Supporting Information for:

Automated system for monitoring trace C_2H_2 in ambient air by cavity ring-down spectroscopy combined with sample pre-concentration

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Section 2 of the main manuscript contains an overview of the design and operation of the automated spectrometer for trace-level C_2H_2 measurements in air. Here, further details are provided about the construction of the gas sampling and pre-concentration components of the apparatus. The air sampling protocols are described and illustrated by a diagram showing the sequence of events used to make a single measurement and the times for each step in the process.

Dual-trap sample pre-concentration methodology

In the dual-trap sample pre-concentration process, ambient air samples were initially passed through a diaphragm pump (KNF, N86 KTE) followed by a mass flow controller, MFC 1 (MKS, 200 sccm, N_2) to regulate the sample flow rate. The air samples were then dried by passage through a Nafion permeation dryer (Brunswick Instrumentation Ltd., MD-050-72S-2) which was continuously counter-purged by a flow of dry N_2 (BOC Edwards, N6 grade containing < 20 ppbv moisture) regulated by a second mass flow controller, MFC 2 (MKS, 500 sccm N_2). The flow of air sample through the dual-trap was controlled by a 12-port 2-position valve (EH2C12WE, Valco Instruments Co. Inc).

Schematic diagrams of the two valve positions are shown in Figure 2 of the main paper. In position A, the sample line was connected to the pre-trap (containing Tenax TA (110 mg, 60/80 mesh size, Supelco)), the main-trap (containing a carbon based molecular sieve, Carbosieve SIII (CSIII, 300 mg, 60/80 mesh size, Supelco)), and the vent. The RDC was simultaneously evacuated as far as port 10 of the 12-port valve by control of two solenoid valves SV1 and SV2 (A2011-V-VO-LB-12VDC, Gems Sensors and Controls). In position, B, the sample line connected directly to the vent, allowing the line to be purged before the traps were loaded. The main-trap was connected to MFC 4 (MKS, 10 sccm, N_2) and this was used to transfer C_2H_2 molecules from the main-trap to the RDC with the aid of heating and a purge flow. A single heating and N_2 purge cycle was sufficient for complete transfer of C_2H_2 from the trap to the RDC. The pre-trap was connected to MFC 3 (MKS, 10 sccm, N_2) and this was used to evacuate heavier VOCs to the vent. With such a configuration of the

valve inputs and outputs, it was possible to clean the pre-trap simultaneously with the desorption of the adsorbed contents of the main-trap to the RDC.

Automated communication protocols

A personal computer (PC) based system controlled and monitored the operation of the valves, air-sampling pump, MFCs and wavemeter through a custom written LabVIEW 8.2 program. The digital and analog communications were controlled through a BNC adapter (BNC-2110, National Instruments) which contained the digital and analog input/output (I/O) circuitry to interface the various components of the automated system with a PC-mounted data acquisition (DAQ) card (PCI-6024E, National Instruments), to which it was connected. The automation controls were designed to make the spectrometer sufficiently compact, robust and portable for future deployment outside the laboratory

The air-sampling diaphragm pump was controlled by a solid state relay (SSR) (MP240D3, 3A 12-280Vac, Crydom) through a digital circuit based on transistor-transistor-logic (TTL) electronics. The logic circuit was connected to a digital I/O terminal of the BNC adapter. The two solenoid valves, SV1 and SV2 were operated independently by TTL circuits, each followed by a SSR (MPDCD3 3A 3-60Vdc, Crydom). The 12-port 2-position valve was electrically actuated using a ten-pin digital I/O cable (P/N I-22537) through the VICI actuator control module with in-built TTL circuitry which enabled switching of the valve between its two positions (denoted A and B). The four MFCs were operated using a controller module (MKS, 247D) connected to the PC by a P6 interface connector, thereby allowing remote setting of the various gas flow rates required in the measurements. An analog output port of the BNC adapter supplied a ramp voltage to the laser driver to scan the laser frequency, which was monitored by the wavemeter, with output readings collected through an analog input to the BNC adapter and PC.

A serial communication protocol was designed to control the heating systems of the traps for desorption of VOCs. Each trap was resistively heated to a temperature of 210 ˚C by applying a high current to a nichrome heating wire wrapped around the trap

exterior. The current was provided by a power supply (PCI Case CRS2040S-2FBH) through a SSR (D1D40, 40A rms 0-100Vdc, Crydom). An E-type butt-welded junction thermocouple (CHCO-015-BW) was attached to the trap to monitor its temperature. The thermocouple was shielded by polyimide tubing (EW-95820-05, Cole-Parmer) and high-temperature heat shrink tubing (polyvinylidene fluoride (PVDF)) was used around the trap to keep all the components together. The desired set point temperature for the main trap was controlled by a PID controller (CN77354-C2, Omega). In this manner, precise, repeatable temperature control of set points was achieved within a few seconds, with temperature fluctuations of ± 1^{o}C. A serial port (RS-232) from the PC was used to communicate with the PID controller. An additional such serial interface was used to control remotely the pressure inside the cavity via a vacuum gauge controller (230002, Oerlikon Leybold, 1500 Torr).

Automation sequence

Figure S1 displays a flow diagram of the automation sequence for each step for a complete adsorption-desorption and measurement cycle. The approximate times for completion of each step are indicated in the flow chart. The whole cycle took ~15 minutes for a complete sample run and the next cycle started ~15 minutes afterwards. This additional period was required to cool the adsorbent traps back to room temperature, but could be reduced by active cooling with a Peltier-based device. Execution of each step was displayed on the front panel window of the LabVIEW 8.2 control program, with indicators to show the sequential operations of the sampling and measurement sequences.

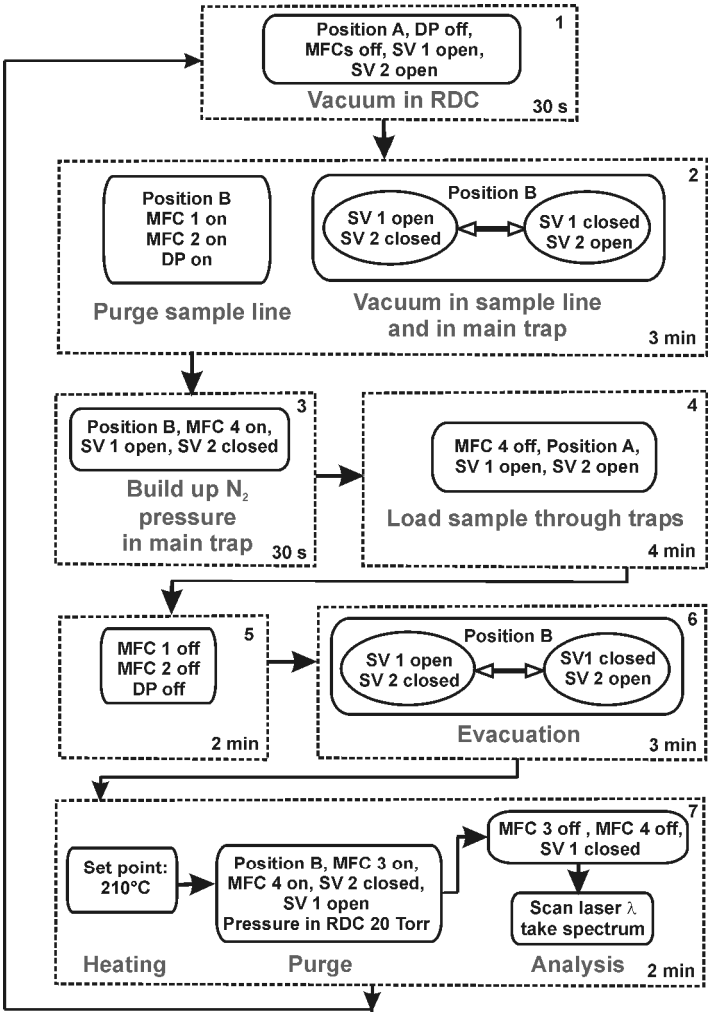

FIGURE S1. Flow chart of the automation sequence for a complete adsorption-desorption and measurement cycle. Each cycle is completed by following 7 steps and the approximate time for completion of each step is indicated. In the chart, DP: diaphragm pump, MFC: mass flow controller, SV: solenoid valve. Positions A and B refer to the two positions of the 12-port valve shown in figure 2 of the paper.