

A supramolecular approach to sub-ppb aromatic VOC detection in air†

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Micromachining technology is coupled to a selective pre-concentration material for the development of a portable sub-ppb level monitoring system for aromatic volatile organic compounds (VOC); the high sensitivity of Metal Oxide (MOX) gas sensors is combined with a supramolecular concentration unit to increase selectivity and reduce the detection limits.

Increasing pollution due to vehicular traffic and industrial activities is a major problem nowadays, particularly in large urban or industrial areas. Widespread air quality monitoring is mandatory to ensure healthy living conditions, but available real-time VOC monitoring systems for in-field environmental monitoring applications are bulky and expensive, being automatic high-end systems derived from laboratory instrumentation.¹ Simple low-cost systems based on solid state gas sensors were recently proposed.² However, the lack of selectivity of MOX gas sensors is one of the major issues in applications where single analytes within complex mixtures must be detected and quantified. Some of the compounds typically found in air samples, like *e.g.* water vapour, though harmless to the population, are present at high concentrations and can vary rapidly with time, producing significant shifts in the baseline of MOX sensors. Instead, the presence of compounds like benzene, which are toxic or even carcinogenic at ppb concentrations, needs to be accurately determined.³

Here we report an innovative approach to sub-ppb level aromatic VOC detection in environmental monitoring. A miniaturized system is proposed, composed of a selective supramolecular concentration unit, a Si-micromachined GC column and a Si-integrated MOX sensor. The issue of achieving at the same time molecular-level selectivity and low-ppb sensitivity for benzene has been solved by disconnecting the recognition element from the detection unit. The recognition event is assigned to a molecular receptor, capable of selectively trapping aromatic vapors at the gas–solid interface.⁴ The selective concentration component is interfaced to a miniaturized Si GC column,[‡] necessary for the separation of the different aromatic compounds released by the trapping unit, which are then individually channeled to the MOX detector.[§]

For the supramolecular trapping unit we have chosen a quinoxaline-bridged cavitand (QxCav, Fig. 1) having a cavity of 8.3 Å deep and 8.0 Å wide, which selectively binds aromatic guests *via* CH– π interactions with the cavity bottom and walls. In

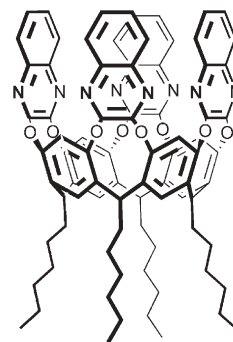


Fig. 1 Molecular structure of QxCav.

particular the complexation properties of QxCav towards aromatic compounds have been demonstrated both in the solid state⁵ and in the gas phase.⁶ QxCav is totally insensitive to aliphatic hydrocarbons, water and to polluting gases present in air like CO, SO_x, NO_x.⁷

The cavitand action in this device is twofold: (i) separate the aromatic components from all the other pollutants and interferences present in air and (ii) concentrate the aromatic VOC to a level sufficient to be detected by the MOX sensor after desorption. To be used in the device, QxCav was crystallized from acetone and the resulting crystalline solid was passed through 35–60 mesh sieves to obtain a powder having homogeneous size distribution.[¶] Decomposition of QxCav occurs above 400 °C under nitrogen as indicated by thermogravimetric analysis.⁸

The experimental setup used for testing the performances of QxCav as a selective concentration unit for aromatic VOC is composed of a gas distribution system comprising several mass flow controllers connected to certified cylinders which provides a calibrated mixture of aromatic VOC at different concentrations eluted in synthetic air, which is sampled by the cavitand in a purge and trap configuration. During sampling the cavitand unit is kept at room temperature. A MOX sensor is mounted in a low-volume chamber and connected to the outlet of the cavitand cartridge (Fig. 2).

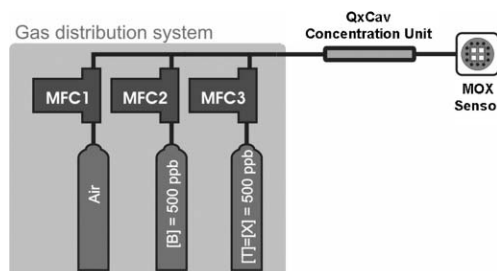


Fig. 2 Apparatus setup for QxCav testing.

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The absorption efficiency of the cavitand is measured by comparing the sensor response in the case of a cartridge filled with QxCav with the response in the case of an empty cartridge. After a given sampling time (15 or 20 minutes), the cartridge is heated with a linear temperature ramp from room temperature to 80 °C in 25 minutes, and the MOX sensor is used as detector of the released volatiles.

In Fig. 3a the typical sensor response during absorption of benzene is shown. The dotted blue plot shows the sensor response in the case of an empty cartridge, representing the sensor response to the injection of 20 ppb of benzene for 15 minutes. The flat black plot represents the sensor response of QxCav under the same conditions. The comparison of these responses clearly shows the high absorption efficiency of the considered cavitand.

In Fig. 3b the sensor responses during the desorption temperature run are compared. The black plot shows the sensor response to the compounds released after a 20 minutes absorption of 20 ppb of benzene, while the dotted blue plot refers to the release of a mixture of 5 ppb of toluene and 5 ppb of *m*-xylene, compared to a reference desorption (gray dashed plot, after sampling of humidified air without any VOC).

In both cases the release has a maximum peak at around 70 °C, which is a temperature low enough to be easily implemented in a miniaturized and portable system. On the other hand, the temperature at which the release occurs is very similar for all of the considered compounds, therefore the selectivity needs to be enhanced for a reliable quantification of each single aromatic compound.

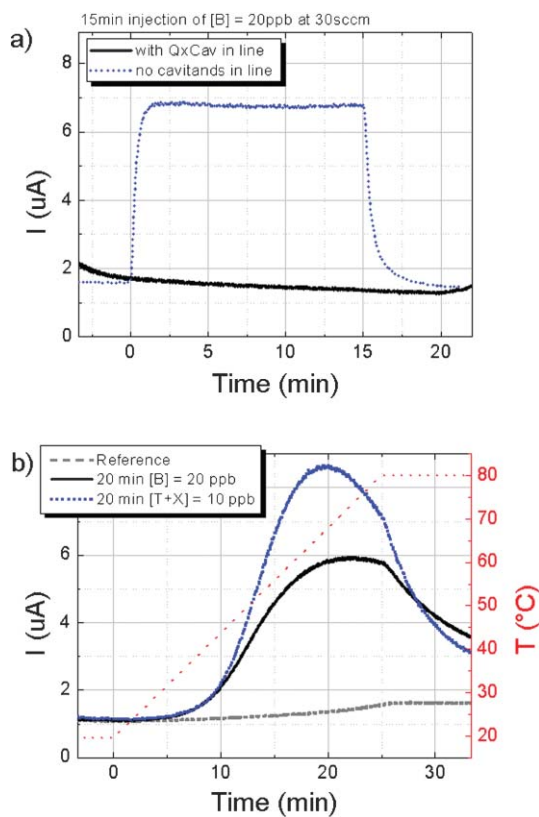


Fig. 3 a) Measurement of QxCav absorption efficiency. b) Measurement of QxCav desorption kinetics. The red dotted trace shows the temperature ramp.

The GC system⁹ was therefore inserted between the QxCav cartridge and the MOX sensor to separate the different aromatic compounds. Benzene, toluene, ethylbenzene and *m*-xylene (BTEX) in concentrations between 0.1 ppb and 5.0 ppb eluted in humidified synthetic air were provided by the gas distribution system shown in Fig. 2 at a constant 500 sccm flow. The sampling pump of the mini-GC was used to sample 200 sccm from this flow for 50 minutes, while the remaining flow was flushed to vent. After 50 minutes of concentration, the QxCav cartridge is heated to the desorption temperature of 100 °C for 2 minutes, and a valve is switched to connect the outlet of the cavitand column to the inlet of the GC pump, which drives the released analytes through the GC separation column to the MOX detector. During the chromatogram acquisition, which lasts approximately 15 minutes, the concentration unit column is cooled down and starts the next concentration cycle. In this way the chromatogram acquisition and the concentration can be performed in parallel, therefore the cycle duration is mainly determined by the chromatogram duration or by the concentration time, whichever is the longest. Obviously, longer concentration times make it possible to reach lower detection limits, while in the case of higher concentrations shorter measurement cycles can be applied.

In Fig. 4 a set of five measurement cycles is reported, with four different analyte concentrations in the range between 0.1 ppb and 5.0 ppb, together with a reference chromatogram relative to humidified air only. The injections were not performed in any increasing or decreasing order, but in a random sequence, to exclude any systematic error due to analyte residues. After a first injection peak at $t < 1$ min, the four peaks relative to benzene, toluene, ethylbenzene and *m*-xylene are released at $t = 2, 5, 7$ and 10 min respectively. The peaks are well separated, and the baseline drift at $t > 4$ min is due to the increase of the GC column temperature to allow a faster release of the heavier analytes (programmed temperature ramp). For all of the concentrations, including the lowest 0.1 ppb injection, the peaks are clearly visible and a peak area can be extracted, which can be correlated to the concentration of the single analytes. The correlation of the chromatographic peak areas of eight different chromatograms with the analyte concentrations for benzene, toluene and *m*-xylene is shown in Fig. 5. A regular trend of the peak area as a function of

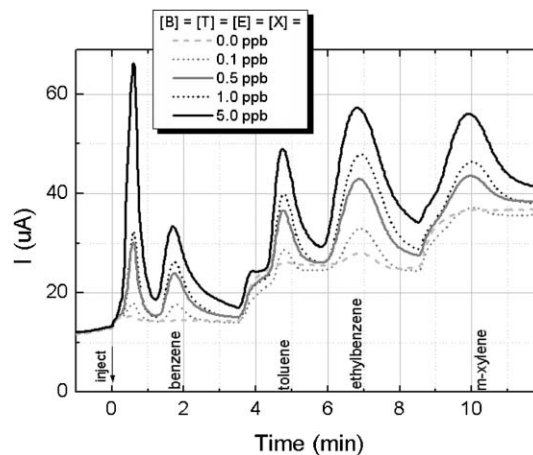


Fig. 4 Set of five chromatograms relative to QxCav desorption of BTEX at different initial concentrations.

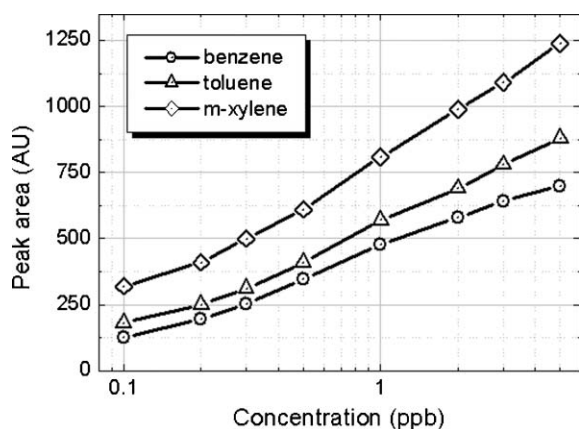


Fig. 5 Calibration curve: peak area as function of analyte concentration for benzene, toluene and *m*-xylene.

the gas concentrations in a semi-logarithmic scale was found, and the nonlinearity of the correlation is due to the non-linearity of the MOX sensors used as detector, which are well known to saturate at higher concentrations. Nevertheless, the regular trend of the slopes of Fig. 5 allows for a precise calibration of the system, and the relation of peak area as a function of gas concentrations was found to be stable and reproducible within two months of measurements. Preliminary measurements in real outdoor air were successfully performed, and the system is now being characterized in direct comparison with a commercial GC used for environmental monitoring.

In summary, a palm-sized sensor prototype for the detection of airborne benzene was fabricated, integrating QxCav as selective concentration material, a micromachined gas chromatographic column and a MOX sensor array as detector. QxCav showed excellent performances as concentration material in terms of absorption efficiency, desorption kinetics and reproducibility. Furthermore, with QxCav being selective as sorbent material, only aromatic VOC are retained from the sampled gas, greatly reducing the necessary resolution of the GC column. QxCav sampling and desorption are not influenced by relative humidity, making the system suitable for direct environmental sampling of aromatic VOC. All these advantages make the proposed monitoring system capable of complying with the strict EU legislation, which requires threshold values for benzene below 0.7 ppb ($\approx 2 \mu\text{g m}^{-3}$) by 2010.³ The direct integration of cavitands on silicon,¹⁰ by coating the inner part of a micromachined Si column with a monolayer of QxCav, is currently in progress.

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Notes and references

‡ The micromachined Si GC columns used in this work are spiral-shaped channels with cross sectional areas up to 0.8 mm^2 and column lengths up to 50 cm, realized by an advanced silicon etching (ASE) process on a 1 mm thick silicon wafer polished on both sides, with etching depths of 850 μm . To control the temperature of the GC column during separation, a platinum heater was fabricated on the bottom of the Si wafer. Finally, a Pyrex wafer with pre-formed drillings for the gas in- and outlet was anodically bonded onto the Si wafer for encapsulation. After encapsulation, the GC columns were filled with a commercial packed gas chromatographic stationary phase, Carbowax 2 + 0.2% Carbowax with mesh 60–80.

§ A Si-micromachined thin-film MOX sensor was used as detector of the concentration-separation system. The sensing layer was deposited by a sputtering process on a Si-microhotplate based Si_3N_4 membrane and with a thin gold layer as catalyst. The thin film metal oxide gas sensors were operated at 400 °C, which was found to be the best temperature for aromatic VOC detection. The sensing layer conductivity was acquired by reading out the sensing layer current under a fixed bias voltage of $U = 1.2 \text{ V}$. Both the control of the sensor heater and the acquisition of the sensor conductivity were performed using a custom electronic interface connected to a PC.

The two micromachined components (GC column and MOX detector), together with the supramolecular pre-concentration unit, were integrated into a simplified GC system together with some commercial components. The system comprises two pumps (KNF NMP09), a zero grade air generator (activated carbon mesh, provided by Environment SA, France) and some commercial 3-way microvalves (by The Lee Company) for gas flow control. All of these components were assembled on a stainless steel pneumatic interconnection board, and connected to specifically designed control and read-out electronics, fabricated using small footprint stacked SMD PCBs. Fig. S1 (ESI) shows a photograph of the complete assembled system, while Fig. S2 (ESI) shows the disassembled system with all of the components visible and compared to a 1 euro coin. The system does not require any external inert gas cylinder, since the carrier gas is generated directly on-board.

¶ In the reported experiments 54 mg of QxCav were packed in a Pyrex purge and trap column of 60 mm length and 1.5 mm inner diameter.

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