An Improved, Automated Whole-Air Sampler and Gas Chromatography Mass Spectrometry Analysis System for Volatile Organic Compounds in the Atmosphere

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Abstract.

Volatile organic compounds were quantified during two aircraft-based field campaigns using highly-automated, whole air samplers with expedited post-flight analysis via a new custom-built, field-deployable gas

25   chromatography – mass spectrometry instrument. During flight, air samples were pressurized with a stainless steel bellows compressor into electropolished stainless steel canisters. The air samples were analyzed using a novel gas chromatograph system designed specifically for field-use which eliminates the need for liquid nitrogen. Instead, a Stirling cooler is used for cryogenic sample pre-concentration at temperatures as low as -165°C. The analysis system was fully automated on a 20-minute cycle to allow for unattended processing of

30   an entire flight of 72 sample canisters within 30 hours, thereby reducing typical sample residence times in the canisters to less than three days. The new analytical system is capable of quantifying a wide suite of C2 to C10

organic compounds at part-per-trillion sensitivity. This manuscript describes the sampling and analysis systems, along with the data analysis procedures which includes a new peak-fitting software package for rapid chromatographic data reduction. Instrument sensitivities, uncertainties and system artifacts are presented for 35 trace gas species in canister samples. Comparisons of reported mixing ratios from each field campaign with

5   measurements from other instruments are also presented.

1. Introduction

Volatile organic compounds [VOCs], chemical species consisting primarily of carbon, hydrogen, and oxygen, are ubiquitous and important components of the atmosphere (Glasius and Goldstein, 2016). VOCs are fundamental to the photochemical formation of ozone and secondary organic aerosol (de Gouw et al., 2005; Edwards et al.,

10   2014; Kanakidou et al., 2005; Trainer et al., 2000), and can have direct and indirect effects upon both air quality and global climate (Hoyle et al., 2009; Monks et al., 2015). Measurements of VOCs can be used to identify and quantify emission sources and photochemical aging processes (Fortin et al., 2005; Mckeen and Liu, 1993; Warneke et al., 2012). Important primary sources for VOCs can vary by location and season – emissions from biogenic, biomass burning, urban/industrial and oil/natural gas extraction have all been characterized by this

15   laboratory and others using in-situ gas chromatography – mass spectrometry [GC-MS] (Gentner et al., 2014; Gilman et al., 2013; Gilman et al., 2015; Goldan et al., 1995; Goldan et al., 2000; Hornbrook et al., 2011).

The use of gas chromatography followed by mass spectrometry for the analysis of VOCs is a well-established technique due to its superior selectivity and sensitivity compared to other chromatography methods (McClenny

20   et al., 1996). For GC-MS, sensitivities can be enhanced by pre-concentration of the analytes, commonly by means of adsorbent(s) or cryogenic trapping (Brown and Purnell, 1979; Greenberg et al., 1994; McClenny et al., 1984; Woolfenden, 2010). Cryogenic sample pre-concentration allows high vapor pressure VOCs and halocarbons to be trapped without the use of strong adsorbents that can produce significant artificial responses (Apel et al., 2003; Sive et al., 2005); however, sufficient volumes of liquid cryogen (e.g., liquid nitrogen) can be

25   difficult to obtain at remote field locations (Tanner et al., 2006; Wang et al., 2012). Cryogen-free systems that allow for low-temperature sample trapping by means of Peltier or refrigeration units suffer from slow temperature response times, lack of portability due to size and weight and/or insufficiently low trap

temperatures to allow trapping of the most volatile gases (e.g., ethane) without adsorbents (Hopkins et al., 2011; Liu et al., 2016; Miller et al., 2008; Sive et al., 2005; Tanner et al., 2006; Wang et al., 2014).

Stirling coolers offer an alternative cooling technology for cryogenic sample pre-concentration and feature low weight and size, modest power consumption, and maintenance-free operation but at the cost of low lift capacity (ter Brake and Wiegerinck, 2002). Conceptually, the Stirling cooler consists of a sealed cylinder filled with a gas (e.g., helium), with a piston that compresses and expands the gas and a displacer that moves the gas from one end of the cylinder to the other out of phase with the piston (de Waele, 2011). Cooler performance is measured in watts of lift capacity, a measure of the amount of heat transfer from one end of the cylinder to the other while maintaining a constant temperature at the cold end. In this application, the warm end of the cooler is subsequently cooled with forced air. Stirling coolers have been used by at least two other gas chromatography groups for air sample pre-concentration, but previous examples either required an extended (20 minute) cooling cycle to achieve cryogenic trapping temperature (Oliver et al., 1996) or were operated at warmer (-80 °C) than cryogenic temperatures (Sala et al., 2014; Obersteiner et al., 2016). For the work presented here, a novel sample trap design has been developed utilizing a Stirling cooler that is capable of achieving cryogenic trapping temperatures on the time scale of seconds, allowing for the fully automated rapid analysis of air samples by GC-MS. This sample trap is incorporated in a new analytical instrument, herein referred to as ACCBAR, "Advanced Cryo-mechanical Chromatograph for Biospheric-Atmospheric Research," which is capable of separating and quantifying a wide suite of C2-C10 VOCs with a 20 minute cycle time and part-per-trillion-by-volume (pptv) sensitivity.

Sample collection of whole air samples by canisters extends the utility of GC-MS analysis to locations and platforms unsuitable for a ground-based detection system or where high time resolution sampling on the order of seconds is required without loss of method sensitivities (McClenny et al., 1991; Wang and Austin, 2006). Electropolished stainless steel canisters have been used for many years for quantifying trace gases, including from aircraft platforms (Colman et al., 2001; Heidt et al., 1989; McClenny et al., 1996; Simpson et al., 2010; Simpson et al., 2014). Due to the space- and weight-constraints of operating a whole air sampling system aboard research aircraft, this laboratory, in conjunction with the National Center for Atmospheric Research (NCAR), constructed a new semi- to fully-automated system, the improved whole air sampler (iWAS), for field

work (Warneke et al., 2016). This system packages 12 electropolished stainless steel canisters in rack-mountable modules that can be rapidly installed in or uninstalled from a wing-pod of the aircraft in sets of six and filled remotely. The sampler design and post-fabrication conditioning protocols have been adopted from the NCAR Advanced Whole Air Sampler (AWAS) and earlier whole air sampler designs (Heidt et al., 1989;

5   Schauffler et al., 1999) and the UC-Irvine whole-air sampling program (Blake et al., 1994; Simpson et al., 2010). The NCAR AWAS system had previously been deployed for the NOAA field campaigns TexAQS II and CalNEX in 2006 and 2010, respectively (Parrish et al., 2009; Warneke et al., 2012). The stability of various classes of compounds in electropolished stainless steel canister systems as a function of canister preparation and sampling and analysis protocols has been well documented in the literature (Kelly and Holdren, 1995; Ochiai et

10   al., 2002).

The combined iWAS/ACCBAR system was deployed during two aircraft-based field campaigns (summarized in Table 1). In summer 2013, the Southeast Nexus (SENEX) field campaign was conducted to investigate the roles of anthropogenic and biogenic emissions upon the formation of tropospheric ozone and secondary aerosol in

15   the Southeast United States (Warneke et al., 2016). Twenty research flights were conducted aboard the NOAA WP-3D aircraft, based in Smyrna, TN, from May to July 2013. During SENEX, over 1100 canister samples were collected and subsequently analyzed in the field, with mixing ratios for 24 species reported. In spring 2015, the Shale Oil and Natural Gas Nexus (SONGNEX) field campaign was conducted to quantify the emissions of trace gases and fine particles from oil and natural gas basins throughout the western United States. The NOAA WP-3D

20   aircraft was based in Broomfield, CO and Austin, TX from March to May, and conducted 19 research flights. Over 1300 canister samples were collected and analyzed, with 24 VOC species reported.

This manuscript presents the instrumental details for the iWAS sampling and ACCBAR GC-MS analysis systems, as well as the methods used to fill and sample the canisters and the post-analysis cleaning process. The data

25   analysis workflow, including peak area integration, normalization and calibration is detailed, as well as a description of a series of instrument tests to identify possible artifacts in either the sample collection or analysis systems. Finally, a comparison of a subset of final reported mixing ratios from two field campaigns with measurements made by other instruments is provided.

2. Instrumental

2.1 Airborne Whole Air Sample Collection

Air samples were collected aboard the NOAA WP-3D aircraft, with the sampling system installed in a wing-pod mounted underneath the starboard wing of the aircraft. The sample train consists of an unheated forward-

5   facing stainless steel inlet (10.2 mm ID) extending 15 cm from the outboard surface of the wing-pod with a reduced diameter outlet (2.2 mm ID) to increase ram air pressure and an orthogonal stainless steel sampling arm (10.2 mm ID). The sampling arm is connected via flexible stainless steel hose (9.5 mm ID) to a 2-stage stainless steel bellows compressor (Senior Aerospace p/n 28823-11) used in series, capable of >50 slpm of air flow at 60 psia (4140 hPa) with the inlet at 25 °C and 14.7 psia. The compressor output is connected in series to

10   six canister modules via welded manifolds of 4.6 mm ID stainless steel tubing with breakable connections made between the canister modules with Swagelok stainless steel metal gasket fittings (VCR) with silver-plated nickel gaskets. Each canister module holds twelve 1.4 L electropolished stainless steel canisters that are isolated from the sampling manifold via pneumatically-actuated stainless steel bellows valves (Swagelok p/n SS-BN4VCR-C). The canister modules were built by UC-Irvine and NCAR's Design and Fabrication Services. After the canister

15   modules, the sample flow is exhausted through a proportional relief valve set at 60 psia, with a bypass port that opens to ambient pressure via a bellows valve. With the compressor operating, air flows through the sample manifold regardless of whether the valve to the bypass port is open.

Sample collection is controlled via a custom-built PC-104 data system (Diamond Systems, Mountain View, CA)

20   running LabView-based software (National Instruments, Austin, TX) in a Microsoft Windows environment. The flight scientist communicates with the data system over the aircraft local area network using Windows remote desktop protocol. After takeoff, the compressor is started with the bypass port open to reduce back-pressure. When the aircraft has reached the sampling area, the bypass port is closed to allow adequate manifold pressure for filling canisters. Air samples are sequentially collected by actuating the stainless steel bellows valve on an

25   individual canister and allowing the canister to be pressurized to 50 psia (3450 hPa). Fill time for a canister with the system at standard sea level pressure is 3 seconds and the time increases with increasing aircraft altitude (decreasing ambient pressure). At an altitude of 5000 masl (meters above sea level), fill time is typically 11 seconds, and the maximum fill time allowed by the flight computer is 15 seconds regardless of fill pressure.

During SONGNEX 2015, ≈95% of samples were collected below 3500 masl and had fill times between 3-7 seconds. At typical air speeds of 100 m/s, these samples average the VOC composition over < 1 km of the flight track. The data system can be operated in a survey mode, whereby canisters are automatically filled at set intervals (typically 180 to 450 seconds between samples). The flight scientist is also able to immediately collect sample(s) with an override function, and can adjust the sample interval as required. Canister fill times are transmitted to the onboard flight scientist over the aircraft local area network and to scientists on the ground along with the aircraft GPS coordinates allowing for real-time mapping of sampling. When all canisters have filled, the sample manifold bypass valve is opened for venting and the compressor is turned off.

2.2 Post-flight analysis via GC-MS

2.2.1 Sampling from the Canisters

Each canister is sequentially analyzed post-flight in the field with ACCBAR [Figure 1]. The canister modules are connected to a welded electropolished stainless steel sampling manifold via 2.2 mm ID passivated stainless steel tubing (Restek Sulfinert-treated). The sampling manifold has eight electropolished stainless steel bellows valves, which isolate individual canister modules as well as a 2-stage diaphragm vacuum pump and a supply of humidified zero air (compressed ultra-zero air passed through a water bubbler). The sample manifold is connected to the GC-MS with a VCR fitting using a stainless steel gasket with a 100 µm orifice, and the remaining flow path to the GC-MS consists of 2.2 mm ID passivated stainless steel; the total internal volume of the sample manifold is approximately 80 cm^3. Once all six canister modules are installed, the entire sample train is evacuated to <0.01 psia to remove any residual liquid water in the canister module manifolds and to check for leaks. Once analysis begins, the sample manifold and target canister module manifold are evacuated to <0.002 psia, then filled with humidified zero air to >30 psia and evacuated again before each sample. The sample analysis system is also tested for artifacts by analyzing the humidified zero air flush gas, typically before running canisters and after each set of 24 canisters has been analyzed. The target canister is opened 6 seconds before the GC-MS sampling valve is activated, allowing the sampling manifold to reach sufficient pressure to deliver sample flow (120 sccm) to the instrument through the orifice and to passivate the manifold surfaces with each sample prior to analysis. The GC-MS control system evaluates the sample manifold pressure one second before opening the sample valve; if the manifold pressure is below 30 psia the GC-MS will automatically switch to an

instrument zero to avoid sampling a vacuum (see below). This condition is typically met as a result of a canister that failed to fill during flight.

2.2.2 Sample analysis and description of GC-MS

5 Conceptually, ACCBAR is a series of traps used to reduce unwanted component(s) from the air sample matrix (i.e. water and carbon dioxide)while concentrating the target analytes, which are subsequently injected on separation columns and detected via mass spectrometry on a 20-minute cycle. The custom-built GC-MS ACCBAR consists of two channels; with channel 1 optimized for C2-C6 hydrocarbons and halocarbons using a PLOT column and channel 2 optimized for C6-C10 hydrocarbons, oxygen- and nitrogen-containing species using a low-

10 to mid-polarity phase column. A single quadrupole mass spectrometer detector (MSD) runs in selective ion mode for increased signal-to-noise response and sequentially analyzes the effluent from the two columns. This instrument is based on a two-channel GC-MS developed by NOAA Chemical Sciences Division and deployed on many field campaigns over the past 15 years (Gilman et al., 2013; Goldan et al., 1995). The new instrument is designed for field-deployment, capable of measuring *in situ* or analyzing canister samples, and is built into a 104

15 cm x 104 cm x 64 cm (H x W x D) rack shock-mounted on casters. ACCBAR requires no cryogen (e.g. liquid nitrogen), consuming only carrier gas (ultra-high purity He), calibration gases (typically zero air and a secondary standard, discussed below) and 120 VAC power (2 x 15A circuits). The new GC-MS was successfully deployed in 2013 for SENEX to the Smyrna/Rutherford County Airport (Smyrna, TN) via a towable laboratory trailer which was parked inside an aircraft hangar; for SONGNEX in 2015, ACCBAR remained in the CSD laboratory since field

20 operations were predominantly from the nearby Rocky Mountain Metropolitan Airport (Broomfield, CO).

Figure 1 presents a schematic of the flow path of ACCBAR, along with alternative settings of the five two-position chromatography valves (Valco Instruments, Houston, TX) used to direct gas flow. Channel 1 is shown with the 10-port valve (1-10) in "flush" mode and the 6-port valve (1-6) in "import" mode, where the sample

25 trap is connected to the separation column with carrier gas (UHP He) flowing through the sample trap and to the column. Channel 2 is shown with the 10-port valve (2-10) in "load" mode and the 6-port valve (2-6) in "backflush" mode, where sample flow is directed through a water trap followed by the sample trap, while the separation column is isolated and back-flushed with UHP He. The 4-port valve is shown directing channel flow from the separation column on channel 1 to the mass spectrometer, while channel 2 flow (UHP He) is vented.

When performing analysis, two 240 cm³ (standard pressure and temperature) air aliquots are simultaneously collected from each canister to both channels over four minutes at a flow rate of 60 sccm controlled by individual mass flow controllers (Pneucleus MicroFlo, Hollis, NH). There is no vacuum pump downstream of the

5   flow controllers which vent to ambient, so positive pressure is required upstream of the GC-MS sample inlet. If the inlet pressure is sub-ambient it is possible that flow will reverse in the sample path, so this condition must be avoided. Carbon dioxide (CO_2), which can freeze and plug the channel 1 sample trap at collection temperature, must be removed. The channel 1 sample passes through a bed of heated (35 °C) granular NaOH-coated silica (Ascarite II) packed in a 10 cm PFA tube (6.3 mm ID) with silanized borosilicate wool at each end

10   (Goldan et al., 2004). No CO_2 trap is required for channel 2, as the sample trap temperature is just warm enough to prevent freezing of CO_2 at the residence time of the trap. Water vapor also must be removed from the air samples to prevent ice buildup in the subsequent sample traps, which would cause plugged flow, as well as to prevent degradation of the PLOT column used for channel 1. Prior to sample trapping, the air aliquot for each channel passes through a water trap, which is a 36 cm loop of 2.0 mm ID PEEK tubing inside a coaxial stainless

15   steel tube resistively heated to control temperature, mounted in an insulated aluminum cold block. The water traps are cooled to -20°C during trapping, then are heated to 100 °C for 12.9 minutes between sample injections while being back-flushed with UHP He. The water trap cold block is chilled with a single-stage mechanical refrigerator (Neslab CC-65) during operation. The water traps are able to cool from purge to trapping temperature in approximately 45 seconds, and are controlled within 0.2 °C of set point during trapping.

After passing through the water traps, analytes from the air samples are pre-concentrated via cryogenic trapping at nominal temperatures of -165 °C and -135 °C for channels 1 and 2, respectively. The sample traps (Figure 2a) are a novel design, using a Stirling cooler (Sunpower Inc., Athens, OH, model CryoTel GT) to achieve trapping temperatures without the need for liquid nitrogen. The CryoTel GT cooler is capable of 16W lift

25   capacity (e.g. heat removal) at -196 °C at maximum power (240W input) while weighing only 3.1 kg. The cold end of the cooler terminates in a threaded cold finger, which is bolted to a small copper plate (25 mm x 25 mm x 6 mm) that is attached to a larger copper cold block (178 mm x 51 mm x 10 mm) via 12 stranded copper wires (10 AWG). This serves to mechanically isolate the cold finger from the cold block while still allowing efficient thermal transfer. The copper cold block is mounted in a 20 cm ID x 6.2 cm cylindrical vacuum chamber,

suspended by two 3.2 mm OD, 2.7 mm ID stainless steel tubes that are sealed with Swagelok Ultra-Torr fittings. The Stirling cooler is mounted to the top of the chamber via a KF-50 vacuum flange attached to the cooler at the terminus end of the cold finger, and a turbomolecular pump is mounted to the bottom of the chamber to reduce pressure inside the chamber below 1×10^{-4} hPa. The vacuum chamber has additional ports to allow for

5   pressure measurement and sensor and heater wiring to the cold block.

The sample traps consist of a 330 mm section of treated fused silica tubing (0.53 mm ID) mounted inside a thin-wall hypodermic stainless steel tube (0.97 mm ID, 1.08 mm OD) that is resistively heated. The treated fused silica tubing used for channel 1 is Al_2O_3/KCl PLOT column (Restek RT-Alumina BOND/KCl), with the Al_2O_3 scraped

10   from each end of the tubing so that only the center 180 mm is coated; channel 2 uses deactivated fused silica (Restek Rxi Guard) without modification. To allow temperature control of the sample trap, a type-T thermocouple is adhered to the outer wall of the hypodermic tubing with shrink tubing, which electrically isolates the heater from the outer support tubing. The ends of the hypodermic tubing – that part of the heater tubing that is not positioned inside the cold block – are plated with 30 μm copper then flashed with gold to

15   reduce the resistance of the heaters at the ends; this avoids overheating the ends of the sample trap while controlling the temperature in the center (Figure 2b). The trap assemblies are installed inside the 3.2 mm OD stainless steel support tubes described above. During typical operation throughout the sample cycle, the Stirling cooler is operated at 220W rather than full power, as this is adequate to maintain an average cold block temperature of -180 °C. At maximum cooler power, it is possible to operate the sample traps at temperatures

20   as low as -200 °C.

Figure 3a shows a typical temperature trace for each sample trap during an analytical cycle. At cycle time (t) = 0 s, the traps are held at temperatures slightly above trapping temperatures (-120 °C and -100 °C for channel 1 and 2, respectively) while being back-flushed with UHP He, to reduce the heat load to the Stirling cooler

25   between sampling periods. Before sample trapping begins, both traps are heated sequentially to >100 °C (at t = 105 s and t = 135 s for channels 1 and 2, respectively) and held at this temperature for 20 seconds to ensure the traps are as clean as possible, then cooled to their trapping temperatures (-165 °C and -135 °C for channel 1 and 2, respectively). The heater design allows for rapid heating and cooling of the sample traps, so the traps can switch from cold to hot set point temperatures in less than 3 seconds, and can be cooled from 100 °C to their

respective trapping temperatures in less than 30 seconds (Figures 3b and 3c). The novel geometry of the sample

trap and the duty cycles of the heaters allows for this performance, while operating within the constraints of

the lifting power of the Stirling cooler.

5   Sample flow is directed to both traps starting at t = 210 s by switching the 10-port valves from "flush" to "load"

position which is maintained for 240 seconds at a flow rate of 60 sccm; during sample collection, the sample

trap temperature is controlled to within 0.2 °C by heating. At t = 450 s, the 10-port valves simultaneously switch

back to the "flush" position stopping sample flow to the traps, which are then back-flushed with UHP He while

maintaining trapping temperatures. This post-collection flush removes most of the untrapped permanent gases

10   (e.g., nitrogen, oxygen, argon) from the sample trap flow path, thereby reducing the chromatogram background

signal at the start of each channel. The sample traps are flash-heated at t = 553 s and t = 796 s of the cycle

(channel 1 and 2, respectively) to 100 °C to inject the analyte onto the separation columns. The trapped volume

is small enough and is injected onto the column quickly/efficiently enough so that no cryofocus is required on

the column heads.

After trapping, the concentrated samples are injected in turn onto the respective chromatography columns.

UHP He is used as the carrier gas, at a constant flow of 2 sccm, with the total chromatogram requiring 780

seconds of run time. After separation, the column effluent is directed sequentially to the MSD via a four-port

valve (Figure 1), with channel 1 measured first, followed by channel 2. Channel 1 uses an Al_2O_3/KCl PLOT column

20   (Restek RT-Alumina BOND/KCl; 30 m length, 0.25 mm ID, 4 µm film thickness), with a temperature profile

ramped from 35 °C to 190 °C in 190 seconds. Channel 2 uses a low- to mid-polarity modified methylpolysiloxane

(Restek MXT-624; 30 m length, 0.25 mm ID, 1.4 µm film thickness), with a temperature profile ramped from 40

°C to 170 °C in 518 s. For both columns, the temperature programs are multi-step ramps with several different

heating rates used to optimize peak separation for each column (Figure 4a). The columns are individually

25   sheathed inside two custom interlocking aluminum spindles (12.2 cm OD, 10.5 cm ID). The columns are

wrapped around the innermost spindle along with resistive temperature detectors (RTDs) for temperature

measurement. The spindles are heated resistively with Kapton thin-film heaters. Both spindles are suspended

inside fiberglass housings by thin (0.38 mm) stainless steel tabs. The housings have 150 x 172 mm fans mounted

on one side to cool the columns; the fans are operated by pulse-wave modulation and can be reduced to ≈ 40%

power allowing for low air flow rates across the heated column spindles thereby improving temperature control at temperatures close to ambient. After each column has completed separation, it is back-flushed with UHP He while heated to 190 °C or 210 °C for channel 1 and 2, respectively, before cooling in preparation for the next sample.

The mass spectrometer (Agilent model 5975C) is usually operated in selected ion monitoring mode, scanning up to 11 masses per window, 28 windows per chromatogram with dwell times between 10 and 20 milliseconds per mass, to optimize instrument sensitivity while providing enough sample points per mass to accurately determine peak area. Beginning with the 2015 SONGNEX campaign, a new peak-integration software package called Tern (Aerodyne Research, Inc.) has been used for automated peak-area retrieval (Isaacman-Van Wertz et al., in preparation). Tern is a custom-designed chromatographic data handler and peak integration package built upon Igor Pro's (Wavemetrics, Inc.) multi-peak fitting functionality. Chromatographic peaks are fit by minimizing the residual of a set of Gaussian and exponentially-modified Gaussian peaks for a subset of the chromatogram (typically 20 seconds) on a single mass. The peak within this optimized fit considered most likely to be the analyte of interest is returned, and the peak area is calculated from the coefficients of the solution. Use of Tern to integrate chromatograms has reduced analysis time to approximately 1.25 minutes per chromatogram, at least an order of magnitude faster than the previous method using Agilent Chemstation and hand-integration, while increasing peak area precision and accuracy (Isaacman-VanWertz et al., 2016).

2.2.3 Canister cleaning and conditioning

After the canisters have been analyzed, they must be prepared and conditioned for reuse. An automated cleaning oven has been constructed that allows for the unattended processing of three canister modules at one time. Each canister manifold, and then each individual canister, is evacuated and leak-tested. The canisters are then heated to 65°C under vacuum using a dry scroll pump, typically to less than 0.01 hPa as measured between the canister modules and the pump. Canisters are then filled with high-purity nitrogen gas (UHP N2 or liquid nitrogen blow-off) and re-evacuated. The nitrogen flush process is repeated a minimum of 3 times. After the final canister pump down, approximately 15 hPa of water vapor is added to the canisters to reduce artifacts in the subsequent air sample collected in the canisters (Ochiai et al., 2002). Note that for the SENEX field campaign, humidified UHP nitrogen was used rather than water vapor, as most canisters were collected in the

summertime southeast U.S. planetary boundary layer where ambient water vapor is adequate to condense liquid water in the sample canisters at sample pressures. A full research flight of 72 canisters (6 modules) requires at least 12 hours of cleaning and conditioning before they are ready to be reused. During a field campaign, the efficacy of the cleaning system is evaluated by filling cleaned and humidified canisters with the

5 same zero air gas used to test for artifacts (see below).

3 Results: Normalization, calibration, artifacts

3.1 Normalization of instrument response

For both chromatograph channels, normalization is required to account for changes in instrument sensitivity

10 primarily attributable to changes in detector response. Halocarbon species long-lived in the atmosphere are used for normalization, effectively serving as internal standards for canister samples. Four halocarbons have been selected (only two were used for SENEX) which are abundant and relatively constant in tropospheric air as a function of latitude over the typical one-month time period of a field campaign: Freon-12 [CF_2Cl_2, dichlorodifluoromethane], Freon-11 [$CFCl_3$, trichlorofluoromethane], CFC-113 [$CFCl_2$–CF_2Cl, 1,1,2-trichloro-

15 1,2,2-trifluoroethane] and carbon tetrachloride [CCl_4, tetrachloromethane]. Expected mixing ratios in ambient air for each halocarbon (Table 1) are estimated from data provided by the NOAA Global Monitoring Division using averaged monthly data from the nearest sampling sites by latitude: Niwot Ridge, CO and Trinidad Head, CA (Montzka et al., 2015). These halocarbons are also added quantitatively to a custom-dilution of a 57-component ozone precursor hydrocarbon standard (Scott Specialty Gases) in UHP nitrogen. This gas mixture

20 serves as a single-point secondary standard during field measurements to characterize instrument response throughout the campaign. The secondary standard is also measured periodically during sensitivity studies (Sect. 3.2), as the analyte consists of standard(s) diluted in UHP nitrogen and therefore has no significant halocarbon mixing ratios.

This allows for quantification of normalization factors in both ambient samples and calibration samples.

A normalization factor is calculated for every sample, based on the raw peak area for CF_2Cl_2 on channel 1 ($CFCl_3$ and CFC-113 were also used for SONGNEX, see below), and CCl_4 on channel 2. The calculation of a normalization factor (NF) is shown in Eq. 1:

$$NF = Raw_{halo}/Target_{halo} \qquad (1)$$

Here, *halo* is a halocarbon used for normalization, *Raw* is the integrated raw counts for a peak, and *Target* is the expected raw counts. The secondary standard has a CCl_4 mixing ratio of 87.5 pptv, with a target response of 15,000 counts; during SONGNEX an ambient mixing ratio of 84.1 pptv as reported by NOAA GMD, and a target response of 14,400 counts was assumed. For SENEX, a single normalization factor was calculated for each channel using Eq. 1. For SONGNEX, three normalization factors (NF_{halo}) were calculated for channel 1 from halocarbon responses spanning that channel's elution time (Figure 4). The final normalization factor was then calculated by linear interpolation, based upon the target analyte retention time (Eq. 2); for species eluting outside these halocarbon retention times, the nearest halocarbon factor was used.

$$NF_{sp} = Raw_{sp}/\left[NF_{halo_2} - \left(NF_{halo_2} - NF_{halo_1}\right) \times \left(RT_{halo_2} - RT_{sp}\right)/\left(RT_{halo_2} - RT_{halo_1}\right)\right] \qquad (2)$$

Here, *sp* is the analyte species of interest, $halo_1$ and $halo_2$ are the halocarbons eluting before and after the analyte, respectively, and RT is retention time. The additional step of fitting multiple halocarbons was performed for channel 1 to account for some additional sensitivity changes independent of the detector response, which may be related to changes in trapping efficiency of the PLOT material in the sample trap. Peak areas are reported as normalized kilocounts (nkcts) simply by dividing the raw peak area by the relevant NF. This method is applied to all samples with known mixing ratios of these halocarbons, either from standards or ambient air, rather than interpolating only between standards in order to improve the accuracy of the normalization. For samples with no or unknown mixing ratios of halocarbons (e.g. instrument zeros, sensitivity calibrations), the normalization factors are interpolated from ambient and calibration samples.

3.2 Sensitivities

Sensitivities for all reported species are individually calculated by measuring the instrument response to a set of dynamic dilutions of gravimetric standards, using humidified UHP nitrogen as the diluent. Typically, at least seven dilution levels are sampled over at least three orders of magnitude; for SONGNEX, this range was 0.03 ppbv – 70 ppbv. Hydrocarbon calibrations are performed with a nominal 1 ppm PAMS 57-component commercial standard (Scott Specialty), with a stated 5% uncertainty of individual component concentrations. Inter-comparisons of multiple PAMS commercial standards across C2-C5 hydrocarbons gave 3-18% differences,

with an average difference of 10%. For other species – oxygenated compounds, alkyl nitrates, monoterpenes –
are calibrated with in-house-made gravimetric standards consisting of 1-10 ppm mixtures of up to 10 species,
with 5% uncertainties. In-house standards include at least two hydrocarbons also found in the PAMS standard,
typically benzene or toluene, in order to confirm that instrument response is consistent across a series of

5   calibration tests. Accounting for additional measurement errors of flows of the dynamic dilution system and
uncertainties in normalization, total uncertainty is estimated at 12% for the calibration method.

Instrument responses for most compounds are non-linear over the dynamic range of the calibrations. This
behavior is consistent with what has been observed on this laboratory's previous GC-MS system, although the

10   non-linear response on the previous generation of this instrument was only significant for later eluting
compounds (those after benzene). The behavior is sigmoidal, in that sensitivity is constant at low mixing ratios,
then transitions to a higher sensitivity at high mixing ratios. The non-linearity is currently attributed to the
water trap. At high mixing ratios the gas-phase analyte reaches equilibrium with adsorbed analyte on the
wetted surfaces of the water trap, while at low mixing ratios this equilibrium is never reached and losses are

15   kinetically determined. Precise control of the water trap temperature and sample flow rate are required to
ensure that the non-linearity is reproducible. Alternative water trap geometries and materials are currently
under investigation to reduce this non-linearity.

3.3 Precision and limits of detection

20   Instrumental precision for most species is determined from the measurement of the secondary standard
described in Sect. 3.1 during field measurements. The secondary standard is typically measured at the beginning
and end of each flight analysis, and at least three times during analysis. For example, during SONGNEX 1327
sample measurements and 138 standard measurements were made. Precision is defined here as relative
deviation from the mean of the normalized response for each species measured in the secondary standard,

25   reported as a percentage. For species that are not in the standard, precision is estimated from the standard
deviation of a dynamic dilution calibration normalized data point near the middle of the calibration dynamic
range. Precision uncertainty is less than 7% for most species reported in Table 2. Detection limits for the
various species (DL; Table 2) may be calculated in units of pptv analyte using the sum of a precision estimate
and the instrument sensitivity:

$$DL = 3 \times \sigma_{prec} \times Sens \qquad (3)$$

where σ_{prec} is the standard deviation of the lowest calibration point (minimum 4 replicates) for any reported

species in units of nkct$s$ and *Sens* is the instrument sensitivity for that species, in units of pptv nkct^{-1} (Oliver et

al., 1996). For most species, the detection limit is less than or equal to 5 pptv and often below 1 pptv, however

5   ACCBAR had significantly higher limits of detection for several oxygenated species. The humidification system

used during dynamic dilutions contributes significant backgrounds for some oxygenated species (e.g. alcohols)

and thereby increasing the standard deviation of those calibration points. To assess the overall analytical

uncertainty further, the measurement of n-hexane, which is quantified on both channels of the GC-MS are

compared. Figure 5 shows a scatter plot of n-hexane measurements for the entire SENEX field campaign. The

10   two-sided linear fit of the data indicates an agreement within 4% with an insignificant intercept and little scatter

(a least-squares fit gives a correlation coefficient, r, of 0.98).

3.4 Sample canister tests

Previous work (Kelly and Holdren, 1995; Ochiai et al., 2002; Palluau et al., 2005) has indicated that samples

15   collected in dry electropolished stainless steel canisters may be subject to significant artifacts due to loss of

certain VOCs to the canister walls, while samples humidified either via addition of water prior to sampling or by

adequate ambient water vapor will be less prone to these effects. The iWAS/ACCBAR system was evaluated for

potential artifacts due to canister preparation, sample collection, and sample aging. This was accomplished via

four sets of tests.

3.4.1 Canister humidification and retrieval efficiency

A series of humidification experiments were performed using ambient air samples collected outside the

laboratory in Boulder, CO in canisters filled with varying amounts of water vapor after the cleaning process

(Figure 6). The goal of these tests was to determine the minimum level of water vapor that should be added to

25   the sample canisters in order to sufficiently reduce analyte losses to the canister surfaces. ACCBAR collected

and measured the ambient air *in-situ* while canister were simultaneously filled, using a common PFA inlet for

both systems. Ambient dew points during these tests varied between -1 − 5 °C (15 − 40 % RH), while air

temperature was between 21 − 28 °C. Fill times for the canisters were approximately 30 seconds; these

extended fill times were achieved by restricting the inlet flow to the compressor and opening multiple canisters at the same time. Canisters were evaluated for retrieval efficiency (Rtv Eff), which is defined as the ratio of canister mixing ratios to *in-situ* mixing ratios for samples collected at approximately the same time.

$$Rtv\ Eff = Mean\ concentration\ canister/Mean\ concentration\ in\ situ \qquad (4)$$

5 Most hydrocarbons show retrieval efficiencies near unity, with considerable scatter due to the difficulty in comparing a 4-minute integrated sample (*in-situ*) with a 30-second integrated sample (canister). For most species, water vapor pressure >10 torr (13 hPa) was found to be adequate to passivate the canisters, although heavy aromatics (>C8) showed significant losses at all levels. Ketones are positively correlated with added water, indicating a possible contamination with the canister humidification system.

3.4.2 Canister blanks

During SONGNEX, the sampling system was evaluated for background signal by filling canisters with zero air immediately after cleaning and humidifying, then allowing the cans to sit 1 – 3 days before analysis. These tests are in contrast to the analysis system blanks (see Sect. 2.2.1) as they identify signal enhancements attributable

15 to canister preparation. These results are presented in Table 2 as blanks in units of pptv. Hydrocarbons and alkyl nitrates have very small signals in the blanks, with ethane being the only species with a mixing ratio greater than 2 pptv. However, a few oxygenated species had blank values at atmospherically-relevant levels. The blanks were significantly larger than the analysis system blanks (the same zero air passed through the sample train) so the artifacts are attributed to the canisters rather than the analysis system. Since nearly all species but

20 oxygenates were below detection limit, the canister cleaning appears to be adequate. Instead, the source of contamination is likely the canister humidification system, confirming the observations noted in Sect. 3.4.1. Because of this contamination, oxygenates are not reported for SONGNEX. For SENEX, sample canisters were not pre-treated with water vapor but with humidified nitrogen (see Sect. 2.2.3), so mixing ratios of oxygenates collected in the planetary boundary layer are expected to be less perturbed for this dataset. Also note that

25 during SONGNEX, ACCBAR showed a significant ethanol contamination that decayed exponentially throughout the campaign, so that the reported ethanol blank value here is likely a combination of instrument and canister artifact.

3.4.3 Canister aging and retrieval efficiency

Additional canister tests were conducted to characterize the retrieval efficiencies and short-term storage (< 100 hour) effects of the iWAS/ACCBAR system using canisters prepared with approximately 12 torr of water vapor. For each sample period, four to nine canisters were filled with air collected from outside the Boulder, CO

5   laboratory while ACCBAR simultaneously measured the air *in-situ*, similar to that in described in Sect. 3.4.1. The ambient dew point during these tests was near 8 °C (45 – 55 % RH) with an air temperature around 18 °C. Due to the configuration of the canister sampling geometry, the canister fill times are not expected to be identical, but rather the first canister in the sample path will fill to full pressure slightly before the next canister. This results in larger variance sample-to-sample than replicate tests (see Sect. 3.4.4), especially for compounds with

10   transient ambient mixing ratios (e.g. aromatics and alkenes due to local auto exhaust). The canister samples were then measured 1, 2 and 4 days after collection. Two example plots are shown in Figure 7, the results are summarized in Table 2 and all test results are listed in Tables S1 and S2 of the Supplemental Information Section. At 95% confidence interval (mean + 2σ), there were only two differences in Rtv Eff between the canisters after 1, 2 or 4 days of aging across all compounds (Table S1), in agreement with the replicate tests

15   described in Sect. 3.4.1. Therefore, the data for these canister tests was grouped together irrespective of age to calculate a single Rtv Eff for each compound, which are shown in Table 2. Generally, hydrocarbon retrieval efficiencies vary near or slightly above unity, with no alkane, alkene or cycloalkane having a Rtv Eff significantly different than 1. Aromatic species and alkyl nitrates have Rtv Eff that are systematically low, although typically within 20% of the *in-situ* measurement. Oxygenated species were not well-behaved with aldehydes and ketones

20   showing large scatter, excluding methyl ethyl ketone and methacrolein. As noted above, the canister humidification system is the suspected source of this contamination. Further work will be required to identify the cause of this contamination in the humidification flow path and eliminate it.

3.4.4 Canister replicates

25   During SONGNEX replicate analysis was performed on full sets of canister samples from three research flights to evaluate the analytical precision of the entire system (rather than just the GC-MS). The research flights were made on April 9th through the eastern Permian Basin of Texas, April 13th in the Denver-Julesburg Basin and Colorado Front Range, and April 23rd through the western Permian Basin of Texas and New Mexico. These

canister sets were aged on average 37, 256, and 92 hours, respectively, between the first and second analysis. Example scatter plots comparing the first and second analysis are shown in Figure 8. For most species, the replicates were not significantly different than unity for the 37- and 92-hour replicates, with the notable exception of alcohols which were enhanced for the second analysis due to temporary partitioning into the aqueous phase (Kelly and Holdren, 1995). Replicate results for aldehyde and ketone species typically agreed within 10%, indicating that the analysis system does not contribute measurement artifacts for these species. For cans aged 256 hours on average, several additional classes of compounds (ketones, alkyl nitrates, aromatics) showed enhancements in the second analysis. For SONGNEX, most canisters (92%) were analyzed within 100 hours of sampling, so only the 37- and 92-hour replicate results are considered to be applicable here. The results of these tests are summarized in Table 2 as the slope of the two-sided linear regression of the combined 37- and 92-hour replicates, ignoring the 256-hour replicate samples.

4 Results: Measurement validation by inter-comparison with other measurements

4.1 SENEX 2013

The iWAS/ACCBAR system was first field-deployed for the SENEX field campaign in the southeast U.S. in late-spring 2013, where canister samples were collected aboard the NOAA WP-3D aircraft. As described in Sect. 2.2.3, the canisters were not filled with water vapor but rather with humidified UHP N2, as the typical boundary layer humidity levels were adequate to produce condensed water in the sample canisters at sample fill pressures. One set of 3 canister modules was not humidified at all, but was flown entirely evacuated during a test flight from Tampa, FL; these canisters were not considered for the orthogonal fits of the data discussed below. During the field campaign, a proton transfer reaction mass spectrometer [PTRMS;(de Gouw et al., 2003)] also flew aboard the NOAA WP-3D and measured 12 VOCs (individually or as grouped response by mass) using a nominal 15 second duty cycle, measuring an individual unit mass for one second. Inter-comparisons between the PTRMS and previous whole-air sampling systems have been published (de Gouw and Warneke, 2007) showing generally good agreement for aromatic species summed by carbon number, isoprene and select oxygenates, with correlation coefficients typically between 0.85 and 0.95.

Due to the large ambient variability of some species, additional scatter in the data is expected from the difficulty of time-aligning these two measurements. Canister sample fill times were less than 8 seconds for more than 95% of all samples during SENEX, so the comparison requires a 15 second averaging window of PTRMS data centered about the mid-point of the canister fill time. For SENEX, six individual or summed species

5   measured by both instruments are compared, as shown in Figure 9a-f. Light aromatic species (benzene and toluene) showed a significant difference in slope between the instruments, with the iWAS mixing ratios lower than the PTRMS. The trend is consistent with observed retrieval efficiency of toluene noted during the canister tests discussed above, but significant benzene losses in canisters have not been observed. Biogenic species were abundant in ambient air during SENEX, and the comparison between instruments compares favorably to

10   previous published work (de Gouw and Warneke, 2007) for both isoprene and summed monoterpenes (i.e., α-pinene, β-pinene, 3-carene and limonene from the canister measurements vs. *m/z* 137 for the PTRMS) (de Gouw et al., 2015). Inter-comparisons of acetone and the summed response of methyl vinyl ketone and methacrolein both show a significant difference in slope between the instruments, with the canister system showing a higher response than the PTRMS, especially for MVK + MACR. Interestingly, the 36 dry canisters –

15   circled in Figure 9e – have a pronounced enhanced signal for acetone, but the MVK+MACR scatterplot does not show the same response. Recent work has found that oxidation products of isoprene may contribute to artificial response in the whole air canister system, and the retrieval efficiency experiments indicated a particular enhancement of MVK in the iWAS canisters, consistent with modeling results (Rivera-Rios et al., 2014; Wolfe et al., 2015). Therefore, the difference between instruments for MVK+MACR is attributed to enhanced response of

20   MVK. Note that all species reported here have a correlation coefficient greater than 0.85, with the exception of acetone, comparable to previous inter-comparisons between whole air samplers and PTRMS techniques cited above.

4.2 SONGNEX 2015

25   For SONGNEX, a more limited set of inter-comparisons with other instruments is available due to the apparent contamination of the canister during preparation by oxygenated species (see Sect. 3.4), and due to the ambient mixing ratios of observed species (isoprene and monoterpenes were at low mixing ratios during early spring). The PTRMS instrument that had been used for previous field missions was replaced with a new hydronium-ion chemical ionization time-of-flight mass spectrometer (H_3O^+-CIMS) (Yuan et al., 2016). A new spectroscopic-

based ethane detector (Yacovitch et al., 2014) was also aboard the NOAA WP-3D aircraft, providing an

additional compound for inter-comparison. Light aromatic species (benzene and toluene) were measured by

both iWAS-ACCBAR and the H_3O^+-CIMS, and scatterplots of these mixing ratios are shown in Figure 10a-b. The

benzene slope is insignificantly different from one given the stated uncertainties of the instruments, while the

5   H_3O^+-CIMS observed slightly higher toluene mixing ratios , which is in-line with the results of the canister tests

described in Sect. 3.4. Comparison of ethane measurements (Figure 10c-d) shows a very tightly correlated

measurement with a significant difference in slope (higher response by the spectroscopic instrument). This

discrepancy is partially attributable to an inconsistency on the order of 10% within the ethane calibration scales

used for the two instruments. If a single calibration scale is applied to both instruments, the measurements

10   agree within 8%, which is within the stated uncertainty for ACCBAR.

An alternative evaluation for the quality of measurements made with the canister system is possible by

comparing measurements made in the same airshed by different instruments at different times. Absolute

mixing ratios are expected to vary with time, but ratios of species with high emission rates and relatively slow

15   atmospheric reaction rates are expected to be stable if emission sources are consistent over the time period of

the inter-comparison. Research flights made during SONGNEX overflew two shale basins that had been recently

characterized by NOAA CSD using an older GC-MS system: Uinta Basin in Utah (Warneke et al., 2014) and

Denver-Julesburg in Colorado (Gilman et al., 2013). Figures 11a-b show inter-comparisons of two different pairs

of alkanes from the Uinta Basin and Denver-Julesburg fields, respectively. The ratio of propane to ethane,

20   determined by the slope of a two-sided linear fit, was statistically equivalent for the Uinta Basin between 2012

and 2015, although the absolute mixing ratios observed during the ground-based campaign are considerably

higher than the aircraft measurements. For Denver-Julesburg, two sets of ground-based measurements have

previously been reported, wintertime measurements made at the southwest edge of the oil and gas exploration

area [NACHTT 2011] and summertime measurements made at the northwest edge of the area near Ft. Collins,

25   CO [BIOCORN 2011]. The ratio of iso-pentane to n-pentane determined by a two-sided linear fit for the

SONGNEX flight data is statistically equivalent to the BIOCORN 2011 data, but the NACHTT 2011 data has a

slightly higher ratio. The difference for the NACHTT data may be due to the difference in season affecting the

relative oxidation rates of iso-pentane and n-pentane, or from the influence of the nearby Denver metropolitan

area where the iso- to n-pentane ratio is higher because of gasoline emissions from mobile sources.

5 Conclusions

A new automated whole air sampler and GC-MS analysis system that relies upon cryogenic sample pre-

5 concentration without the need for liquid nitrogen has been designed, built and field-deployed. The whole air

sampler typically fills 72 sample canisters during a single research flight; post-flight analysis requires 30 hours

with minimal interaction with the operator. A new peak integration software package allows for the automated

retrieval of peak areas, thereby reducing post-analysis data processing time by an order of magnitude. Over

2400 air samples were analyzed during the SENEX 2013 and SONGNEX 2015 field campaigns, with mixing ratios

10 reported for a wide range of hydrocarbons (alkanes, alkenes, aromatics), alkyl nitrates, monoterpenes and

select oxygenated species. The system limit of detection is typically below one part-per trillion with precision

uncertainty (at 1σ) less than 10%. Significant sampling artifacts were observed from the canister samples for

several classes of oxygenated species (aldehydes, ketones, alcohols) along with significant losses of heavy

aromatics (C9+). Inter-comparison with other measurements indicates good results for light aromatics and

15 biogenic hydrocarbons, with improved agreement for the SONGNEX 2015 campaign.

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Table 1. Summary of measurement parameters for SENEX 2013 and SONGNEX 2015 campaigns.

Parameter	SENEX 2013	SONGNEX 2015
Field work dates	May-June 2013	March-April 2015
Location of field work	Southeast U.S.	Central/Western U.S.
Canisters analyzed	1115	1326
Median time between collection and analysis (h)	89	62
Canister humidification method	Humidified N_2	Water vapor
Chromatogram analysis method	Manual integration	Semi-automated
Species reported as of publication	24	24
Expected ambient halocarbon mixing ratio (pptv)		
CF_2Cl_2	523	518
$CFCl_3$	not used	234
CFC-113	not used	73.8
CCl_4	85.4	84.1

Table 2. Precision, detection limits [DL], canister backgrounds [Blank] and canister test results for select VOC species measured by iWAS/ACCBAR. Replicate compares two analyses of the same sample canister performed within 100 hours of each other. Retrieval efficiency [Rtv Eff] is the ratio of the observed mixing ratio between canister and *in-situ* samples collected simultaneously, with the canisters then analyzed within 100 hours of collection. Values in parenthesis are 1σ uncertainties in the reported mean values. Bolded values are significantly different than 1 at 95% confidence interval and within the precision of the measurement.

Compound	Channel	Precision [%]	DL [pptv]	Blank [pptv]	Replicate	Rtv Eff
Ethane	1	8	0.6	6 (1)	0.98 (0.01)	1.06 (0.14)
Propane	1	6	3	B.D.L.	0.93 (0.01)	1.05 (0.21)
i-Butane	1	5	1	0.9 (0.3)	0.95 (0.01)	n/a
n-Butane	1	5	0.8	B.D.L.	0.97 (0.01)	1.13 (0.07)
i-Pentane	1	3	0.8	B.D.L.	0.97 (0.01)	0.95 (0.07)
n-Pentane	1	3	0.8	B.D.L.	0.99 (0.01)	1.04 (0.06)
n-Hexane	1	4	5	B.D.L.	0.98 (0.01)	0.95 (0.04)
n-Hexane	2	3	1	B.D.L.	1.01 (0.01)	0.94 (0.06)
n-Heptane	2	4	0.8	B.D.L.	0.97 (0.01)	1.07 (0.10)
n-Octane	2	3	1	B.D.L.	0.97 (0.01)	1.09 (0.11)
n-Nonane	2	5	2	B.D.L.	0.98 (0.01)	1.05 (0.07)
Ethene	1	8	3	B.D.L.	0.98 (0.01)	1.05 (0.33)
Isoprene	1	7	3	B.D.L.	1.11 (0.03)	0.98 (0.06)
α-Pinene	2	1	1	B.D.L.	0.92 (0.35)	1.05 (0.09)
β-Pinene	2	1	2	B.D.L.	n/a	1.16 (0.10)
Ethyne	1	5	0.5	B.D.L.	1.02 (0.01)	1.02 (0.08)
Methylcyclopentane	2	3		B.D.L.	1.06 (0.01)	1.13 (0.08)
Cyclohexane	2	4	2	B.D.L.	**1.11 (0.02)**	1.18 (0.09)
Methylcyclohexane	2	5	1	B.D.L.	0.94 (0.01)	1.03 (0.08)
Benzene	2	2	0.6	0.5 (0.1)	0.97 (0.01)	0.99 (0.07)
Toluene	2	4	2	B.D.L.	0.96 (0.01)	0.87 (0.06)
Ethylbenzene	2	6	1	B.D.L.	0.95 (0.01)	0.92 (0.09)
m,p-Xylenes	2	2	1	B.D.L.	**0.94 (0.01)**	**0.78 (0.08)**
o-Xylene	2	4	1	B.D.L.	0.98 (0.01)	**0.82 (0.08)**
Nitrate, ethyl	2	2	4	B.D.L.	0.96 (0.01)	0.98 (0.14)
Nitrate, i-propyl	2	2	3	B.D.L.	1.00 (0.01)	**0.87 (0.02)**
Nitrate, n-propyl	2	2	4	B.D.L.	1.00 (0.01)	0.91 (0.07)
Methanol	2	4	15	100 (50)	**1.28 (0.02)**	1.6 (1.3)
Ethanol	2	4	12	600 (150)	**1.35 (0.02)**	1.26 (0.15)
Acetone	2	2	5	180 (110)	0.95 (0.03)	-0.8 (85)
Methyl ethyl ketone	2	1	3	25 (25)	**0.95 (0.01)**	1.03 (0.12)
Methyl vinyl ketone	2	2	5	12 (5)	**1.06 (0.01)**	32 (154)
Acetaldehyde	2	3	8	390 (280)	**1.07 (0.02)**	31 (32)
Propanal	2	2	3	40 (40)	0.95 (0.03)	42 (76)
Methacrolein	2	2	3	B.D.L.	**1.11 (0.02)**	1.25 (0.16)

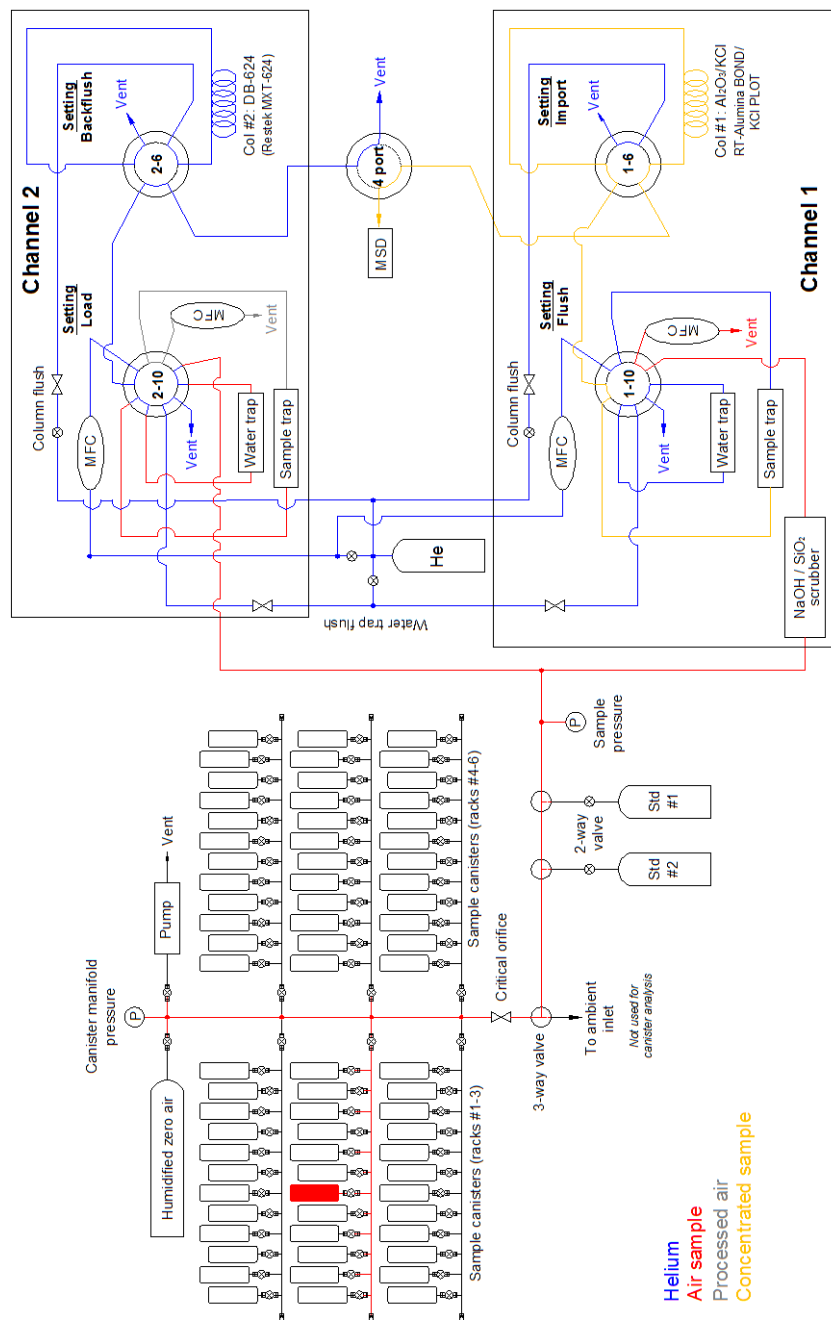



Figure 1. Schematic of instrument with flow path and valve position. Figure shown with open valve for a canister of middle-left sample module, Ch 1 flushing sample trap effluent to separation column, and Ch 2 loading sample trap.

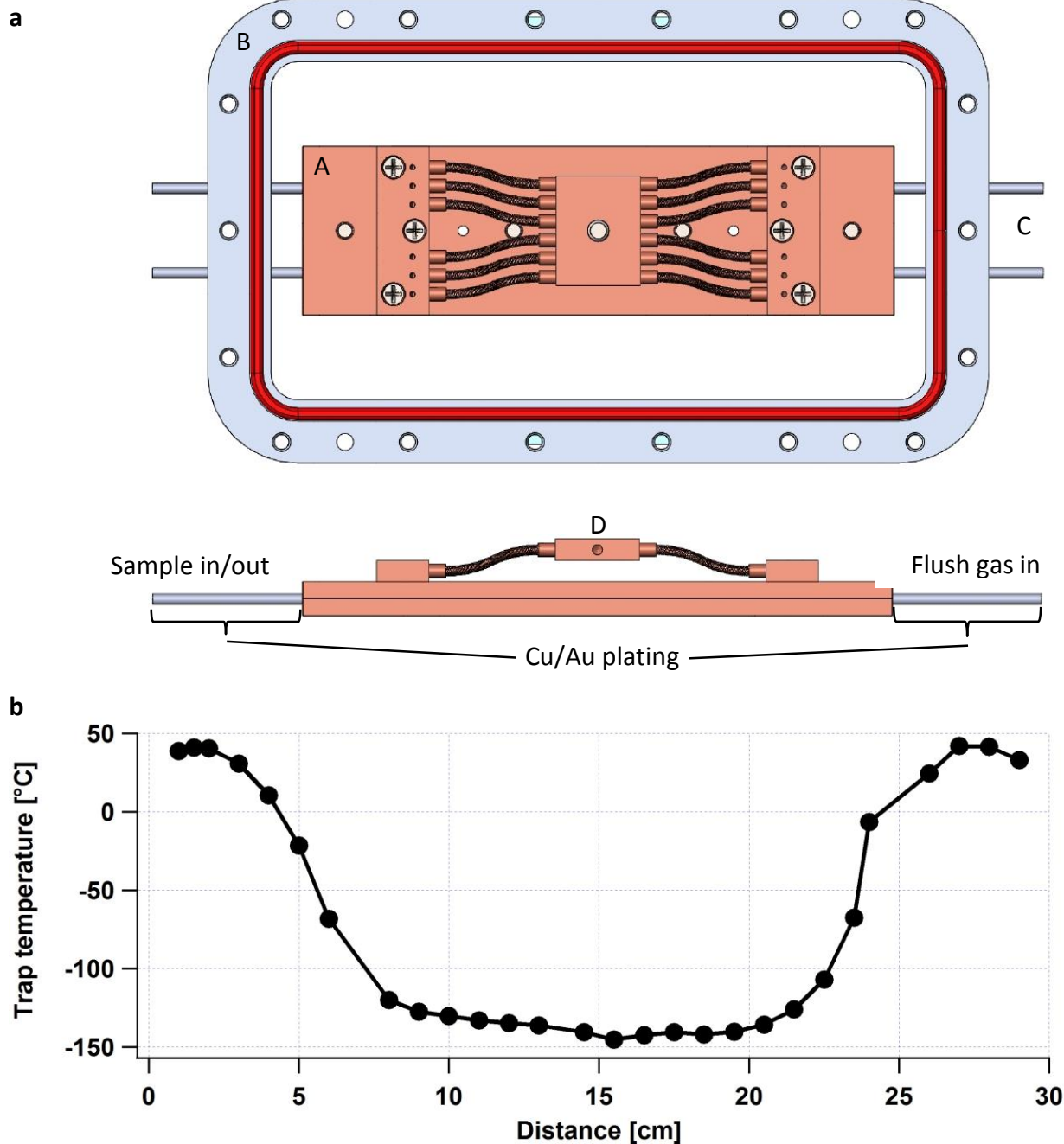



Figure 2. a) Drawing of ACCBAR sample trap (top view, side view). The cold block (A) is mounted inside a vacuum chamber (B), suspended upon two 3.2 mm OD stainless steel tubes (C). The Stirling cooler cold finger (not shown) bolts to the floating stage (D) centered above the cold block. b) Temperature profile of Ch #2 sample trap at nominal -135°C.

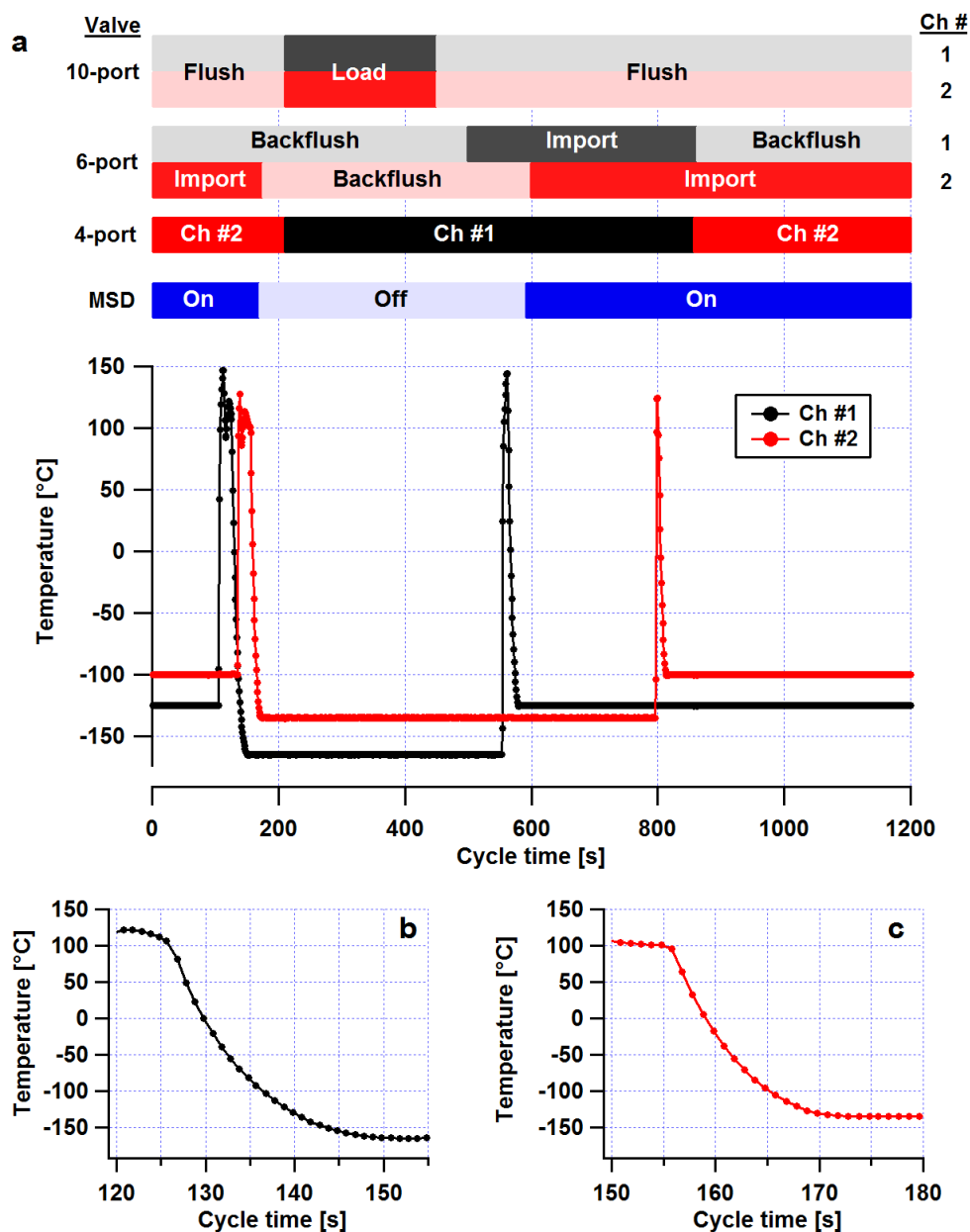



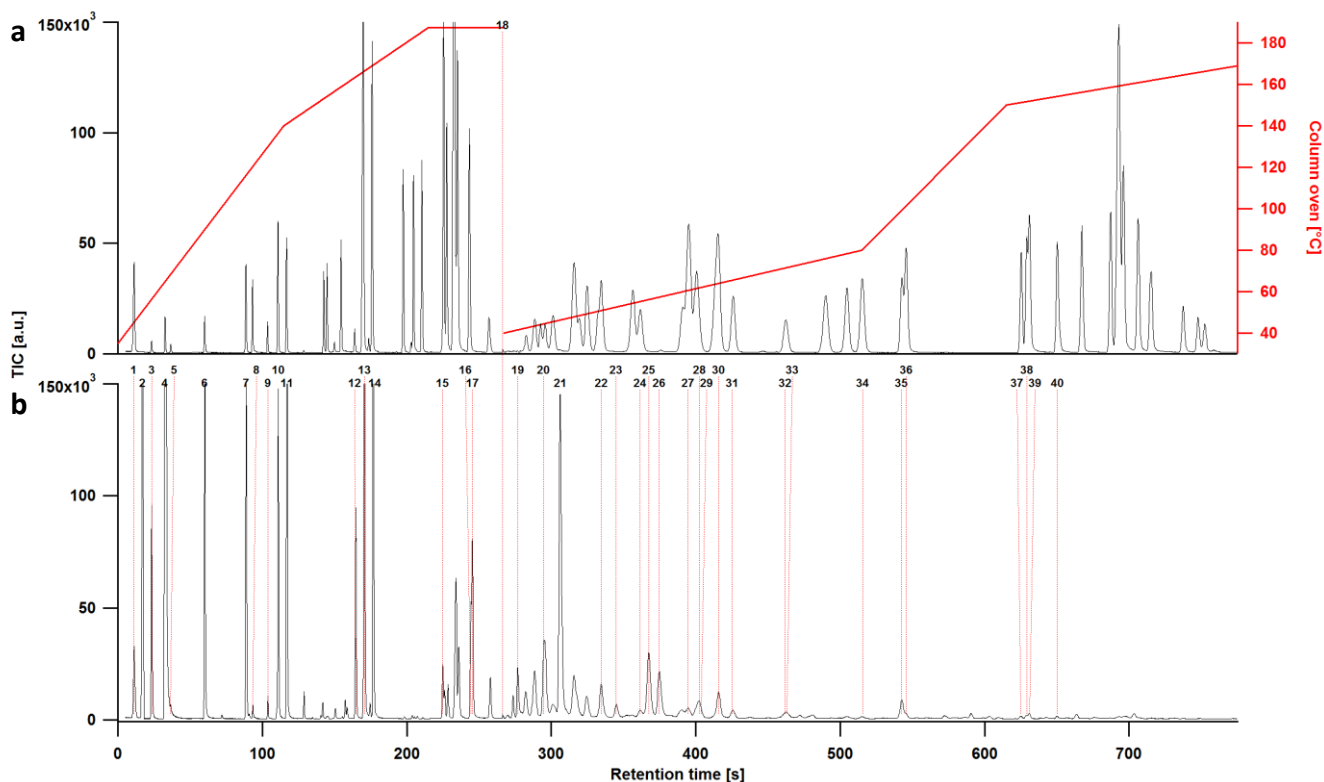
Figure 3. a) Valve positions and temperature profile of sample traps for an analysis cycle. The 10-port valves control flow to the water and sample traps, the 6-port valves control flow to the separation columns and the 4-port valve controls flow to the detector. b) For Ch #1 trap, the exponential rate of cooling ≈ 8.4 sec and the trap is cooled from 100 °C to -165 °C in 25 sec. c) For Ch #2 trap, the exponential rate of cooling ≈ 7.0 sec and the trap is cooled from 100 °C to -135 °C in 18 sec.

1	Air spike	9	Ethyne	17	Isoprene	25	Methyl vinyl ketone	33	Nitrate, i-propyl-
2	Xenon	10	Butane, iso-	*18*	*Start of channel 2*	26	Methyl ethyl ketone	34	Nitrate, n-propyl-
3	Ethane	11	Butane, n-	19	Methanol	27	Cyclohexane	35	Toluene
4	Nitrous oxide	**12**	**Freon-11 (CFCl₃)**	20	Ethanol	28	Carbon tetrachloride	36	Octane, n-
5	Ethene	13	Pentane, iso-	21	Acetone	29	Nitrate, ethyl-	37	Benzene, ethyl-
6	Propane	14	Pentane, n-	22	Hexane, n-	30	Benzene	38	Nonane, n-
7	**Freon-12 (CF₂Cl₂)**	**15**	**CFC-113 (CFCl₂-CF₂Cl)**	23	Methacrolein	31	Heptane, n-	39	Xylenes, m&p-
8	Propene	16	Hexane, n-	24	Cyclopentane, methyl-	32	Cyclohexane, methyl-	40	Xylene, o-

Figure 4. Chromatograms displayed as total ion count (TIC) with select peaks identified. Top panel (a) shows secondary standard, along with temperature ramp for each GC channel. Bottom panel (b) shows air sample collected in the Haynesville oil & gas field near Shreveport, Louisiana, 25-Apr-2015.

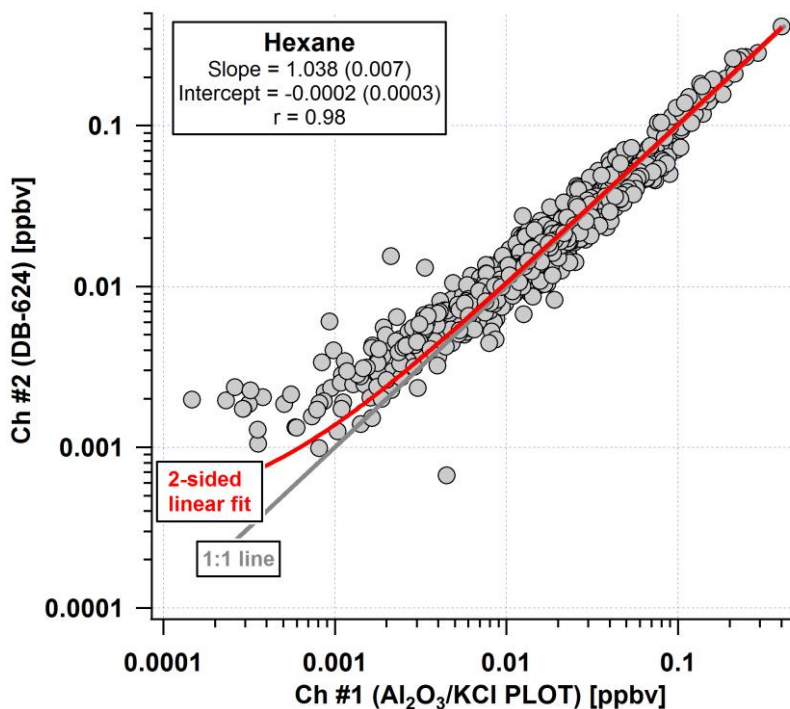



Figure 5. Inter-comparison of n-hexane measurements made by the two different channels of iWAS-ACCBAR system during SENEX 2013.

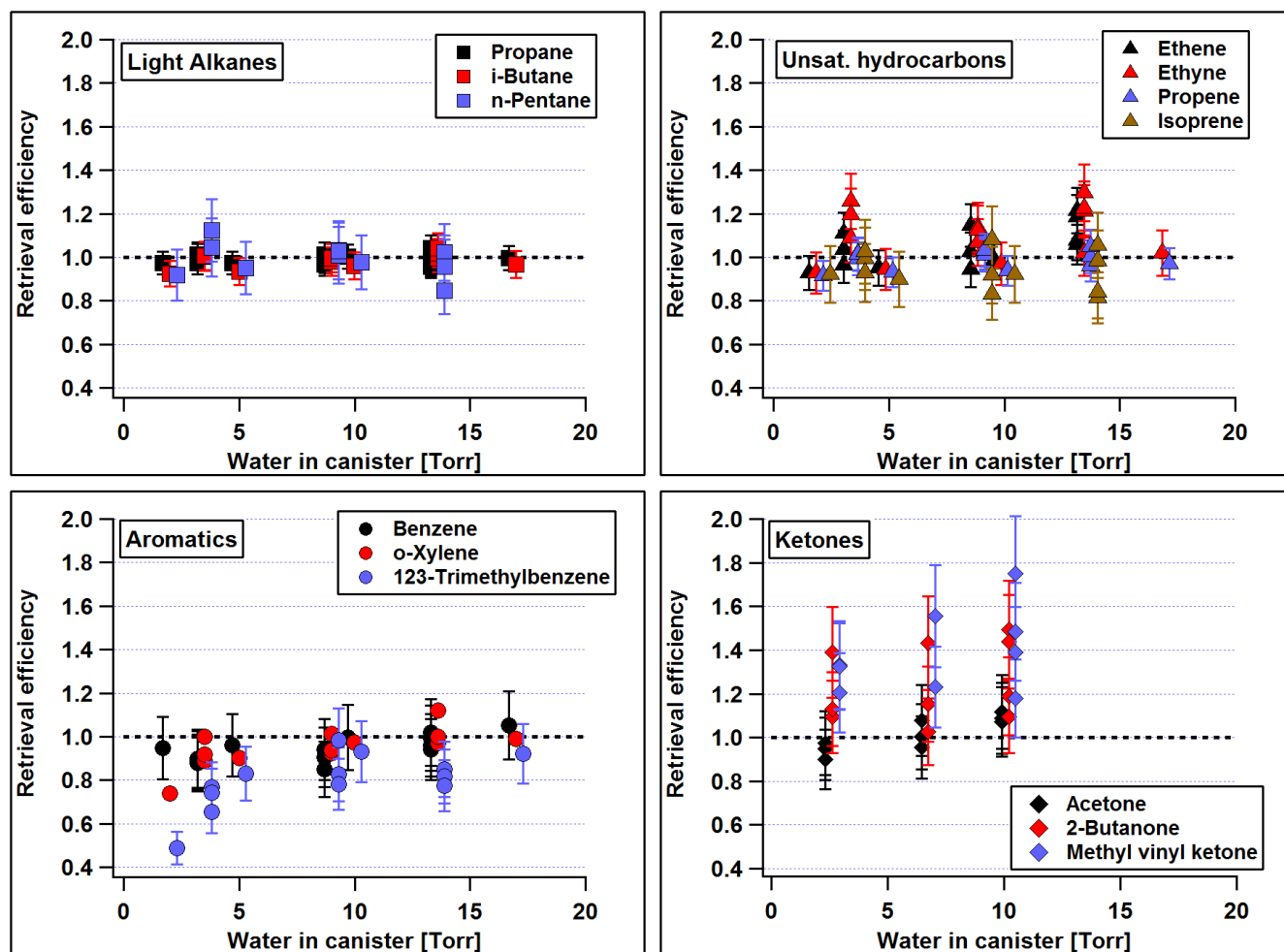



Figure 6. Retrieval efficiency as a function of added water vapor to sample canisters after cleaning. Data points are the ratio of observed mixing ratios in canister samples versus ambient mixing ratios measured by ACCBAR during the time period the canisters were filled. Error bars indicate standard deviation of multiple canisters filled simultaneously. Data are offset on x-axis for easier viewing.

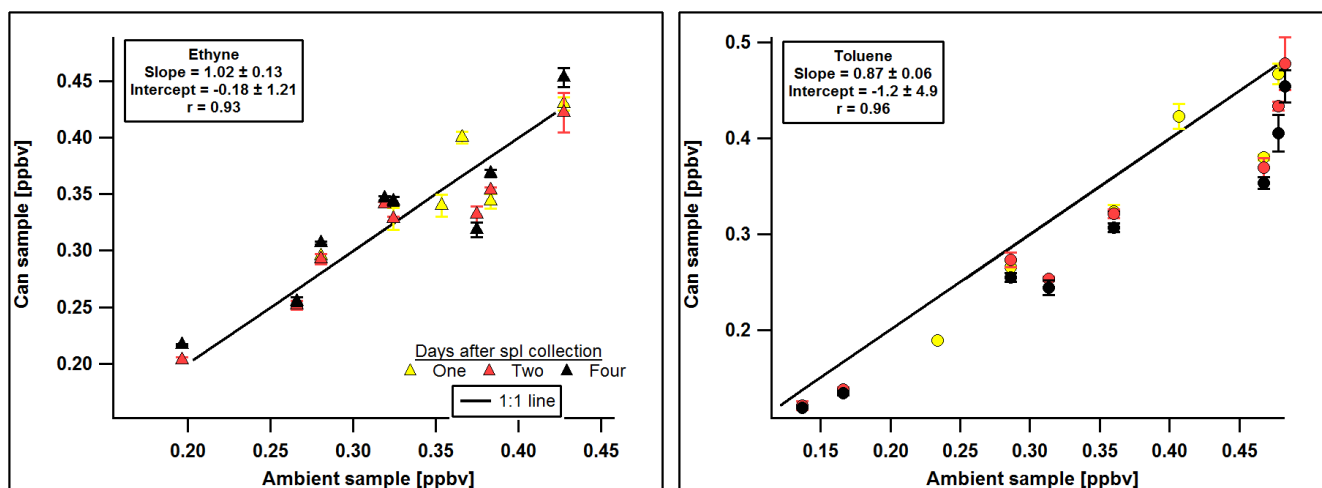



Figure 7. Canister samples versus in-situ ambient samples collected in Boulder, CO, using sample canisters humidified to 12 torr water vapor during the cleaning process. Error bars indicate standard deviation of replicate canister samples.

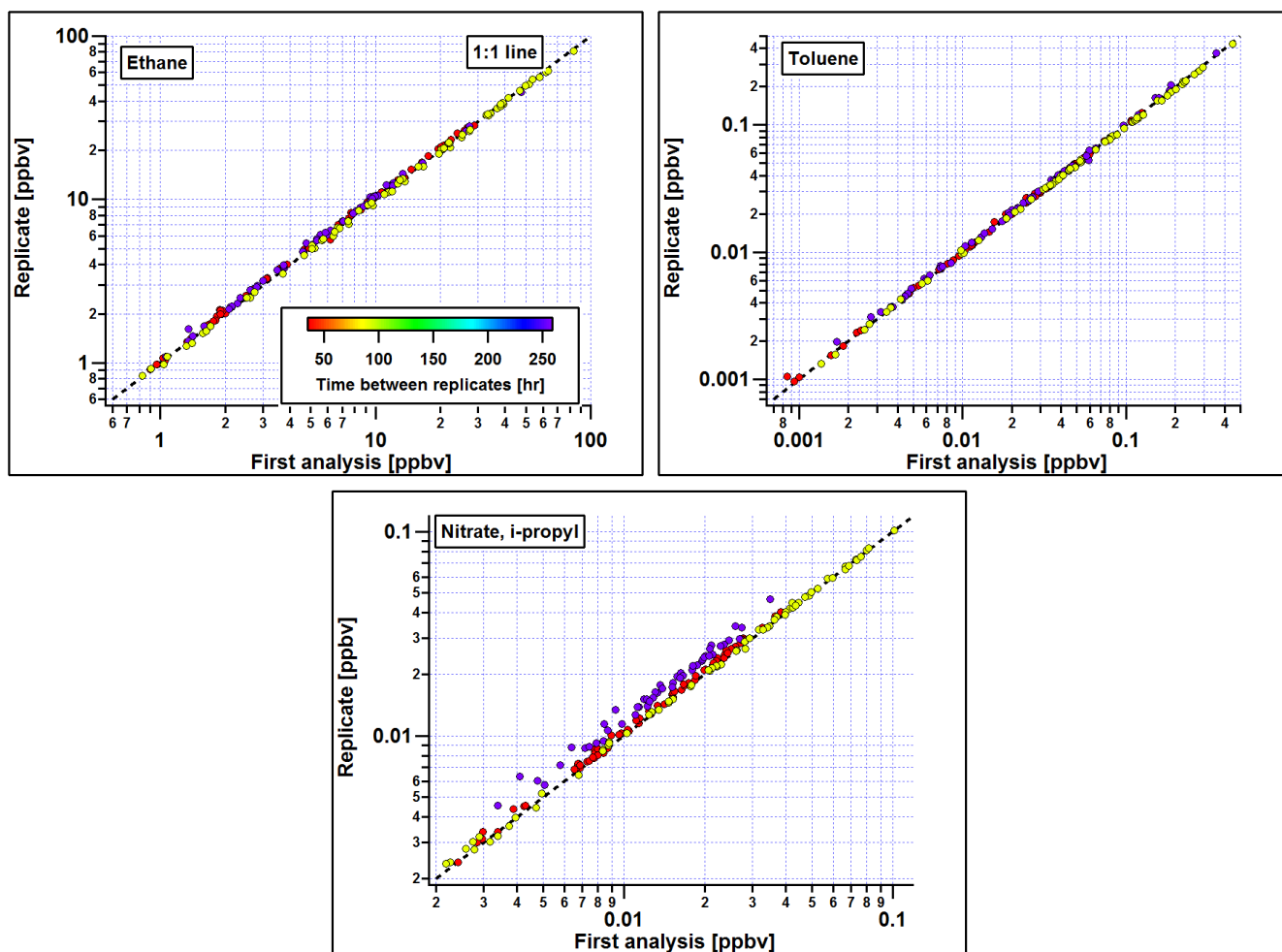



Figure 8. Comparison of replicate analyses from the same sample canister sets from three flights during SONGNEX 2015 (flight dates: April 9, April 13, April 23).

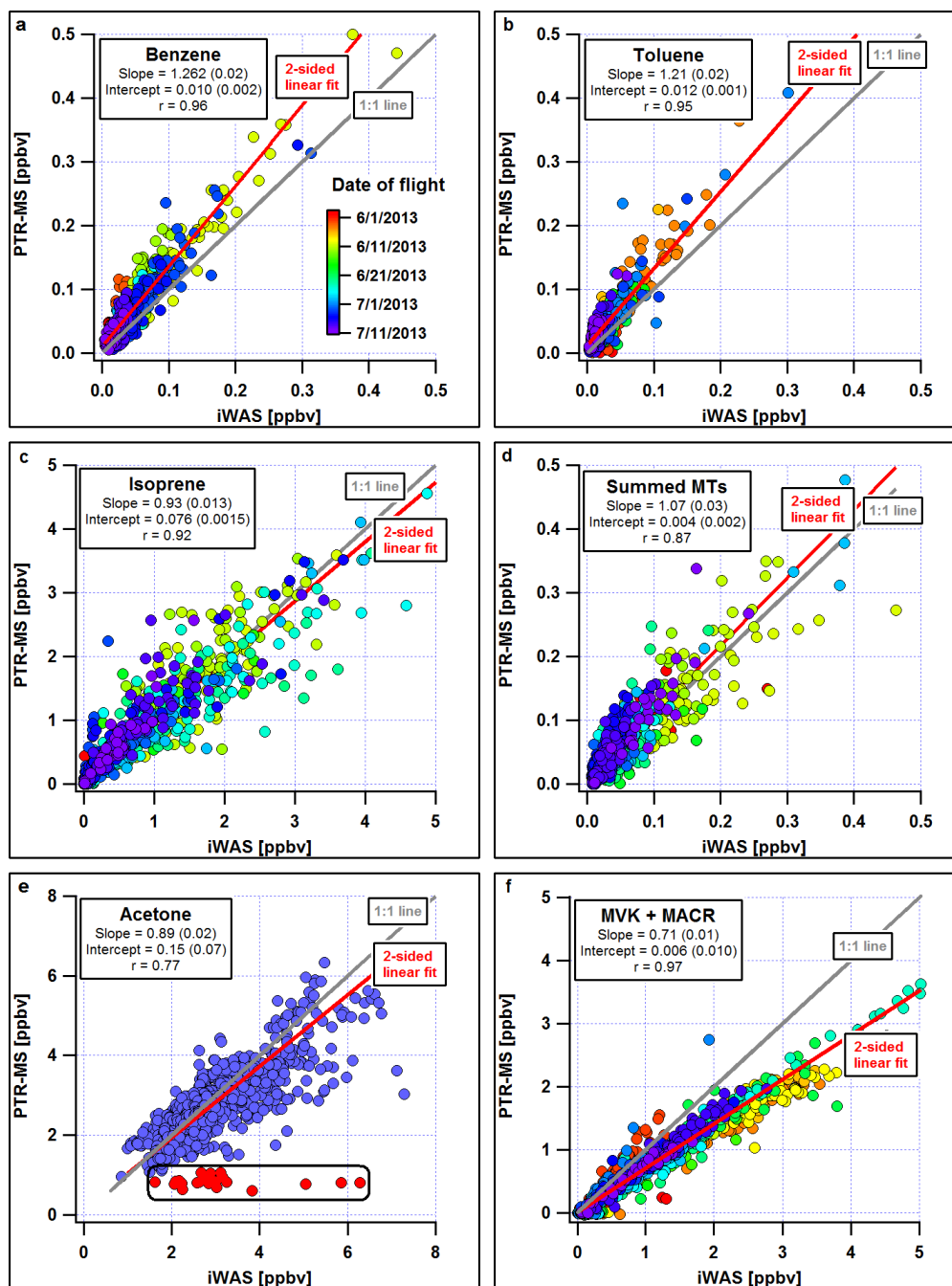



Figure 9a-f. Inter-comparison with PTR-MS of select VOCs from SENEX 2013. Slopes and intercepts from two-sided linear fits of the data are presented, along with correlation coefficients (r) from one-sided linear fits. The red points circled in 8e show data collected in dry canisters during a test flight from Tampa, FL, and are not used for the linear fits.

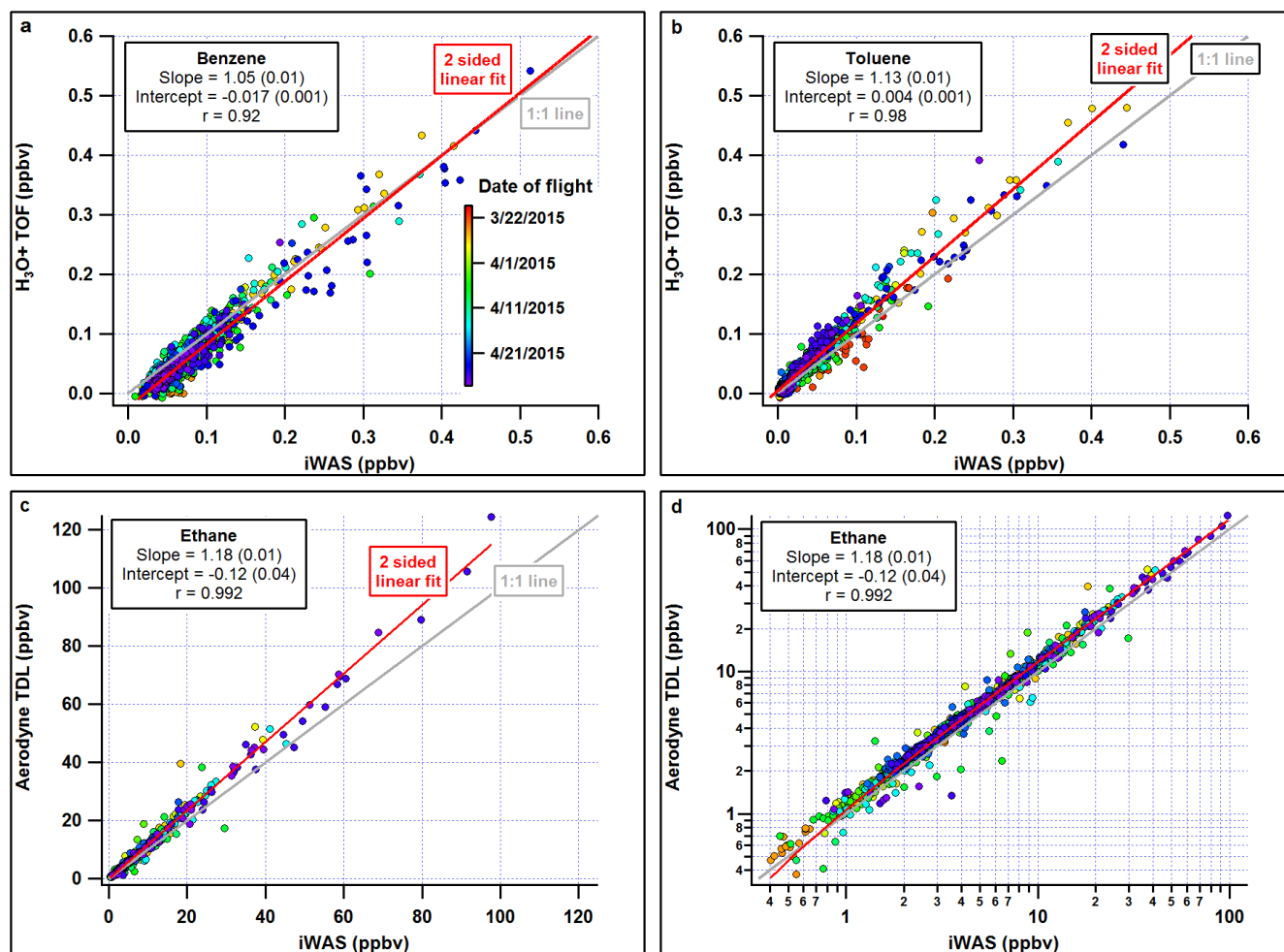



Figure 10a-b. Inter-comparison with H₃O⁺-CIMS of benzene and toluene, respectively, from SONGNEX 2015. Slopes and intercepts from two-sided linear fits of the data are presented, along with correlation coefficients (r) from one-sided linear fits. Figure 10c-d. Ethane inter-comparison for SONGNEX 2015. Slopes and intercepts from two-sided linear fits of the data are presented, along with correlation coefficients (r) from one-sided linear fits.

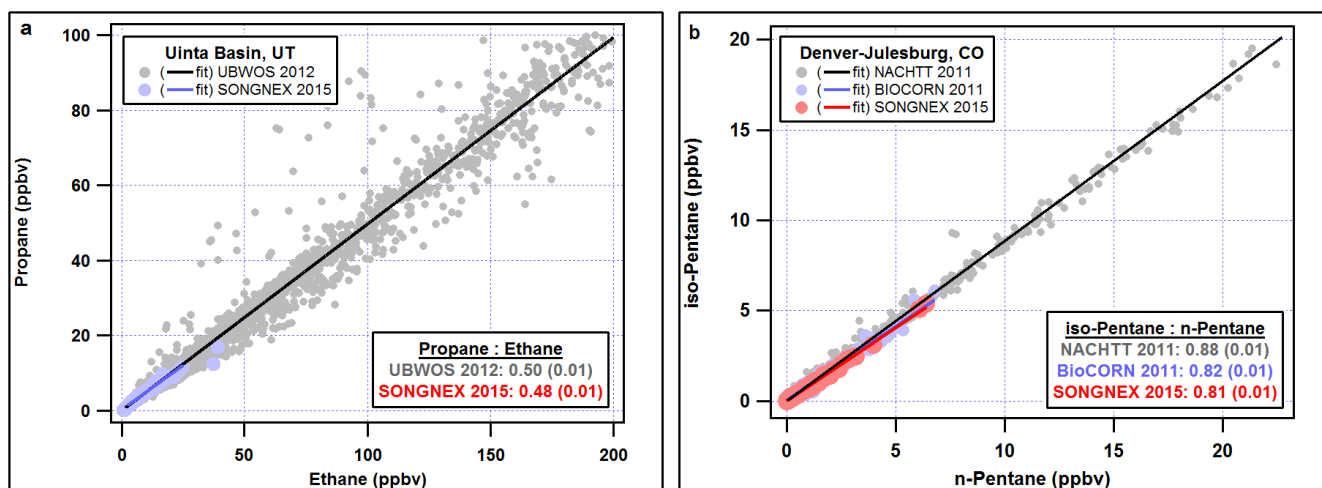



Figure 11a-b. Inter-comparison of alkane measurements made in oil and natural gas fields using a ground-based in-situ GC-MS (UBWOS 2012, NACHTT 2011, and BIOCORN 2011) and airborne WAS during SONGNEX 2015.