Advances in offline approaches for chemically speciated measurements of trace gas-phase organic compounds via adsorbent tubes in an integrated sampling-to-analysis system

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A B S T R A C T

Gas-phase organic compounds across a range of volatilities, including volatile organic compounds (VOCs), are key components of outdoor air, indoor spaces, and a variety of other anthropogenic and biogenic systems. The collection of offline samples on adsorbent-packed tubes for analysis on laboratory instrumentation has been in use for decades, but with limited sensitivities and compound coverage. We present and evaluate our integrated sampling-to-analysis system that enables offline detailed chemical characterization of multi-faceted organic mixtures at trace concentrations. Its capabilities extend across a diverse variety of VOCs with different molecular features, as well as intermediate and semivolatile organic compounds (I/SVOCs). Samples can be collected manually or via automated devices that have been applied in chamber, field, and aircraft platforms. The laboratory instrumentation can be coupled to both a high resolution mass spectrometer (MS) and a traditional quadrupole MS, though performance metrics presented in this study are determined via the traditional MS. We demonstrate capabilities for detailed chemical characterization and routine performance for a wide range of compound functionalities at sub-part per trillion (ppt) concentrations, and as low as <100 parts per quadrillion (ppq), yielding 3300 observed unique compound peaks in a single indoor air sample. These limits of detection and compound coverage were accomplished through a holistic optimization of the entire system and lifecycle of adsorbent tubes. We present our best practices for all aspects of tube production, handling, sampling, and analysis, and an examination of commercially-available materials and our custom adsorbent tubes using a diverse mix of VOC, IVOC, and SVOC standards, including difficult to measure analytes across a range of polarities and functionalities. In many aspects, the commercially-available materials and tube conditioners tested were insufficient for achieving low-ppt measurements.

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1. Introduction

Gas-phase organic compounds, including volatile, intermediate-volatility, and semivolatile organic compounds (VOCs, IVOCs, SVOCs, respectively) play prominent roles in outdoor and indoor air quality, and act as important markers of chemical and biological processes in a variety of systems. They can be primary pollutants, but they have a larger impact on secondary air pollution through the formation of detrimental tropospheric ozone and secondary organic aerosol (SOA), which comprises a variable, prominent fraction (20–90%) of ambient $PM_{2.5}$ (particulate matter with diameters $\leq 2.5\,\mu m$) [1–5]. This process occurs over multiple generations of oxidation reactions, where gas-phase organic compounds either fragment into smaller oxidized compounds or functionalize and partition into the particle/aqueous phase (i.e. SOA), with branching ratios dependent on molecular structure and atmospheric conditions [6–8].

Major uncertainties remain related to the emissions, airborne concentrations, and chemical transformations of IVOCs, SVOCs, and non-traditional VOCs that require detailed measurement techniques to resolve [9–11]. The large number of isomers and diversity of functional groups leads to the chemical complexity of the (formerly) "unresolved complex mixture" and makes full chemical

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speciation difficult, especially considering functionalized compounds can be lost in sampling or measurement instrumentation.

Current measurement methods fall into two major categories: online and offline. Online methods are popular for atmospheric measurements because high temporal resolution data is collected in real-time. Common examples include Chemical Ionization-Mass Spectrometry (CIMS), which includes Proton Transfer Reaction-Mass Spectrometry (PTR-MS) [12,13]. However, these methods are often expensive and require significant resources to make field measurements. CIMS measurements have been limited by the mass resolving power of field deployable mass analyzers, the inability to separate complex mixtures of isomers, detection limits, and less controlled ionization conditions. Online gas chromatographs (GCs) for field measurements exist, but most are limited to a narrow range of VOCs and still require significant resources to deploy in the field.

With offline measurements, collected samples are analyzed with lab-based instruments. Offline sampling techniques traditionally include the use of metallic gas canisters or VOC-adsorbent materials in a variety of configurations: packed tubes, SPME (solid phase micro-extraction) fibers, and coated denuders, filters, or surfaces (e.g. badges) [14]. Gas canisters (typically 0.5–100 L) are used for whole air sampling. Their quantitative chemical range is limited to small compounds (e.g. C_{1-9}) in large concentrations due to the loss of larger or more functionalized analytes to the canister walls during storage and transport, along with interactions with collected water vapor and oxidants.

Offline sampling on adsorbents involves the concentration of gas-phase organic compounds from large volumes of air onto a small mass of adsorbent, which can then be desorbed thermally or with solvent; however, thermal desorption directly into a GC is more typical. A wide range of adsorbents have been used, including porous polymers, graphitized carbon, molecular sieves, zeolites, polyurethane foam, quartz/glass wool, and beads [14–16]. Tenax TA, a porous polymer of 2,6-diphenylphenol, is proven as an effective adsorbent for wide range of analytes, though it has a propensity to degrade, causing positive and negative artifacts upon reaction with atmospheric ozone [17,18] and has a tendency to lose monoterpenes [19–21]. To overcome the limitations of a single adsorbent, multi-layered adsorbent-packed tubes have been employed to extend the volatility range of analytes captured with each adsorbent targeting a complementary range of compounds.

The current problems that limit adsorbent tubes are 1) that commercially-available tubes have high background contamination that affects limits of detection and restricts measurements to high parts per billion (ppb) concentrations; 2) that most struggle with breakthrough at higher flow rates or volumes; 3) inconsistency in sampling conditions or tube-to-tube variability; and 4) other inconsistencies in preparation, handling, and analysis. These issues have impeded their ability to acquire reliable offline measurements at part per trillion concentrations (ppt) or lower across a wide range of volatilities. The integrated sampling-to-analysis system presented here addresses these challenges by optimizing limits of detection in the ppt to parts per quadrillion (ppq) range, transmission efficiency through our coupled sampling-analytical system, and speciation of complex analyte mixtures.

Offline analysis of adsorbent tubes on our system opens new opportunities for very detailed chemical characterization across the VOC, IVOC, and SVOC ranges. While adsorbent tubes provide less temporal resolution than online instruments, they allow for the identification and quantification of a broader range of compounds by providing flexibility for laboratory analysis on one or more detectors, including those that are unavailable for field deployment. Additionally, offline analysis of adsorbent tubes enables detailed chemical speciation of samples collected with highly portable field sampling systems to collect spatially-resolved samples. Our high chemical resolution offline measurements are not intended to supplant online techniques–they aim to augment them with complementary data that enable chemically-comprehensive characterization.

The overall objective of this study is to design and optimize an offline integrated sampling-to-analysis system that enables automated, high-throughput measurements of gas-phase organic compounds with unprecedented sensitivity and chemical detail. Specifically, we (1) describe our optimized, integrated sampling-to-analysis system for sub-ppt offline measurements of VOCs, IVOCs, and SVOCs; (2) evaluate a range of system parameters, including the composition of adsorbent tubes and sample collection conditions; and (3) present best practices for the design, preparation, and pretreatment of adsorbent tubes prior to sampling, sample collection, transport and storage, thermal desorption, and GC–MS analysis.

2. Experimental

2.1. Reagents and materials: adsorbent tube description

Borosilicate glass tubes (6.35 mm OD, 4 mm ID, 88.9 mm length, Yale Glassblowing Shop) containing a 1.9 mm ID constriction near the inlet side were filled with single adsorbents or multi-bed combinations (see below). The tubes were labeled with ceramic decals (Wale Apparatus) for identification. Prior to packing, all adsorbents were thermally cleaned in 5.5 grade nitrogen (0.5-1 L min^{-1}) for several hours at the material-specific maxima (see Table S1 for details) in a tube furnace (Lindberg/Blue M Mini-Mite, Thermo Fisher), which was pre-cleaned in air at 450 °C for 8 h. This aggressive pretreatment eliminates contaminants on the adsorbents prior to their packing in tubes.

High-purity quartz wool (LECO), in tandem with the constriction and a stainless steel tension spring at the outlet (Sigma), was packed on both ends to secure adsorbent beds. Quartz wool also acts as an adsorbent for I/SVOCs and functionalized VOCs at the inlet side prior to the sample reaching the other adsorbents. Two primary multi-bed adsorbent combinations in this study are QBT (quartz wool-glass beads-Tenax TA) and QBTX (quartz wool-glass beads-Tenax TA-Carbopack X). The quartz wool, glass beads (50/70 mesh, unwashed, Sigma) and Tenax TA (60/80 mesh, SUPELCO) were selected to collectively capture I/SVOCs (C_{12}-C_{27}) and larger VOCs (C_{7+}). In QBTX tubes, Carbopack X (60/80 mesh, SUPELCO) was added as a stronger adsorbent for C_4-C_{10} VOCs. Tubes containing Res-Sil B or C silica packings held in place with quartz wool plugs were also tested (B 80/100 mesh; C 80/100 mesh; and B 80/100 mesh with 5% Rtx-1 doping). Packed tubes were conditioned in large batches at their maximum conditioning temperature (material-dependent) with 500 mL/min nitrogen for six or more hours in the tube furnace followed by secondary conditioning and spot checking in the thermal desorption unit. After conditioning was complete, the tubes were immediately sealed with brass Swagelok caps and PTFE ferrules to prevent passive sampling via diffusion [22].

2.2. Instrumentation and software: integrated sampling-to-analysis system description

2.2.1. Sample collection equipment

Samples were collected for analysis with the use of a pump (e.g. Pfeiffer) and a high-accuracy mass flow controller (Alicat). When appropriate, we have designed systems (See: Novel Sampling Approaches) to automate the collection of multiple samples. Sodium thiosulfate doped quartz filters were used upstream of the tubes to prevent potential ozone reactions with the analytes and Tenax TA [18–20,23–25]. Tubes can be cooled to 5–15 °C during trapping using thermoelectric coolers, since chilling tubes to near-
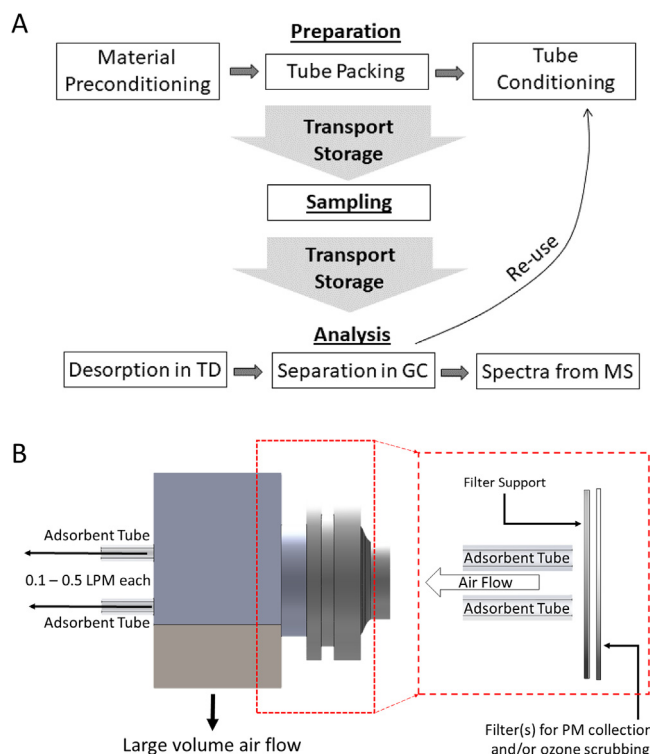
A

B

Fig. 1. (A) A holistic consideration of the lifecycle of adsorbent tube production, sample collection and analysis is required for high-accuracy low concentration measurements. This spans raw materials preconditioning, to tube packing, reconditioning, storage/transport, sampling, analysis, and reconditioning prior to re-use. (B) Example of one of our sample collection devices as a Solidworks schematic and a close-up internal diagram (red-dotted border) of our dual filter and adsorbent tube sampler. Aerosol samples are collected at 17 LPM and adsorbent tubes simultaneously subsample from the centerline immediately behind the filter to reduce the potential wall losses in this system with a minimal inlet (typically <1-2 ft). Particles and ozone are removed prior to adsorbent tube gas collection. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

freezing temperatures increases adsorption efficiency [26]. After sample collection, samples were immediately capped and stored in a sample-dedicated freezer or cooler. Samples were stored and transported with either ice packs or dry ice. If they have been exposed to high concentration samples or other possible contamination, brass caps may be thermally treated or sonicated as necessary prior to sampling and following analysis in order to avoid cross-contaminating samples.

2.2.2. Novel sampling approaches: automated sampling on research aircraft

The Yale Airborne Sampler (YAS) is an automated device that collects adsorbent tube samples during research aircraft flights (Fig. S1), such as the NOAA SONGNEX campaign (Feb.-Apr. 2015). The YAS incorporates mass flow (MKS), pressure (Bronkhorst), and temperature measurements, and has the capability to take 14 samples in one flight. LabVIEW code through a LabJack T7 DAQ device automates valve states, which directs air flows through 4-way 316 L stainless steel cross manifolds and two Rheodyne 10/11 port valves pulled by an oil-free vacuum pump (Pfeiffer). To interface with the NOAA P-3 aircraft, the YAS sampled air via a winglet.

2.2.3. Novel sampling approaches: portable field sampling with minimized inlet losses

At the 2016 PROPHET field campaign, gas and aerosol phase organic compounds were simultaneously collected via a uniquely constructed sampling device (Fig. 1B). The adsorbent tube inlets

were placed approximately 2 mm behind a 47 mm diameter Teflon filter (Pall), which was installed upstream of every tube pair to collect aerosol samples and prevent particulates from entering the tubes. Stainless steel Teflon filter holders were passivated (AMCX) to reduce sample losses to the holder walls. An 84 mesh (210 μm) stainless steel screen was placed ahead of the Teflon filters to prevent large particles (>10 μm) and insects from depositing on the filter. The downstream end of each tube pair was connected to a pump via valves and mass flow meters. The flow valves were automated and connected to a computer through a LabJack T7 signal recording and transmission unit.

2.2.4. Analytical instrumentation

Adsorbent tubes are analyzed via thermal desorption into a gas chromatograph (Agilent 7890B) and subsequent detection by multiple mass spectrometers or a flame ionization detector (FID), but a traditional vacuum EI-MS is used for the data here. For thermal desorption, adsorbent tubes' brass caps were replaced with DiffLok (diffusive) caps and placed in an automated thermal desorption system (modified TD-100, Markes). Tubes were thermally desorbed with helium gas at 300 °C for 10 min and focused onto a −10 °C cryogenic trap packed with quartz wool, Tenax TA, and Carbopack X. This cold trap was then desorbed onto the GC column at the calculated optimal linear velocity, going from −10 °C to 325 °C and held at 325 °C for ten minutes. All transfer lines are maintained at 200 °C to reduce analyte losses via adsorption.

Analytes were primarily separated in helium gas on a HP-1-MS column (Agilent, 30 m x 320 μm x 3 μm), held initially at 31 °C for 6 min, ramped at 25 °C per minute to 260 °C (6 min hold), and then ramped at 40 °C per minute to 280 °C (2 min hold). The chromatograms shown in Fig. 5 used an HP-5-MS (Agilent, 30 m x 250 μm x 0.25 μm) or a DB-624UI-MS (Agilent, 30 m x 250 μm x 1.4 μm) column. Column effluent in our system can be split between a vacuum electron-impact (EI) quadrupole mass spectrometer (Agilent 5977 A GC/MSD) and a second detector, usually an atmospheric pressure chemical ionization (APCI), quadrupole time-of-flight mass spectrometer (Agilent 6550 Q-ToF MSxMS), or sometimes a flame ionization detector (FID). Spectral results from chromatographic peaks were compared to a NIST database (MS Search 2.2) and analytical standards (Apel-Riemer, AccuStandard) for identification confirmation and quantification. In future ambient measurements with our system, authentic analytical standards will be used wherever possible to identify and quantify observed analytes using both their GC retention time as well as their mass spectra and molecular ion. Compounds will be calibrated for and quantified on single ion responses that are specific to a given compound or a similar set of isomers. Where standards are unavailable, compounds will be characterized based on their mass spectra (referenced against the NIST library), high resolution molecular ion, and GC retention time, with their abundance constrained by the response factors of analogous standards or their FID response if appropriate for the application. Tentative identifications will be assigned (and clearly labeled as such) only if there is sufficient information from these data streams to provide a molecular formula or specific isomer.

2.3. Methods: system evaluation & adsorbent tube evaluation

Our study used a multicomponent gas cylinder standard containing 44 compounds at ppb-level concentrations (Apel-Riemer, Table S2) ranging in volatility from ethanol to n-tridecane with diversity in molecular functionalities (e.g. carbonyl, alcohol, organic nitrate, acetate). The compound concentrations for analytes in the standard cylinder were assumed to be consistent with the manufacturer's gravimetric production and confirmation analysis, which reported uncertainties less than or equal to ±5% of final concen-

trations. The valves and regulator (ProStar Platinum) connected to the cylinder (Luxfer N150) are composed of high purity stainless steel. A short (66 cm) piece of PEEK tubing, an ultra-low flow MFC (5 sccm max., Alicat) with 316 stainless steel walls, and a stainless steel T-union (316 with Inertium passivation, AMCX) were used to transfer the appropriate flow of standard to the adsorbent tube. Zero air (Aadco generator) controlled by an MFC (500 sccm max., Alicat), entered the other port of the T-union to dilute the standard and transport analytes into the tube at the typical sampling flow rates tested in this study. To reduce the risk of analyte losses, the sample delivery system was allowed to come to equilibrium at the set flow rates for an hour before adsorbent tubes were collected. In addition to the multicomponent gas cylinder standard, select liquid standards (AccuStandard) were also used for methods experimentation and system verification.

Ratios of peak areas relative to o-xylene's peak area were calculated to analyze the stability and storage data (See S.2 in the SI for calculations), with o-xylene chosen as an internal standard because it 1) is well resolved (no co-elutions); 2) has approximately median retention index and functionalization; 3) changes in peak area with a majority of the other compounds over time; 4) is not an artifact of any of the adsorbents; and 5) is well trapped by all tube variants, with minimal breakthrough. In the stability tests, a subset of compounds are similarly normalized to 1-methylnaphthalene.

2.3.1. Blank comparisons

Conditioned tubes were compared to a selection of commercially-available adsorbent tubes. These commercial stainless steel tubes contained: quartz wool and Tenax TA (Commercial Tube #1) and quartz wool, Tenax TA, Carbograph 1, and Carboxen 1000 (Commercial Tube #2), and were delivered "preconditioned". After extensive additional conditioning following the same process as our tubes, more than 10 of each type were run on the TD-GC–MS to assess their background signal.

2.3.2. Breakthrough

Extensive breakthrough tests were conducted for the five adsorbent tube types (QBT; QBTX; Res-Sil B, C, and B with 5% Rtx-1) at various total sampling rates and volumes of the multicomponent standard. A sample chromatogram can be found in Fig. S2. Compound-dependent breakthrough was determined by installing an additional back tube (QBTX) to capture any compounds that "broke through" the adsorbents in the front tube. All tubes were analyzed on the TD-GC–MS system. Sampling times were dictated by the flow rate and total volume for each test, but the total standard cylinder volume spiked, and thus mass, were kept consistent at 15 mL. A range of potential sampling conditions were simulated. QBTX tubes were tested at sampling volumes and flow rates of 6 L (125 sccm, triplicate), 10 L (125 sccm), 15 L (125 sccm), 25 L (125 sccm and 250 sccm), and 50 L (50 sccm). QBT was tested at 10 L with flow rates of 125, 200, 300, and 500 sccm, and also at 6 L and 15 L (125 sccm for both). For Res-Sil materials, experiments were conducted at 6 L and 125 sccm in triplicate. All tests were run at room temperature.

2.3.3. Limits of detection

Limits of detection (LODs) were determined by using a multi-point pg-level calibration in triplicate at analyte mass loadings that approached or extended past the observed limits of detection. LODs were determined on individual m/z fragments for each standard compound and were defined as a peak with a signal to noise ratio of 3. Standards at average mass loadings of 40, 120, 240, and 480 pg per compound (which varied with relative cylinder concentrations) were spiked on QBTX tubes and run in triplicate. A calibration curve for peak area vs. mass loading was created for each compound, and the regression was used to determine the expected mass loading

at the LOD peak area with signal to noise ratio of 3. These mass loadings were then converted into concentrations dependent on sampling volumes to determine the range of attainable LODs in terms of concentration.

2.3.4. Stability

We analyzed drift in the complete analytical system (i.e. TD-GC–MS) to assess day-to-day deviations and changes over a 2-month period. Adsorbent tubes were spiked with the multicomponent cylinder that contained a broad range of compounds. QBTX tubes were spiked in triplicate with 15 mL of standard (normalized to STP) over 3 min, ranging 3.0–16.9 ng (i.e. 45–753 ppt in a 6 L sample) for each compound. QBT and Res-Sil-containing tubes were also tested for five triplicate trials on five consecutive days.

2.3.5. Storage effects

Storage tests were conducted at time intervals of 1 day, 1 week, 1 month, and 2 months to assess analyte losses and artifact formation on QBTX tubes with some tests of Res-Sil. For each time interval, four tubes were spiked with 15 mL of the multicomponent standard. Three were stored at −30 °C, one was left at room temperature, and 1 blank was stored at −30 °C. All tubes were sealed with brass caps and PTFE ferrules, and seals were checked after cooling down. After storage, changes in the spiked standard compounds were compared to each other. For each tube type, compounds that were not efficiently collected on an adsorbent tube's bed(s) were removed for this analysis (e.g. isopentane on Res-Sil). The formation of artifacts during storage was also evaluated (Fig. S3).

In both the stability and storage tests, changes in the composition or relative ratios of samples were used to evaluate compound-dependent losses during storage or system drift. The peak area ratio of each compound to o-xylene was determined for each time point. Geometric means of the ratios across all time points were determined and each time point ratio was divided by the geometric mean to examine compound-dependent losses and drift (See SI for equations). Subtracting these by 1 provided a deviation % above/below 0% to look for an upward or downward trend.

2.3.6. Samples: system demonstration in real-world studies

For the purposes of demonstration, indoor air samples were collected from 2 separate buildings: one in an indoor office common area; and another from one of five large air conditioning units sampled. In the first location, tube samples were collected in pairs with two 500 sccm mass flow controllers (Alicat) and a pump (Pfeiffer) for a range of sample volumes: 6, 30, 50, 60, and 96 L. In the second, 5.4 L samples were collected (120 sccm for 45 min). In addition, test samples were collected from a large-volume oxidation chamber experiment of n-dodecane at high-NO$_X$ at UNC-Chapel Hill (J. Surratt Group).

3. Results & discussion

3.1. Adsorbent background contamination and tube preparation

Throughout our system design and testing we observed significant heterogeneity between adsorbent materials with respect to their initial contamination, cleanability, and persistent artifacts. This variability occurs between material types, but also between material providers and batches. Extensive thermal treatment of loose raw materials (and empty tubes) in high-purity nitrogen prior to packing was essential to achieve the blank chromatograms and limits of detection presented here (Fig. 2). Packed tubes without pretreated materials were well short of the standard level of cleanliness for those pre-cleaned materials and
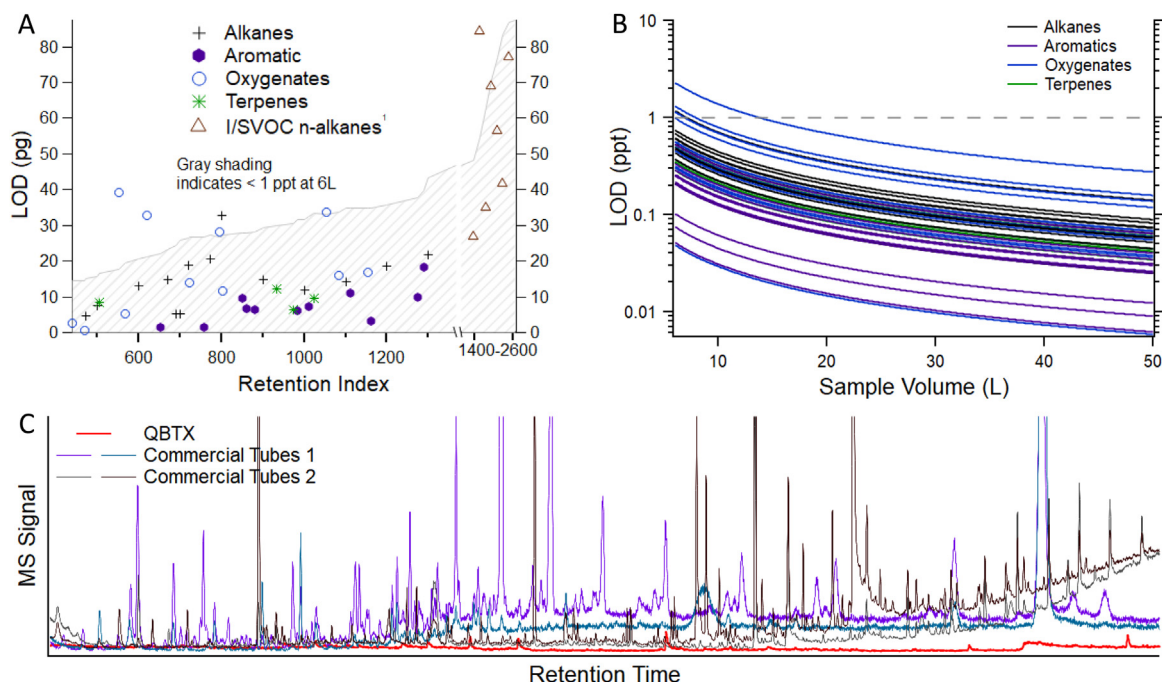
Fig. 2. Limits of detection (LOD) and background "blank" contamination. (A) Limits of detection are presented as analyte mass (pg), with colors/shapes designating the four major compound classes in the multicomponent standard cylinder and diesel range organic (DRO, brown) liquid standard for n-alkane I/SVOCs. The gray shading demarcates the approximate 1 ppt boundary for a 6 L sample, where most compounds can be detected at concentrations <1 ppt at 6 L (see Fig. S4 for compound names). (B) LODs as a function of sample volumes greater than 6 L show that large volume samples enable measurements at ~100 ppq or lower. (C) Background contamination in "blanks" are compared as chromatograms (from C_5 VOCs and up) between a custom tube produced in the Gentner Lab (red) against two commercially-available adsorbent tubes with similar adsorbents, showing high levels of persistent background contamination that inhibit low concentration measurements. Commercial Tube 1 was run on an HP-1 column while the other two types were run on the same HP-5 column, and shows some variability in column bleed at later retention times. The pairs of commercial tubes were chosen as common lower and upper limits of baseline contamination. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

exhibited an elevated contamination baseline even after extensive conditioning and did not improve with further conditioning. However, for some materials, initial contamination could not be resolved with thermal cleaning. Similarly, we have found that commercially-available packed tubes and commercially-available "tube cleaning units" were insufficient and inconsistent to reach the minimal contamination necessary for ppt-level measurements of most compounds. Even additional extensive thermal cleaning of commercially-packed tubes following our cleaning program produced unsatisfactory results. This contamination inhibits limits of detection, increases uncertainty, and can also interfere with analyte adsorption/desorption especially for functionalized analytes.

High-purity materials are a necessity but alone, they may not guarantee low background contamination. Through testing, quartz wool out-performed glass wool since glass wool was observed to physically degrade at elevated temperatures and silanized glass wool produced greatly enhanced siloxane signatures in our chromatograms. Diatomaceous earth with 20% RTX doping had a persistent siloxane signal (e.g. m/z 73, 267) and was removed from consideration. While a number of options exist for glass beads, some can off-gas acids from their commercial pretreatment (e.g. acid-washed).

Tenax TA has a number of known artifacts that we also observed in our system: benzaldehyde, benzacetaldehyde, acetophenone, phenol, nonanal, and decanal [27]. These often do not completely depart, even with conditioning, but can be accentuated by recent or past oxidation by ozone or other oxidants (e.g. OH, NO_3, NO/NO_2). Whereas, we found that Res-Sil B and C (w/o doping) had relatively few artifacts once well-cleaned, albeit with some batch variability. Both of these materials maintained their relatively clean baselines even after two months storage in the freezer. We observed minimal positive artifacts from Carbopack X, which confirms previous

literature findings [27]; however, some graphitized adsorbents are known to cause molecular rearrangement [19], so using them as the last adsorbent in tubes minimizes the number of analytes that reach them.

3.2. Limits of detection

The LODs of the compounds tested from the standard cylinder had a median of 11.3 pg (ranging from 1 to 40 pg), had a geometric mean of 9.56 ± 0.95 pg, and were lower than 1 ppt for 36 out of 40 compounds in 6 L samples when quantified on single ions at unit mass resolution (e.g. m/z 91). These 36 compounds included most aromatics (e.g. BTEX), alkanes, oxygenates (e.g. MVK, furfural, nonanal), and all terpenes included. Fig. 2A shows LODs in pg against retention index and demonstrates our ability to measure sub-ppt concentrations with 6 L samples of VOCs, IVOCs, and SVOCs—ranging in volatility from ethanol to n-hexacosane (i.e. n-C_{26}) and across a wide variety of functionalization, with few exceptions. Furthermore, Fig. 2B shows that we can reach LODs of 10–100 ppq for most analytes with larger sample volumes up to the maximum volumes tested for breakthrough in this study. The same figure also serves as a reference for expected LODs in ppt at various sampling volumes, with larger samples enabling lower LODs.

Background contamination or instrumental noise can also affect the achievable LODs. Fig. 2C shows a comparison between our tubes and commercially-available tubes containing similar or identical adsorbents, all cleaned with the same rigorous conditioning process described in Section 2.1 and Table S1. We also report that lower noise and LODs are achievable when any minor leaks across the whole TD-GC system are continuously checked and resolved, which represents a much larger flow path in some TD systems.

3.3. Adsorbent tube breakthrough

Analyte breakthrough during trapping was investigated in depth for the QBTX and QBT tube types across sampling volumes and flow rates, and the adsorbent capabilities of Res-Sil beads were tested at baseline conditions of 6 L and 125 sccm. While breakthrough volume can be defined as penetration of 50% of analyte [28,29], we pursue stricter tolerances of breakthrough and look at the absolute percentage of analyte that breaks through to the backup tube. QBTX tubes performed very well under the conditions tested, even down to iso-pentane. Under most conditions, all analytes were trapped with 95% or greater efficiency and nearly all data were >85% (Fig. 3A). This included challenging sample volumes up to 25 and 50 L. However, any future work should reconfirm breakthrough with new sampling conditions or apparatuses.

The QBT tubes trapped larger compounds well (i.e. C_{9+}), but exhibited a S-curve trend, where the most volatile compounds broke through completely and the less volatile compounds exhibited less breakthrough with a sharp transition region (Fig. 3B). These results are consistent with previous characterization of Tenax TA [14], and we reiterate the need for caution when using it to trap compounds smaller than C_9. We also observe that α- and β- pinene are poorly retained on QBT tubes for these tests. Unsurprisingly, VOCs from iso-pentane to n-heptane are not retained by QBT and are thus trapped on the Carbopack X layer in the QBTX tubes.

Sampling flow rates up to 500 sccm through QBT tubes had a minimal dependence on flow rate for C_9 and larger compounds. For these flow rates, the sigmoid curves cross 50% at roughly the same retention index (Fig. 3B). Additionally, in the compound-by-compound comparison, those compounds where the largest difference would be expected (i.e. breakthroughs between 20–80%) varied statistically insignificantly with respect to flow rate (Fig. S5). This observation can be advantageous in certain field sampling situations where a high flow rate allows for shorter time resolved samples or for increased sample collection, which provides more mass loading to detect I/SVOCs and C_{9+} VOCs appearing in trace concentrations. In our QBT tube tests from 6 to 15 L, sampling volume did not significantly affect trapping efficiencies for C_{9+} compounds (Fig. S7). These volumes are not different enough from each other to pass through the breakthrough volume of the compounds in the standard.

Breakthrough tests on all 3 Res-Sil materials showed that certain compounds were not efficiently captured by the Res-Sil tested. Similar to QBT, the lightest non-oxygenated VOCs (e.g. isopentane, isoprene, to n-hexane) were consistently not retained by the materials, even for a 0.9 L sample. Larger analytes and oxygenated VOCs were retained better (Fig. 3C). The Res-Sil B with 5% Rtx doping performed the best for the light alkanes, while the Res-Sil C showed the most breakthrough. From these tests, we conclude that Res-Sil can perform similarly to QBT tubes and Tenax TA, but with better retention of α- and β- pinene.

3.4. Other sample collection considerations

Beyond analyte breakthrough, other sampling system features must be considered when collecting offline adsorbent tube samples. To reduce inlet losses, we design our sampling systems to reduce analyte residence time upstream of adsorbent tubes and to keep flow paths as inert as possible. In recent years, even "inert" materials such as PTFE have been shown to contribute to wall losses, and now require a vapor wall-loss correction for chamber studies to more accurately model the kinetics [30–32]. Therefore, we use passivated (i.e. Inertium[TM]-coated) stainless steel 316 L, which has shown good transmission of functionalized analytes [33]. Further, heated inlets (i.e. 50–70 °C) minimize analyte losses via adsorption. However, such systems still allow for analyte-wall interactions,
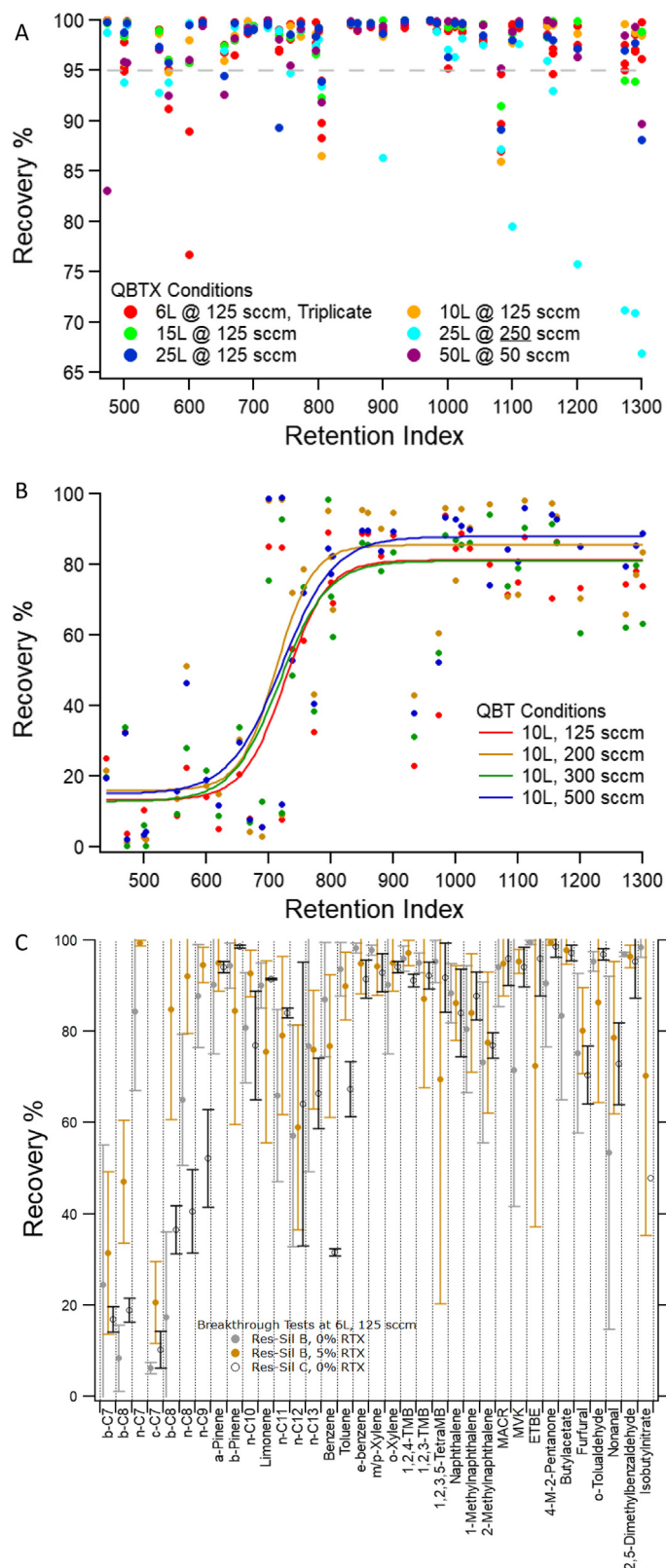

Fig. 3. Breakthrough testing results for all adsorbent tubes produced in Gentner Lab: (A) quartz wool-glass beads-Tenax TA-Carbopack X mix (QBTX), (B) quartz wool-glass beads-Tenax TA mix (QBT), and (C) 3 types of Res-Sil held in place with quartz wool (1 type per tube). A–B are shown as a function of retention index and C is grouped by compound class with error bars representing 1σ of percentages away from the average. QBTX tubes show excellent trapping with the vast majority of data over 95%. QBT shows a sharp transition in trapping that is fit with a Sigmoid curve (See Fig. S5 for 6 and 15 L data). Res-Sil-only performance varies with analyte characteristics and Res-Sil type (See Fig. S6).

which can be mitigated by "wall-less inlets" with centerline skimming of sampled air. All valves and flow/pressure controllers are placed downstream of adsorbent tubes when possible to reduce the surface area and substrate variety contacted by analytes, and oil-less pumps reduce potential contamination.

Atmospheric oxidants, particularly ozone, can react both with adsorbents (esp. Tenax TA) and with trapped analytes (e.g. olefins). We use sodium thiosulfate ($Na_2S_2O_3$) coated filters to remove ozone when necessary, and other methods exist (e.g. potassium iodide coated scrubbers, addition of NO or small reactive olefins among others), but are limited due to their reactions with target analytes or persistence in analytical systems [20]. Quartz filters (and Teflon filters) represent a surface area upon which gas-phase analyte loss occurs, but this risk is reduced in our system design by using high flow rates ($\geq$17 LPM) that minimize the residence time of vapors near filter fibers. The use of Res-Sil in place of Tenax TA will reduce the likelihood of artifacts from adsorbent-oxidant reactions, but not analyte-oxidant reactions occurring on the adsorbent surface, so ozone must still be removed when measuring alkenes or other species that are highly reactive with ozone. Also, water vapor can accumulate on some adsorbents, but does not preferentially adsorb onto the adsorbents tested here, such as Tenax TA, which is hydrophobic [26]. Yet in warm, humid environments, water vapor can condense in cooled adsorbent tubes and must be removed upstream, which can present challenges to analyte transmission.

3.5. System stability

We evaluated the stability of the complete TD-GC–MS system using the 44-component standard cylinder, both day-to-day over a 13-day trial and over the 1 day to 2 month storage tests. Day-to-day changes in raw peak areas, normalized to the arithmetic mean across the sampling duration, of standard compounds (in triplicate) show some drift across the 13-day measurement period with most days remaining within ±10% of the overall mean and an average standard deviation of 12.3% by compound (Figs. 4A, S8A), with compounds in the middle of the tested volatility range exhibiting the most stable relative behavior (including 4-methyl-2-pentanone, both trimethylbenzenes, methacrolein, ethyl tert-butyl ether, and the four terpenes). Some deviation beyond ±10% is observed on several days. This deviation was statistically-consistent across compound classes, and occasionally statistically different by volatility. The exact cause of the drift is unknown, but could include MS detector response drift, TD unit variability, or by way of experimental design, a contribution from the standard cylinder or its spiking system (esp. for low-volatility or functionalized compounds). The influence of MS detector drift is well-known and shown in the literature to potentially contribute a 20%+ over even short timescales [34].

Firstly, these results demonstrate that offline adsorbent tube samples from a measurement campaign are best run altogether in one consecutive period to minimize drift that may be occurring over longer timescales.

Secondly, these results demonstrate the importance of internal standards with offline adsorbent tube sampling, preferably deuterated with multiple chemically-diverse internal standards spread across the analyte volatility space. When we correct for the drift using the multicomponent gas cylinder as a reference (i.e. o-xylene and 1-methylnaphthalene for compounds with RI > 1050 and multi-oxygen-containing species), stability across the 13-day period improved to an average standard deviation of 9.2% with tighter individual-compound distributions around ±5% (Fig. 4B, S8B) though some unexplained deviation remains, in particular for oxygenated compounds. To minimize these uncertainties in future studies, internal standard will be delivered via a liquid injection of dilute internal standards (in solvent) after sampling or by standard cylinder. Care must be paid to the delivery of internal standard such that all of the standard is effectively delivered to the adsorbent beds, such that it will not suffer losses during handling or storage. Ideally a trace gas can be bled into the sample flow so that it can be uniformly deposited onto the adsorbent bed with the analytes.

Changes in these peak area ratios for each type of adsorbent were calculated (Fig. 4C) as a measure of long-term analytical stability. For all the adsorbent bed materials and combinations tested in this paper, the average long-term stability was well within 20% throughout a two-month period for QBTX tubes, Res-Sil B, and Res-Sil B (5% Rtx-1 doping), with only Res-Sil C exhibiting significant deviation, specifically at the one week and two-month time periods. Thus with careful usage of internal standards, long-term system stability in peak areas is possible. However, clustering all offline samples together for consecutive analysis along with the use of frequent calibrations (at least daily) are encouraged to reduce any effects of system drift.

3.6. Storage effects

We evaluated the effect of adsorbent tube storage for analyte losses and the formation of positive artifacts over 1 day, 1 week, 1 month, and 2 month periods primarily with QBTX tubes, with some tests for Res-Sil tubes. Tubes spiked with cylinder standard were stored in the $-30\,^\circ$C freezer (3 tubes) and at room temperature, and were compared to the stored blanks and tubes run at the time of analysis. Specifically, we checked for changes in the relative composition of analytes in the tubes that would indicate compound-specific analyte loss processes during storage. For QBTX tubes, changes in peak area ratios to o-xylene show some variance over time, with a median of 1.9% change over two months and within ±20% for most individual analytes (Fig. 4D). Furthermore, regressions of all these (triplicate) sample ratios over time show 7 compounds with significant downward trends (i.e. slopes greater than 1σ and r>0.5). Results for all Res-Sil tubes have fewer individual compounds with significant downward trends and a median change of 0.42% across all types (compound specific results in Fig. S9). These tests signal that while a few compounds show a general loss in storage over time, the majority of compounds do not vary with respect to the internal standard o-xylene, and variability may be attributed to the stability issues rather than cold storage.

Across several tests, we observed that Tenax-containing tubes left at room temperature (or higher) build up significant concentrations of artifacts (Fig. S10). The specific identities of these artifacts are similar to artifacts observed in Tenax TA adsorbent oxidation, with benzaldehyde, acetophenone, phenol, nonanal, and decanal the most prominent compounds observed. Some compounds (benzaldehyde and acetophenone) show increased concentrations with storage time for warm conditions compared to cold conditions, while others, such as decanal and phenol, do not (Fig. S10B). This difference in trends may be attributed to variations in the production mechanisms – some may occur more as a product of degradation during storage, while others may arise from degradation due to exposure to other factors during sampling or handling and are thus more constant over storage. These artifacts increase background contamination and the uncertainty of measurements, especially for trace gas-phase measurements. Storing unused tubes in sample-dedicated freezers limits the formation of storage artifacts that appear more often and form at greater rates at room temperature rather than at cold temperatures. Additionally, for all materials stored at room temperature, we observe minimal losses through one month of storage, but losses (up to 25%) become significant at the two month time point (Fig. S11). Thus, cold storage is recommended given the increased potential for chemical reactions or analyte diffusion at higher temperatures and is consistent with the best practices for aerosol filter sample storage.
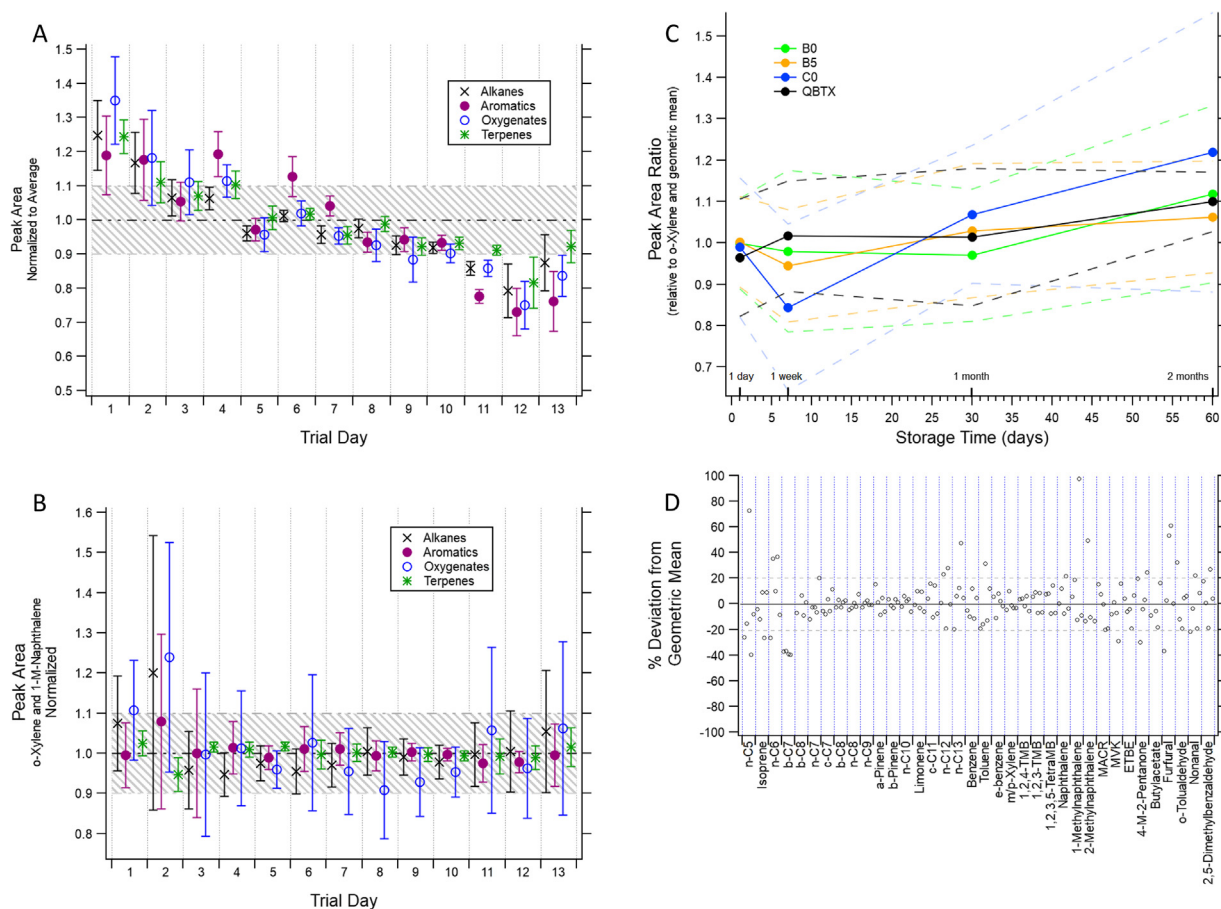
Fig. 4. Stability of integrated sampling-to-analysis system over time and the effect of storage of analyte concentrations. (A) Raw peak areas from 13-day stability test with QBTX tubes (i.e quartz wool-glass beads-Tenax TA-Carbopack X mix) centered over a arithmetic mean (shown with ±10%), which are then corrected by o-xylene and 1-methylnaphthalene (B) as internal standards to reduce the impact of system drift. Error bars represent 1σ away from the geometric mean. (C) Long-term stability over 2 month periods are shown as averages and standard deviations by adsorbent tube type, with all types performing within ±20%, except Res-Sil C. Similarly, the error lines represent 1σ. (D) Storage tests by compound for QBTX tubes show 1 day, 1 week, 1- and 2-month tests (left to right in each compound column) that are corrected by o-xylene and compared to the geometric mean to check for changes in analyte-specific response over time. Fig. S9 contains compound-specific data for the Res-Sil materials.

As part of minimizing potential losses throughout our entire sampling-to-analysis system, the transport of adsorbent tubes prior to analysis is also important. Sample tubes may encounter high concentrations of organic compounds or high temperatures, both of which can contribute to sample contamination. This can be mitigated by ensuring a good seal with brass caps and PTFE ferrules and keeping sampled tubes cold with either ice packs or dry ice. It is also important to check tube seals after they have been resealed and placed in freezers to make sure that the air-tight seal remains, as the tubes, brass cap and PTFE ferrule will shrink under the cold temperatures. However, caps sealed too tightly or carelessly can damage the ends of glass tubes.

3.7. System demonstration: sample data & observed analytes

Test samples were used throughout the development of our integrated sampling-to-analysis system to evaluate the performance of the system and examine specific variables. Across them, our system has observed a wide array of compound classes from samples or standards that include typical hydrocarbons (incl. aliphatic and aromatic compounds), functionalized, and multi-functional compounds. Examples include single- and multi-oxygen-containing compounds (e.g. alcohols/polyols, ketones, aldehydes, furans, acids, esters, ethers, phthalates), nitrogen- or sulfur-containing compounds (e.g. organic nitrates, thiophos-

phates), halogenated species (e.g. CFCs, HCFCs, HFCs, chlorinated aromatics), and siloxanes.

Fig. 5 shows three chromatograms from real world applications of our system from ambient environments and controlled experiments that all include a range of VOCs, IVOCs, and SVOCs. These chromatograms include measurements of organic compounds from the interior of an air conditioning unit (Fig. 5A), from an indoor office common area (Fig. 5B), and from an oxidation chamber reaction of n-dodecane (Fig. 5C). n-Dodecane oxidation under high-NOx conditions produces an impressive collection of organic compounds spanning the gas-phase volatility range, including carbonyls, acids, diols, dicarbonyls, and dihydrofuranones, which is consistent with previous n-dodecane oxidation studies [35].

For the indoor air measurements in the office common area, across several large volume samples we observed between 2159–3295 unique compounds across the VOC, IVOC, and SVOC ranges. While the samples were taken at separate times, the number of observed unique compounds tends to increase with greater sample volumes, especially when the minimum QC/QA peak area threshold is increased. These measurements were all made with traditional unit-resolution vacuum MS that fragments most analytes during electron impact ionization. More powerful detectors and less destructive ionization methods can provide further information on the speciation with a greater number of unique peaks. For future applications, high resolution mass spectrometers with soft ionization that preserves the molecular ion can be connected to
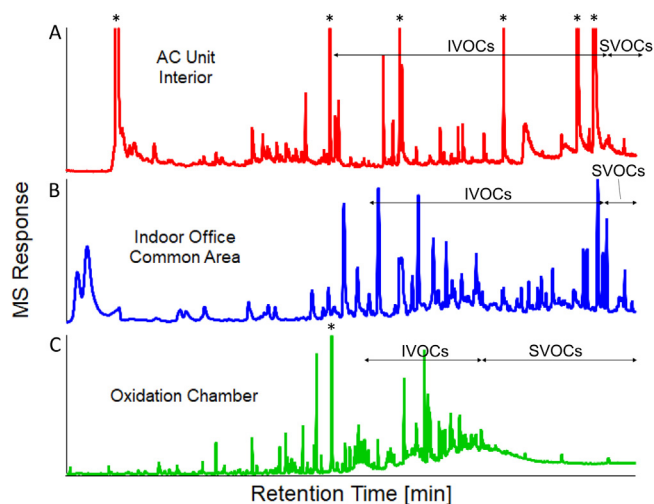
Fig. 5. Example total ion chromatograms (TICs) from three different studies showing a diverse range of VOCs, IVOCs, and SVOCs with a range of unoxidized, functionalized, and multi-functionalized analytes, from (A) a commercial air conditioning unit in West Haven, CT; (B) an indoor office common area (New Haven, CT); and (C) a large volume PTFE oxidation chamber (Durham, NC) with n-dodecane oxidation at high-NOx. Samples were analyzed at different times, and on different GC columns (see text). Peaks higher than the axis boundaries are marked with *.

the integrated sampling-to-analysis system and provide additional chemical resolution to speciate complex mixtures and identify analytes.

3.8. Other considerations for analysis

3.8.1. Laboratory contamination

Laboratory environments often contain much higher gas-phase concentrations of organic chemicals than sampling environments, which presents risk of contamination to adsorbent tubes. Handling of tubes in the lab right before analysis can introduce contamination, so operators should avoid potential contamination and minimize the time uncapped tubes are exposed to room air during TD loading. However, even with negligible time spent in the laboratory and no obvious exposure pathways, we have observed sample contamination. Exposed, inactive flow paths in thermal desorption units can collect lab air contaminants via surface adsorption that will be desorbed and observed in the subsequent sample. To minimize potential lab contaminants into sample desorption flow paths, we constructed a polycarbonate enclosure for the TD that is constantly purged with a positive pressure of zero air from a zero air generator (Aadco).

3.8.2. Thermal desorption efficiency

The incomplete desorption of analytes from adsorbent tubes is a major risk of bias in measurements since incomplete analyte transmission affects the original sample and carryover affects subsequent samples. We observed a strong sensitivity to the maximum desorption temperature and duration, and use a 10 min desorption (at the maximum temperature allowed by tube adsorbent composition) to fully desorb analyte mass and reduce any effects of carryover. Similarly, all flow paths carrying these analytes are inert and set to their highest temperature (200 °C) to minimize losses to the walls. As part of system diagnostics, users should routinely check for analyte carryover on tubes with repeat desorption of samples, and also for system carryover with empty tubes following sample desorption. We also evaluated the thermal desorption and transfer efficiency by comparing chromatogram peak areas between liquid standards injected directly into adsorbent tubes with zero air flow to direct injection into the inlet of our gas chro-

matograph (without the TD). We observed near full transmission of analytes through the TD, within the typical limitations of GC transmission of highly-polar functionalized analytes. Deactivated, ultra-inert columns and unions can help improve transmission into and through the GC, but users are also likely to observe sensitivities to thermal desorption parameters, where some functionalized analytes can decompose with rapid thermal desorption. Slower temperature ramps on the adsorbent tubes and focusing traps can help reduce the risk of fragmentation or isomerization.

4. Conclusions, future work, and summary of recommended best practices

Through the application of our integrated sampling-to-analysis system, we extend the capabilities of offline adsorbent tubes to lower concentrations (i.e. ppq) across a diverse range of analytes. This enables future applications of very powerful mass spectrometers that have been physically confined to the laboratory and can produce very detailed chemical speciation of complex mixtures of gas-phase organic compounds. Applications range across outdoor and indoor environments, laboratory experiments, and commercial/industrial monitoring and research. These include powerful collaborations in which offline methods, such as GC-resolved, high-accuracy MS and tandem MS, can identify and speciate the complex mixtures of ions and isomers observed by high time-resolution online instrumentation (i.e. TOF-CIMS, PTR-HTOF). Future work on the instrumentation includes: new configurations of adsorbent tube sampling devices that are more compact with greater capacity; the optimization of internal standard mixtures and delivery methods to improve stability corrections; experiments to evaluate and minimize losses of IVOCs and SVOCs to sodium thiosulfate quartz filters and Teflon filters; and longer storage tests to determine the ability to store or archive adsorbent tubes over extended periods. Opportunities also exist for the commercial and research community to minimize the TD flow path length (with more inert and non-absorptive materials) to increase transfer efficiency of unstable or reactive analytes. While our QBTX mix tubes were demonstrated as versatile sampling media for VOCs through SVOCs, we show that Res-Sil B (without RTX doping) is a potential alternative to Tenax TA with fewer artifacts and similar adsorbent performance, especially if used in multi-bed traps preceding a stronger adsorbent that captures smaller VOCs (i.e. $\leq C_7$).

To help improve the accuracy of research with adsorbent tubes across the field at the levels presented in this paper, we summarize our recommendations for best practices across the tube production through analysis lifecycle (Fig. 1):

Tube production & conditioning:

- Raw, unpacked adsorbent materials should be thermally cleaned for several hours (see Table S1) prior to tube packing (and stored in clean air-tight containers). This is in addition to the re-conditioning of packed tubes before sampling.
- Cold storage of unused tubes can reduce the formation of artifacts that contribute to background contamination.
- New types or batches of materials should be checked for contamination following pretreatment, as some materials have persistent contamination or degradation products.
- While the application should inform adsorbent choices, multi-bed adsorbent tubes work for a wider range of analytes, using hydrophobic adsorbents when possible to avoid water collection.
- Custom or commercial tube conditioning systems and procedures should be carefully validated to reduce background contamination and routinely checked for efficacy of cleaning used tubes, which can vary depending on prior sample composition.

- Re-used adsorbent tubes need to be properly re-conditioned and spot checked in order to avoid background contamination and achieve sub-ppt limits of detection.

Sampling:

- Breakthrough confirmation tests are warranted with the introduction of new sampling conditions (i.e. temperature, pressure, RH), flow rates, sampling volumes, or sampling equipment, since small changes in conditions could affect breakthrough. Transfer efficiency tests with complete sampling instrumentation are also recommended to characterize sampling losses.
- A multicomponent internal standard (ideally deuterated) should be spiked in each sample tube to track variability across the full sampling-to-analysis system.
- To monitor external contamination during transport, "shipping blanks," in addition to normal field blanks, should be included with shipments of adsorbent tubes.
- Ozone scrubbers (ideally sodium thiosulfate) should be used upstream of adsorbent tubes to reduce oxidation of analytes or adsorbents.
- All surfaces and flow paths in the sampling and analytical systems (e.g. tubing, valves) should be heated and consist of inert or passivated materials to minimize wall losses form adsorption or reactions.

Storage & analysis:

- Tubes should be stored in a sample-dedicated freezer ($-30\,^{\circ}$C or colder) away from concentrated standards, solvent, and other chemicals, and transported in cold/isolated conditions. Storage caps need to be checked after the initial temperature drop to confirm a proper seal.
- Additionally, adsorbent tubes should be isolated from contamination during transport and in laboratory environments where high concentrations of organic chemicals often exist.
- Samples from an experiment or campaign should be run consecutively in a short time period to reduce the potential impacts of instrument drift.
- Daily calibration checks with a standard in triplicate each day during sample analysis provides crucial information on system stability and monitors for changes in desorption or transmission efficiency.
- Tunable instrument parameters provide useful approaches to optimize analyte transmission (i.e. TD or GC temperature programs) but should be set prior to analysis of field sample sets.

Acknowledgements

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.chroma.2018.09.014.

Figs. S1–11 and Tables S1–2 can be found free of charge online.

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