat sink and fan as it requires cooling.

Figure 2. One temperature cycle of the Peltier device.
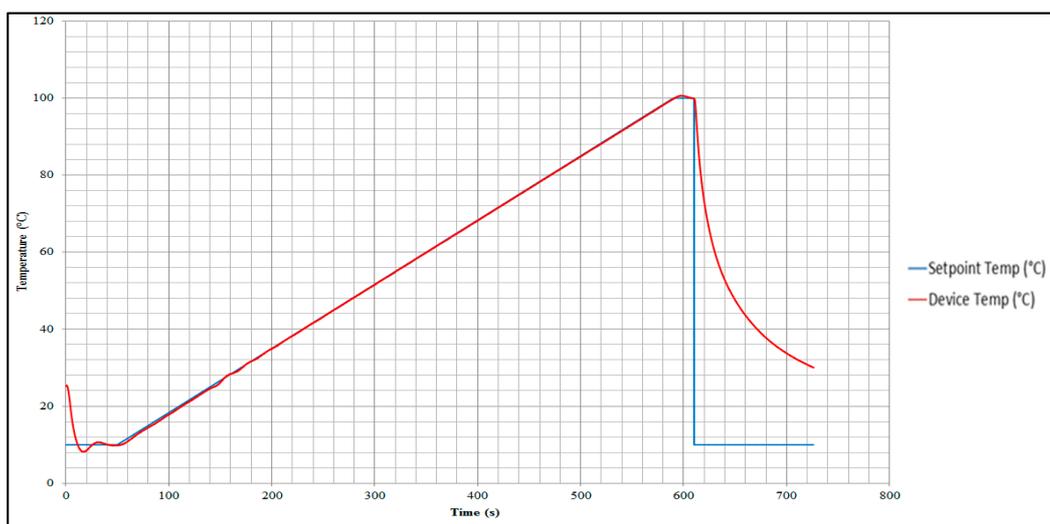
To test the performance of the Peltier device for continuous sequential runs, five such temperature cycles were set to run and the resulting temperature profiles are shown in the Figure 3. It was noted that the set point and device temperatures were almost identical for the majority of each ramp and that there was no thermal wind-up in the system – that is the starting 10 °C could be achieved reproducibly each time.

Figure 3. Five cycles of the Peltier device used for GC chip temperature control.
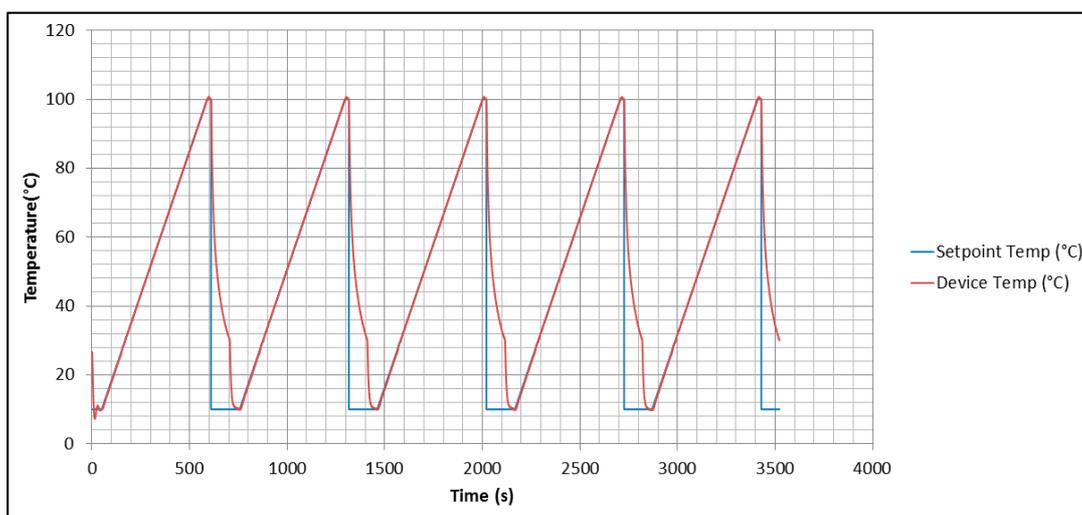
Features of note are the slight overshoot at the initial and final temperatures, and the slight wobble through room temperature region as the voltage polarities are reversed. These can be optimised for a set

of conditions, however in significantly different ambient conditions the Proportional Integral Derivative gains may need to be re-tuned if these differences to the set point become too large. As it is, the discrepancies are never more than about 1°C (except the initial overshoot, which is often around 2°C).

The total power used in this set up is about 40W, which relates to about 24kJ per cycle of 10 minutes. This is a considerably lower power consumption compared to a laboratory gas chromatography oven which uses on average 1kW over 30 minutes – that is, 1.8MJ per cycle.

4. Separation performance in a laboratory GC with PID

A key barrier to portable GC systems has been a lack of a suitable detector for the field. The most simple lab detector is FID, but that is orientation specific and requires a hydrogen supply. Here we have focussed attention on a low-cost (~200 USD), commercially available PID (PID-AH, Alphasense) as the detection method for VOCs measurement following GC. The PID used here is designed primarily for a solvent alarm, not a GC detector, so we have undertaken experiments to understand its capabilities if modified for this purpose. The ultraviolet lamp of the PID provided 10.6 eV for compound ionisation and the device was used as supplied, with the exception of the deliberate removal of a filter inlet placed over the detection grids. High purity helium (BIP Air Products, Keumiee, Belgium) was used as the carrier gas for GC. Separation was performed on a BPX5 column (50 m x 0.32 mm x 1.0μm, length x internal diameter x film thickness) with two split outlets, one going to a time-of-flight/mass spectrometer (TOF/MS) and the other going directly into the PID. This allowed for the comparison of the detector results of the PID with the TOF/MS. The oven was programmed to run at 40°C for 3 min, then ramp at 15°C min^{-1} to 125°C, then at 20°C min^{-1} to 250°C and held for 5 minutes. Figure 4 shows how a capillary column is connected to the PID and Figure 5 shows the close-up set-up of the PID to the GC.

Figure 4. Capillary column connected to a PID.


Figure 5. GC-PID set-up.
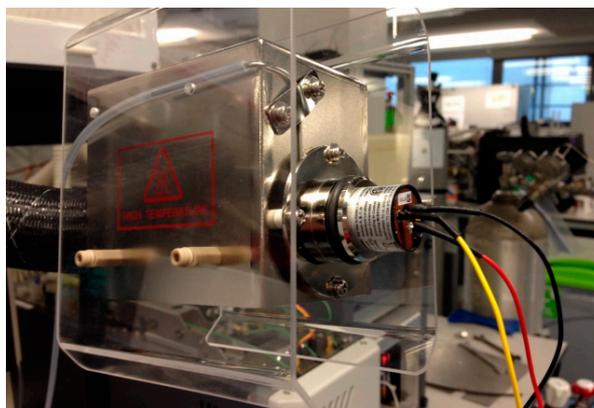
A standard mixture including 4 nmol/mol (molar ppb) of benzene, 2,2,4-trimethylpentane, heptane, toluene, octane, ethylbenzene, m-xylene, p-xylene, o-xylene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene and 1,2,3-trimethylbenzene was introduced into a thermal desorption unit (Markes Unity Series 2 Thermal Desorption Unit) prior to separation on the GC column. 1000ml of gas was sampled at 100 ml/min. The trap was purged for 1 minute at 100 ml/min and heated from -30ºC to 300ºC at the maximum heating rate of the system and held for 3 minutes.

4.1. Data capture with 12-bit ADC LabJack

The results for detection with TOF/MS and PID are shown in Figures 6 and 7 respectively. The results obtained with the PID shows good separation between the components with symmetrical peak shape comparable to that obtained with TOF/MS. The high PID response of the compounds gave a good signal to noise ratio. This PID chromatogram was generated with approximately 6.5 – 10 ng of each compound. Peak skew is less than 1.8 for all peaks (with half of them less than 1.2) which we considered acceptable. The chromatogram indicates around 67000 theoretical plates as measured for toluene. It is worth noting that this PID result was achieved without any direct heating of the PID itself.

Figure 6. Separation of the 4 ppb standard gas mixture and detection by laboratory standard TOF/MS detector.
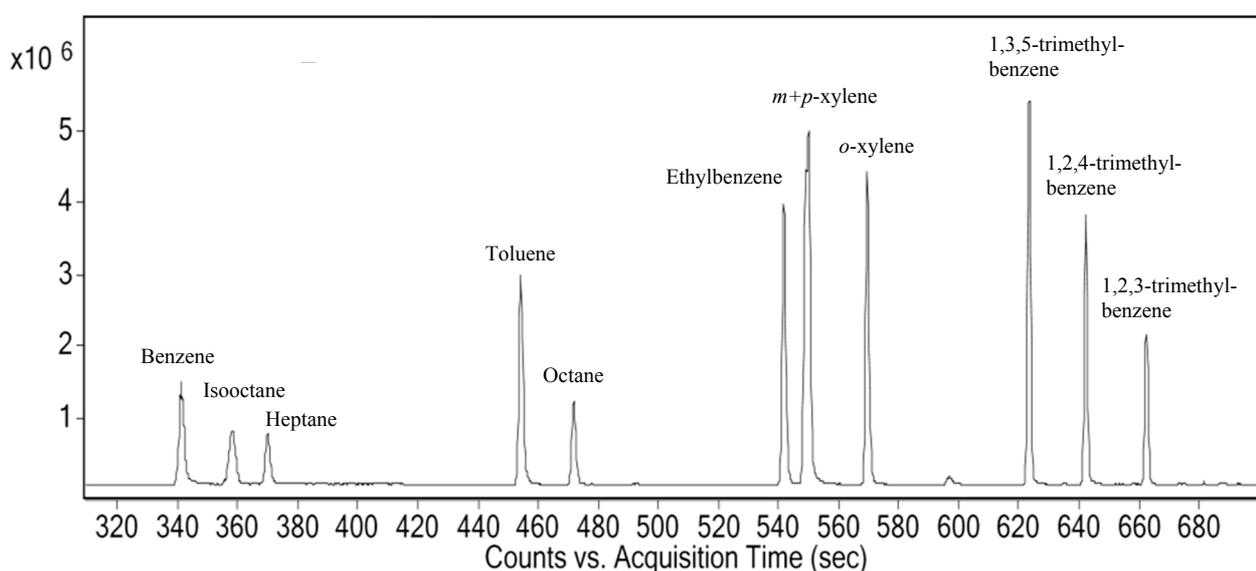
A second gas mixture containing approximately 26 ppb of isoprene and 77 ppb toluene was introduced separately. Parameters of the set up were identical to those used previously, but in this case only 100 ml of gas was sampled at 100 ml/min.

The results for detection with TOF/MS and PID are shown in Figures 8 and 9 respectively. The results obtained with the PID shows symmetrical peak shape comparable to that obtained with TOF/MS. The high relative PID response of the compounds resulted in a good signal to noise at the ppb level. The PID chromatogram was generated with approximately 3.69 ng of isoprene and 14.78 ng of toluene at detector. Peak skew is around 1.0 for both compounds, with 68000 theoretical plates as measured for toluene.

Figure 7. Separation of the 4 ppb standard gas mixture and detection by low-power low-cost PID.
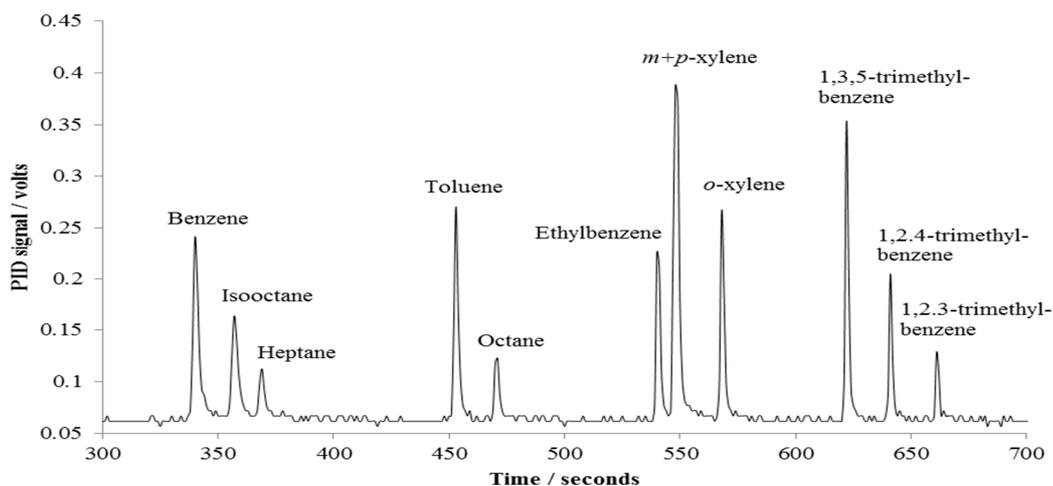

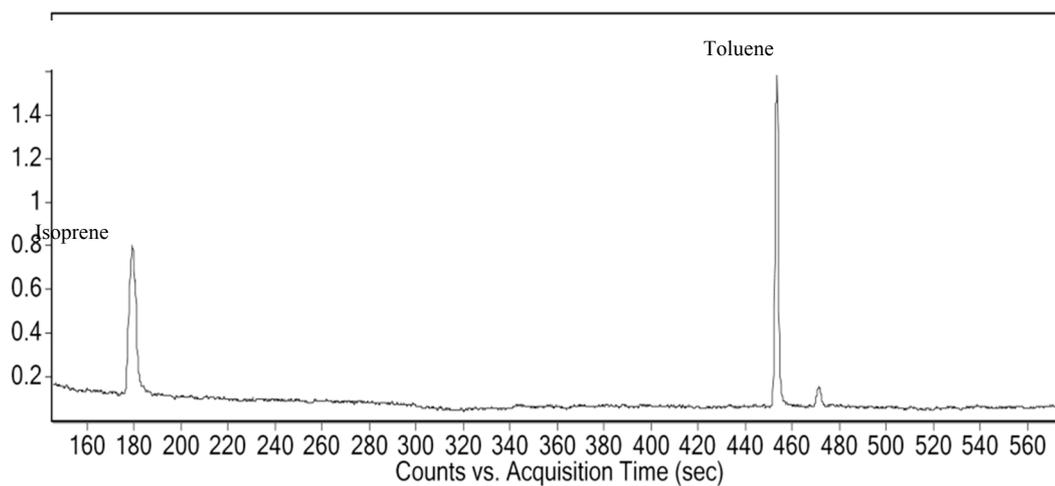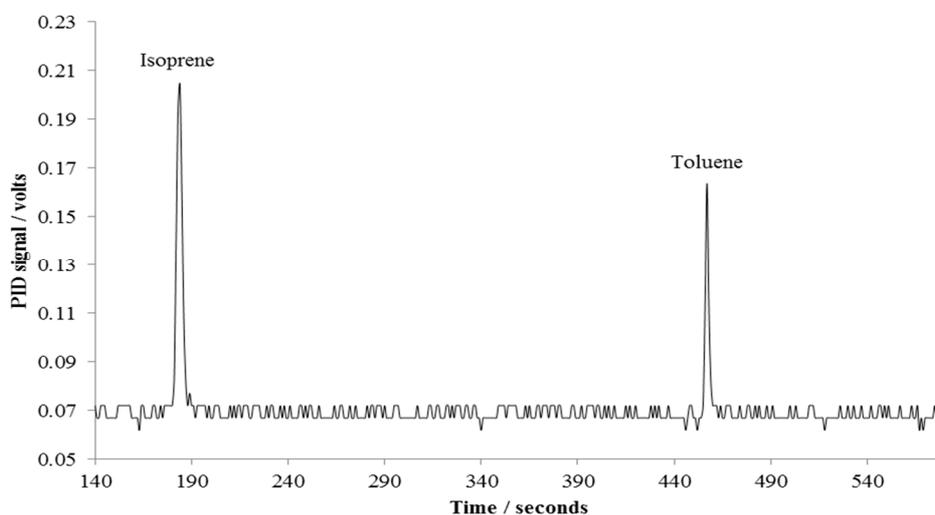**Figure 8.** Separation of the isoprene and toluene gas mixture and detection by TOF/MS.

Figure 9. Separation of the isoprene and toluene gas mixture and detection by low-power low-cost PID.

From the data obtained using the PID, digital noise could be observed at the baseline of the chromatograms (see Figure 9). The current analogue-to-digital converter (A/D) has a resolution of 12 bit. To improve the resolution of the data capture, further tests were carried out using an A/D with a higher resolution of 18 bit.

4.2. Data capture with 18-bit ADC LabJack

Using a higher resolution data capture hardware, the digital noise observed previously at the baseline of the PID chromatograms had been eliminated. 1000 ml of the 4 nmol/mol standard gas mixture was sampled at the same conditions as described previously. The results for detection with TOF/MS and PID are shown in Figures 10 and 11 respectively.

Compounds with retention times before that of benzene are allocated to their respective peaks based on information obtained from their mass spectra and their boiling points. It was observed from the enlarged chromatograms of the early eluting peaks that the resolution of the peaks from the PID were comparable to, if not better than, that of the TOF/MS. This is because the MS may not be as proficient in detection of compounds with smaller masses; the smaller compounds are fragmented to even smaller masses which "disappear" into the background of the chromatograms.

With the elimination of the digital noise at the baseline of the PID chromatograms, the limit of detection (LOD) of the PID detection method could then be evaluated. 200 ml of the 4 nmol/mol standard gas mixture was sampled at the same conditions as described previously. The result for detection with PID is shown in Figure 12.

Figure 10. Separation of the 4 ppb standard gas mixture and detection by laboratory standard TOF/MS detector.
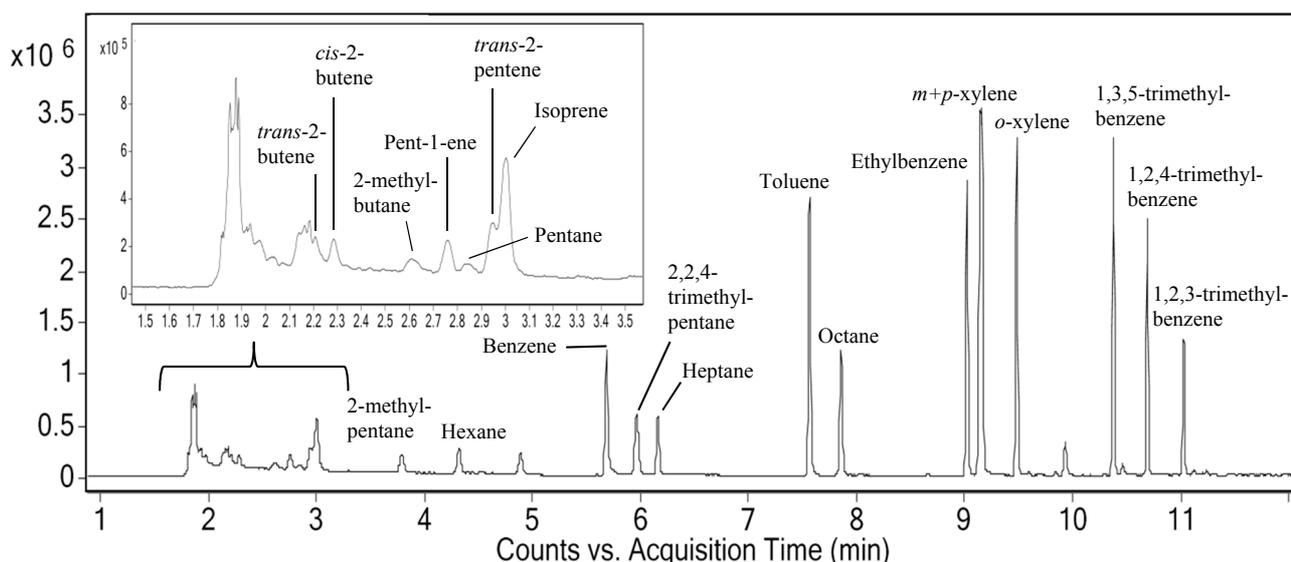
Figure 11. Separation of the 4 ppb standard gas mixture and detection by low-power low-cost PID.
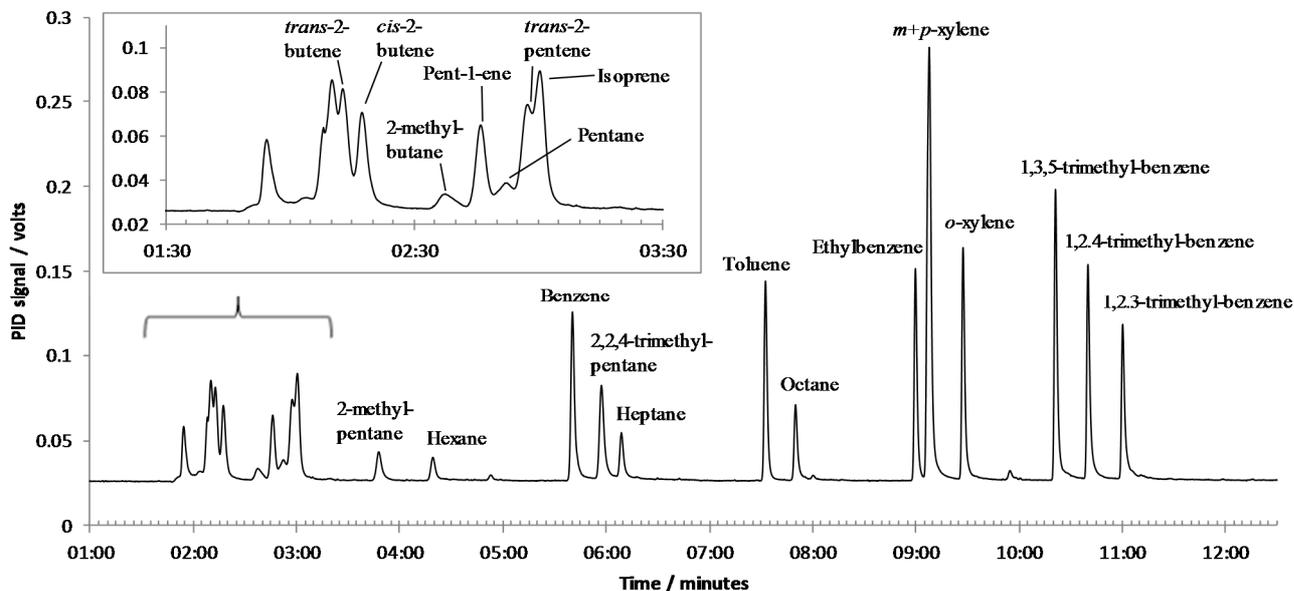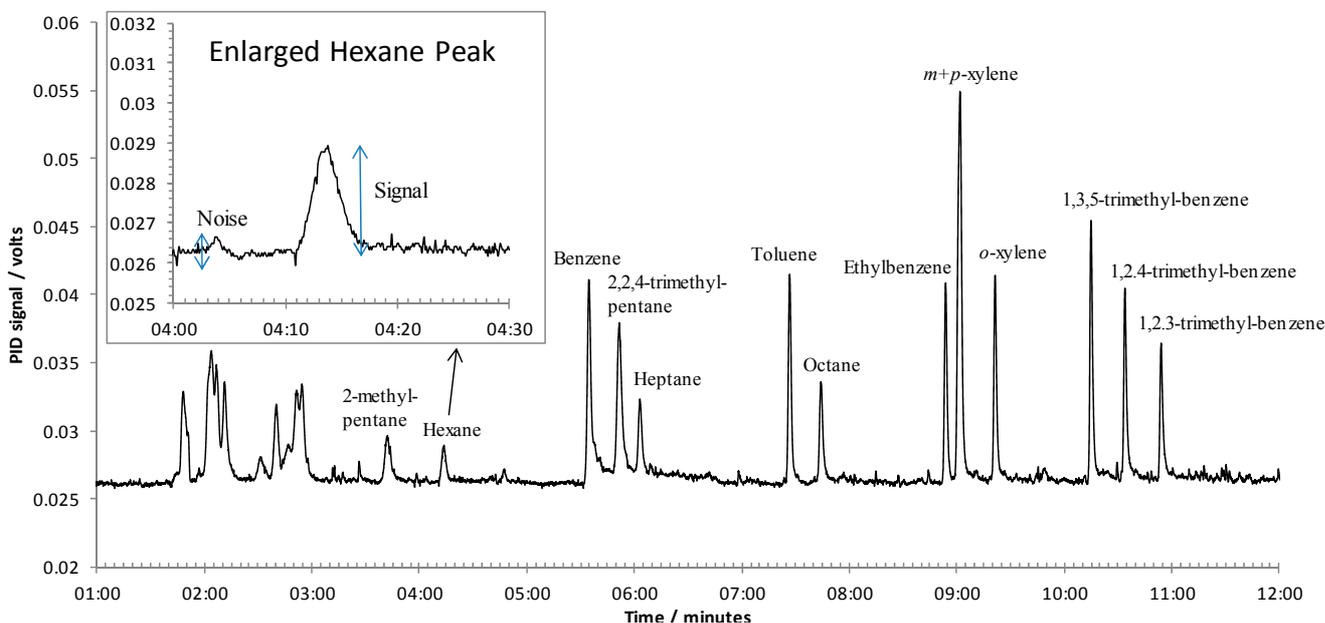

Figure 12. Separation of the 4 ppb standard gas mixture and detection by low-power low-cost PID.

The signal to noise ratio for hexane in the sampling of 200 ml of the 4 nmol/mol standard mixture is about 3:1. Hence the LOD of hexane for this described method of detection is about 1.4 ng. The LOD for the other compounds were calculated based on extrapolation from the LOD of hexane and the values are tabulated as shown in Table 2.

Table 2. LOD of compounds with PID as detection method.

Compounds	LOD (ng)	LOD (ng/s)	LOD (ppb)
2-methylpentane	1.2	0.24	0.34
Hexane	1.4	0.24	0.40
Benzene	0.29	0.19	0.088
2,2,4-trimethylpentane	0.55	0.24	0.12
Heptane	0.97	0.33	0.23
Toluene	0.32	0.38	0.085
Octane	0.87	0.38	0.18
Ethylbenzene	0.40	0.35	0.090
m+p-xylene	0.41	0.51	0.046
o-xylene	0.38	0.35	0.086
1,3,5-trimethylbenzene	0.34	0.33	0.069
1,2,4-trimethylbenzene	0.47	0.33	0.094
1,2,3-trimethylbenzene	0.67	0.33	0.13

Table 2 also includes the LOD (ng/s) based on a sampling amount of 200 ml. In this calculation, the absolute amounts (ng) of the compounds sampled were divided by their peak widths (seconds). The LOD in concentration (ppb) of the listed compounds were also calculated assuming a sampling of 1 litre of air for analysis.

5. Conclusions

We have made important progress in the development of the subcomponents needed for a low power and low cost VOC device. The GC – LOC will take a squarish spiral design to fit standard off-the-shelf Peltier devices that are available commercially. PDMS is considered a good material of choice because of its low manufacturing cost and ease of fabrication, although considerable testing work remains to be completed.

The use of a Peltier device to control the temperature of a GC column removes the dependence on the bulky and power hungry GC oven. We achieve precise control of the temperature set points and gradients of a Peltier based system through Proportional Integral Derivative control. A Peltier device with switchable polarities allows the initial temperature of the column to be as low as 10ºC, offering substantial advantages of the analysis of VOCs without the need for cryogenic cooling in standard GC ovens.

PID was chosen as the detector in this work as it offers substantial potential for the development of a field portable air quality sensor. When paired with a commercial GC system, the peaks produced by the PID were comparable to those produced by the TOF/MS, with acceptable peak skews and theoretical plates of >65000 for toluene. Peak tailing was observed to be minimal. These experiments highlighted the need for relatively high resolution data capture in order to fully exploit the inherent sensitivity of the PID. With the 18-bit data capture hardware, the digital noise observed previously at the baseline of the

PID chromatograms had been eliminated. The LOD for the PID detection method was evaluated to be about 0.3 – 1.4 ng for the various compounds present in the standard mixture.

The ability to control the temperature of the chip with a low power function, and good evidence for the PID performance in producing peaks comparable to that of a TOF/MS, allows us to proceed to GC column testing and integration to produce a complete functional system.

Acknowledgments

Conflict of Interest

The authors declare no conflict of interest.

References and Notes

1. Directive 2004/42/CE of the European Parliament and of the Council of 21 April 2004 on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain paints and varnishes and vehicle refinishing products. European Union Publications Office: EUR-Lex.
2. Environment Canada - Pollution and Waste - Volatile Organic Compounds - Background. https://www.ec.gc.ca/cov-voc/default.asp?lang=En&n=59828567-1 (accessed 10/04/2014).
3. Palli, D.; Saieva, C.; Grechi, D.; Masala, G.; Zanna, I.; Barbaro, A.; Decarli, A.; Munnia, A.; Peluso, M., DNA bulky adducts in a Mediterranean population correlate with environmental ozone concentration, an indicator of photochemical smog. *International Journal of Cancer* **2004,** *109* (1), 17-23.
4. Pang, X.; Lewis, A. C., A microfluidic lab-on-chip derivatisation technique for the measurement of gas phase formaldehyde. *Analytical Methods* **2012,** *4* (7), 2013.
5. Jacobson, M. Z., *Atmospheric Pollution: History, Science and Regulation*. Cambridge University Press: Cambridge, United Kingdom, 2002.
6. Edwards, S. J.; Lewis, A. C.; Andrews, S. J.; Lidster, R. T.; Hamilton, J. F.; Rhodes, C. N., A compact comprehensive two-dimensional gas chromatography (GC×GC) approach for the analysis of biogenic VOCs. *Analytical Methods* **2013,** *5* (1), 141.
7. de Gouw, J.; Warneke, C., Measurements of volatile organic compounds in the earth's atmosphere using proton-transfer-reaction mass spectrometry. *Mass spectrometry reviews* **2007,** *26* (2), 223-57.
8. Black, R. M.; Clarke, R. J.; Cooper, D. B.; Read, R. W.; Utley, D., Application of headspace analysis, solvent extraction, thermal desorption and gas chromatography—mass spectrometry to the analysis of chemical warfare samples containing sulphur mustard and related compounds. *Journal of Chromatography A* **1993,** *637* (1), 71-80.

9.   Robbat, A.; Liu, T. Y.; Abraham, B. M., On-site detection of polycyclic aromatic hydrocarbons in contaminated soils by thermal desorption gas chromatography/mass spectrometry. *Analytical Chemistry* **1992,** *64* (13), 1477-1483.

10.   Ochiai, N.; Sasamoto, K.; Kanda, H.; Yamagami, T.; David, F.; Tienpont, B.; Sandra, P., Optimization of a multi-residue screening method for the determination of 85 pesticides in selected food matrices by stir bar sorptive extraction and thermal desorption GC-MS. *Journal of Separation Science* **2005,** *28* (9-10), 1083-1092.

11.   Sandra, P.; Tienpont, B.; David, F., Multi-residue screening of pesticides in vegetables, fruits and baby food by stir bar sorptive extraction–thermal desorption–capillary gas chromatography–mass spectrometry. *Journal of Chromatography A* **2003,** *1000* (1–2), 299-309.

12.   Ochiai, N.; Sasamoto, K.; Takino, M.; Yamashita, S.; Daishima, S.; Heiden, A.; Hoffman, A., Determination of trace amounts of off-flavor compounds in drinking water by stir bar sorptive extraction and thermal desorption GC-MS. *The Analyst* **2001,** *126* (10), 1652-1657.

13.   Ochiai, N.; Sasamoto, K.; Takino, M.; Yamashita, S.; Daishima, S.; Heiden, A.; Hoffmann, A., Simultaneous determination of preservatives in beverages, vinegar, aqueous sauces, and quasi-drug drinks by stir-bar sorptive extraction (SBSE) and thermal desorption GC–MS. *Analytical and bioanalytical chemistry* **2002,** *373* (1-2), 56-63.

14.   Wu, C.-H.; Feng, C.-T.; Lo, Y.-S.; Lin, T.-Y.; Lo, J.-G., Determination of volatile organic compounds in workplace air by multisorbent adsorption/thermal desorption-GC/MS. *Chemosphere* **2004,** *56* (1), 71-80.

15.   Waterman, D.; Horsfield, B.; Leistner, F.; Hall, K.; Smith, S., Quantification of Polycyclic Aromatic Hydrocarbons in the NIST Standard Reference Material (SRM1649A) Urban Dust Using Thermal Desorption GC/MS. *Analytical Chemistry* **2000,** *72* (15), 3563-3567.

16.   Zhu, J.; Aikawa, B., Determination of aniline and related mono-aromatic amines in indoor air in selected Canadian residences by a modified thermal desorption GC/MS method. *Environment International* **2004,** *30* (2), 135-143.

17.   Draeger, Draeger-Tubes & CMS Handbook: Handbook for short term measurements in soil, water and air investigations as well as technical gas analysis. 16th Edition ed.; Draeger Safety AG & Co KGaA: Luebeck, 2011.

18.   Fine, G. F.; Cavanagh, L. M.; Afonja, A.; Binions, R., Metal oxide semi-conductor gas sensors in environmental monitoring. *Sensors (Basel)* **2010,** *10* (6), 5469-502.

19.   Halliday, J.; Lewis, A. C.; Hamilton, J. F.; Rhodes, C.; Bartle, K. D.; Homewood, P.; Grenfell, R. J. P.; Goody, B.; Harling, A.; Brewer, P.; Vargha, G.; Milton, M. J. T., Lab-on-a-Chip GC for Environmental Research. *LC GC EUROPE* **2010,** *23* (Article), 514-523.