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**$\mu$ Dirac: an  
instrument for  
halocarbon  
measurements**

B. Gostlow et al.

# $\mu$ Dirac: an autonomous instrument for halocarbon measurements

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## Abstract

We describe a new instrument ( $\mu$ Dirac) capable of measuring halocarbons in the atmosphere. Portability, power efficiency and autonomy were critical requirements in the design, and the resulting instrument can be readily deployed unattended on a range of platforms: long duration balloon, aircraft, ship and ground based stations. The instrument is a temperature programmed gas chromatograph with electron capture detector (GC-ECD). The design requirements led to  $\mu$ Dirac being built in-house with several novel features. It currently measures a range of halocarbons (CFCs and shorter-lived halocarbons having biogenic and anthropogenic sources) with measurement precisions ranging from  $\sim 1\%$  sd ( $\text{CCl}_4$ ) to  $\sim 9\%$  sd ( $\text{CH}_3\text{I}$ ). Since the prototype instrument was first tested in 2005 the instrument has been proved in the field on technically challenging aircraft and ground based campaigns. Results from one aircraft and two ground-based deployments are described.

## 1 Introduction

Halocarbons in the atmosphere were first observed by Lovelock (1971) using a gas chromatograph (GC) after his invention of the electron capture detector (ECD – Lovelock and Lipsky, 1960; see also Morris and Ettore, 2007). His initial atmospheric use for his GC-ECD was to measure CFC-11 and CFC-12, but it was soon also used to measure  $\text{CH}_3\text{I}$  and  $\text{CCl}_4$  in air and water (Lovelock et al., 1973). Since those early beginnings, observations of atmospheric halocarbons have proven essential to improving our understanding of the interplay between different atmospheric processes in many regions of the atmosphere. Due to the wide range of atmospheric lifetime (hours to centuries) and varied sources (natural and anthropogenic; marine and terrestrial), halocarbons are valuable in tracing air mass origins and understanding dynamical and chemical processes. Observations of short-lived compounds can reveal the presence of biogenic sources (e.g. oceanic, biomass burning).

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based on a GC-ECD system and is capable of making measurements of halocarbons with a range of atmospheric lifetimes and sources, including a number of short-lived gases such as  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Br}_2$ ,  $\text{C}_2\text{Cl}_4$ ,  $\text{CHBr}_2\text{Cl}$ ,  $\text{CHBr}_3$ , and  $\text{CH}_3\text{I}$  present at and below part per trillion (ppt) levels. The flexible, lightweight and autonomous design of  $\mu$ Dirac means that a range of uses can be envisioned, with only relatively minor adaptations being required. In this paper we describe in Sect. 2 the core GC instrument which is common to all deployment scenarios. In Sect. 3 we describe instrument adaptations which are specific to the type of deployment: MIR (Infra-Red Montgolfier) long-duration balloon; lower tropospheric aircraft and ground based campaigns. Section 3 discusses instrument performance in terms of halocarbon sensitivity, measurement precision, accuracy and sampling frequency. Recent results are presented in Sect. 4.

## 2 Instrument description

$\mu$ Dirac is a gas chromatograph (GC) with electron capture detector (ECD) which makes in situ measurements of halocarbons. To meet the exacting requirements of flight on MIR balloons it had to be lightweight, low power and able to operate autonomously for several weeks; as such it has been almost completely designed and made in-house. Section 2.1 describes the instrument core which is common to all uses. Specific requirements for MIR balloon, aircraft and ground based deployments are presented in Sect. 2.2–2.4.

### 2.1 Core GC

The core GC has a modular design which consists of: an inlet manifold for selection of sample/calibration air or helium purge gas; a sample adsorption/desorption system; a temperature programmed column for separation; and an ECD for detection (Fig. 1). Nitrogen and helium carrier gases are pressure-controlled as is the detector cell. Sample (or calibration) air passes through an adsorbent-containing micro-trap which re-

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moves the halocarbons from the flow stream. After the sample has been collected, the micro-trap is flash heated and the desorbed halocarbons are passed through a chromatographic column with temperature and flow programming capability. After temporal separation in the column, the target compounds pass through the ECD. The absolute calibration is determined by reference to on-board NOAA-ESRL calibration standards. The overall time resolution is determined by the timing sequence and is typically 8–15 min depending on the range of species being measured (Fig. 2). We now describe each element of the core GC in more detail.

*Inlet manifold.* This consists of: three solenoid valves acting as stream selectors; a Valco valve; a flow isolation solenoid valve; and a flowmeter for volume determination. The three solenoid valves are independently controlled and allow sample air, calibration gas or helium purge gas to be selected. The helium purge gas passes through a stainless steel purifier tube packed with 40/60 mesh molecular sieve 13X and 40/60 mesh SK4 charcoal to remove moisture and other contaminants. The solenoid valve actuators (Pneumax, model N372-3) are mounted on custom made polyetheretherketone (PEEK®) bases made by Valco Instruments Co. Inc. (VICI). The Valco valve is a 6 port, 2 position rotor valve with 1/32" 0.25 mm ID ports (VICI, model 4N6WE) and it is actuated by a metal geared servo motor (Hitec, model 645MG). Downstream of the Valco valve, a solenoid valve directs flow through the flow meter (Sensirion, model ASF1430) until the target volume is reached. All tubing used on the inlet manifold is 1/32 OD, .020" ID PEEK® (Upchurch Scientific, part no. 1569).

*Sample adsorption/desorption system.* Halocarbons present in the sample air or calibration gas pass through the inlet manifold to the Valco valve. Mounted across the Valco valve is an in-house adsorption/desorption tube made from a 200 mm length of 0.8 mm OD, 0.53 mm ID methyl deactivated metal tubing (Varian, part no. CP6540). The tube contains two beds of carbon molecular sieve adsorbent, the first is ~1 mg of 60/70 mesh Carboxen™ 1016 and the second bed is ~1 mg 45/60 mesh Carboxen™ 1001. Sample air (or calibration gas) reaches the bed of Carboxen™ 1016 first and this preferentially adsorbs compounds with a high boiling point. Compounds with low

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boiling points pass readily through the bed of Carboxen™ 1016 and are adsorbed by the Carboxen™ 1001. The adsorption stage is typically performed within a temperature range of 15 to 25°C. For the desorption stage the tube is first purged with helium to remove oxygen before the Valco valve is turned to the “inject” position. The adsorbent tube is then flash heated to match pre-determined set points (typically 170°C for 15 s) in a reverse flow of helium carrier gas. The target compounds are rapidly desorbed and pass with the helium carrier flow onto the separation column. A typical trap has a mass of 0.35 g and resistance of 560 m Ω. Before flash heating the control software checks that the trap resistance falls within a safe window and that the under-load output of the battery is satisfactory (>7.5 V and typically 8.12 V). With over 100 W available the trap reaches the set-point temperature in about half a second. The trap temperature is calculated from the resistance using prior oven calibrations. Mark space control is applied to maintain the resistance of the trap within a mΩ or so of the set point until the flash period is complete.

*Temperature programmed column.* The capillary column is a 10 m long, 0.18 mm ID MXT502.2 (Restek®, model 71891). This Silcosteel® treated stainless steel column has an inner wall coating of Crossbond® diphenyl/dimethyl polysiloxane phase with a film thickness of 1 μm. The column is mounted in an armature consisting of two waterjet cut anodised aluminium end plates held apart by Vespel spacers. The column is double wound and supported by a series of Teflon® “combs”. The armature and column together have a mass <40 g. The column inlet is linked to the Valco valve by a 30 cm length of 0.4 mm OD, 0.18 mm ID Silcosteel® treated stainless steel transfer line (Restek®, model RE51166). Direct electrical heating is applied to the column, 10 m of which has a resistance of ~112Ω. A centre tap is made and the two halves heated in parallel (28Ω) and a 24 V supply provides at most 26 W. An additional 30 W heating is applied to the aluminium endplates through pairs of 75Ω patch heaters (Minco, part no. HK913F type F). The response of the column is extremely fast compared to the endplates, but 26 W alone is not enough for fast ramping of the column temperature. In operation the endplates may fall behind by perhaps 10°C but the fast response and the

direct heating of the column ensure that the desired temperature profile is achieved with a very small error. Column and endplate heating are under PID mark-space control. A typical temperature program consists of a 2 minute run-in at 25°C followed by a linear ramp to 175°C at 30°C min<sup>-1</sup>, finishing with a 2 min isothermal run-out at 175°C (Fig. 3).

For aircraft and ground based deployments the column and cage are mounted in an oven enclosure made from 5 mm foamboard and internally insulated with Microtherm® thin sheet and Mylar® film. At the end of each heating cycle, a small 40 mm fan cools the column to the initial starting temperature for the next cycle. For the MIR balloon deployment the column assembly is mounted in a polystyrene housing which is located underneath the instrument away from solar radiation. This allows the column to be cooled by a fan drawing in external air at an ambient temperatures as low as -60°C.

*Helium pressure controller.* To achieve reproducible peak retention times it is necessary to control the helium carrier gas flow, and a novel regulator has been developed to achieve light weight and software control. A Pneumax N372-3 solenoid valve controls the input of helium into small reservoir through a restrictor formed from a 20 cm length of 1/32" OD 0.0035" ID PEEK® capillary tube. The pressure in the reservoir is sensed using absolute pressure sensors (Honeywell, model ASDX030A24R) and once it falls below a dynamic threshold the valve is opened to admit helium until the upper threshold is reached. This results in a saw-tooth pressure profile. A second reservoir is connected by a 15 cm length of 1/32" OD 0.0035" ID PEEK® capillary tube forming, by analogy, a low pass filter. The pressure in this second, output, reservoir is also measured and fed into the PID control. In this way the column head pressure is controlled to within 0.2% relative standard deviation (RSD) of the setpoint. The column head pressure is programmable and can be ramped with set points and ramp rate held in eeprom. As the column temperature goes up, the increase in viscosity of the helium carrier gas results in a decreased flow for a constant column head pressure. To maintain the optimum carrier flow rate (~0.3 cm<sup>3</sup> min<sup>-1</sup>) the helium column head pressure is ramped. A typical helium pressure program is 127 kPa for the 2 min isothermal run-in followed by a linear ramp to 143 kPa at 3 kPa min<sup>-1</sup>, finishing with a 2 min run-out at

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143 kPa. The outflow from the pressure controller is passed through an in-house purifier. At the end of the cycle a solenoid valve quickly vents enough helium to return the pressure to the initial value.

*Detection system.* The column outlet is electrically isolated by a PEEK® union and connected to the detector by a 30 cm length of 0.4 mm OD, 0.18 mm ID Silcosteel® treated stainless steel transfer line. Target halocarbon molecules pass into the cell of the micro-volume ECD (Agilent Technologies, model G2397-60510) where they are ionised within an electron field formed by ionisation of a nitrogen make-up gas from primary electrons emitted from a  $^{63}\text{Ni}$  foil. An electrometer maintains a constant current across the cell and the pulse frequency increases when electron-capturing molecules enter the cell. The electrometer has an ultra-low bias current operational amplifier (Burr Brown OPA129) at its front end. Control over “constant” current and offset is made possible using digitally controlled potentiometers. At the output a 16 bit analogue to digital converter “oversamples” at 20 ms intervals and averages to produce the final 5 Hz output. The sensitivity of the ECD is highly temperature dependent and so the detector temperature is precisely controlled (typically at 260°C). The detector is coupled to an aluminium heating block with cartridge heater and PT100 temperature sensor; the detector heater is PID controlled to within 0.1% RSD of the setpoint. The detector assembly is mounted in an stainless steel vacuum flask for thermal insulation. The detector has an internal cell of  $0.15\text{ cm}^{-3}$  and is ideally suited to capillary column chromatography. The detector has a hidden anode design to minimise the need for cleaning and is furnished with a nitrogen anode purge flow in addition to a nitrogen make-up gas flow.

*Nitrogen pressure controller.* Nitrogen is used for the anode purge and make-up flow. Precise control of these flows is achieved by a pressure controller similar to that used for controlling the helium carrier head pressure but without the need for a vent valve. The output nitrogen pressure is controlled to within 0.1% RSD of the setpoint. The make-up flow is typically  $5\text{ cm}^3\text{ min}^{-1}$  and the anode flow is typically  $0.5\text{ cm}^3\text{ min}^{-1}$ . Flow rates can be adjusted by changing the output pressure set point or by changing

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the length of the PEEK® capillary flow restrictors. The nitrogen is purified at the exit of the pressure controller using an in-house purifier.

*Back pressure controller.* The detector response is sensitive to changes in atmospheric pressure which can be large during airborne deployments. In addition, changes in atmospheric pressure during ground-based deployment can cause small changes in peak retention times. It is thus necessary to control precisely the ECD cell pressure (back pressure). This is achieved by using a pressure controller similar in design to the nitrogen pressure controller but controlling an upstream (back) pressure rather than a downstream head pressure. The back pressure is typically 110 kPa and is controlled to within 0.2% RSD of the setpoint.

*Electronics backplane.* Software control is integral in the design of  $\mu$ Dirac. The electronic design is modular and consists of a backplane with sockets for nine small plug-in boards and linked peer-to-peer by RS485. Each board has its own PIC microcontroller so that the processing tasks (e.g. flow control, ECD electrometer, column oven ramping) are distributed. The “primary” control board runs the chromatographic method in flash memory and can store data locally on removable 32 MB Sandisk MMC. It handles communication with the PC user interface. For aircraft and ground based deployments it is convenient to store data on the PC using USB flash memory. The user interface was developed using Visual Basic 6.0 (Microsoft®) and permits remote operation.

*Control.* A consistent design aim has been to make all parameters configurable and held either in eeprom or flash memory. The instrument is either quiescent, where parameters such as gas pressures are maintained or it is operating in program mode. The chromatographic method is written as a .csv file using a spreadsheet such as Excel before being compiled and passed to the instrument where it is held either on SanDisk MMC or in flash memory. The user has almost complete freedom to configure temperatures, pressures, timings and so on. In addition the user can call for parameters to be recorded in a system file at run time, for example, sample volume for later analysis. Once the instrument has been deployed, it is possible to remotely view/edit instrument parameters or download a different chromatographic method. Remote operation is

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possible using LogMeln control software.

*Power supplies.* The core GC is designed to operate from a 24 VDC supply to allow flexibility of deployment. The column and detector ovens use this supply directly. DC/DC converters provide regulated power for solenoid valves at 12 VDC with further regulation to 5 VDC for the electronics. The electrometer requires regulated  $\pm 15$  VDC power which is provided from a DC/DC converter. The thermal desorption system requires a 12 VDC high current supply, provided by a battery pack using NiMH cells and maintained by a trickle charge. If 100/240 VAC mains power is available the instrument can be powered from a regulated 24 VDC power supply backed up by a commercially available uninterruptible power supply (UPS). Alternatively, batteries may be used: primary lithium cells (Saft, part no. G62) in the example of MIR balloon deployment; pairs of 12 VDC battery packs set in series, each consisting of 10 rechargeable NiMH cells; lead acid car batteries.

## 2.2 Requirements for MIR balloon deployment

The MIR balloon platform has been in development since 1977 by the Centre National d'Etudes Spatiales (CNES, Toulouse, France). It is a hot air balloon of 36 000 to 45 000 m<sup>3</sup> though it is lifted to the stratosphere by helium which exits from the balloon during the first few days of flight. The balloon is heated by radiative fluxes from the sun by daytime and upwelling infrared fluxes during the night which causes the balloon to rise at dawn and descend at sunset, enabling vertical profiles to be measured. The night-time air temperature inside the balloon envelope needs to be  $>15^{\circ}\text{C}$  higher than the ambient air to keep a balanced float level and for this reason the envelope is optimized to capture infrared fluxes rising from the earth (about  $250\text{ Wm}^{-2}$  available at float level). The balloon can carry a maximum payload at its hook of  $\sim 50$  kg.

This is the most technically challenging deployment for  $\mu\text{Dirac}$  as the core GC needs to make scientifically useful measurements at very low atmospheric pressure (5 to 80 hPa) and at very low air temperatures ( $-20$  to  $-60^{\circ}\text{C}$ ). The gondola (supplied by CNES) provides protection during launch and thermal insulation when aloft, power and

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communication throughout the 30 day mission. We now describe how each of these technical requirements is achieved.

*Sampling pump and inlet.* The challenge for the pump is to deliver an uncontaminated supply of sample air at high enough pressure to generate a flow through the sampling manifold including the Valco valve and adsorbent trap. A commercial diaphragm or metal bellows pump cannot be used due to power, weight and contamination issues. Instead the design is in-house, based on two 100 cc glass laboratory syringes each with a solenoid valve for flow control. The syringes are each driven by a gas actuated cylinder with magnetic/reed switch stroke detection and are operated 180° out of phase (Fig. 4). A differential pressure sensor is used to determine when the pump pressure is sufficiently high to be directed into the sample stream selector valve of the core GC. The target sample volume was 5 cm<sup>3</sup> at standard temperature and pressure (STP) which could be obtained by about 3 pump cycles at an ambient pressure of 20 hPa. Each syringe is fitted with a 2 m length of high purity Teflon PFA inlet tubing which reaches outside and below the gondola to allow sampling of uncontaminated air during descent.

*Helium and nitrogen gas supply.* The core GC requires sufficient nitrogen, helium and calibration gas for the duration of the MIR balloon flight. We assume a duration of 30 days, though MIR balloons have previously remained aloft for over 11 weeks. The nitrogen and helium supplies are stored in 1.5 litre aluminium/glass fibre composite cylinders (Structural Composites Industries Inc., part no. ALT816E), each equipped with a three way filling valve (Swagelok, part no. SS-42GXF2). The cylinders are filled to ~200 bar with grade 6.0 nitrogen and helium. The helium and pressure controllers in the core GC require an input pressure of 3 to 5 bar absolute and this is delivered by high purity absolute pressure regulators (Swagelok, HF series). The sampling pump actuators also require a delivery pressure of 3 to 5 bar and this is supplied from the output of the HF series helium regulator via a tee.

*Calibration gas supply.* The core GC requires regular calibration during the balloon flight. Typically a calibration chromatogram should be run at the start and end of each

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vertical profile. There is also a calibration mode which generates a five point calibration response curve to enable correction for instrument non-linearity effects. The calibration gas supply is stored in a 75 cc double ended Sulfinert treated cal gas cylinder (Restek, model 24130), equipped with a stainless steel bellows filling valve (Swagelok, model SS-4H-V51). The cylinder is rated for a filling pressure of 120 bar, in practice we fill to  $\sim 68$  bar (the bellows valve rated pressure) by decanting from a 29.5 litre Aculife-treated aluminium cylinder containing Niwot Ridge air which is compared to NOAA-ESRL halocarbon standards (Hall et al., 2001). The core GC requires a calibration gas pressure of  $\sim 2$  bar absolute delivered by a high purity absolute pressure regulator (Swagelok, HF series). The output port from the pressure regulator is connected to the calibration stream selector valve using  $1/32''$  OD  $0.0035''$  ID PEEK capillary tube which restricts the flow through the core GC to  $\sim 5 \text{ cm}^3 \text{ min}^{-1}$ .

*Power consumption.* The overall power consumption while measurements are being made reaches a peak of 50 W and drops to 10 W or less while the instrument is in quiescent mode. When flying, it only measures for a few hours each day when the balloon altitude changes at sunrise and sunset so that it can be quiescent for most of the time. The CNES gondola provides power from primary lithium cells together with a nominal 24 V electrical supply from 6 solar panels. During daylight the solar power is configured to heat the detector oven and minimise drain of the on-board lithium battery.

*Armature, housing and weight.* The core GC, pump and gas supply are all supported on an armature constructed from light weight honeycomb composite sheet (Aim Composites, Flitelam) (Fig. 4a). The instrument is housed inside the CNES gondola made from polystyrene (EPS150 of  $25 \text{ Kg/m}^3$ ) which also contains the lithium battery packs and communications module (Fig. 4b). The column oven is situated in the base of the gondola to assist in rapid cooling at the completion of each sample run. The overall weight of the MIR instrument (core instrument, pump and gas packs) is  $\sim 11$  Kg.

*Communication.* Each balloon profile is initiated by sunrise or sunset and the instrument needs to anticipate these events by an hour. On receiving a ‘wake-up’ command from a CNES payload service board (PSB) the instrument becomes active, tempera-

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ture and pressure set points stabilise and a calibration run is carried out. Data is then passed to the PSB module for upload via a CNES module which is in direct communication with the INMARSAT satellite network. Throughout the profile, as each run is completed, data is passed to the PSB module. Through commands input in Toulouse, the PSB is also able to switch the instrument between 7 different operating modes or methods. The PSB is equipped to turn the instrument on or off.

All these features were tested at low temperature and low pressure prior to flight in the CNES stratospheric simulator, with  $\mu$ Dirac successfully running (a) overnight at  $-60^{\circ}\text{C}$  and (b) simultaneously at 100 hPa and  $-60^{\circ}\text{C}$ . The full communications system between the instrument and the CNES PSB was also tested up to and including upload of data to satellite via ISBA and download to Toulouse and the mirror site in the Seychelles.

### 2.3 Requirements for aircraft deployment

Here we describe the technical requirements needed to support the core GC for a low altitude (<5 km) deployment on the NERC airborne research and survey facility (ARSF) Dornier 228 aircraft in the Cape Verde Islands. This was a technically easier deployment than the MIR balloon flight as aircraft power was available, sample collection was easier (higher ambient pressure), the degree of required autonomy was lower (typical aircraft flight was 4 h duration) and the thermal environment was less extreme.

*Sampling pump and inlet.* For low altitude operation the sampling pump is located at the exit of the core GC to minimise the risk of sample contamination as the required pressure differential across the inlet manifold can easily be obtained from a partial vacuum reservoir. In practice, the sampling pump (Uno International Ltd, model Boxer DF-18) maintains a sub-ambient reservoir of  $\sim 16$  kPa inside a 600 ml canister. Using a reservoir in this way provides the means to control the flow-rate through the core GC between 5 and  $20\text{ cm}^3\text{ min}^{-1}$ . The sample inlet line of the core GC is connected to the aircraft's main inlet tubing. The main inlet is a  $\sim 10$  m length of high purity Teflon PFA 1/4" OD 0.188" ID tubing and is flushed at a flow rate of  $\sim 1\text{ L min}^{-1}$  using a miniature

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rotary vane pump. The sample flow passing into the core GC is dried using a dessicant membrane drier (Perma Pure LLC, model DM-060-24).

*Helium, nitrogen and calibration gas supply.* The core GC requires sufficient helium, nitrogen and calibration gas for several days of operation as refilling the gas cylinders is difficult on an aircraft. For the Dornier 228 deployment a gas pack separate to the core GC was constructed from honeycomb composite sheet which secures the cylinders inside the housing. The 6.0 grade helium and nitrogen are stored in aluminium cylinder (Catalina Cylinders). Each cylinder is equipped with a three way filling valve (Swagelok, part no. SS-42GXF2). The cylinders are filled to 120 bar and protected from over-pressure by a burst disc. The calibration gas system is identical to that for the MIR deployment except that a larger cylinder with a volume of 150 cm<sup>-3</sup> is used. A full gas pack can run the instrument for ~10 days of continuous operation.

*Power supply and batteries.* The instrument was run indirectly from 240 VAC aircraft power. A regulated power supply is used to supply 24 VDC power (maximum 5.24 amps) to the core GC. To provide unbroken power to the core GC during engine startup and shutdown we configured a UPS from pairs of 12 VDC battery packs set in series.

*Housing.* On aircraft the need for a strong housing is paramount over weight considerations, and so the core GC and gas pack are housed in a steel 19 inch 9U rack enclosure. The core GC and gas pack are on a slide-out shelf to provide ease of access. The enclosure is fitted with 10 cm fans to remove heat from the instrument. Cooled air is also provided to the column cooling fan from a thermally insulated plastic box mounted on the top of the instrument enclosure. The air inside the box is cooled to ~5°C below ambient air temperature by a 58 W peltier heat pump (Supercool, part no. AA060-24220000). Power to the peltier pump at 24 VDC is from a regulated power supply running on 240 VAC aircraft power.

*Flight computer.* Although the instrument is designed to run autonomously (and usually flies unattended on the Dornier 228) a flight computer is used to interface the instrument before flight and to store data in-flight. We use a low power, single board

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computer system (Eurotech Ltd, part no. GX1-ICE). This features built-in UPS protection and uses solid state disk drives rather than mechanical drives which can fail at reduced ambient pressure. Data from the GC is stored on a USB flash drive. The flight computer is installed with Windows XP embedded operating system (Microsoft) which runs the in-house control interface and front end. For user interaction a laptop running terminal emulation software (RealVNC Ltd., VNC server/viewer) can be connected via a crossed network patch cable. A monitor and keyboard can be directly connected if needed.

## 2.4 Requirements for ground based deployment

Here we describe the technical requirements needed to support the core GC for long ground-based or ship deployments where the instrument is likely to be unattended for long periods. Two  $\mu$ Dirac instruments have been deployed in Sabah (Malaysian Borneo). This work has involved sampling at different heights on a 100 m tower located in an area of tropical lowland rain forest at Bukit Atur, Danum Valley (see Sect. 3.4) as well as multi-month measurements at forest and coastal sites. The technical requirements are similar to those required for use on aircraft. The main design requirements are a longer flushed sample inlet, sufficient support gases for several months deployment and a robust power scheme to handle power outages.

*Sampling pump and inlet.* The sampling pump system is identical to that used for aircraft deployment. However, a much longer inlet is needed to ensure that sampling is clear of building contamination and other local infrastructure. For inlet lengths up to 20 m we use high purity Teflon PFA 3/16" OD 0.125" ID tubing and for long inlet lengths up to 80 m we use high purity Teflon PFA 1/4" OD 0.188" ID tubing. Tests in the laboratory and in the field show no measurable interference. Ingress of rain at the top of the inlet is avoided by an upturned glass funnel plugged at its inlet by glass wool to exclude insects and large particles. The inlet is flushed by a pump located downstream of the instrument inlet tee. The air flow down the inlet tubing can be controlled by a tee piece on the pump input which allows the pump to draw air from the inlet tube and

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through a flow restrictor on the tee. By adjusting this flow restriction the inlet flow can be changed without impairing the operation of the pump. A counter-flow membrane drier (Perma Pure LLC, model DM-050-12P-2) is used to dry the sample flow passing into the core GC using the detector exhaust gas as the counter flow.

5 *Helium, nitrogen and calibration gas supply.* The core GC requires sufficient helium, nitrogen and calibration gas for several months unattended operation. Space and weight issues are not important for this type of deployment so for helium and nitrogen supplies small commercially available rental cylinders are used. Cylinders with a volume of 10 L filled to 200 bar with 6.0 grade nitrogen and helium are sufficient for 9 and  
10 45 months of continuous operation, respectively. The cylinders are fitted with high purity single stage pressure regulators set to an output pressure of 4 bar. The calibration gas system is identical to that for the MIR balloon but with a larger cylinder (500 cm<sup>-3</sup>) of the same series, with a capacity of 34 liters of calibration gas, sufficient for 4 months typical operation. For longer deployments NOAA-ERSL standards contained in 34 litre stainless steel cylinders are used directly.

15 *Power supply and batteries.* Where 100/240 VAC mains power is available the instrument is supplied from a regulated 24 VDC power supply backed up by a commercially available uninterruptible power supply (UPS). In the absence of mains power the instrument can be operated off-site (e.g. on the forest floor) by employing pairs of 12 VDC  
20 battery packs set in series, each consisting of 10 rechargeable NiMH cells and supplemented by two 12 VDC lead acid car batteries. These packs can keep the instrument running for hours to days.

25 *Housing.* The core instrument is housed in a lightweight (4 kg) plastic 19" 8U rack enclosure which can easily be carried for off-site use. Cooled air is provided to the column cooling fan and adsorbent trap using a Peltier heat pump mounted on a plastic box identical to that used for aircraft deployment. Power to the Peltier pump at 24 VDC is from a regulated power supply running on mains 240 VAC power (UPS protected).

*Computer.* A low power, low heat, single board computer system (Eurotech Ltd, part no. GX1-ICE) identical to that used for aircraft deployment is used to run the user

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interface and data collection software. A flat panel monitor, keyboard and mouse are connected, though these are removed for off-site deployment. Data from the GC is stored on a USB flash drive for ease of removal during periodic personnel visits. Power for the computer at 24 VDC is delivered either from a regulated power supply or from batteries (off-site deployment).

### 3 Instrument performance

Here we describe the instrument performance based on laboratory tests and on the results of recent field deployments. High quality geophysical data is possible only after detailed attention to instrument calibration, accuracy/precision, sensitivity and comparison with established instruments. We now describe each of these performance aspects in turn.

#### 3.1 Calibration

Absolute calibrations are determined by reference to a NOAA-ESRL calibration gas standard. The standard is a pressurised sample of air from Niwot Ridge, CO, USA which is a site representative of remote continental air. The standard was then spiked with a few ppt of  $\text{CH}_3\text{I}$ ,  $\text{CHBr}_3$  and  $\text{CH}_2\text{Br}_2$  and compared to NOAA-ESRL working standards and analysed using GC-ECD and GC-MS techniques enabling accurate ppt determination for 21 halocarbons. Typical uncertainty in the calibration gas is  $<0.5\%$  for the CFCs and other long-lived halocarbons and  $<5\%$  for the shorter-lived halocarbons (B. D. Hall and J. W. Elkins, personal communication, 2005). In Cape Verde (May–June 2007), calibration chromatograms of the same volume as the samples ( $\sim 20 \text{ cm}^3$ ) were run after typically every 6 sample chromatograms (the calibration frequency can be changed in the method file). A blank chromatogram was also run just before every calibration to check on system impurities. The instrument method now includes calibration response curves (several calibrations covering a range of volumes) which allow

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for the tracking of small changes in detector non-linearity. Figure 5 shows the complete set of measurements of  $C_2Cl_4$  at Danum Valley from 26 June to 3 July 2009), though it should be noted that not all gases have as linear a response as  $C_2Cl_4$ .

### 3.2 Accuracy and precision

5 Taking into account additional uncertainties such as that introduced during the transfer of gas to the on-board standard, we estimate that an overall accuracy of <2% can be achieved for the long-lived halocarbons and <10% for the shorter-lived compounds. The estimated accuracies of the measurements of individual halocarbons are given in Table 1. The overall precision cannot be estimated directly in the samples. One  
10 way to assess this is by repeating the measurement of the gas standard several times consecutively and calculating the RSD of the peak heights for each target compound. Using this approach in the laboratory we obtain RSDs ranging from 0.2% (CFC-11) to 8.5% ( $CHCl_3$ ) (Fig. 6a). To show the measurement precision in the field, we look at the real-time calibration chromatograms run typically after every six samples (Fig. 6b)  
15 in the Cape Verde campaign. The precisions obtained here vary from 1.1% for  $CCl_4$  up to 9.3% for  $CH_3I$  and are given in Table 1. Both the laboratory and the field station tests were carried out in relatively stable conditions in terms of operating temperature, ambient pressure, etc., and so the estimates given here for accuracy and precision are probably smaller than what can be achieved in the more adverse conditions encountered during a balloon flight. However  $\mu$ Dirac has been designed so that its operating  
20 conditions are as stable as possible in order to minimise any additional error contributions.

### 3.3 Sensitivity

The instrument has been optimised for high sensitivity. The micro-volume ECD is arguably the most sensitive ECD available commercially and has the lowest internal cell  
25 volume. This allows capillary columns to be used with low make up gas flow (the flush-

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ing time of the cell is shorter than a conventional ECD). The nitrogen make up flow is typically set at  $5 \text{ cm}^3 \text{ min}^{-1}$  in order to further improve sensitivity. The electrometer and ADC have both been designed to minimise noise interference with the result that detector noise approaches the quantisation step of the ADC. Although we have optimised the method for an adsorption volume of  $20 \text{ cm}^3$  it is also possible to increase sample volume and thus improve detection limit (though this may be at the expense of chromatographic resolution). Volumes much larger than  $50 \text{ cm}^3$  would require a larger adsorption trap and may also require an increase in the scale of the system (e.g. larger bore column).

In addition, the attention paid to optimizing the precision has resulted in  $\mu$ Dirac being a highly sensitive instrument. A common way to assess sensitivity is by calculating the limit of detection from the signal to noise ratio (SNR) with the limit of detection defined as twice the signal to noise ratio. Here we calculate the SNR as the ratio between the peak height of interest and the root mean square (RMS) of the baseline noise. For example, the smallest known peak in Fig. 6b is  $\text{CH}_3\text{I}$  with a peak height of 128 and the RMS of the baseline noise is 2.05 giving a SNR of 62. The concentration of  $\text{CH}_3\text{I}$  in the calibration standard is 3.4 ppt, resulting in a detection limit of 0.1 ppt (SNR 2) for a sample volume of  $20 \text{ cm}^3$ . The detection limits for the halocarbons measured by  $\mu$ Dirac are given in Table 1 assuming that a sample of  $20 \text{ cm}^3$  is collected.

An additional quantity used in assessing sensitivity is the limit of quantification which is the smallest detectable amount of a compound which is statistically larger than zero. The ideal way to test for this is to introduce known amounts of each halocarbon at a concentration just above the limit of detection. Then by measuring the RSD of repeat chromatograms we can deduce if the measurement precision for a very low SNR is the same as that for a high SNR. This test has yet to be carried out for  $\mu$ Dirac so here we estimate the limit of quantification by assuming that the precision measured from the calibration gas at high concentration is an absolute measure of precision. So for  $\text{CH}_3\text{I}$  the estimated precision at 3.4 ppt is 9.3% or, in absolute terms, 0.3 ppt which we estimate is the limit of quantification for this compound.

### 3.4 Comparison with UEA GC-MS instrument

From April to July 2008, a  $\mu$ Dirac instrument was operated at the measuring tower of the Bukit Atur GAW station at Danum Valley, Malaysia (5° N, 118° E) as part of the Oxidant and Particle Photochemical Processes (OP3) field campaign. At the same time the University of East Anglia (UEA) had a GC-MS installed at the GAW station. This was an Agilent 6890/5973N operating in negative ion, chemical ionisation mode (NICI) with CH<sub>4</sub> as reagent gas. The GC column was a 105 m×0.32 mm×1.8 $\mu$ m RTX-502.2, temperature ramped from 35°C to 235°C. One litre air samples were processed on a Markes Unity thermal desorption unit. CH<sub>2</sub>Br<sub>2</sub> and CHBr<sub>3</sub> are referenced to the NOAA-ESRL (2003) calibration scale. Further details can be found in Worton et al. (2008). The two instruments were sampling almost identically with just an 18m difference in the inlet height. Figure 7 shows the atmospheric concentrations of CHBr<sub>3</sub> and CH<sub>2</sub>Br<sub>2</sub> measured by the two instruments from 4–21 July. For CHBr<sub>3</sub> there is an excellent agreement in the absolute mixing ratios and the trend and for CH<sub>2</sub>Br<sub>2</sub> the  $\mu$ Dirac mixing ratios are lower by 20–30% than those of UEA although the trends in the two data sets are similar. Both instruments use the NOAA-ESRL calibration scale, but it is still very reassuring to see such a high level of agreement. Gaps in the measurement record occurred as a result of power failures with problems caused by the consequent shut-down of the air-conditioning. Similar, though not quite so good performance is seen for CHCl<sub>3</sub>, though there is a calibration offset of currently unknown cause.

## 4 Results and discussion

$\mu$ Dirac has participated in several ground based deployments, two aircraft and two balloon campaigns. In this section we describe the fateful MIR balloon flight and then demonstrate the field performance of  $\mu$ Dirac by presenting results from one aircraft campaign and two ground-based deployments.

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## 4.1 Attempted MIR long duration balloon flight

On the evening of 17 February a long duration version of  $\mu$ Dirac was launched on a MIR balloon from Mahé International Airport, Seychelles (4.68° S, 55.53° E). The balloon ascended to 38 km and began tracking west across the Indian Ocean towards the East African coast some 1600 km distant. The instrument was programmed to be in standby mode during the night and to start the first sampling sequence at dawn. However, on the first morning, a serious communication problem developed between the ground control station and the CNES balloon flight control gondola. For several hours CNES personnel attempted to regain communication and control of the balloon but with no success. At the end of this period an automatic timer triggered a cut-down of the balloon (standard safety practice in the event of a major communication failure). The equipment below the balloon descended by parachute and entered the Indian Ocean at 5.80° S, 46.82° E. No recovery attempt was possible at short notice and the instrument was lost. No data was recovered as the communication failure occurred before the end of the first sampling sequence. There was no immediate flight opportunity for the back-up instrument which is being kept in case of a future flight opportunity.

## 4.2 Cape Verde Dornier flights

The NERC (ARSF) Dornier 228 aircraft was stationed on São Vicente Island, Cape Verde (São Pedro Airport, 16.83° N, 25.06° W) between 25 May and 1 June 2007. The aircraft contained an atmospheric chemistry instrument payload from the Universities of York, Leeds and Birmingham and also carried a Cambridge  $\mu$ Dirac instrument. Twelve short, local survey flights (3 per day) were performed in the vicinity of the Cape Verde Atmospheric Observatory and an additional three longer 'rendezvous' flights were made to the NERC RRS Discovery ship which was cruising around Cape Verde on campaign (Reactive Halogens in the Marine Boundary Layer – RHaMBLe). Vertical profiles of  $\text{CHCl}_3$ ,  $\text{C}_2\text{Cl}_4$ , and  $\text{CHBr}_3$  indicate that the aircraft predominately flew

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in background air remote from anthropogenic influence (Fig. 8). The greater variability of all three gases in the lower boundary layer is consistent with the ground-based observations which started at this time (O'Brien et al., 2009), with the concentrations of  $\text{CHCl}_3$  and  $\text{C}_2\text{Cl}_4$  being elevated when the air had previously passed over W. Europe and high variability in the  $\text{CHBr}_3$  concentrations.

### 4.3 Weybourne Atmospheric Observatory (WAO)

From 28 March to 3 April 2007  $\mu\text{Dirac}$  was deployed at WAO, Norfolk, UK (52.95° N, 1.12° E). Measurement time series of  $\text{CHCl}_3$  and  $\text{C}_2\text{Cl}_4$  indicate that the site was influenced by two different air mass source regions during this period (Fig. 9). Between 28 and 31 March high variability in  $\text{CHCl}_3$  and  $\text{C}_2\text{Cl}_4$  was observed indicating that the air mass was under the influence of industrial sources. The period from 31 March to 4 April was characterised by lower values of  $\text{CHCl}_3$  and  $\text{C}_2\text{Cl}_4$ , more indicative of background air. The values in this second period are similar to those seen at the Mace Head Observatory. Back trajectories indicate that the more polluted air arriving at WAO in late March had passed over W Europe, whereas the cleaner background air in early April had come from above the boundary layer over Greenland and down the North Sea.

### 4.4 Operation in Malaysian Borneo

In 2008, the NERC OP3 project studied the forest emissions over Borneo. The ground-based segment was based at the Global Atmospheric Watch station at Bukit Atur in a tropical lowland dipterocarp forest in Danum Valley. As part of this, two  $\mu\text{Dirac}$  instruments were deployed. One was based permanently at the GAW station and one was used to make exploratory measurements in the rain forest and at the coast. Halocarbon measurements were also made at the GAW station by the GC-MS of the University of East Anglia, and Fig. 7 shows the time series for both instruments for  $\text{CHBr}_3$  and  $\text{CH}_2\text{Br}_2$ . The two sets of measurements agree well for both gases, with agree-

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ment in variations in the sub-ppt range. At present,  $\text{CH}_2\text{Br}_2$  co-elutes with  $\text{CHBrCl}_2$  in  $\mu\text{Dirac}$  chromatograms leading to an overestimation of 10–30% in the marine atmosphere (O'Brien et al., 2009). The two ground-based  $\mu\text{Dirac}$  instruments remained in Sabah, Malaysian Borneo after the end of OP3, with one instrument at the Bukit Atur GAW station and the other on the coast near Tawau (4.22° N, 118.00° E). This dual instrument deployment is the first step in a larger scale project to generate a long time series of halocarbon (and later hydrocarbon) measurements from several coastal sites in the west Pacific. In addition to the coastal measurements, a  $\mu\text{Dirac}$  instrument will be deployed aboard a container ship to make long duration transect measurements in coastal and open waters, including in SE Asia.

## 5 Summary

A new lightweight micro-GC is described. It uses a Carboxen adsorbent trap and a temperature and flow programmable chromatographic column. A central feature is the on-board, autonomous, precise control of all aspects of the instrument. Designed for use on a long duration balloon, it is lightweight (11 kg without batteries), has low power consumption and can run autonomously for long periods. Unfortunately it could not prove itself on the long duration balloon due to a balloon failure. However, the novel design needed for the long duration deployment has resulted in a versatile instrument capable of running reliably at the ground for months at a time. The calibration procedure allows any changes in linearity of response to be monitored as well as changes in sensitivity, giving increased confidence in the quality of the measurements. The measurements of  $\text{CHCl}_3$  and  $\text{C}_2\text{Cl}_4$  at the Weybourne Atmospheric Observatory were made in one period where the site was influenced by industrial emissions from Europe and immediately followed by a second period where background Northern hemisphere values were observed. Comparison with the UEA GC-MS at Bukit Atur shows excellent agreement for the biogenic gases  $\text{CHBr}_3$  and  $\text{CH}_2\text{Br}_2$ . The reliability of the instrument for continuous operation has been demonstrated in Malaysian Borneo since Septem-

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ber 2008, with continuous operation from November 2008 until present.

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**Table 1.** *μ*Dirac target compounds and measurement performance during the Cape Verde ground based campaign.

Compound name	Formula	Atmospheric lifetime	VMR in NOAA-ESRL cylinder <sup>a</sup>	Estimated Accuracy (%) <sup>b</sup>	Estimated Precision (%) <sup>c</sup>	Limit of detection (ppt) <sup>d</sup>	Limit of quantification (ppt) <sup>e</sup>	Typical RT, minutes
CFC-11	CFCI <sub>3</sub>	45 years	251.5	0.3	2.6	0.02	6.5	1.95
CFC-113	CCl <sub>2</sub> FCClF <sub>2</sub>	85 years	80.8	0.6	3.9	0.05	3.2	2.39
methyl iodide	CH <sub>3</sub> I	5 days	3.4	0.1	9.3	0.11	0.3	2.72
chloroform	CHCl <sub>3</sub>	5–6 months	9.93	3.0	4.0	0.10	0.4	3.95
methylchloroform	CH <sub>3</sub> CCl <sub>3</sub>	5 years	17.84	1.0	2.6	0.05	0.5	4.21
carbontetrachloride	CCl <sub>4</sub>	26 years	95.0	0.3	1.1	0.02	1.0	4.39
dibromomethane	CH <sub>2</sub> Br <sub>2</sub>	3–4 months	4.8	2.0	5.4	0.03	0.3	5.12
tetrachloroethene	C <sub>2</sub> Cl <sub>4</sub>	3–4 months	2.01	3.0	4.2	0.01	0.1	6.02
bromoform	CHBr <sub>3</sub>	26 days	9.0	2.0	4.5	0.05	0.4	7.22

<sup>a</sup> certified at time of filling, December 2005;

<sup>b</sup> 1 standard deviation;

<sup>c</sup> 1 standard deviation of 6 calibration chromatograms made in a single day;

<sup>d</sup> based on signal to noise ratio of 2;

<sup>e</sup> derived by assuming estimated precision measurement is absolute.

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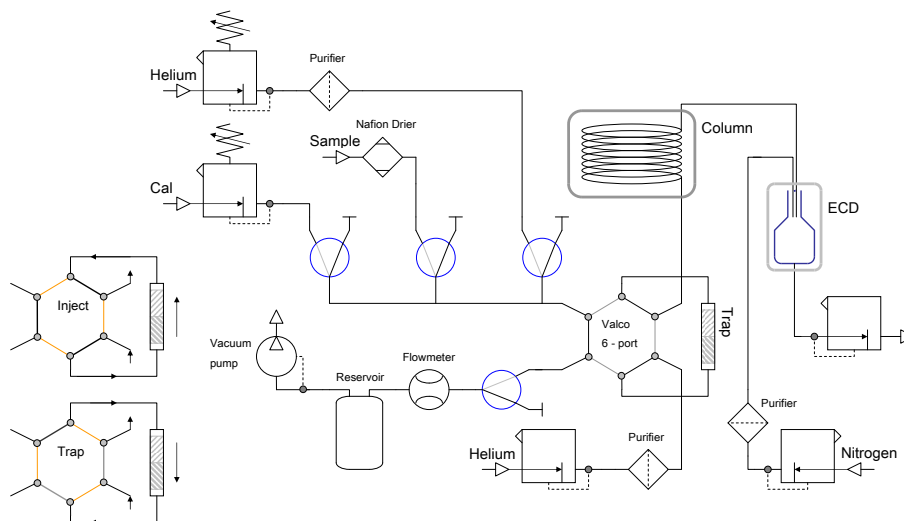
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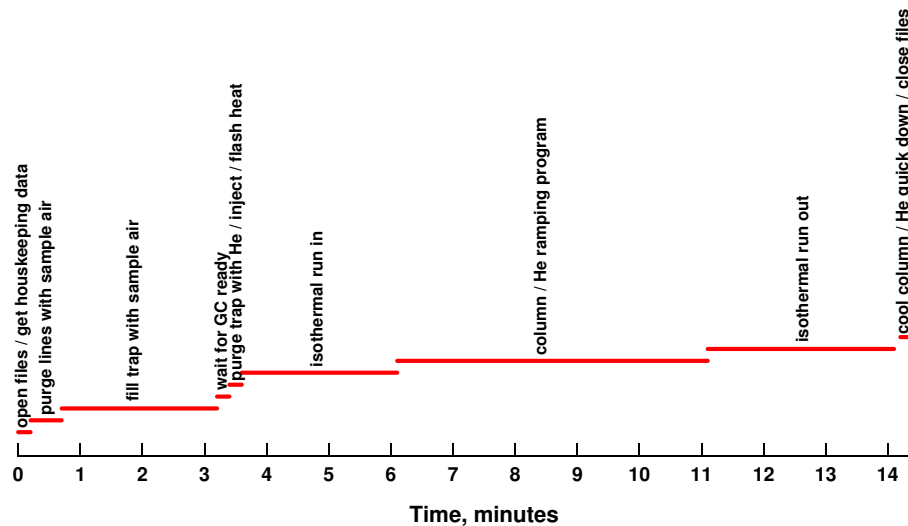


**Fig. 1.** Schematic of the core gas chromatograph. The smaller schematics in the lower left show the Valco valve flow paths for the “inject” and “trap” positions.

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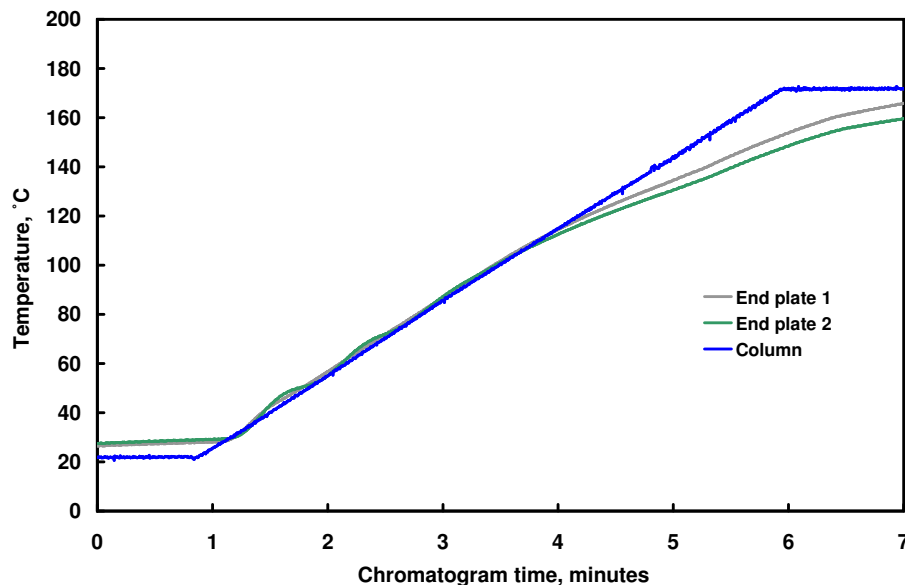


**Fig. 2.** Typical timing sequence for  $\mu$ Dirac operation with a 15 min overall cycle time.

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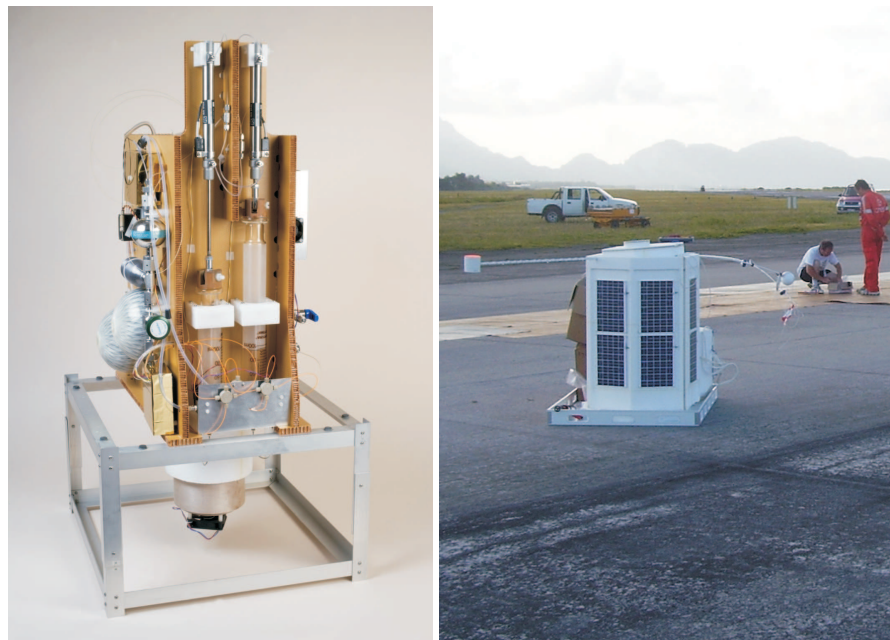
**Fig. 3.** Performance of the programmed column oven during a linear rise from 20 to 175°C at 30°C min<sup>-1</sup>. The three lines show the simultaneous temperatures of the oven end-plates (grey and green) which provide the bulk of the power and of the column itself (blue) which provides additional regulations from direct heating.

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**Fig. 4.** (a) MIR  $\mu$ Dirac armature showing twin syringe sample pump; (b) MIR flight housing on the launch pad in Mahé, Seychelles.

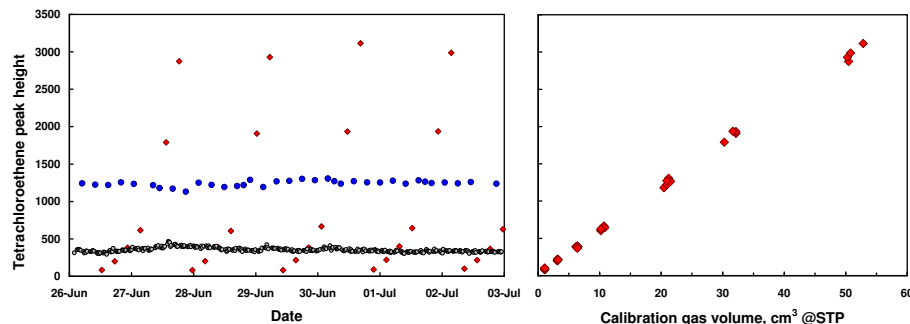
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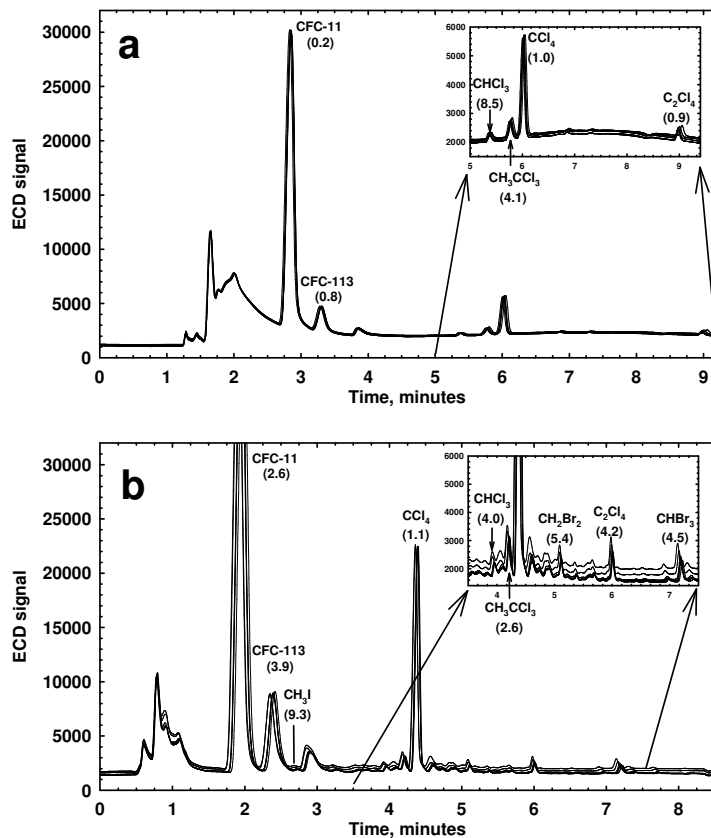


**Fig. 5.** (left) Typical  $\mu$ Dirac calibration/sampling sequence showing raw peak height data for tetrachloroethene. Sample peak heights are shown as grey circles. Precision calibrations (blue circles) are used to derive measurement precision and to allow for correction to sensitivity drift. Response curves (red circles) are used to make corrections for non-linearity effects (right). The response curves with peak height as a function of volume of calibration gas. The measurements were made in June 2009 during remote operation at Bukit Atur, Malaysia.

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**Fig. 6.** Overlaid chromatograms of calibration gas samples during operation in **(a)** the laboratory and **(b)** Cape Verde in June 2007. The precision of the peak heights (RSD%) are shown in parentheses, each chromatogram is generated from a  $20\text{ cm}^3$  volume of Niwot Ridge air (NOAA-ESRL) spiked with  $\text{CH}_3\text{I}$ ,  $\text{CH}_2\text{Br}_2$  and  $\text{CHBr}_3$ .

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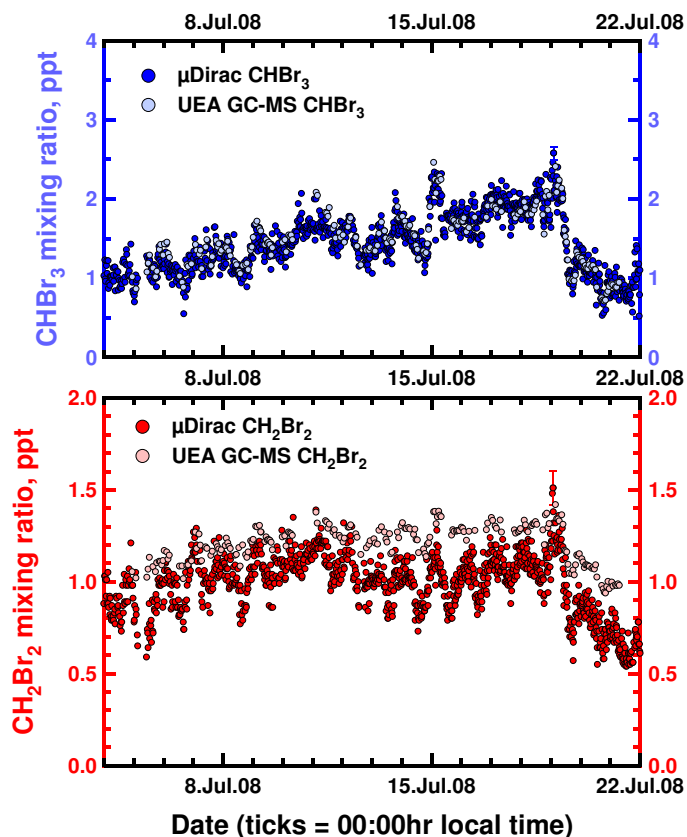
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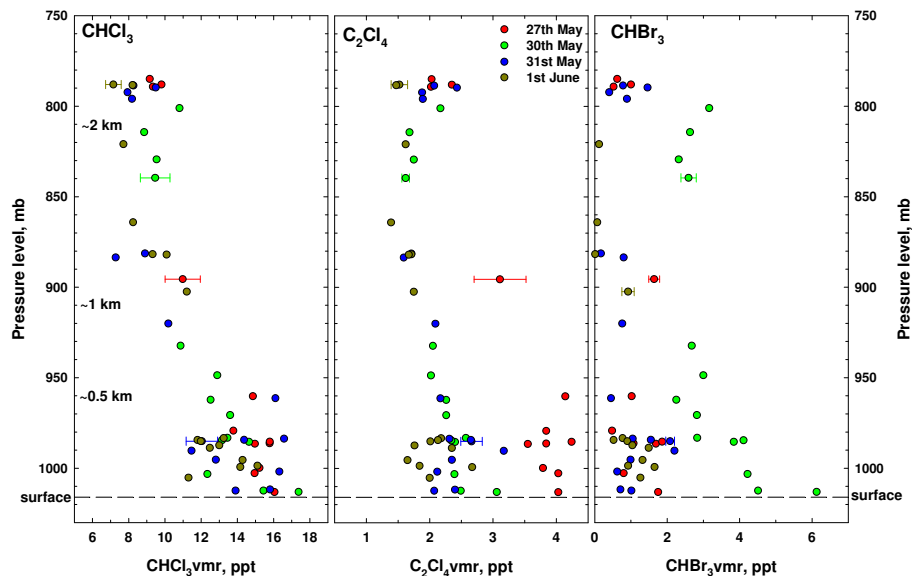


**Fig. 7.** Mixing ratios of  $\text{CHBr}_3$  and  $\text{CH}_2\text{Br}_2$  measured at the Bukit Atur GAW station in Danum Valley, Borneo in June/July 2008. The dark symbols are measurements made by  $\mu$ Dirac and the light symbols are measurements made by the UEA GC-MS. Both instruments used the same measurement tower with inlets which were 18m apart in height. The estimated 1 s.d. precisions are:  $\text{CHBr}_3$  –  $\mu$ Dirac 3% and GC-MS 5%;  $\text{CH}_2\text{Br}_2$  –  $\mu$ Dirac 6% and GC-MS 5%.

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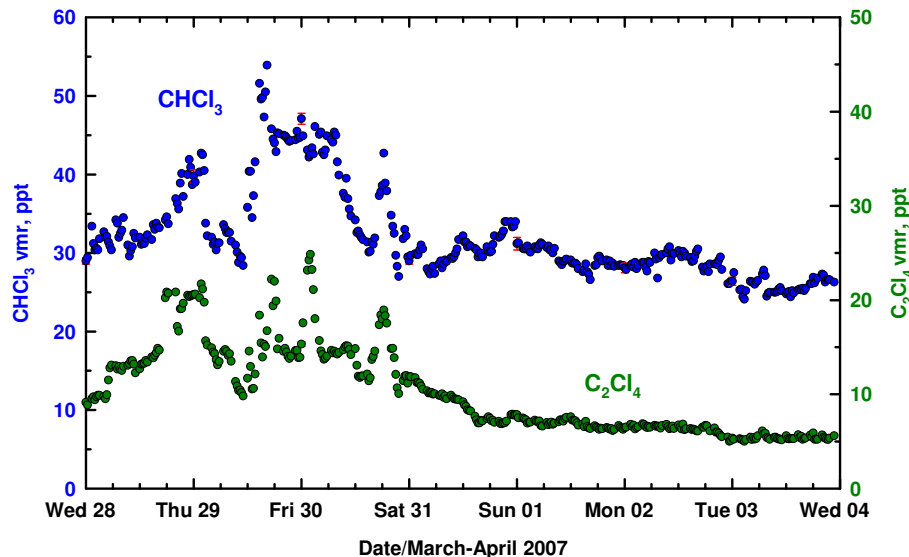


**Fig. 8.** Vertical profiles of  $\text{CHCl}_3$ ,  $\text{C}_2\text{Cl}_4$  and  $\text{CHBr}_3$  mixing ratios measured near the Cape Verde Islands by  $\mu$ Dirac aboard the Dornier 228 aircraft in May/June 2007.

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**Fig. 9.** Time series of CHCl<sub>3</sub>, and C<sub>2</sub>Cl<sub>4</sub> mixing ratios measured by  $\mu$ Dirac during a test deployment at Weybourne, Norfolk in March/April 2007.

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