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Atmospheric Measurement Techniques Discussions

Dynamic Solution Injection: a new method for preparing pptv-ppbv standard atmospheres of volatile organic compounds

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Abstract

Proton Transfer Reaction-Mass Spectrometry (PTR-MS) and thermal desorption Gas Chromatography-Mass Spectrometry (GC-MS) allow for absolute quantification of a wide range of atmospheric volatile organic compounds (VOCs) with concentrations in the ppbv to pptv range. Although often neglected, routine calibration is necessary for accurate quantification of VOCs by PTR-MS and GC-MS. Several gas calibration methods currently exist, including compressed gas cylinders, permeation tubes, diffusion tubes, and liquid injection. While each method has its advantages and limitations, no single technique has emerged that is capable of dynamically generating accurate concentrations of complex mixtures of VOCs over a large concentration range (ppbv to pptv), is technically simple and field portable, and affordable. We present the development of a new VOC calibration technique based on liquid injection with these features termed Dynamic Solution Injection (DSI). This method consists of injecting VOCs (0.1–0.5 mM) dissolved in cyclohexane (PTR-MS) or methanol (GC-MS) into a 1.0 slpm flow of purified dilution gas in an unheated 25 mL glass vial. Upon changes in the injection flow rate (0.5–4.0 µL min^{-1}), new VOC concentrations are reached within seconds to minutes, depending on the compound, with a liquid injection flow rate accuracy and precision of better than 7% and 4%, respectively. We demonstrate the utility of the DSI technique by calibrating a PTR-MS to seven different cyclohexane solutions containing a total of 34 different biogenic compounds including volatile isoprenoids, oxygenated VOCs, fatty acid oxidation products, aromatics, and dimethyl sulfide. In order to validate the new DSI method, a GC-MS and PTR-MS calibration intercomparison with VOC standards generated by dynamic dilution of NIST traceable permeation tubes (α-pinene, acetone, and ethanol) and a compressed gas cylinder (acetaldehyde) was made. The results revealed that while calibration of acetone is comparable between the methods, calibration curve slopes for other VOCs obtained by using permeation tubes and the compressed gas cylinder are lower than those obtained by the DSI technique by up to a factor of 2. This implies that concentration measurements of some

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VOCs may be overestimated using permeation tubes and/or compressed gas cylinders for calibration. Because of its high accuracy and precision, small size, low cost, and simplicity, we conclude that the Dynamic Solution Injection method will be of great use to both laboratory and field VOC studies.

1 Introduction

Measurements of gas-phase volatile organic compound (VOC) concentrations are critical for studying fundamental physical, chemical, and biological processes occurring in the atmosphere. However, this poses a technical challenge because the species of interest are usually present in very trace quantities and an extremely sensitive instrument is required to directly measure them. While a few high sensitivity VOC sensors are currently available, the number of important atmospheric species continues to increase (Goldstein and Galbally, 2009). With current calibration techniques, our ability to accurately identify and quantify these species is limited, especially during remote field campaigns where a small portable calibration system is needed.

Standard gas mixtures can be made by two fundamental methods; static and dynamic (Barratt, 1981). Preparation of static ppbv concentrations of gas-phase VOCs has been achieved volumetrically by evaporating small volumes (5–10 µL) of dilute VOC solutions in a gas sample bag filled with a known volume of air (Bouvier-Brown et al., 2007) and gravimetrically with N_2 in gas cylinders (Rhoderick and Yen, 2006). A major disadvantage of using static methods for the preparation of VOC standards is the absorptive losses on surfaces like bags and gas cylinder walls. This loss is difficult to account for and is particularly significant for VOCs with low vapor pressures like semi-volatile organic compounds and other compounds with strong surface interactions like oxygenated VOCs. Despite this issue, static calibration methods are commonly used in many environmental monitoring programs, often by dilution of a high concentration gas cylinder (ppmv) (Apel et al., 1998). In the dynamic mode of VOC standard generation, compounds are introduced into a known steady flow of purified dilution gas and the mixture is then homogenized. Pure dynamic methods minimize wall effects, allow rapid variations in concentration, and enable the generation of standards when needed. VOC standards prepared dynamically have been achieved by passing a dilution gas flow over permeation (Spinhirne and Koziel, 2003; Mitchell, 2000; Cardoso et al., 1996; Jakoubkova et al., 1986; Teckentrup and Klockow, 1978; Godin and Boudene, 1978) or diffusion (Thompson and Perry, 2009; Helmig et al., 2003; Komenda et al., 2001) tubes in temperature-controlled ovens. However, these methods often suffer from long and tedious gravimetric calibration periods where permeation rates are determined by a change in mass over time (weeks for diffusion tubes, months for permeation tubes), the limited commercial availability of compounds (permeation tubes), and their associated high prices (typically $200–$1000 for a single permeation tube). Other disadvantages are the need to accurately and precisely control the permeation chamber temperature, degradation of reactive VOCs with time (hydrolysis, hydration, oxidation, etc.), changes in the permeation characteristics of the diffusion membranes over time (permeation tubes), and difficulties preparing complex mixtures of VOCs (each permeation tube is often certified at a different temperature).

To avoid some of these disadvantages, liquid injection techniques have been developed for the generation of VOC standard atmospheres. In this technique, liquid VOC standards are directly injected at a known rate into a dilution air or N_2 stream. The key assumption of this approach is that the evaporation of the liquid standard into the air stream is complete, which is then homogenized in a mixing chamber. Previous configurations have suffered from complicated designs with liquid VOCs sprayed into heated air warmed by air/gas combustion (Jaouen et al., 1995). More recently, a stepper-motor driven syringe has been used to inject pure liquids into a dilution gas flow (Rosenberg et al., 2001). While simpler than previous designs, this system lacks the ability of continuous operation (due to the need of a syringe-fill cycle) and requires a heated liquid injection manifold (to promote evaporation of liquid standard) and a separate mixing chamber.

In this paper, we present the development of a new simplified calibration system based on a stepper motor controlled syringe-less pump capable of delivering continuous liquid flow rates with values spanning six orders of magnitude (nL/min to mL/min). This system combines the injection and mixing chamber into a single glass vial, eliminates the need for heating the injection manifold by utilizing VOC solutions in solvents with high vapor pressure (methanol or cyclohexane), and expands the calibration of PTR-MS and GC-MS to a much larger range of VOCs.

2 Materials and methods

2.1 Dynamic Solution Injection (DSI) system

The experimental setup of the Dynamic Solution Injection system (DSI) is shown in Fig. 1 and consists of a liquid pump, a calibration solution vial, a mixing vial, and Teflon® (PFA) tubing and fittings. A syringe-free stepper motor driven pump (M6 liquid handling pump, Valco Instruments Co., Inc) was used to control the injection flow rate of a calibration liquid solution into a mixing vial. The M6 pump was controlled with the included PC software (M6-LHS). While not employed here, this software also provides the capability of controlling a liquid sampling valve for the automated selection of one of multiple calibration solutions as well as allowing for the development of a liquid flow rate method in which flow rates can be automatically changed over time. Approximately 20 mL of a liquid standard calibration solution was placed in a 25 mL glass vial fitted with a Teflon® sealed cap and one end of a 1/16 in O.D.×1 ft tube was submerged in the liquid calibration solution after piercing through the septum while the other end was connected to the inlet of the M6 pump. An additional tube (1/16 in O.D.×1 in) was inserted through the septum to allow room air to enter the calibration solution vial when liquid solution was pumped out. From the pump outlet, another 1/16 in O.D.×1 ft tube was pierced through the septum of a mixing glass vial (empty) while 1.0 slpm of ultra high purity (UHP) N_2 flowed into the mixing vial via a separate 1/16 in O.D. tube that was also pierced through the septum. The flow rate of the UHP N_2 was controlled with a mass flow controller (Cole-Palmer, USA) calibrated with a primary flow meter (Defender 220, Bios International). The outflow of the mixing chamber passed through a third tube (1/8 in O.D.×6 in) that was also inserted into the septum of the mixing vial and connected to a 1/8 in O.D. tee. One of the ports on the tee was vented to an exhaust via a 1/8 in×6 in tube while the other was connected either to a Proton Transfer Reaction-Mass Spectrometer (PTR-MS) or a thermal desorption Gas Chromatograph-Mass spectrometer (GC-MS). Both instruments require ~50 sccm, resulting in the majority of the flow from the mixing vial vented to an exhaust.

For the purposes of calibration, dilute VOC solutions were made as shown in Table 1 with either cyclohexane (PTR-MS) or methanol (GC-MS) as the solvent. Each solution was prepared by diluting 5.0 µL each of an authentic, neat liquid standard (Sigma-Aldrich) in 100 mL of the appropriate solvent to produce concentrations in the range of 0.22 to 0.89 mM. Once a liquid calibration solution was added to a new sample vial, the M6 pump was purged at 100 $\mu L\,min^{-1}$ for 15 min (<100 µL internal volume). During this time, the liquid output was collected in a separate vial (flush). During liquid injection in the mixing vial, the M6 pump was set to deliver a flow rate of 4.0 $\mu L\,min^{-1}$ or less to ensure a complete evaporation of solvent and VOC solutes into the UHP N_2. For solutions in methanol, injection flow rates were kept below 2.0 $\mu L\,min^{-1}$ to ensure complete evaporation. Gas-phase VOC concentrations produced by the DSI system ranged between 0–40 ppbv.

2.2 Permeation tube and gas cylinder standards

For validation of the DSI technique, a comparison was made between calibration slopes (GC-MS and PTR-MS) obtained with a compressed gas cylinder (acetaldehyde) and permeation tubes (ethanol, acetone, and α-pinene). After obtaining a blank (UHP N_2), a four point calibration curve was obtained for acetaldehyde, by diluting 2.0, 5.0, and 10.0 sccm of a 2.0 ppmv gravimetrically prepared standard (Apel Riemer Environmental Inc, USA) in UHP N_2 to produce gas-phase concentrations between 0–19.8 ppbv.

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For acetone, ethanol, and *α*-pinene, National Institute of Standards and Technologies (NIST) traceable permeation tubes (KIN-TEK Laboratories, Inc.) placed in a temperature controlled permeation chamber (VICI Valco Instruments Co. Inc.) with 100 sccm of UHP nitrogen flowing through was used to generate known concentrations of acetone (456 ppbv), ethanol (579 ppbv), and *α*-pinene (313 ppbv). Upon dilution with high flow rates of UHP zero air (15.0, 10.0, and 5.0 slpm), the resulting concentrations ranged between 0–35 ppbv. All flow rates were controlled with mass flow controllers (Cole-Parmer and Omega Engineering) and calibrated using a primary flow meter (Defender 220, Bios International).

2.2.1 Proton Transfer Reaction-Mass Spectrometry (PTR-MS)

VOC calibration gas samples produced from the three calibration systems (DSI, permeation tubes, and compressed gas cylinder) were measured using Proton transfer reaction-mass spectrometry (PTR-MS). PTR-MS has been used extensively to measure the concentrations of atmospheric volatile organic compounds (VOCs) with proton affinity greater than water. The technical details of the PTR-MS have been previously described (Lindinger and Hansel, 1997; de Gouw and Warneke, 2007). A commercial high sensitivity PTR-MS instrument (IONICON, Austria, with a QMZ 422 quadrupole, Balzers, Switzerland) was used for this study. The PTR-MS was operated with a drift tube voltage of 600 V and drift tube pressure of 2.1 mb. During each PTR-MS measurement cycle, the mass to charge ratios *m/z* 21 ($H_3^{18}O^+$) and *m/z* 32 (O_2^+) were sequentially monitored with a dwell time of 20 ms. From these, the primary ion signal (H_3O^+) was calculated to be between 1.5–2.0×10^7 cps. For the PTR-MS calibrations, the seven solutions were chosen so that in a given solution, no two compounds had the same molecular weight. For calibration solutions 1–4, additional mass to charge ratios corresponding to the protonated VOCs shown in Table 1 were sequentially measured, each with a dwell time of 0.5 s. The total PTR-MS cycle time (each mass to charge ratio measured once) was 30.3 s. In order to determine the time required for gas-phase concentrations to stabilize once the liquid injection flow is changed, a reduced set of mass to charge ratios were monitored for solutions 5–7. In addition to *m/z* 21 and *m/z* 32, additional mass to charge ratios were monitored as follows; Solution 5: *m/z* 45, Solution 6: *m/z* 81, 137, and Solution 7: *m/z* 47, 59. This resulted in a decreased PTR-MS cycle time of 1–5 s. The PTR-MS was calibrated to each solution by measuring the calibration gas generated from the DSI system with liquid injection flow rates of 0.5, 1.0, 2.0, and 4.0 µL min^{-1}. Each flow rate was measured for at least 30 min and UHP N_2 flowing through a separate line was also measured for background signals.

2.3 Thermal Desorption Gas Chromatography-Mass Spectrometry

Identification and quantification of VOCs produced from the three calibration systems (DSI, permeation tubes, and compressed gas cylinder) was made with a Series 2 air server connected to a Unity 2 thermal desorption system (MARKES International) interfaced with a 5975C series gas chromatograph/electron impact ionization mass spectrometer with a triple-axis detector (GC-MS, Agilent Technologies). Calibration air samples were collected at 50 sccm for 10 min (0.5 L) on an internal sorbent tube (water management cold trap, MARKES International) held at 30 °C and purged with UHP helium at 30 sccm for 5 min. During injection, the trap was heated to 300 °C for three minutes while backflushing with carrier gas at a flow of 6.5 sccm. In order to improve peak shape, 5 sccm of this flow was vented through the split while the remaining 1.5 sccm was directed to the column (Agilent DB624 60 m×0.32 mm×1.8 µm) temperature programmed with an initial hold of 3 min at 40 °C followed by an increase to 230 °C at 5 °C min^{-1}. The mass spectrometer (Agilent 5975C) was configured for scan mode (*m/z* 40–300) with a 5.5 min solvent delay (methanol). Identification of VOCs was made by comparison of mass spectra with the National Institute of Standards and Technologies (NIST) database. Quantification of VOCs was performed from peak areas of *m/z* 43 (acetaldehyde), *m/z* 45 (ethanol), *m/z* 43 (acetone), and *m/z* 93 (α-pinene). The GC-MS was calibrated to solutions 5–7 by measuring the calibration gas generated from the DSI system with liquid injection flows of 0.5 µL min^{-1}, 1.0 µL min^{-1}, and 2.0 µL min^{-1}. An assessment of the UHP N_2 results demonstrated that peak areas for

VOC blanks were negligible.

3 Results and discussion

A series of experiments was carried out to evaluate the function of the DSI system as well as the accuracy and precision of the analytical procedure. To access the accuracy and precision of the pump, we measured the liquid mass acquired by a glass collection vial after dispensing 50 µL of methanol with the M6 pump at flow rates of 0.5, 1.0, and 2.0 µL min^{-1} (three repeat mass flow calibrations each). Assuming a methanol density of 0.79 g mL^{-1}, the accuracy of the nine individual flow settings was found to be within +0.3% to −6.8% of the expected mass (39.6 mg) with an average of −2%. The flow rate precision was found to be 3.9% (nine flows, one standard deviation). To access the precision of the entire analytical system (DSI, GC-MS), a full calibration was performed five times with a liquid injection flow rate of 0.5, 1.0, and 2.0 µL min^{-1}. For all flow rates, the compound specific (acetone, ethanol, *α*-pinene) peak area precision ranged between 9 and 15% RSD. These results show excellent reproducibility, well within the 20% required for ambient air sampling. This analytical precision range falls within those found by other studies during repeat calibrations employing a similar thermal desorption GC-MS system (Ma et al., 1997). Our observations suggest that in the range of flow rates used in this study, the M6 pump offers a repeatable and accurate method for liquid standard injections.

After flushing the fresh liquid calibration solution through the M6 pump and tubing, regardless of the liquid flow (0.5–4.0 µL min^{-1}), the liquid calibration solution did not produce visible liquid drops at the end of liquid injection tube in the mixing vial, suggesting that that the liquid delivery rate determines the evaporation rate for both cyclohexane and methanol solutions. We also conclude from these results that the evaporation process is complete without the need for heating.

PTR-MS measurements demonstrate that upon switching from measurement of UHP N_2 (background signals) to measurement of the DSI system running with cyclohexane solution #1 at a liquid injection rate of 0.5 µL min^{-1}, a rapid increase in signals corresponding to the presence of the protonated compounds (MW+1) occurred (Fig. 2). Due to the lower proton affinity of cyclohexane than water, the presence of high cyclohexane concentrations in the drift tube of the PTR-MS did not affect the primary ion intensity or the proton transfer reactions between the primary ion (H_3O^+) and VOCs. These signals remained stable for the 30-min measurement period indicating establishment of a steady state evaporation process controlled by a constant liquid delivery rate. Upon increasing the liquid injection flow rate to 1.0, 2.0, and 4.0 µL min^{-1}, the PTR-MS signals increased in a step wise fashion and stabilized after a few minutes. Upon decreasing the solution #1 flow rate from the high (4.0 µL min^{-1}) to the low (0.5 µL min^{-1}) setting, the PTR-MS signals returned rapidly to the original values (data not shown). This result suggests that in the flow rates used, steady state conditions rapidly form and that an accumulation of unevaporated calibration solution in the mixing vial did not occur.

To demonstrate the feasibility of calibrating the PTR-MS to a variety of compounds using the DSI system, solutions 1–5 were analyzed. These solutions contained a variety of structural classes including isoprenoids, oxygenated VOCs, fatty acid oxidation products, aromatics, and dimethyl sulfide. Care was taken to avoid using compounds with limited solubility in cyclohexane such as organic acids. The results show that linear calibration plots for large mixtures of compounds can be produced with the DSI technique (Fig. 3). Different calibration curve slopes represent different sensitivities of the PTR-MS to each compound. Sensitivities are influenced by differences in transmission efficiencies, fragmentation channels, and proton transfer reaction rate constants. Instead of changing the solution injection rates used in this study, we recommend that lower or higher gas-phase concentrations be generated by preparing lower or higher concentrations of VOCs in solution. This would avoid the potentially lower accuracy and precision of solution delivery from the M6 pump at low flow rates (5 nL min^{-1}) and incomplete evaporation at higher flow rates.

In order to validate the DSI system, PTR-MS and thermal desorption GC-MS calibrations were done with α-pinene, ethanol, and acetone permeation tubes and an acetaldehyde compressed gas cylinder. These results were compared to calibrations of the same compounds done with the DSI system (Fig. 4). For both GC-MS and PTR-MS, the acetone calibration slopes for the DSI and permeation tube methods show good agreement (within 24% of each other) (Fig. 4, row 1). These results suggest that both the DSI and permeation tube techniques offer an accurate method for calibration of acetone. However, when calibration slopes for ethanol and α-pinene permeation tubes were compared with the DSI results, the DSI slopes were greater than those from the permeation tubes on both the PTR-MS and GC-MS by a factor of 1.5–2.3 (Fig. 4, rows 2 and 3). For PTR-MS measurement of acetaldehyde, the DSI calibration slope was also greater than the slope obtained from the compressed gas cylinder standard by a factor of 1.6 (Fig. 4, row 4). However, when the same experiment with acetaldehyde was repeated using GC-MS, the DSI calibration slope was lower than the PTR-MS slope (DSI slope was 18% lower than the compressed gas cylinder slope). This apparently inconsistent result may be explained by a significant appearance of methyl acetate in the GC-MS chromatogram from DSI samples (Fig. 4, bottom row) but not from compressed gas cylinder samples. The appearance of methyl acetate suggests that some of the acetaldehyde reacted with the solvent (methanol) to form methyl acetate in the DSI technique. The increase in methyl acetate peak area compared with acetaldehyde peak area supports this idea. Therefore, a drawback of the DSI method is that care needs to be taken to ensure that calibration solution compounds do not react with the solvent (like acetaldehyde and acetic acid in methanol) or with other compounds in the solution (like alcohols and acids).

4 Conclusions

Despite its many drawbacks including low accuracy for some compounds, high cost, low field portability, and dangers associated with the use of compressed gas cylinders, the static method for the generation of low concentration (ppbv–pptv) VOC standards is routinely used in industrial, academic, and government settings. Dynamic methods for the generation of low concentration gas standards are preferred due to the minimization of wall effects, but the current techniques (permeation and diffusion tubes) can suffer from poor accuracy that can change over time, long calibration times, high costs, low compound availability, and difficulties preparing complex mixtures. The DSI system overcomes these limitations and may provide an alternative to dangerous and non-portable compressed gas cylinders and expensive permeation tubes in most cases. The flexibility and versatility of the DSI system stems from the fact that liquid calibration solutions containing complex mixtures of VOCs can be used to generate a wide range of gas-phase concentrations with high accuracy and precision. However, care must be taken to assure that compounds present do not react with each other or the solvent, and that the compounds are soluble in the solvent. Another major advantage of the DSI technique is the low consumption rate of the purified dilution gas. Unlike diffusion and permeation tube methods where the calibration gas concentrations are achieved by dilution with high flow rates of UHP N_2 or zero air, the DSI technique utilizes a constant 1.0 slpm of dilution gas.

When PTR-MS and GC-MS calibration curve slopes were compared between the DSI technique and permeation tubes, discrepancies were observed. In our comparison, calibration curves for acetone showed good agreement between the permeation tube and DSI techniques. In contrast, calibration curve slopes for ethanol and α-pinene obtained using permeation tubes were significantly lower than those obtained by the DSI technique (up to a factor of 2). By PTR-MS the calibration curve slope obtained for acetaldehyde from a compressed gas cylinder was also larger relative to the DSI technique (results using GC-MS were obscured by the formation of methyl acetate from a reaction between acetaldehyde and the methanol solvent). These results suggest that for some compounds, permeation tubes and compressed gas cylinders generate lower concentrations than initially certified. This would result in an overestimation of VOC concentrations in air samples by up to a factor of 2. This may be due to loss processes that are difficult to characterize including absorptive losses in gas cylinders, chemical decomposition processes in permeation tubes, and changes in permeation tube membrane properties over time. Since our DSI method does not involve addition of heat, this technique may be very useful for the calibration of labile and reactive VOCs as well as "sticky" VOCs like oxygenated VOCs and semi-volatile organic compounds. Because of its high accuracy and precision, small size, low cost, and simplicity, we anticipate the dynamic solution injection method will benefit many applications in future laboratory and field VOC studies.

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Table 1. Seven cyclohexane solutions used to calibrate the PTR-MS using the DSI technique. Solutions 5–7 were also prepared in methanol for GC-MS calibration. Both PTR-MS and GC-MS were also calibrated to alpha-pinene, ethanol, and acetone using permeation tubes and to acetaldehyde by using a compressed gas cylinder.

Solution	Compounds	MW	PTR-MS (m/z)	mM
1	dimethyl sulfide	62.13	63	0.68
1	methyl acetate	74.08	75	0.63
1	benzene	78.11	79	0.56
1	3-methyl-2-buten-1-ol	86.13	87	0.49
1	heptanal	114.19	115	0.36
2	ethyl vinyl ketone	84.12	85	0.50
2	3-hexen-1-ol	100.16	101	0.42
2	benzaldehyde	106.12	107	0.49
2	benzyl alchohol	108.14	109	0.48
2	acetophenone	120.15	121	0.43
2	phenethyl alcohol	122.16	123	0.42
2	p-cymene	134.22	135	0.32
2	3-hexenyl acetate	142.20	143	0.32
2	methyl salicylate	152.15	153	0.39
3	2-butanone	72.11	73	0.56
3	3-methyl-2-butenal	84.12	85	0.52
3	2-penten-1-ol	86.13	87	0.50
3	trans-2-hexenal	98.15	99	0.43
3	3-hexanone	100.16	101	0.41
3	1-octene	112.21	113	0.32
3	2-heptanone	114.19	115	0.36
3	guaiacol	124.14	125	0.45
3	nonanal	142.24	143	0.29
3	ethyl benzoate	150.17	151	0.35
3	decanal	156.27	157	0.27
4	hexanal	100.16	101	0.41
4	3-pentanone	86.13	87	0.47
4	3-buten-2-one	70.09	71	0.61
4	homosalate	262.35	139	0.17
4	caryophyllene	204.36	205	0.22
5	acetaldehdye	44.05	45	0.89
6	alpha pinene	136.23	137	0.32
7	ethanol	46.07	47	0.86
7	acetone	58.08	59	0.68

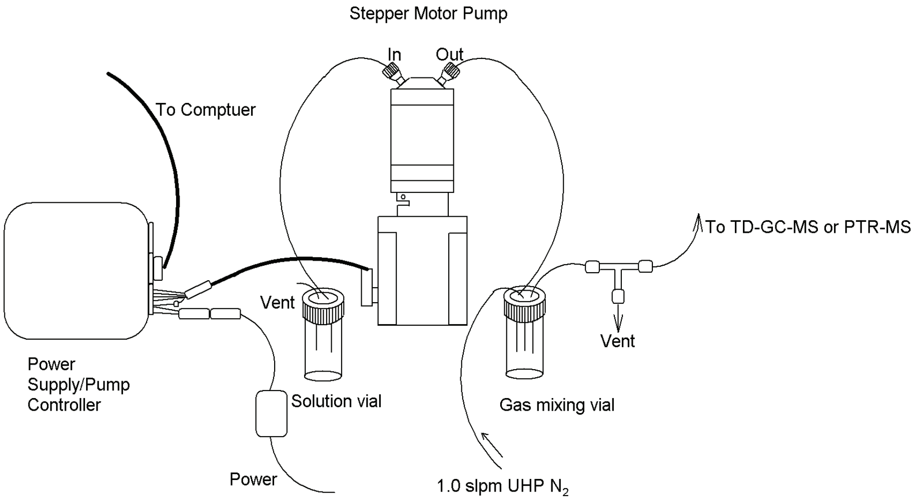

Fig. 1. Diagram of the Dynamic Solution Injection (DSI) system. A calibration solution vial is connected to the inlet of a liquid stepper motor pump that injects a known flow of liquid into a gas mixing vial where 1.0 slpm of dilution gas (UHP nitrogen or air) is added.

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Interactive Discussion

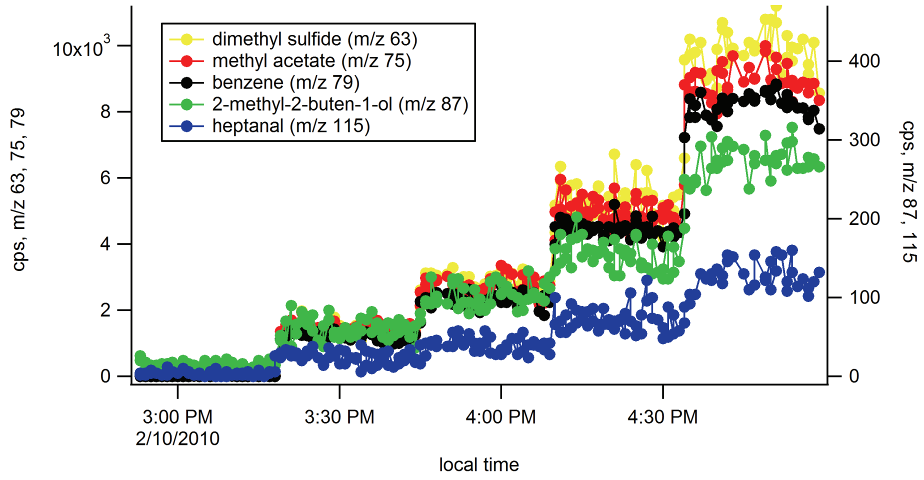

Fig. 2. Example time series of PTR-MS signals (counts per second, cps) during dynamic injections of solution 1 into a 1.0 slpm UHP N_2 flow. Solution flow rates were injected at 0.0, 0.5, 1.0, 2.0, and 4.0 µL min^{-1} sequentially.

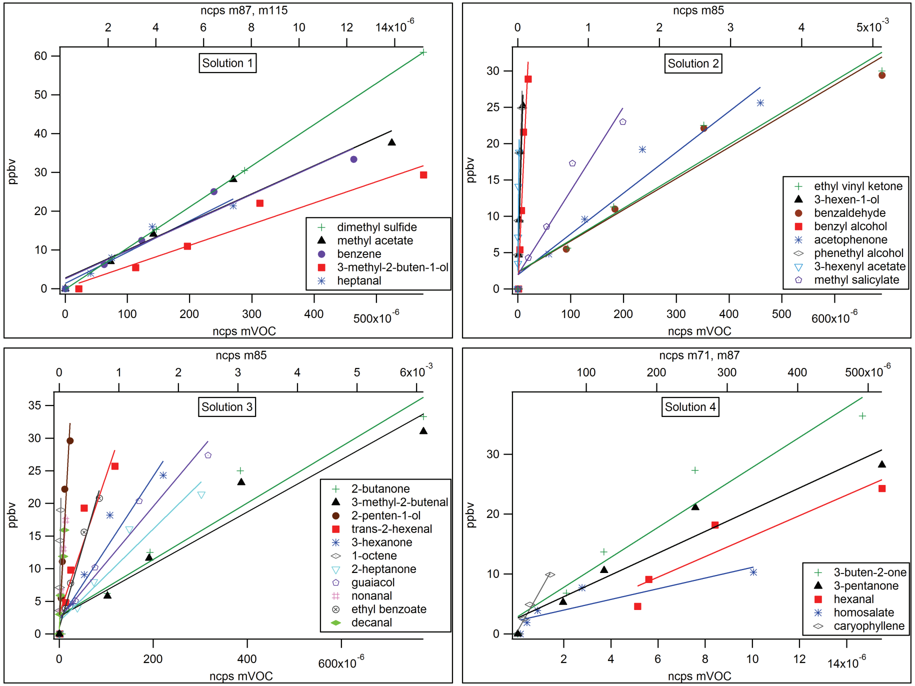

Fig. 3. Calibration of the PTR-MS to 30 different compounds in 4 different cyclohexane solutions using the DSI technique. VOC concentrations generated by the DSI system are plotted versus normalized counts per second (ncps).

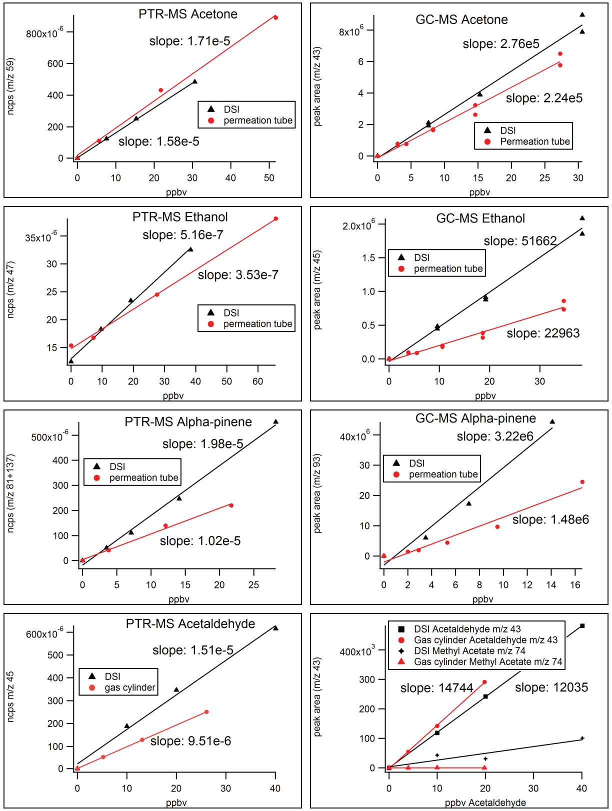

Fig. 4. Quantitative comparison of calibration slopes using DSI method and permeation tube/compressed gas cylinder methods for ethanol, acetone, *α*-pinene, and acetaldehyde. PTR-MS measurements are shown on the left and GC-MS measurements are shown on the right. Using GC-MS, the DSI technique resulted in the loss of acetaldehyde and the production of methyl acetate.