Supporting Information

for

High Temperature Mass Detection Using a Carbon Nanotube Bilayer Modified Quartz Crystal Microbalance as a GC Detector

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Content: The supporting information contains a description of the in-house built, portable gas chromatograph (GC). The document also contains further chromatographic data in support of the manuscript.

Figure S-1 shows a block diagram of the portable gas GC system with integrated QCM detector. The sample introduction takes place via thermal desorption by inserting a sample swab into the inlet.

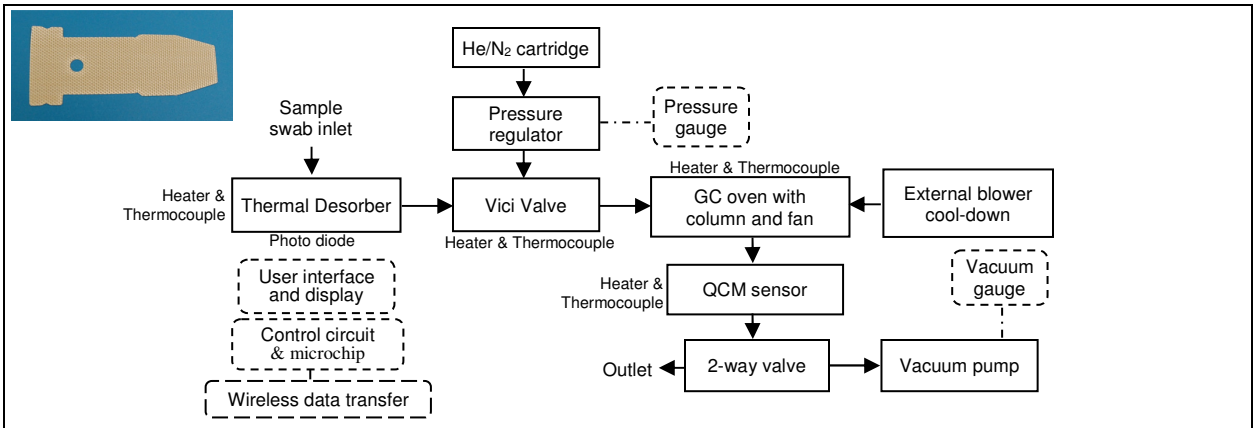

Figure S-1. Block diagram of portable gas chromatograph system. The figure shows the flow path and a component overview. The sequence of events is as follow: 1) Sample inlet/ desorption (from sample collection swab); 2) GC column (sample separation) in a temperature controlled oven; 3) Quartz crystal microbalance (detection) specialized for high temperature measurements. The picture in the upper left corner shows a commercially available sample swab, typically used for Ion Mobility Spectrometers.

All components from the thermal desorber, the Vici valve, the GC oven and the QCM sensor can be independently temperature controlled via PID control. The heating mechanism is either based on NiCr wiring or heater cartridges. The thermal desorber and the Vici valve are set to a constant temperature, whereas the GC oven and the QCM detector are subject to a temperature ramp profile.

The system operates in suction/vacuum mode pulling in ambient air as the carrier gas at 40 kPa whenever it is in rest mode as well as at the beginning of a measurement (sample introduction). The GC oven profile starts at 120˚C with a 30 seconds isothermal step that is followed by a ramp to 220˚C at 25˚C/min. At a programmed point in time, the system switches from vacuum mode to pressure mode at 55 kPa utilizing the attached inert gas miniature cartridge. In order to avoid thermal oxidation of the column's stationary phase, the switch from ambient air to inert carrier gas takes place at the latest at 150˚C. The system switches back to ambient air on cool-down when the column is below that temperature.

Besides the GC profile and QCM temperature ramp, additional parameters such as the desorption time and the desorber and valve temperature had to be optimized in order to achieve the chromatographic performance described in the manuscript. For all contraband drug measurements, the desorption time was set to 60 seconds, with the desorber and valve temperature at 210˚C.

Figure S-2 shows a picture of the in-house built GC prototype. The sample swabs used in this study (shown as being inserted into the desorber inlet) are commercially available from DSA Detection (North Andover, MA; part # ST1318) and Morpho Detection (Wilmington, MA; part # M0001964). The dimensions of the system are 10"x12"x8" (d/w/h). All individual components correlate to the block diagram shown in Figure S-1. An interface block was designed that connects the GC column to the QCM holder and acts as a minute flow cell. Pressure gauges measure the system's pressure and vacuum respectively.

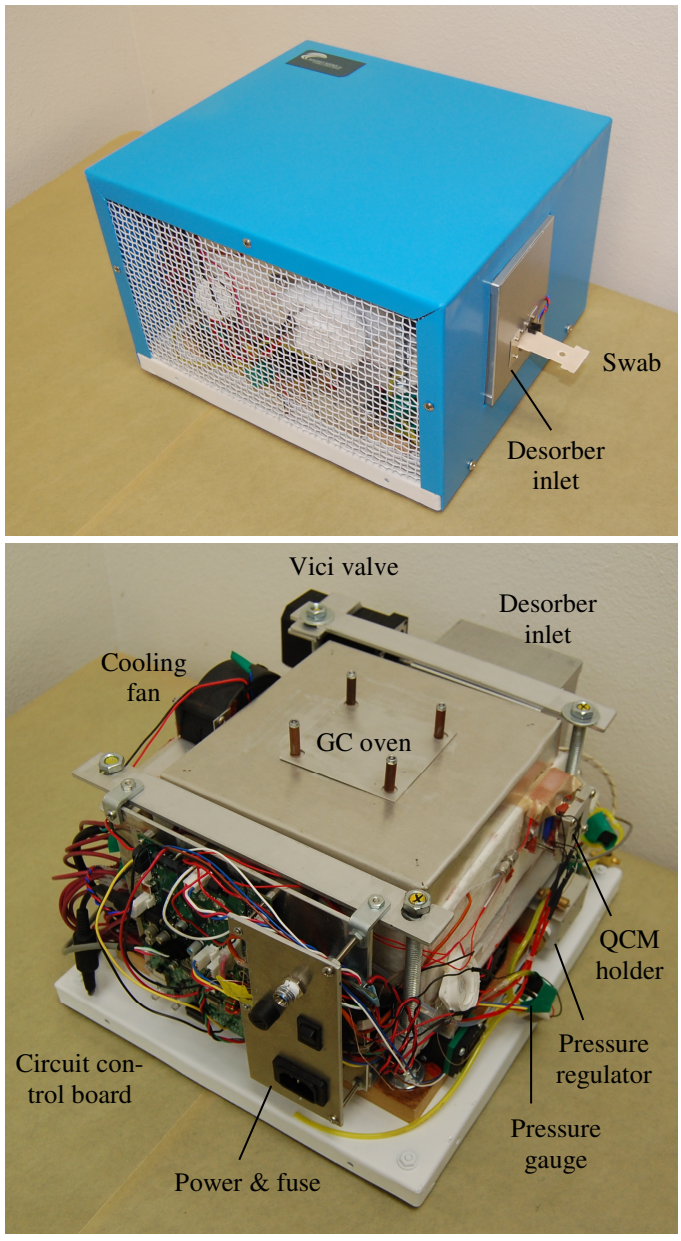

Figure S-2. Picture of the portable GC system with and without chassis.

Figure S-3 shows a typical chromatogram of a blank sample as well as a calibration sample with 3µg of the PCP standard solution (allowed to evaporate prior to injection). The measured retention time of the PCP peak onset can be entered into the GC software to correct all library retention times for possible drifts. The valve switch takes place after the sample introduction (via suction) to a helium or nitrogen carrier gas (pressure mode). This change of the carrier gas is the cause of the QCM frequency spike at around 60 seconds in the graph below. The valve switch can be preprogrammed to take place at a given time of column temperature. The initial peak at around 20 seconds is related to the sample swab insertion into the thermal desorber.

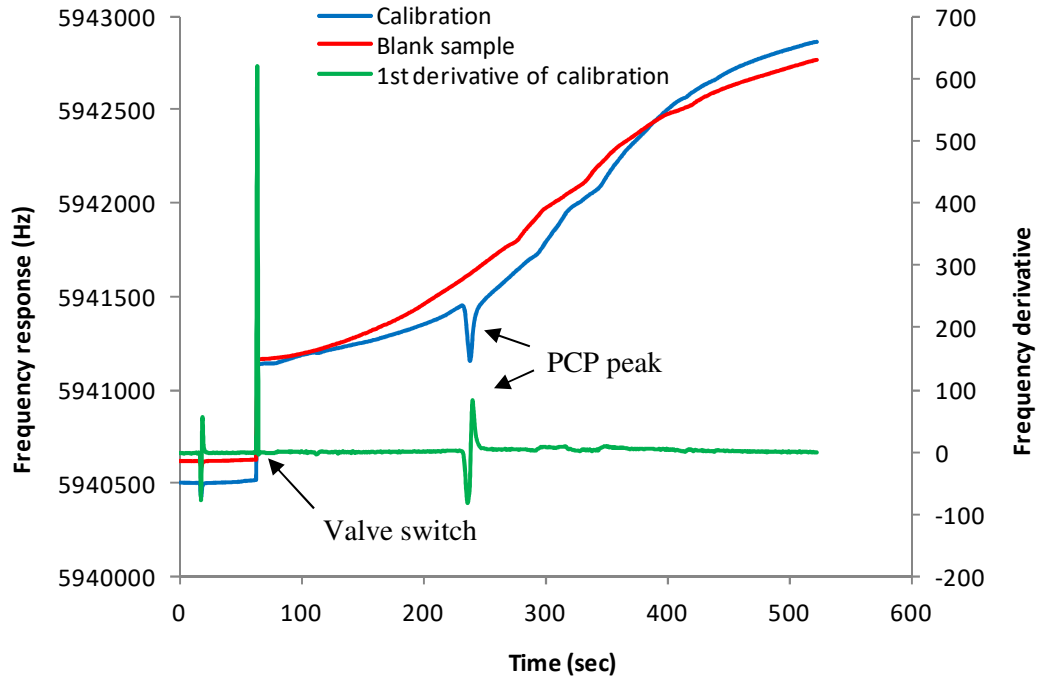

Figure S-3. Chromatogram of a blank and a calibration sample (PCP standard). The first and second derivatives of the frequency response are used for the determination of peak onset and peak maxima.

Figure S-4 shows a collection of random sampling events of different objects from floors, bench top to the sampling of the palm of a hand. One of the objects was purposely spiked with 10µg of PCP (2nd tool box sampling). The GC software correctly identified the controlled substance as positive detection despite the added noise in the chromatogram. Another sampling event of a cabinet door resulted in a false positive detection of Ephedrine. The rate of false positive detection is currently below 6%. This rate can be reduced by tightening the margins around each compounds' library retention times. These tolerances are currently set to ± 2 to ± 6 seconds, depending on the retention time of the compound. Alternatively, the minimum peak height/area threshold can be increased to reduce the number of false positives. As a comparison, the false positive alarm rate of commercially available Ion Mobility Spectrometers (IMS) is at a minimum 1%.[1]

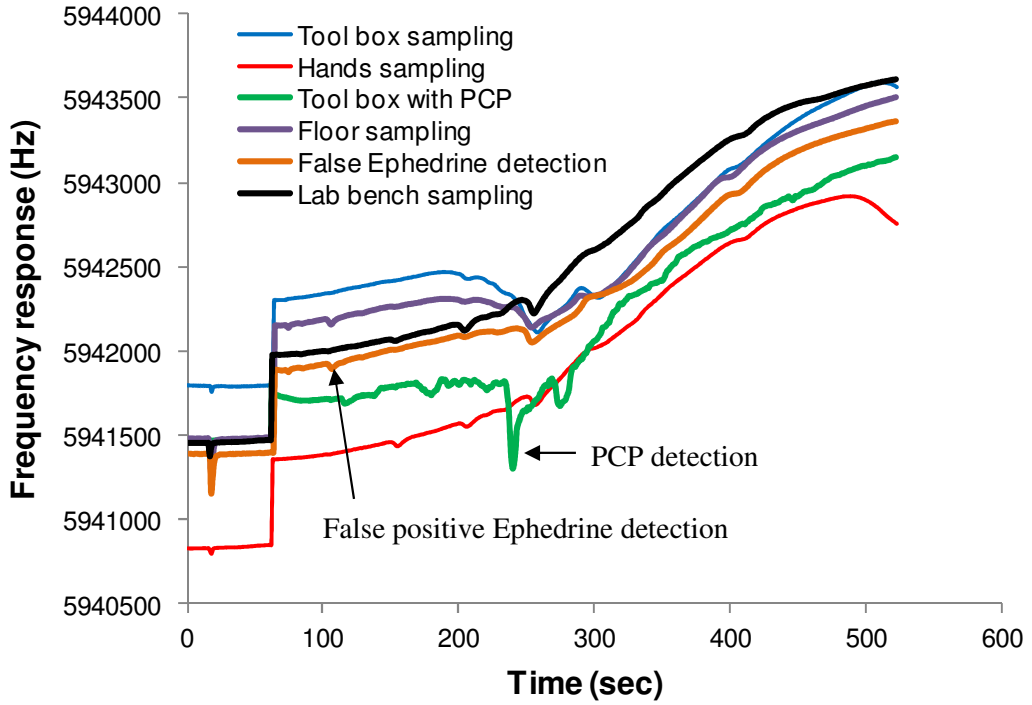

Figure S-4. Chromatogram of several sampling events of various objects. The green marker shows the results of a sample where 10µg of PCP was placed on a tool box that was subsequently sampled. Shown in the middle of the graph is the sampling event of a cabinet surface that resulted in a false positive detection of Ephedrine.

[1] Eiceman, G.A., Karpas, Z., Hill, H.H., Ion Mobility Spectrometry, 3rd Edition, 2014, CRC Press