iDirac: a field-portable instrument for long-term autonomous measurements of isoprene and selected VOCs

Conor G. Bolas[1], Valerio Ferracci[2], Andrew D. Robinson[3], Mohamed I. Mead[2], Mohd Shahrul Mohd Nadzir,[4] John A. Pyle[1,5], Roderic L. Jones[1] and Neil R.P. Harris[1,2]

5 [1]Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, UK
[2]Centre for Environmental and Agricultural Informatics, Cranfield University, College Road, Cranfield, MK43 0AL, UK
[3]Schlumberger Cambridge Research, Madingley Rd, Cambridge, CB3 0EL, UK
[4]School of Environmental and Natural Resource Sciences, Universiti Kebangsaan Malaysia, 43600, Bangi, Selangor, Malaysia
[5]National Centre for Atmospheric Science, NCAS, UK

10 *Correspondence to*: Neil R.P. Harris (neil.harris@cranfield.ac.uk)

Abstract

The iDirac is a new instrument to measure selected hydrocarbons in the remote atmosphere. A robust design is central to its specifications, with portability, power efficiency, low gas consumption and autonomy as the other driving factors in the instrument development. The iDirac is a dual-column isothermal oven gas chromatograph with photoionisation detection (GC-
15 PID). The instrument is designed and built in-house. It features a modular design, with novel use of open-source technology for accurate instrument control. Currently configured to measure biogenic isoprene, the system is suitable for a range of compounds. For isoprene measurements in the field, the instrument precision (relative standard deviation) is ±11%, with a limit of detection down to 38 pmol mol^{-1} (or ppt). The instrument was first tested in the field in 2015 in a ground-based campaign, and has since shown itself suitable for deployment in a variety of environments and platforms. This paper describes
20 the instrument design, operation and performance based on laboratory tests in a controlled environment, and during deployments in forests in Malaysian Borneo and in Central England.

1 Introduction

Isoprene (C_5H_8) is one of the most important non-methane biogenic volatile organic compounds (BVOC) emitted into the atmosphere. It has a global emission rate estimated at around 500 TgC year^{-1} (Guenther et al., 2006) and its oxidation products
25 make it a major factor determining ozone and secondary organic aerosol production. Emitted by vegetation, it has been linked to temperature regulation, reducing drought-induced stress and other physiological processes within plants (Sharkey, 2013; Sharkey et al., 2008). A dialkene, isoprene is prone to oxidation by reaction with the hydroxyl radical (OH), as well as by ozonolysis and reaction with the nitrate radical (NO_3) (Stone et al., 2011). Isoprene oxidation pathways are complex (Archibald et al., 2010) and result not only in a number of oxygenated volatile organic compounds (OVOCs *e.g.*, formaldehyde,
30 methacrolein, methyl vinyl ketone) but also in a suite of low-volatility stable products and intermediates that can act as precursors of secondary organic aerosols (Claeys, 2004; Liu et al., 2016).

Due to its high reactivity, isoprene is relatively short-lived, with a typical lifetime of the order of one hour in a temperate (Helmig et al., 1998) forest. Isoprene emissions are mainly driven by incoming solar radiation and temperature, and as a result
35 exhibit a distinctive diurnal cycle which peaks around midday. Local abundances can change rapidly in response to meteorological variations, such as changes in incoming photosynthetically active radiation (PAR), temperature and atmospheric dynamics (Langford et al., 2010). High time resolution data is required to capture trends in isoprene concentrations in real time. It is expected that isoprene emissions will be affected by global change (increasing temperatures, land use change, increasing CO_2) in the coming decades (Bauwens et al., 2018; Hantson et al., 2017; Squire et al., 2015). However, the overall
40 magnitude and sign of changes in isoprene emissions is still uncertain due to the many variables at play and the uncertainties

in our emission models. This, coupled with its large variability, makes it highly desirable to improve the temporal and spatial coverage of isoprene measurements so that our understanding of its emissions via models can be validated against field data.

Measurements of atmospheric hydrocarbons such as isoprene are challenged by the difficulty in making measurements in
5   remote places. To date, in-situ measurements of isoprene have been carried out using existing commercial bench-top instruments, such as gas chromatographs (Jones et al., 2011) and mass spectrometers (Noelscher et al., 2016; Yáñez-Serrano et al., 2015). These techniques differentiate between VOCs either by separation (gas chromatography) or by identification of their molecular ions based on mass-to-charge ratios (mass spectrometry). These instruments, while offering high precision and stability, are not built to withstand field conditions for long periods of time due to their need for power, temperature-
10   controlled environments and speciality carrier gases. This is especially true in under-sampled regions of high isoprene emissions, which are typically in remote or challenging environments (e.g., tropical forests). In these locations instrument size, portability, autonomy, power demand and gas consumption severely limit the length of a deployment. In addition, instrument cost and maintenance limit the number of instruments deployed at any one time, and hence the spatial coverage of a field campaign.

An alternative method to detect environmental VOCs is with grab samples. These can either be whole air samples or adsorbent tubes, where air samples (or some specific air components) are collected in an inert vessel and analysed at a later date. While grab samples can be deployed in relatively large numbers, they typically provide low temporal resolution, making this approach unsuitable to capture the rapidly changing concentrations of isoprene. In addition, reactive compounds can degrade over time
20   before analysis, and using this method for long periods, even with some degree of automation, is very time and resource intensive.

All the limitations in the instruments currently used for VOC detection drive the need for a field instrument that is:

- lightweight, so that it is portable and can easily be carried and installed in environments difficult to access with traditional instrumentation;
25   - low-power, so that it is capable of running off-grid, allowing measurements in locations with no mains power;
- autonomous, so that it minimises operator involvement and maintenance;
- low gas use, so that it minimises the cylinder size required and the number of site visits to replace gas cylinders;
- rugged and durable, so that it can withstand challenging environments; and
- relatively low-cost, so that many instruments can be deployed at one time, maximising spatial coverage.

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Here we describe the development and validation of the iDirac, an instrument that fulfils the requirements listed above. It follows on from the philosophy of the μDirac (Gostlow et al., 2010), with portability, modularity, power efficiency, and autonomy at the centre of its design. The iDirac also incorporates inexpensive microcontroller board processors for advanced control and remote access to the instrument. The core GC instrument and its operation are described in Section 2, while Section
35   3 presents the software used to control the instrument. Instrument performance is discussed in Section 4, including calibration, accuracy, precision, sensitivity and separation ability. Finally, results from trial runs in the controlled environment of a laboratory and deployments in Malaysian Borneo and Central England are presented in Section 5. Results have been published on the impact of herbivory on canopy photosynthesis and isoprene emissions in a UK woodland (Visakorpi et al., 2018) and on isoprene concentrations near the Antarctic peninsula (Nadzir et al., 2019).

2 Practical description of the iDirac

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The iDirac is a portable gas chromatograph equipped with a photoionisation detector (GC-PID): the VOCs in an air sample are separated on chromatographic columns and then sequentially detected by the PID. The instrument is built in-house and is

lightweight, low-power and able to operate for up to several weeks or months autonomously. Its specifications are shown in Table 1. Section 2.1 describes the basic outline of the instrument and Section 2.2 describes the specific configuration of the instrument for isoprene.

Table 1: iDirac specifications

Power	12 W
Weight	10 kg
Voltage Requirements	10–18 V
Dimensions	$22 \times 61.6 \times 49.3$ cm
Carrier Gas	High Purity Nitrogen (Grade 5)
Calibration Gas	10 nmol mol^{-1} (or ppb) high-accuracy isoprene in nitrogen
Limit of detection	38 pmol mol^{-1} (or ppt)
Precision	11 %

2.1 Core gas chromatograph physical design

The iDirac is built in a modular fashion, so that the various components are housed in 6 main plastic boxes (Piccolo Polycarbonate Enclosures, IP67) packed in foam inside a protective waterproof case (Peli 1600), as shown in Figure 1. Details on the boxes and their contents are given below, and shown within the instrument in Figure 1:

- Valve Box, containing 8 solenoid valves to control gas flow from the four inlets;
- Control Box, containing microcontroller boards (Arduino and Raspberry Pi), a number of electronic components (e.g.. solid state relays), the flowmeter and SD card for data storage;
- Oven Box, containing the dual-column system, (pre- and main columns), heating element and Valco® valve;
- PID Box, containing the photoionisation detector (PID);
15
- Pump Box, containing the pump and pressure differential sensor;
- Power Box, contains power regulators and electrical fuses.
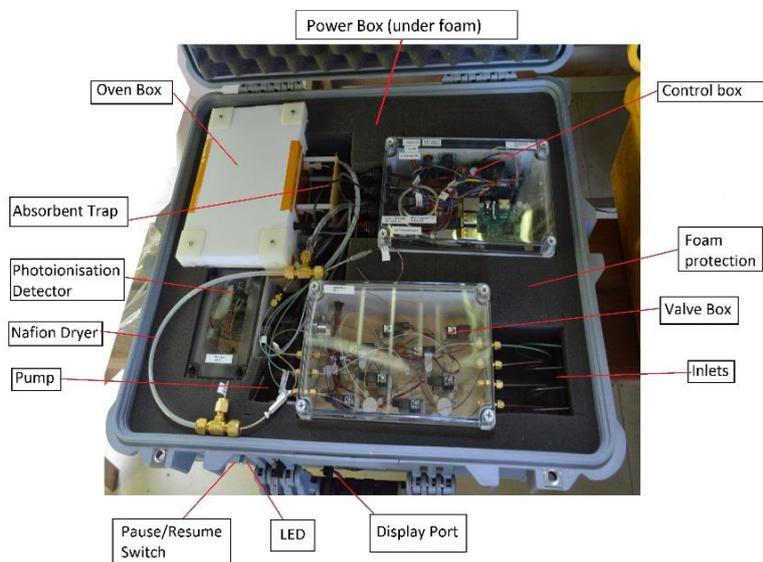
Figure 1: Interior of the iDirac showing the modular design of its component parts inside the main Peli case (22 × 61.6 × 49.3 cm).

On the exterior, the iDirac has a power socket, and four inlets for gas input. The inlets are for the nitrogen carrier gas, a calibration gas and two sample lines (Sample 1 and Sample 2) between which the instrument can alternate.

The general pneumatic design of the instrument is built around two phases in the analysis cycle which are represented schematically in Figure 2: a loading phase (Load Mode – pink), in which the analyte of interest is pre-concentrated on an adsorbent trap, and an injection phase (Inject Mode - purple), in which the analyte is desorbed from the trap and directed into the oven for separation and, eventually, detection. These two modes are controlled by a 2-way 10-port Valco® valve (VIDV22-3110, mini diaphragm 10 port 2-pos 1/16" 0.75mm, Thames Valco) in the Oven Box, which is activated by pneumatic actuation, by the set of solenoid valves in the Valve Box, and by the pump.
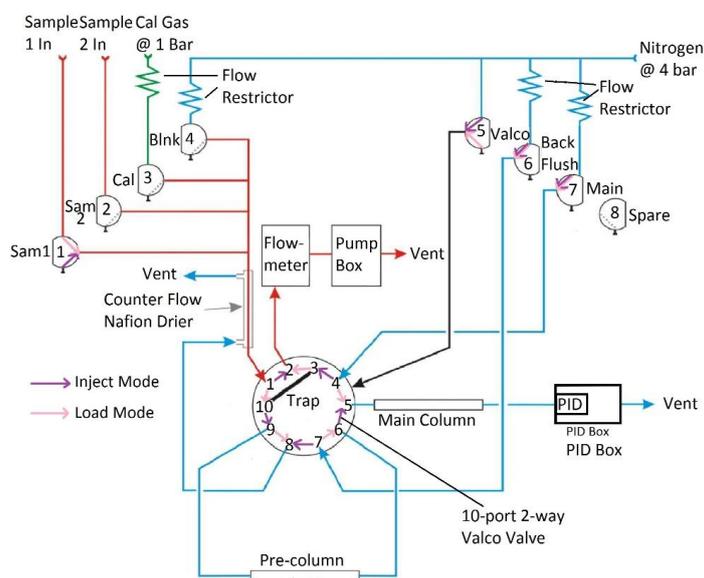
Figure 2: Schematic representation of the iDirac operation. When in Load Mode (valve 5 off - pink), the contents of a gas source chosen between valves 1-4 are pre-concentrated on the adsorbent trap. In Inject Mode (valve 5 on - purple), the VOCs in the trap are injected into the dual-column system for separation and, eventually, detection.

In Load Mode (Valco valve not activated, i.e. valve 5 off), one of four inlet gases (either sample 1, sample 2, calibration gas or blank gas) is selected by switching on the appropriate solenoid valve (valves 1, 2, 3, or 4 respectively). By activating the pump, gas is drawn through the selected inlet valve, dried in a Nafion counter-flow system and passed through an adsorbent

5   trap where the analyte is pre-concentrated. The sampled gas is vented into the Peli® case and then to the outside. A flowmeter is placed in series with the sample flow and measures the gas flow through the trap. Once a pre-defined volume of gas has been sampled, the pump stops and the instrument enters Inject Mode.

In Inject Mode, the trap is flash-heated to approximately 300 °C for 9 s to desorb the analyte from the adsorbent material. The

10   Valco® valve is then pneumatically activated by switching valve 5 on: the nitrogen carrier is flowed through the trap in the direction opposite to trap-loading, delivering the desorbed compounds into the dual-column system where they undergo chromatographic separation. The oven consists of a pre-column, which screens for large bulky molecules (e.g., the monoterpenes) whilst allowing smaller molecules through, and a main column, which performs the critical separation of the relevant analytes. The main column eluent is incident on the PID membrane, where the signal from the changing composition

15   of the gas exiting the main column is detected.
More details on the individual parts of this cycle are given below.

Inlet manifold and sample preparation. The inlet ports protrude from the side of the Peli® case via 1/16" inch bulkhead unions (Swagelok) and connect directly to the Valve Box, containing 8 solenoid valves that act as gas selectors. The Sample 1 (via valve 1), Sample 2 (via valve 2), calibration gas (via valve 3) and blank nitrogen (via valve 4) lines are all combined in

20   a 4-way Silconert-treated stainless steel Valco manifold (Z4M1, 1/16" manifold 4 inlets, Thames Valco). This manifold leads to the adsorbent trap via a Nafion dryer (Nafion gas dryer 12", polypropylene, PermaPure MD-050-12P-2) which drives excess water vapour out of the gas flow by diffusion through a membrane with a counter flow of dry high-purity nitrogen. Valve 5 is a direct line from the nitrogen inlet to the Valco valve for actuation, which requires a higher pressure (typically 4 bar). Valves 6 and 7 control the nitrogen flow through the columns: valve 7 activates the nitrogen flow through both columns in Inject

25   Mode (when valve 5 is on), and through the main column only in Load Mode (when valve 5 is off). Valve 6 activates the nitrogen flow through the pre-column for the backflush in Load Mode. The nitrogen counter-flow needed for the Nafion dryer is provided by Valve 6 in Inject Mode and by the pre-column backflush vent in Load Mode. Gas lines downstream from valves 5, 6 and 7 leave the box via manifolds on the side of the box. Valve 8 is a spare valve with no current function.
Flow restrictors upstream from valves 3, 4, 6 and 7 ensure that the flow from the pressurised inlet lines does not exceed the

30   maximum flow through the flowmeter, and also reduce the gas demand of the instrument. The restrictor tubing used for the calibration line is red PEEK flow restrictor (1/32" OD, 0.005" ID) and the one used for the nitrogen lines is black PEEK (1/32" OD, 0.0035" ID). The rest of the tubing is Silconert-treated stainless steel (Thames Restek, 1/16" OD, 0.04" ID), which does not restrict the gas flow.

Sample adsorption/desorption system. From the Nafion drier, the sample gas passes through ports 1 and 10 of the Valco

35   valve and into the adsorbent trap when the instrument is in Load Mode. The trap consists of wide bore stainless-steel tubing (HI-Chrom, 1/16" OD, 0.046" ID) containing one bed of adsorbent material between two beds of glass beads, both crimped in place, with a coiled nichrome wire heating element surrounding the section of the tube corresponding to the adsorbent. The adsorption of isoprene and other VOCs takes place on a bed of approximately 10 mg Carboxen 1016 (Supelco, 60/80 mesh, 11021-U); Carboxen 1016 is a carbon molecular sieve that has been selected for its optimised recovery rate of unsaturated

40   short chain hydrocarbons upon thermal desorption. Different sorbent materials can be used for other species. The gas exiting the trap, now scrubbed of VOCs, flows via ports 3 and 2 on the Valco valve into the flowmeter (Sensirion, ASF1430) which monitors the flow rate through the trap. This is then integrated across the duration of sampling to calculate the total volume of gas sampled. When the desired volume is reached, the valves from the sample inlet are closed and the pump is halted to stop

the flow of gas through the trap. The heating coil is flash-heated to desorb the analyte from the adsorbent, while the Valco valve is switched to Inject Mode and valve 7 is activated, flushing the desorbed VOCs onto the pre-column in the oven box with the high-purity nitrogen carrier.

Isothermal oven. The flow containing the sample leaves the trap and enters the thermally insulated oven box. This enclosure,

5 housed in insulating material (Lightweight display board, Kerbury Group), is heated to 40 ºC using a heating element (PTC element enclosure heater, 15W 12-24V 40C) which is fixed to the base-plate of the oven using conductive paste. A fan mixes the air inside the oven to ensure a uniform temperature throughout.

The sample is injected onto the pre-column (5% RT-1200, 1.75% Bentone-34, SILPT-W, 100/120, 1.0 mm ID, 1/16"OD SILCO NOC, Custom Packed, Thames Restek, ~70 cm in length) via ports 10 and 9 on the Valco valve. Here, isoprene and

10 other small molecules travel faster through the pre-column than bulky VOCs. After a set time (typically, 30 s), once isoprene has passed through the pre-column, the Valco valve is switched off, with Valve 5 closing and Valve 6 opening, so that the pre-column is back-flushed. This way lighter species, including isoprene, elute onto the main column while larger molecules that are still in the pre-column when valve 5 is switched off are removed from the column system via the back-flush. This is important to avoid large, less volatile species from entering the main column.

15 The main chromatographic separation occurs on the main column (OPN-RESL-C, 80/100, 1 mm ID, 1/16"OD, SILCO NOC, Custom Packed, Thames Restek, ~70 cm in length), based on the boiling point and polarity of the VOCs. This way, different species elute onto the detector at different times.

Photoionisation detection system. The sample is directed from the outlet of the main column into a photoionisation detector (PID). The PID (Alphasense Ltd™, PID-AH) operates by ionising any gas diffusing through a membrane covering a krypton

20 lamp. Near-vacuum UV radiation from the lamp ionises any molecule with an ionisation potential of less than or equal to 10.6 eV. Isoprene, with an ionisation potential of 8.85 eV (Bieri et al., 1977), is readily photolysed and hence detected by the PID with a sensitivity of 140% relative to that of isobutylene, which is used by the manufacturer as a reference compound in terms of PID response. The ions generated by photoionisation produce a voltage change across an electrode system which is converted to a digital signal by an analogue to digital converter (ADC) (16-Bit ADC 4 Channel, Adafruit). The PID is turned

25 on for the duration of the elution from the dual-column system, and the data is collected at a frequency of 5 Hz. The chromatography run finishes once isoprene has eluted from the main column (typically 60-75 s after starting the back-flush). The data from the PID is then saved to a new file on an SD card by the Arduino Mega. A typical chromatogram showing an isoprene peak is shown in Figure 3.

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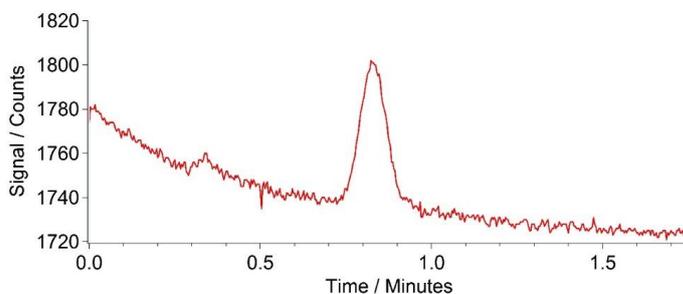


Figure 3: Typical chromatogram showing the isoprene peak detected by the PID around the 0.8 min mark.

2.2 Instrument operation specifications

Carrier gas and calibration gas. Two gas cylinders are required to operate the iDirac: a pure nitrogen supply and a calibration

35 gas. Nitrogen is used as carrier gas through the dual column system, as sample gas for the blank runs and also to actuate the

Valco valve. The nitrogen supply is of at least Grade 5 purity (corresponding to ≥ 99.999 % nitrogen) to minimise interference from impurities with the detection of isoprene. Typically, we use high purity BIP+ Nitrogen (Air Products). The logistics of the measurement dictate the size of the nitrogen cylinder used: for mobile deployments in the field, small portable cylinders (1.2 L) are ideal, whilst larger cylinders (10 L) are more suitable for long-term measurement as they minimise the need for

5 maintenance visits to replace the nitrogen cylinder. Typically, the iDirac can run continuously on a 10 L nitrogen cylinder supplied at 200 bar for approximately 2 months. The calibration gas consists of a binary gas mixture of approximately 10 nmol mol^{-1} (or ppb) isoprene in nitrogen stored in a Silconert-treated 500 mL stainless steel cylinder (Sample Cylinder Sulfinert, TPED, 1/4", Thames Restek). The use of cylinders with passivated internal walls minimises the adsorption of isoprene on surfaces, which would introduce biases in the measurement. The accurate concentration of the calibration gas is determined

10 by comparison with a primary gas standard. The calibration routine is described in detail in Section 4.1.

Power requirements for operation. The instrument requires a power supply between 9 and 18 V. This can either be mains power, or alternatively, a battery. The incoming power is smoothed and regulated with two regulators to stable 5 V and 12 V outlets. The Arduino board monitors the supplied voltage in between runs in the case of the battery losing charge or power cuts. If the voltage drops, the iDirac switches to a power-save mode, where the oven, PID and valves are turned off to conserve

15 power and the instrument waits for 20 minutes before again checking the input voltage. Once a high enough voltage (typically 9 V) is detected, the various components are turned on again.

Flow control through the instrument. The flow through the instrument is driven by either upstream pressure (in the case of the nitrogen and calibration gas flows) or by the pump box (in the case of Samples 1 and 2). The pump box is an air-tight container with an inlet line and a vent. A diaphragm pump (DF-18, Boxer) withdraws air from the pump box and vents it

20 outside, reducing the pressure inside the enclosure. The reduced pressure within the pump box causes air (from the Sample 1 and 2 inlets) to be drawn through the system, via the trap and the flowmeter. A pressure sensor (differential pressure sensor, Phidgets) monitors the pressure differential between the inside and the outside of the pump box. During a pump cycle, the pump is only activated when the pressure differential falls below a pre-specified value (typically, 20 kPa). This method ensures a uniform flowrate and enables control over low flowrates (~ 20 mL min^{-1}), thus reducing the uncertainty in the volume

25 integration of the air sampled.

3 iDirac software and hardware control and data analysis

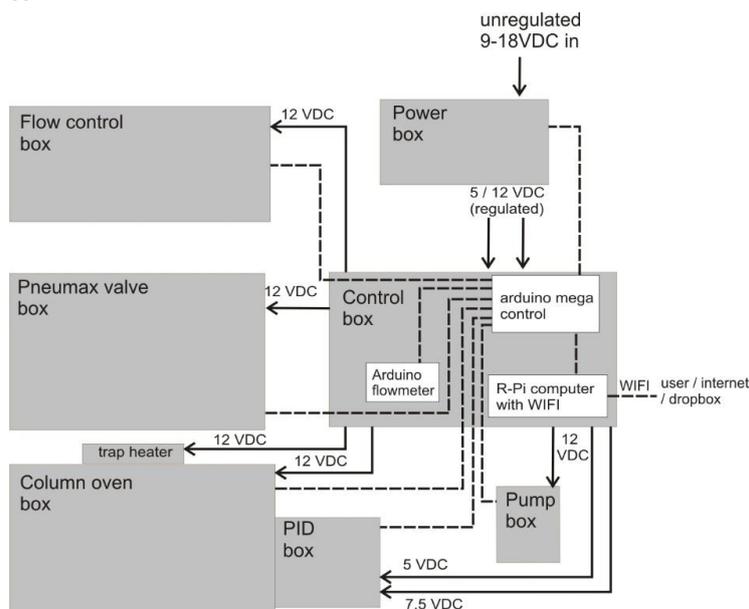
The iDirac is controlled using a dual Arduino system: an Arduino Micro board controls the gas flow components of the instrument, whilst the main instrument control is achieved with an Arduino Mega board. These two units communicate with all of the sensors inside the instrument and read their outputs. A Raspberry Pi computer acts as the interface between the user

30 and the Arduino boards. A Python script is run on the Raspberry Pi, allowing the user to configure the instrument with the desired parameters and read the sensor output from that of the Arduino. The Raspberry Pi desktop can be accessed remotely via an ad-hoc network, allowing connection with a variety of interfaces. This control system allows many of the parameters described above (e.g., sample volume, time spent in each column) to be changed.

3.1 Arduino control of internal electronics

35 The instrument is controlled primarily using an Arduino Mega 2560 board (Arduino Mega 2560, Arduino). This microcontroller has a number of analogue and digital ports and runs Arduino code (C and C++ commands) to control these ports. An SD breakout board is used (microSD Card Breakout Board, Adafruit) to facilitate the use of an SD card to store data in, while a real time clock (RTC) board is used (Real Time Clock, ChronoDot Ultra-Precise, Adafruit) for time-keeping. Figure 4 illustrates the various connections on the Arduino Mega.

40 An Arduino Micro board (Arduino Micro, Arduino) controls specifically the altimeter pressure sensor (located in the PID box) and the flowmeter, and sends these readings to the Arduino Mega via a serial port. The use of the Arduino Micro is justified

as it simplifies the code on the Arduino Mega, particularly as the flowmeter requires the use of a shifter to convert the RS232 serial signal and several subsequent mathematical manipulations. The Arduino boards do not have a shutdown procedure and can simply be unplugged.

5   **Figure 4: Schematic of Arduino Mega connections**

3.2 Description of Raspberry Pi user interface

The iDirac uses a Raspberry Pi (Raspberry Pi Model B V1.1, Raspberry Pi) as a user interface, allowing the instrument to be controlled from a familiar desktop environment. The Raspberry Pi uses a Wi-Fi dongle to set up its own ad-hoc network, which can be connected to by laptops and mobile phones in a fashion similar to a standard Wi-Fi network. Once connected to the
10   network, a graphical desktop sharing system such as VNC viewer (VNC Viewer, RealVNC) allows the user to navigate the Raspberry Pi desktop and manipulate the instrument.

Upon opening the Raspberry Pi desktop a purpose-written Python script is launched automatically. A terminal window is opened displaying the serial output from the Arduino Mega and transmitting data to the Arduino Mega via a serial port connection. The latest version of this Python script is freely available (https://github.com/cgb36/iDirac-scripts). The Python
15   script decodes incoming serial bytes from the Arduino Mega and displays them in a user friendly command line window. It is also possible to restart and shutdown the instrument from the Raspberry Pi desktop. The Raspberry Pi requires a shutdown procedure, which can be done either physically with a switch on the side of the control box, or from the virtual desktop environment.

3.3 Processing of chromatograms

20   To process numerous chromatograms in an automated fashion, a script was created that uses calibration runs to accurately identify isoprene peaks in the sample runs and convert their integrated peak areas into mixing ratios. This script is written in Mathematica (v11.1.1). Figure 5 shows a flow diagram for the main algorithms of the script. Firstly the data is read in, making sure that all the files are the correct size and do not contain any erroneous runs (e.g., corrupted or truncated files) that may jeopardise the running of the script. Each chromatogram file has an index field, either S, X, C or B which indicate if the
25   chromatogram is a sample 1, sample 2, calibration or blank chromatogram respectively.

The calibration data is processed first. This involves selecting all calibration chromatograms (those with index 'C') and plotting them for visual inspection. The next step is to locate the isoprene peak and to fit a Gaussian curve to it to obtain peak height, width and position (equivalent to elution time), as well as the error in the fit. The elution time of the peak is retained in an interpolated function over time. The blank runs (with index 'B') are included in this routine as they effectively represent

5 calibrations with zero isoprene concentration. Subsequently, the peak area is plotted against the calibration volume multiplied by the isoprene concentration in the gas standard to obtain a response curve. A quadratic curve is fit to this data, which captures any slight deviations from linearity. Calibration procedures are described in depth in Section 4.1.

The sample chromatograms are then selected as either Sample 1 (runs with index 'S'), or Sample 2 (runs with index 'X') and, as with the calibration runs, they are plotted to visually inspect the data. Following that, a section of each sample chromatogram

10 is selected as the region where the isoprene peak is likely to reside. This is achieved by interpolating the retention times from adjacent calibration runs to the time of each sample runs, thus ensuring that the isoprene peak is identified correctly. A Gaussian is fitted to this section of the sample chromatogram to calculate all the peak parameters. The Gaussian function has certain boundaries set, to further ensure that it is fitted to the correct peak. Using the sample peak area, the sample volume and the calibration curve, the isoprene mixing ratio in the sample can be calculated.

15 When there are insufficient calibration chromatograms to determine the isoprene peak retention time, it can be estimated using the column temperatures from the nearest calibration runs. If the spacing between calibration points is too great or the calibration is done separately to the sampling, the interpolated calibration retention time values may not span the region where the isoprene peak resides. In this case the column temperature and retention time of the most recent calibration chromatograms are used to define a linear relationship. It is then possible to derive the isoprene retention time from the column temperature

20 of the sample chromatogram.

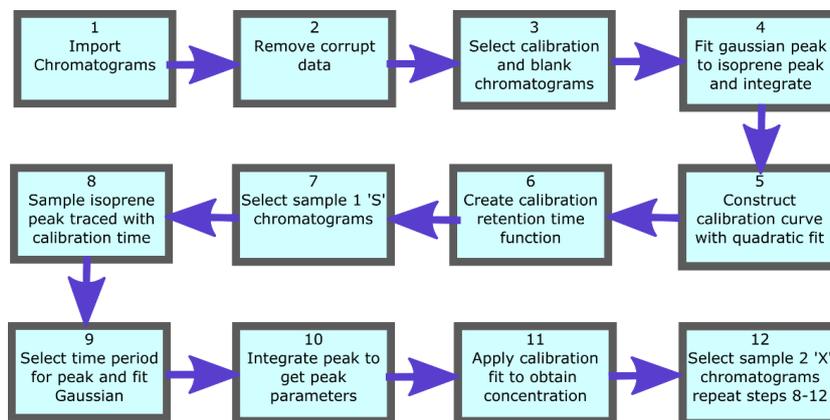



Figure 5: **Analysis script flow diagram**

4 Instrument performance

4.1 Calibration of output chromatograms

25 The PID response to isoprene is calibrated using a primary gas standard supplied by the National Physical Laboratory (NPL), certified as containing 5.01 ± 0.25 nmol mol^{-1} (or ppb) isoprene in a nitrogen matrix. The gas mixture is stored in a 10 L Experis cylinder (Air Products); this type of cylinder has been demonstrated to provide maximum stability for VOC mixtures over time (Allen et al., 2018). The primary standard is only used for calibration in the laboratory; for field deployments, a smaller secondary gas standard is used instead. This is prepared manometrically by diluting a higher concentration parent

30 mixture (100 nmol mol^{-1} isoprene in nitrogen, BOC) to approximately 10 nmol mol^{-1} with high-purity nitrogen (BIP+, Air Products). This secondary gas standard is prepared in a 500 mL Silconert-treated stainless steel cylinder (Sample Cylinder

Sulfinert, TPED, 1/4", Thames Restek). This type of treated cylinder exhibits very good long-term stability for a number of VOCs (Gary Barone et al. Restek Corporation, 2010). The exact isoprene amount fraction in the secondary standard is determined by validating it against the NPL primary standard. This way the measurements from the iDirac are traceable to accurate primary standards.

5   Frequent calibration is needed not only to convert chromatogram peaks into mixing rations, but also to monitor long-term trends in the detection system, including detector drift and decreasing performance of the adsorbent trap. Any changes in isoprene elution time, which may be caused by changes in oven temperature, can affect the correct peak assignment in chromatograms with multiple peaks. These effects can be easily addressed if frequent calibration chromatograms (which only have, by definition, one peak) are available.

10   Calibration frequency is specified by the user in the instrument set-up by selecting the number of samples to run between calibrations. For example, a calibration frequency of '4' would correspond to a run of four sample chromatograms, followed by a calibration run. No calibrations can be selected by inputting '999' (e.g., when there is no access to calibration gas), whilst a calibration-only run can be selected by inputting '0'. It is good practice to perform a calibration run periodically to ensure that the position of the isoprene peak can be traced. The exact number of sample chromatograms that can be run in that time

15   depends on the duration of the chromatographic run (which is designated by the user by specifying an 'inject time' and a 'backflush time') as well as on the volume of air sampled (also specified by the user), which in turn dictates the duration of the step in which the sample is pre-concentrated in the trap.

The calibration cycle is programmed to be preceded and followed by a blank run, in which the system samples from the high-purity nitrogen supply from Valve 4. This allows any residual isoprene in the trap to be desorbed before and after calibration,

20   and to monitor the efficiency of desorption over time.

A calibration curve is obtained by varying the volume sampled in each calibration run. When configuring the instrument, the user specifies a calibration volume in mL, which is sampled every other calibration run. For the remaining calibration runs, the instrument is programmed to sample a volume picked randomly from 5 possibilities: the user-specified calibration volume, the user-specified calibration volume multiplied by 2 or 4, and the user-specified calibration volume divided by 2 or 4. For

25   instance, for a run configured with a calibration volume of 12 mL, half the calibration runs would be of 12 mL samples and half a random mixture of 3, 6, 12, 24 and 48 mL samples. A typical time sequence of isoprene peak areas from different calibration volumes is shown in Figure 6. A calibration curve is then obtained by plotting these peak areas against the effective isoprene concentration (defined as the sample volume multiplied by the isoprene mixing ratio in the calibration cylinder). The zero concentration point is obtained from the blank runs. A quadratic is fitted to the calibration data. A typical calibration plot

30   is shown in Figure 7. The equation for the quadratic fit allows the determination of the fractional isoprene amount in the samples by extrapolation or interpolation, provided the sample volume and peak area are known.

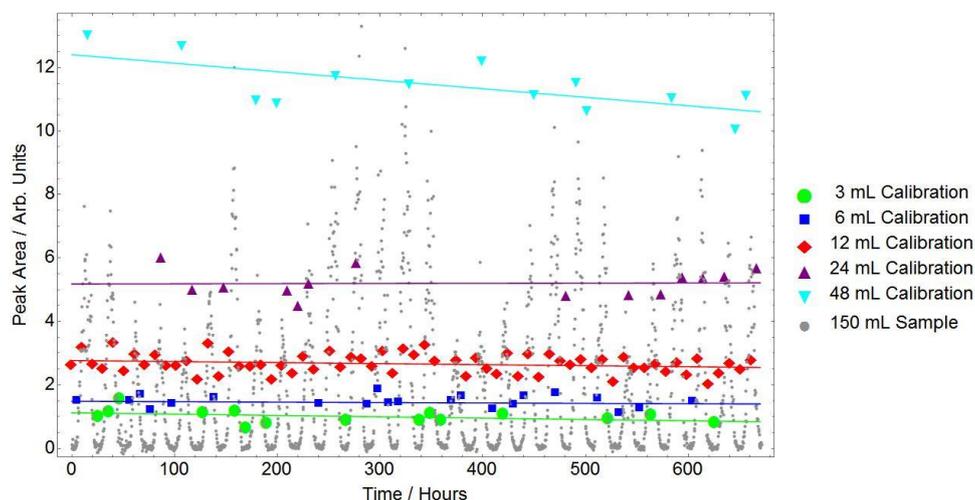



Figure 6: Typical sequence of isoprene peak areas for runs with varying calibration volumes. These are used to produce a calibration curve (see Figure 7). The calibration runs with the standard user-specified sampled volume (red data points) are used to calculate the instrument precision (see Section 4.2). Peak areas from sample runs (grey data points) are also shown to illustrate how the calibration peak areas span the entire range of sample values, minimising the need for extrapolation. This plot was produced using data from the Wytham field campaign (see Section 5.2).

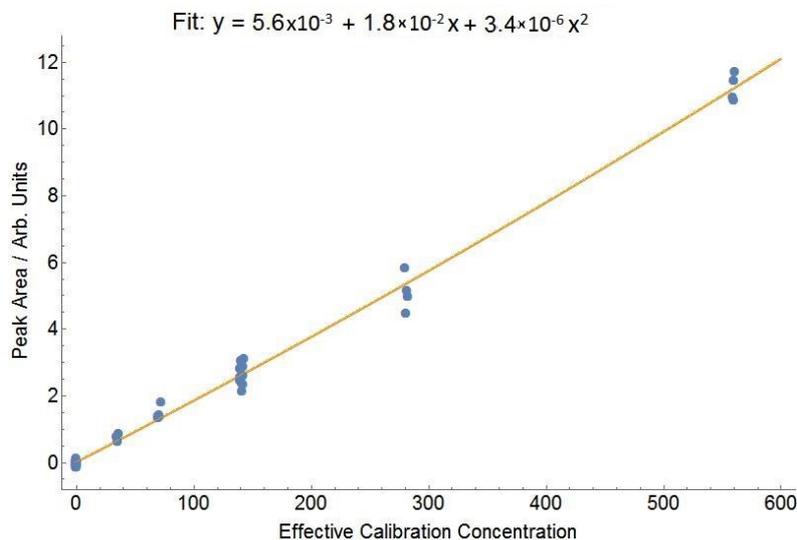



Figure 7: Typical calibration curve for isoprene. The x-axis ('Effective Calibration Concentration') consists in the calibration volume (in mL) multiplied by the isoprene concentration in the gas standard (in ppb).

As interpolation carries lower uncertainty than extrapolation, it is important to choose an appropriate value for the user-specified calibration volume, so that the points in the calibration curve span the entire range of the sample runs (as is the case in Figure 6). Typically, 12 mL is suitable in an environment with relatively low (< 1 ppb) isoprene concentrations (e.g. remote oceans), whilst a higher value (20 mL) is more appropriate when measuring in areas such as tropical forests.

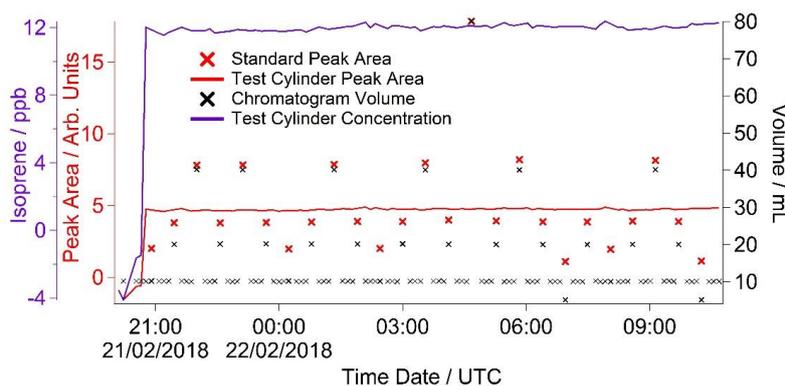
4.2 Precision and accuracy of iDirac data

Precision. The precision of the instrument was determined as the relative standard deviation in isoprene peak area from calibration chromatograms with the same user-specified volume (typically, more than 50% of the total calibration runs in any given measurement sequence, as detailed in Section 4.1) and from the same calibration cylinder. For instance, in the calibration sequence shown in Figure 6 and Figure 7, this corresponds to the runs of 12 mL samples. Following analysis of the scatter of

these data points, the instrument precision determined is ± 11.3% in the field (compared to <5% in the laboratory). This procedure means that the measurement precision can be routinely monitored over time which is especially useful in long deployments.

Accuracy. The accuracy of the instrument is dictated primarily by the uncertainty in the isoprene amount fraction in the NPL

5   standard, and how this is propagated to the isoprene amount fraction in the secondary gas standard used in the field. It is therefore essential that the concentration of the secondary calibration cylinder is determined as accurately as possible by comparing it to the NPL primary standard. This is carried out in the laboratory, typically before and after each field deployment. An example of this concentration determination is shown in Figure 8. XLGENLINE, a generalised least-squares (GLS) software package for low-degree polynomial fitting (Smith, 2010) is used to estimate the final uncertainty in the isoprene

10   amount fraction in the secondary calibration cylinder by inverse regression from the calibration curve. For most secondary calibration cylinders, this is estimated to ~ 7% at the $k = 2$ level (providing a coverage probability of approximately 95%). A similar procedure is applied to calibration and sample data from the field to estimate the uncertainty in the ambient isoprene concentrations. This is estimated to ~20-25 % at the $k = 2$ level.

15   **Figure 8: Summary plot of a concentration determination experiment. The primary reference gas mixture is used as the standard in the calibration runs, and the secondary gas mixture under test is used as sample.**

4.3 Sensitivity of the iDirac to isoprene

The instrument's sensitivity can be adjusted by changing the volume of the sample being analysed. For high concentrations (e.g. strong leaf emissions) a smaller volume should be used as the high concentration of isoprene would risk poisoning the

20   adsorption trap. The instrument has an effective upper volume limit of 250 mL (see Section 5.1) and a lower limit of 3 mL. The volume integration becomes unreliable below 3 mL due to the additional uncertainty brought about by the dead volume before the trap (approximately 1.6 mL). On the other hand, when ambient levels of isoprene are low (< 500 ppt), large sample volumes (200 mL) should be used. Sample volumes lower than or equal to 200 mL are used in order not to exceed the trap breakthrough volume (see Section 5.1).

25

The limit of detection is determined for a specific set of runs by allowing a signal-to-noise ratio (S/N) of 3. The blank runs are used to calculate the noise, which is defined as the standard deviation in the PID signal in a section of the blank chromatogram corresponding to the isoprene elution time. The instrument response factor is calculated from the isoprene peak height in the calibration runs and the isoprene amount fraction in the standard. This allows the calculation of the minimum concentration

30   needed to give rise to a signal that would return a S/N of 3. This is identified as the limit of detection and is calculated for two versions of the iDirac, the grey and the grange instruments. From the average of 20 calibration chromatograms, the limit of detection of the orange iDirac is 108 ppt and that of the grey iDirac is 38.1 ppt. This difference is attributed to the traps used

(i.e., a trap with more adsorbent would retain more analyte, resulting in a larger signal), as well as to the performance of the PID detector. The limit of detection can be monitored routinely during a deployment.

5 Tests in the laboratory and field deployments

The iDirac has been tested in a series of laboratory evaluations, at a deployment at a field station in a tropical forest in Sabah,
5   Malaysia and in a research forest in Wytham Woods, UK.

5.1 Laboratory Tests

Intercomparison of two versions of the iDirac. Two iDirac instruments (orange and grey) were compared against one another, with the two instruments sampling from a chamber containing a controlled isoprene concentration which was varied over time. The orange and grey iDiracs both had inlets inside the chamber with identical filters (polyethersulfone, 0.45µm
10   pore-size) and the same 1.5 m length of PTFE 1/16" tubing, placed as close to one another as possible. The gas within the chamber was well mixed with two large fans. Gas from a 700 ppb isoprene in nitrogen mixture (BOC) was flow-controlled into the chamber at 80 mL min^{-1} for different time periods to change the concentration. The chamber was not flushed and the only exchange out of the chamber was slight seepage through several small holes around the inlets. The concentration was varied stepwise from 0 to 12 ppb. The instruments were calibrated using the same calibration standard (8.3 ± 0.6 ppb isoprene
15   in nitrogen), which was connected to both instruments via a t-piece.

The results from this experiment are shown in Figure 9. The orange iDirac under-reads by 6.6% relative to the grey iDirac, and this is particularly evident at high concentrations. Figure 10 shows this data as a scatter plot of the 15-minute average values from either instrument, again it can be seen that the orange iDirac under-reads slightly. This under-reading is likely due to differences in the absorbent trap, leading to a lower sensitivity for the orange instrument. This is supported by the calibration
20   curve for the orange iDirac, which curves more at high concentrations, resulting in lower peak height than in the grey iDirac for the same concentration. Another artefact of this is that the noise visible on the orange output is greater. Adsorbent traps can be replaced on a regular basis to minimise such artefacts.

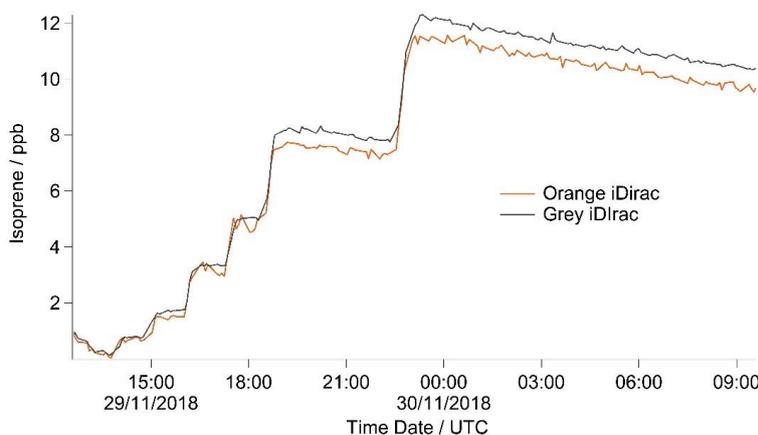



Figure 9: Time series plot showing isoprene mixing ratios from the grey and orange iDiracs

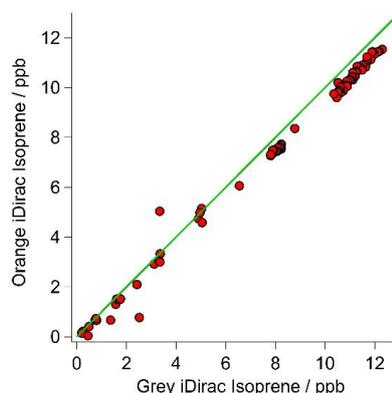



Figure 10: Scatterplot with 1:1 line showing 15 minute average values for the grey and orange iDiracs

Breakthrough tests. The breakthrough volume for the adsorbent traps used in the iDirac was determined. This is a test which

5   evaluates what volume of gas is so great as to cause isoprene to pass through the trap in a single sample run, and is typically

independent of the analyte concentration (Peters and Bakkeren, 1994). This test is performed by placing an additional adsorbent

trap in the instrument upstream of the main trap, at the exit of valves 1-4 from the valve box. Each run sampled 10 mL of an

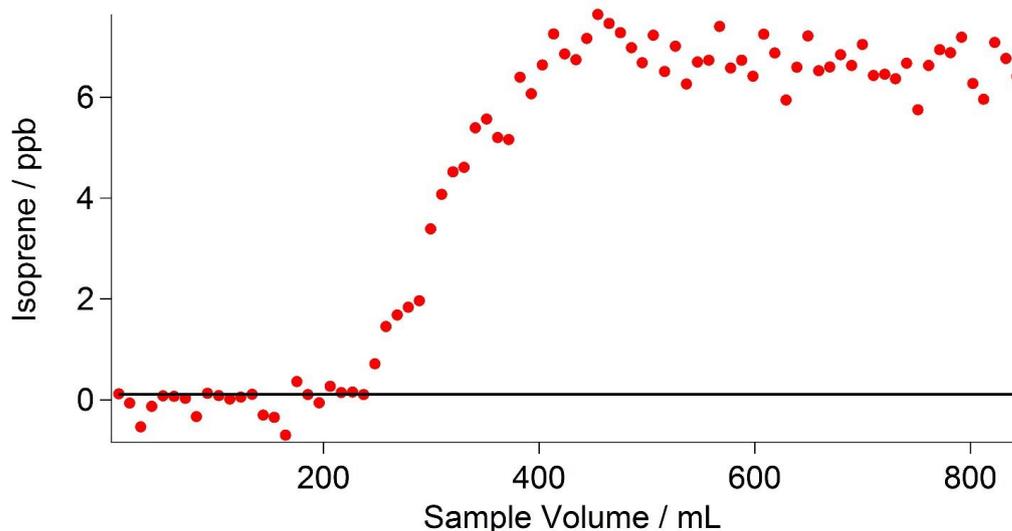
isoprene mixture of known concentration. When the breakthrough volume of the additional trap is exceeded, isoprene

effectively 'breaks through' onto the main trap, so that it is injected onto the dual column system and a peak is observed in the

10   chromatograms. The sum of all the volumes of the runs in which isoprene was not observed (i.e., pre-breakthrough) gives the

breakthrough volume. This value effectively acts as an upper limit of the volume of gas that the instrument can sample. Figure

11 shows a typical example of such test, in which a breakthrough volume of 250 mL was determined. The instrument is

therefore set to sample volumes up to 200 mL, so that the breakthrough volume is never exceeded.

15   **Figure 11: Results of the breakthrough volume tests. Each data point is an individual sample run of 10 mL. A solid black line indicates a threshold (set at LOD of 0.108 ppb), above which the breakthrough volume is exceeded.**

Co-elution of interfering species. The PID used in the iDirac is sensitive to all molecules with ionisation energies less than

or equal to 10.6 eV, which includes the vast majority of biogenic and anthropogenic VOCs with the exclusion of ethane,

acetylene, propane, methanol, formaldehyde and a number of halogenated hydrocarbons. It is therefore possible that species co-eluting at the same time as isoprene might be detected and erroneously identified as isoprene, thus leading to reporting of spurious concentrations. The stationary phase in the main column is selected to achieve good separation of isoprene from VOCs of similar polarity and boiling point. This is tested in a series of co-elution experiments, in which the elution time of a

5 number of potentially interfering species was determined and their separation from isoprene assessed. The VOCs under test were chosen based on the column specifications reported by the manufacturer, which identified i- and n-pentane, 1-pentene, trans- and cis-2-butene, 2-methyl-1-butene and 2-methyl-1-pentene as potentially co-eluting with isoprene. Gas samples containing 10-20 ppb of each interfering VOC are prepared in 3 L Tedlar bags by two-step dilutions from the pure substance using high-purity nitrogen. For each interfering species, the iDirac alternated between sampling from one of the Tedlar bags

10 and sampling from a gas cylinder containing only isoprene in nitrogen. The results of these measurements are summarised in Figure 12. Figure 12a illustrates overlaid chromatograms for each species, whilst the individual chromatograms are shown in Figure 12b-h. Figure 12i summarises the different elution times taking into account the width of each peak (full-width, half maximum) to better assess separation. The isoprene peak is well separated from all interfering VOCs, while we observe poor separation between cis- and trans-2-butene (which are not separated at all and appear as a single peak in Figure 12d) and 2-

15 methyl-1-butene, as well as between i- and n-pentane. These results lend confidence to the unequivocal assignment of the isoprene peak in each chromatogram. Work is ongoing to determine the elution time of a wider range of compounds, including oxygenated products from the oxidation of isoprene.

Co-elution and multiple peaks appearing in a chromatogram are also addressed in the Mathematica script described in Section 3.3. To ensure that the isoprene peak is correctly assigned, the script looks for a peak in a relatively narrow region of the

20 chromatogram, which is based on an interpolation of the elution time from the two nearest calibration runs. This algorithm has relatively low tolerance, so that peaks that are more than 4 s away from the predicted isoprene elution time are not considered. We observe a consistent discrepancy in isoprene elution time between the calibration and sample runs. The elution time of isoprene is typically 1.7 s greater in a sample run than in a calibration run. This is an artefact of the trap adsorption process and the resulting tailing of the peak. For large volumes and low concentrations (e.g., a 150 mL field sample at 0.5 ppb), the

25 isoprene band in the adsorbent trap is very broad and resides in the trap for a longer time, so it tails very strongly. For a high-concentration low-volume sample (e.g., a 12 mL calibration run at 10 ppb), the isoprene band in the trap adsorbent is very sharp; it desorbs quickly and hence it tails less. This difference in elution times is much smaller than the distance to nearest interfering species (2-methyl-1-pentene, which elutes ~7 s before isoprene).

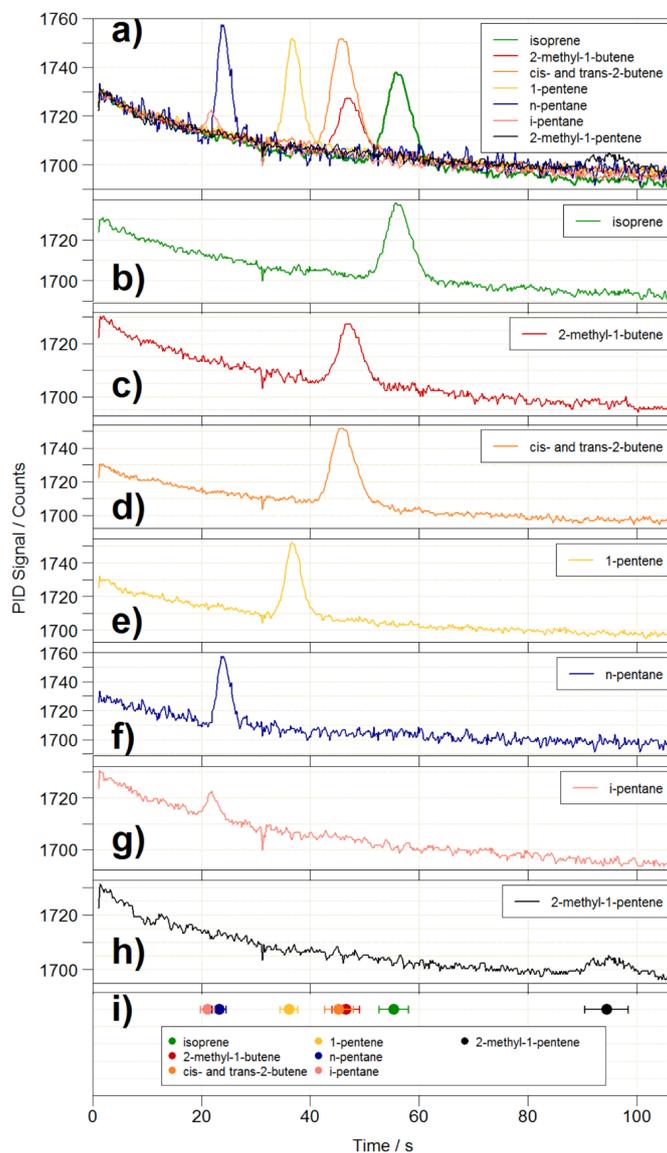



Figure 12: Results of the co-elution tests on the iDirac. a) Overlaid chromatograms of isoprene (green line) and six potential interfering species: 2-methyl-1-butene (red line), cis- and trans-2-butene (orange line), 1-pentene (yellow line), n-pentane (blue line), i-pentane (pink line) and 2-methyl-1-pentene (black line). The chromatograms of each individual species are shown in panels b)-h). The co-elution tests are summarised in h), where the elution time of each species (filled circles) is plotted along with its peak width (FWHM, error bars) to assess peak separation.

Long-Term Tests. The performance of the instrument in the field for long periods of time has been assessed in several deployments. These are described in detail in Section 5.2

5.2 Deployment of the iDirac in Sabah, 2015

Following laboratory development and testing, the iDirac had its first field deployment in Sabah (Malaysian Borneo) as part of the Biodiversity and Land-use Impacts on Tropical Ecosystem Function (BALI) Plant Traits campaign. This campaign ran from May to December 2015. The instrument was principally used to carry out individual leaf measurements in the field. The results from the individual leaf measurements are being written up for publication elsewhere.

The other type of measurements taken in Sabah during this timeframe were longer duration runs, in which the instrument took autonomous measurements of ambient air at the field site continuously. These measurements consisted in attaching the iDirac to a tree at a height of approximately 1 m, with a battery and a 1.2 L N_2 cylinder attached to it, and running repeat samples until either the battery ran flat or the gas supply was exhausted. The aim of these measurements was to obtain an isoprene

5 diurnal profile and observe how this varied with different types of forest. These tests also allowed us to test the feasibility of leaving the instrument running for long periods of time. A picture of the iDirac measuring ambient air in the rainforest in Borneo is shown in **Error! Reference source not found.**.

The ambient air measurements demonstrated that the instrument can easily measure the changes in isoprene concentration in the ambient air and that the inlet drying system could cope with the high humidity of the rainforest. An example from a

10 secondary forest site is shown in Figure 14. This was the first deployment for the iDirac, and it proved to be a success in taking reliable measurements. It also highlighted areas for instrument development (e.g., calibration routine) and several issues with instrument function (e.g., warm-up time) that had been addressed in subsequent versions.

Figure 13: iDirac deployed in a tropical forest environment

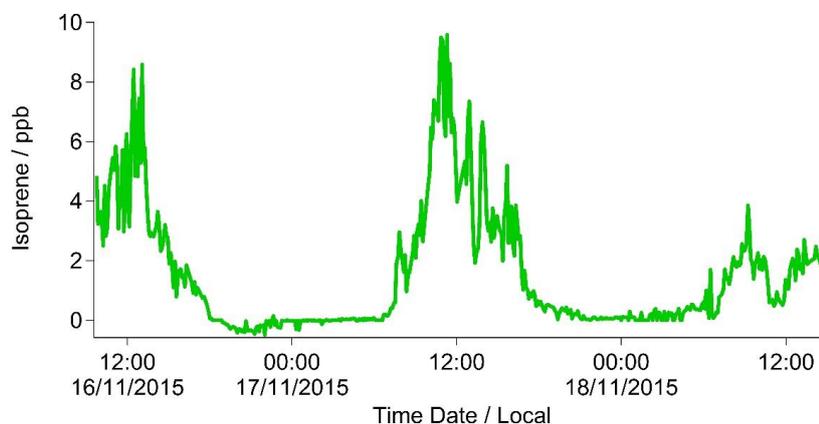



Figure 14: Time series for isoprene at secondary forest site in Sabah (Malaysian Borneo) in 2015

5.3 Deployment of the iDirac in Wytham Woods (University of Oxford)

5.3.1 Experiment description

The instrument was deployed at Wytham Woods (Oxfordshire, UK), a temperate mixed deciduous forest owned and managed by the University of Oxford. A large fraction of trees at this site are Pedunculate Oaks (*Quercus robur*), which are known

5   strong isoprene emitters (Lehning et al., 1999). One iDirac was deployed on the canopy walkway facility, a platform ~15 m above ground resting on a scaffolding support allowing access to crown-level measurements, while another iDirac was installed at ground level. As each instruments has two inlets, this allowed sampling at four heights across the canopy with a view to investigate the isoprene concentration gradient within the canopy. Both iDiracs were run off-grid, powered only by solar-powered batteries. The experiment and results are described in detail in Ferracci, et al., *in prep*. Data was collected from May

10   – October 2018, and here the performance of the instruments is assessed for more than five months of continuous use in a forest environment.

5.23.2 Results and discussion

The iDirac captured isoprene concentrations from 25 May to 29 October 2018. Gaps in the data were generally due to power issues arising from insufficient solar charging of the batteries. A section of the isoprene time series is shown in Figure 15. The

15   diurnal pattern of isoprene is clearly visible, and the vertical concentration gradient is also apparent.

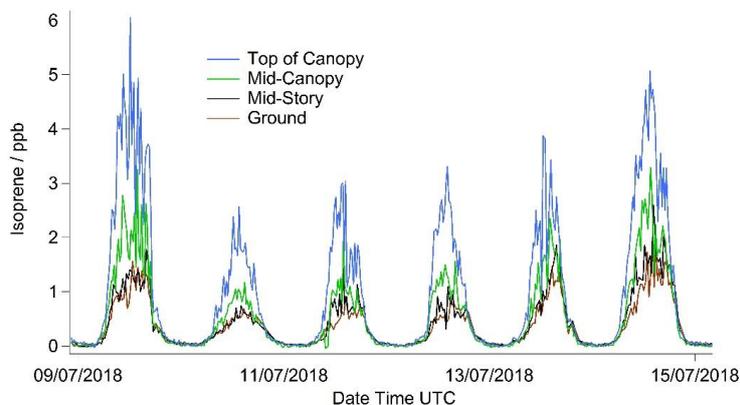



Figure 15: Portion of the isoprene mixing ratio time series measured at Wytham Woods (UK) at four heights within a forest canopy in the summer of 2018.

The iDirac proved capable of measuring isoprene abundances continuously through the day, spanning from concentrations as

20   high as 8 ppb in the height of the summer and to effectively zero at night-time.

The lifetime of the absorbent trap can be assessed by examining the calibration curves over time. The dataset is analysed in weekly segments, with a calibration curve constructed for each week. This allows for the calibrated data to account for any drift in sensitivity. The calibration plots exhibit a clear drift as time progresses, as shown in Figure 16, with calibration chromatograms later in the time series showing lower peak area for the same concentration.

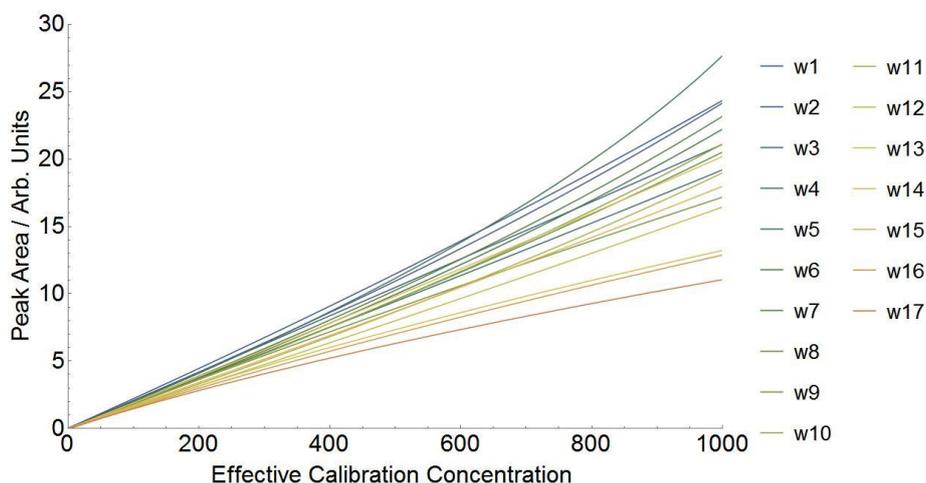



Figure 16: Calibration curves plotted in weekly intervals, showing decreasing sensitivity over time.

This drift is attributed to the gradual degradation of the trap as a result of repeated absorption/desorption cycles, with exposure to high concentrations of VOCs and oxygen. It is likely that the absorbent in the trap becomes 'poisoned' over time and

5 eventually needs to be replaced. We are contemplating ways to mitigate this effect, including using a combination of adsorbent materials within the trap so that large VOCs can be prevented from poisoning the adsorbent bed sensitive to isoprene.

A slight curvature can be seen in the calibration curves. This behaviour increases over time and is attributed to the occurrence of a slight breakthrough, as at high concentrations and/or high volumes, some isoprene is not absorbed by the trap. This further supports the implementation of frequent calibration runs in the current measurement sequence used.

10 Decreasing sensitivity would obviously affect the limit of detection of the instrument. During a particularly long deployment such as that in Wytham Woods, it is important to monitor the sensitivity by means of plots such as that in Figure 16 to establish better when the trap needs to be replaced.

6 Conclusions and future work

We described the development and subsequent deployment of the iDirac, a novel autonomous GC-PID for isoprene

15 measurements in remote locations. The instrument pre-concentrates ambient VOCs on an adsorbent trap and then separates them in a dual column system kept in an isothermal oven before detection by a photoionisation detector, achieving a limit of detection for isoprene down to 38 ppt. The rugged design and modular construction make the instrument easily customisable, while the open source software control results in a straightforward instrument configuration. Designed for field deployments in remote environments with limited power supply, the iDirac weights 10 kg (excluding gas supply), consumes minimum

20 power and gas, can be run autonomously for months with little maintenance and can be exposed to harsh environmental conditions. The sensitivity and linearity of the instrument response can be tracked effectively with regular calibrations, increasing confidence in the quality of the data. The instrument has been demonstrated to function as desired in a tropical and temperate forest in two lengthy field campaigns, in particular in summer 2018 in an Oxfordshire forest with near continuous operation for almost 6 months. While this paper focused on using the iDirac for isoprene measurements, the instrument

25 configuration can be changed to target different analytes. Future work will focus on monitoring different VOCs (e.g., DMS and ethylene), as well as improving on some of the current limitations of the instrument, such as implementing a more sophisticated and interactive control over the oven temperature.

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