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Development and validation of a portable gas phase standard generation and calibration system for volatile organic compounds

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Abstract

We report on the development of an accurate, portable, dynamic calibration system for volatile organic compounds (VOCs). The Mobile Organic Carbon Calibration System (MOCCS) combines the production of gas-phase VOC standards using permeation or diffusion sources with quantitative total organic carbon (TOC) conversion on a palladium surface to CO_2 in the presence of oxygen, and the subsequent CO_2 measurement. MOCCS was validated using three different comparisons: (1) TOC of high accuracy methane standards compared well to expected concentrations (3% relative error), (2) a gas-phase benzene standard was generated using a permeation source and measured by TOC and gas chromatography mass spectrometry (GC-MS) with excellent agreement (<4% relative difference), and (3) total carbon measurement of 4 known gas phase mixtures were performed and compared to a calculated carbon content to agreement within the stated uncertainties of the standards. Measurements from laboratory biomass burning experiments of formic acid by negative-ion proton-transfer chemical-ionization mass spectrometry (NI-PT-CIMS) and formaldehyde by proton transfer reaction-mass spectrometry (PTR-MS), both calibrated using MOCCS, were compared to open path Fourier transform infrared spectroscopy (OP-FTIR) to validate the MOCCS calibration and were found to compare well (R^2 of 0.91 and 0.99 respectively).

1 Introduction

Volatile organic compounds (VOCs) are emitted to the atmosphere from a variety of sources, both natural and man-made. In the atmosphere, the photo-oxidation of VOCs leads to formation of ozone and organic aerosol, which are both significant pollutants and alter radiative forcing in the Earth's climate system. Accurate measurements of ambient VOCs in the atmosphere or laboratory using analytical techniques such as

gas-chromatography (Rappengluck et al., 2006) or PTR-MS (de Gouw and Warneke, 2007) rely on the accuracy of the calibration methods used. For many VOCs, but especially for "sticky" compounds that have a high affinity for metal surfaces, accurate calibration systems are not readily available. VOC standards for instrument calibration
5 are generally produced either statically or dynamically. Static methods rely on mixtures of gases in closed containers of known volume, while dynamic processes involve mixing a continuous flow of analyte into a dilution or carrier stream. A comprehensive review of standard generation processes for VOC can be found elsewhere (Barratt, 1981; Namiesnik, 1984; Naganowska-Nowak et al., 2005)
10 Modern static techniques most commonly utilize mixtures of gases in treated high-pressure cylinders (Apel et al., 1994, 1998; Rappengluck et al., 2006). Static techniques are the preferred calibration method for many field and laboratory investigations due to the portability and robust nature of high-pressure gas cylinders. Standard mixtures are stable for many VOCs; however, wall losses and degradation become
15 significant for highly polar and reactive compounds.

Dynamic standard generation can avoid the problem of wall losses and degradation by continuously flowing analyte into a carrier stream. This method is more suitable for polar and reactive species which would otherwise be lost to surfaces at low mixing ratios (Barratt, 1981). The two most commonly used techniques are standard generation
20 through the use of diffusion cells (Thompson and Perry, 2009; Altshuller and Cohen, 1960; Possanzini et al., 2000; Namiesnik et al., 1981; Williams et al., 2000) and permeation sources (Okeeffe and Ortman, 1966). Diffusion sources are often used in place of permeation sources when the latter is unavailable or behavior of a substance in a permeation source is nonideal (i.e. degredation, low permeation rate, etc.) (Barratt,
25 1981). A combination of static and dynamic standard generation is also often used where a high mixing ratio (ppmv) static mixture is diluted dynamically. This allows for convenient portability but losses are not as significant as with very low mixing ratio static sources.

Total carbon measurement by conversion to CO_2 and nondispersive infrared (NDIR) sensor analysis has long been used for analysis of a range of environmental samples ranging from natural waters to bulk collected aerosol particles. Total organic carbon (TOC) measurements of gas phase nonmethane hydrocarbons using oxidative cata-
lysts, followed by reduction to methane, have been used in previous work (Maris et al., 2003; Roberts et al., 1998). Ambient VOC levels are frequently below the detection limits of these gas phase TOC measurement techniques, which need to account for the large concentrations of ambient CO_2, methane, and carbon monoxide and make them unsuitable for ambient analyses. The TOC technique is however particularly well suited
for the analysis of calibration standards where the mass loading can be user-varied to fall within a measureable range and the effects of carrier gas CO_2 can be eliminated. While the technique used here is similar to TOC methods utilizing the catalytic conversion of organic carbon, we use a direct measurement of the CO_2 produced in this process as a calibration measurement.
In this work we developed a mobile organic carbon calibration system (MOCCS) for the generation and absolute measurements of calibrated VOC mixtures in air that is relatively inexpensive and easy to set up. The MOCCS combines the production of standards using permeation or diffusion sources, quantitative catalytic conversion of carbon containing species to CO_2, and subsequent CO_2 measurement. Validation of
this technique was performed in a three-part analysis: (1) two high accuracy methane standards were analyzed and compared to their known concentrations, (2) comparison of measurements by gas chromatography mass spectrometry (GC-MS) and MOCCS of a benzene standard generated using a permeation source with the system described here, and (3) several complex gravimetrically prepared VOC standards were analyzed
for total carbon content.

2 Experimental details

2.1 Mobile Oxidative Carbon Calibration System (MOCCS)

MOCCS, shown in Fig. 1, consists of 16 flow and temperature controlled permeation tube housings, a thermostated palladium catalyst at 350 °C to readily convert VOCs to
CO_2, and a CO_2 detector (Beckman Industrial Model 870 NDIR or LI-COR LI-6252). The entire assembly was mounted in a portable rack that includes a high-pressure zero air cylinder and an uninterruptable power supply. These features allow MOCCS to be temporarily removed from power for transport while providing continuous temperature control and flow over the permeation sources.

The housing was designed to hold 16 permeation sources at a controlled flow. Four aluminum blocks were drilled for 1/2″ o.d. PFA Teflon sleeves to house four permeation sources each. A temperature probe was inserted in the center of each block and the temperature regulated using individual controllers. Each permeation housing can be operated at a separate temperature with each block housing up to four permeation sources. Sections of 1/16″ o.d. stainless steel capillary tubing ~15 cm long were crimped until a flow of ~10 sccm was provided to each of the 16 channels at 30 psi. Due to slight variations in the inlet pressure, the flow is measured for each channel at the time of calibration.

A typical permeation source calibration is based on the mass loss of the permeation tube and usually requires running for several weeks under stable conditions. MOCCS measures real time emission rates of permeation sources after equilibrating within hours. As a result, any constant VOC source can be used thereby eliminating the necessity of obtaining certified permeation sources that can be quite costly. In this work, permeation sources were made in-house using pure compounds placed into 1/4″ or 1/8″ Teflon permeation tubes purchased from VICI Metronics and sealed with Teflon plugs with crimped stainless steel bands. Adjusting the temperature of the permeation housing can easily vary the output of the sources.

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The catalyst is comprised of a 3″ length 1/4″ o.d. stainless steel tube packed with 10% Pd on Kaowool (Johnson-Matthey, Ward Hill, MA.) and capped with a small amount of glass wool, to prevent the palladium from exiting the catalyst. A thermocouple is attached to the midpoint of the stainless steel tubing and then wrapped in a single layer of insulated Nichrome wire. The finished catalyst is well insulated and placed into an aluminum box with 1/4″ Swagelok bulkhead unions. A 24 Volt temperature controller is used to supply power to the Nichrome wire and set the temperature to 350°C. This catalyst design is based on that used for PTR-MS background measurements (de Gouw and Warneke, 2007).

The flow system was designed for the sample stream to be analyzed for both background CO_2 in the carrier gas and total organic carbon. A schematic of the flow system is shown in Fig. 1. The system was designed to continuously cycle between background CO_2 measurement and standard calibration on a user-defined timescale. Background CO_2 measurements are made by flowing the carrier gas through the permeation directly source into the CO_2 analyzer bypassing the catalyst. Measuring the background in this manner accounts for any CO_2 present in the carrier gas as well as any potential interference from the IR absorption of VOCs. This background is subtracted from the total organic carbon measurement. The presence of VOCs in the carrier gas must also be corrected for by subtracting a TOC measurement of the carrier gas (∼400 ppbv) prior to addition of a permeation source. The catalyst is kept under constant flow by flushing with 10 sccm zero air when the background is being measured.

A Beckman Industrial Model 870 NDIR was used to measure the CO_2 concentrations for most results presented here. Four CO_2 standards in ultrapure air (Scott-Marin Inc.) ranging from 2.065±0.207 ppmv up to 50.1±0.5 ppmv were used to calibrate the NDIR. The results of the calibration are shown in Fig. 2. The precision in NDIR CO_2 measurements through the calibrated concentration range was ±1% of the measurement +30 ppbv. The accuracy of CO_2 measurements through the 2 ppmv to 50 ppmv concentration range was ±4% of the measurement +400 ppbv. Significant improvements

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in both precision and accuracy were made by substitution of a LI-COR LI-6252 CO_2 analyzer and will be presented later in this discussion.

This TOC technique has been previously used to calibrate standards from diffusion sources for organic acids in the development of negative-ion proton-transfer chemical-ionization mass spectrometry (NI-PT-CIMS) (Veres et al., 2008). The diffusion flow system used in that particular study was identical to that described in Williams et al. (2000).

2.2 GC-MS

A custom built gas chromatograph with a quadrupole mass spectrometer detector (GC-MS) was used to independently verify the concentrations of two benzene standards generated and calibrated by the MOCCS. A detailed description of the GC-MS is described by Goldan et al. (2004). The output of the benzene permeation tube was first diluted in humidified nitrogen by factors of $9.78\,(\pm0.11)\times10^{-4}$ and $8.62\,(\pm0.11)\times10^{-4}$. This was done in order to avoid overloading the GC-MS, which normally operates in the pptv to ppbv range. The GC-MS collected each sample directly from the diluted sample stream before subsequent analysis. A minimum of 10 replicate samples were analyzed for each benzene concentration with an overall measurement precision of 3% or better. Benzene measured by the GC-MS was independently calibrated using more than 20 single- and multi-component VOC mixes with an overall measurement uncertainty of ±20%.

2.3 NI-PT-CIMS

Negative-ion proton-transfer chemical-ionization Mass Spectrometry (NI-PT-CIMS) provides gas-phase acid measurements with one-second time resolution. A detailed description of NI-PT-CIMS can be found elsewhere (Veres et al., 2008). Briefly, NI-PT-CIMS consists of (1) a [210]Po source to produce acetate ions ($CH_3C(O)O^-$) from acetic anhydride, (2) a flow tube reactor, in which $CH_3C(O)O^-$ undergoes proton transfer

reactions with inorganic and organic acids, (3) a collisional dissociation chamber (CDC) to decluster ions, and (4) a quadrupole mass spectrometer for the detection of both reagent and product ions.

2.4 OP-FTIR

The open path Fourier transform infrared (OP-FTIR) instrument included a Bruker Matrix-M IR Cube spectrometer and a thermally stable open White cell. The White cell path length was set to 58 m. The spectral resolution was set to 0.67 cm^{-1} and the spectrometer acquired spectra every 1.5 s (four co-added spectra). A pressure transducer and two temperature sensors were located adjacent to the optical path and were logged on the instrument computer and used for spectral analysis. Mixing ratios were obtained by multi-component fits to sections of the IR transmission spectra with a synthetic calibration non-linear least-squares method (Griffith, 1996; Yokelson et al., 2007).

2.5 PTR-MS

Proton transfer reaction-mass spectrometry (PTR-MS) utilizes proton-transfer reactions of H_3O^+ to detect various atmospheric trace gases, usually as the MH^+ion. PTR-MS allows for the detection of numerous volatile organic compounds with high sensitivity (10–100 pptv) and response time (1–10 s). This technique has been used extensively in aircraft, ground-based and laboratory studies. A more complete discussion of the PTR-MS system used in this study can be found elsewhere (de Gouw and Warneke, 2007).

2.6 Gas standards

A detailed list of the standards used in this work is shown in Table 1. VOC mix 1–4 are high-pressure gas cylinder standards prepared at NOAA ESRL/CSD laboratory using gravimetric techniques. The error in each component in these laboratory-generated

standards is estimated to be no greater than 20%. Two high accuracy methane standards that were prepared gravimetrically with an uncertainty of ±0.2% (Dlugokencky et al., 2005) were borrowed from NOAA's Global Monitoring Division (Boulder, CO) and analyzed for TOC. The stated standard concentrations of CH_4 (a) and CH_4 (b) were 5.75±0.11 ppmv and 10.79±0.22 ppmv respectively. A laboratory-made benzene permeation source was equilibrated and calibrated by MOCCS for analysis.

3   Validation of the MOCCS

3.1   Data analysis

The results of the measurement of a benzene standard generated using the MOCCS as an example is shown in Fig. 3. Interpolated background measurements are subtracted from the total organic carbon measurements to obtain a concentration for the source compound. Dividing the result by the number of carbons in the parent molecule (6) gives the original standard concentration on a molar basis, assuming a conversion ratio of 1:1 for the oxidation of carbon to CO_2. The signal after the initial response time is then averaged to obtain an average standard concentration for each cycle. The inset in Fig. 3 shows the stability of the MOCCS that had a measured precision of better than 1% over 5 days. All of the TOC measured concentrations reported here are the averages of a minimum of 10 cycles. The duration of each cycle can be readily adjusted to allow for different time responses of the system to various compounds, which is dependent on their unique chemical properties (e.g. volatility, polarity, etc.).

3.2   Methane conversion to CO_2

The results of the two comparisons for the methane standards are shown in Fig. 4a as CH_4 (a) and CH_4 (b). The TOC determined methane concentration was determined as 5.9±0.6 ppmv for CH_4 (a) and 10.8±0.8 ppmv for CH_4 (b). The relative

errors in concentration between the TOC system and provided standard concentration were less than 3% in both cases and the two determinations agreed within the stated uncertainties.

3.3 Benzene conversion to CO_2

A benzene permeation source in the MOCCS was measured using both GC-MS and TOC. The results of the comparison are shown in Fig. 4b. Two permeation temperature settings were used to generate different concentrations, 7.36±0.14 ppmv and 3.79±0.10 ppmv as measured by TOC. The source output was diluted for analysis with GC-MS: dilution factors of $9.78\,(\pm 0.11) \times 10^{-4}$ and $8.62\,(\pm 0.11) \times 10^{-4}$ were used. GC-MS-measured benzene concentrations, after taking dilution into account, were 7.11±1.42 ppmv and 3.65±0.73 ppmv respectively. The relative difference between TOC and GC-MS measurements is less than 4% for both standards measured.

3.4 TOC of VOC standard mixtures

Results of the total carbon analysis are shown in Fig. 5 for each of the VOC mixtures available. The CO_2 concentration reported is the total carbon concentration of the standards (striped bars), also detailed in Table 1. Error in the NOAA generated standards is estimated to be about 10% based on the propagation of uncertainties in the gravimetric preparation method. TOC measured concentrations are shown in solid grey. Error (1σ) in the measurements shown in Fig. 4 represent the RMS of the standard deviation from the average of multiple TOC cycles (5%), the error associated with the calibration of the Beckman NDIR ±4% of the measurement +400 ppbv, and error in the dilution flows (2%). The agreement for all measurements is within the estimated error of the laboratory standards. The absolute error in the calculated total VOC concentration in the four standards analyzed as measured by MOCCS is less than 15%.

3.5 MOCCS field calibration

MOCCS was recently used during the Smoke Understanding through Regional Fire Simulations (SMURFS) 2009 study preformed at the combustion facility at the US Department of Agriculture (USDA) Forest Service, Fire Sciences Laboratory (FSL) in Missoula, MT. A more in-depth discussion of the SMURFS 2009 study can be found in a future publication (Veres et al., 2010). Briefly, emissions of controlled laboratory biomass fires were sampled directly from a stack in which the fire emissions were completely entrained. A negative-ion proton-transfer chemical ionization mass spectrometer (NI-PT-CIMS) was calibrated for formic acid using a permeation standard that was generated and calibrated with MOCCS. A proton-transfer-reaction mass spectrometer (PTR-MS) was calibrated for formaldehyde measurements using MOCCS. Simultaneous measurements of both formic acid and formaldehyde were made using open-path Fourier transform infrared spectrometer (OP-FTIR) and were used to validate the MOCCS calibration of NI-PT-CIMS and PTR-MS. Figure 6 shows time profile for both formic acid, measured by NI-PT-CIMS and OP-FTIR, and formaldehyde, measured by PTR-MS and OP-FTIR.

The results of a comparison of NI-PT-CIMS and OP-FTIR formic acid emission measurements from a single laboratory biomass fire are shown in Fig. 6a. A scatter plot of the data shown gives a NI-PT-CIMS/OP-FTIR formic acid ratio of 0.91±0.02 with a correlation (R^2) of 0.91. This agreement is well within the stated uncertainty of both instruments. Figure 6b shows the results of a comparison of PTR-MS and OP-FTIR formaldehyde emission measurements from the same laboratory controlled biomass fire shown in Fig. 6a. The PTR-MS/OP-FTIR formaldehyde ratio is 1.06±0.02 with a correlation (R^2) of 0.99 from the corresponding scatter plot. The detection of formaldehyde by PTR-MS is humidity dependent (Hansel et al., 1997); however, the humidity dependence is ignored here, the relative humidity during calibration and fire measurements were similar for this particular experiment. A study of the sensitivity of PTR-MS for formaldehyde as a function of humidity is beyond the scope of the present work.

The agreement between PTR-MS and OP-FTIR in this comparison is well within the estimated uncertainty of both instruments. The agreement between these two sets of independently calibrated measurements validates the use of the MOCCS for VOC standard production and calibration.

3.6 Comparison of CO_2 analyzers

A recent improvement to the MOCCS was the replacement of the Beckman model 870 NDIR CO_2 analyzer with a LI-COR LI-6252 CO_2 analyzer. Table 2 summarizes the results of a comparison of the two CO_2 analyzers. Significant improvements in the instrument response times and detection limits are observed with the LI-COR analyzer. Figure 7 shows the results of a comparison in formic acid response times and detection limits as defined by one complete MOCCS cycle. The formic acid response time, defined as the time required for a calibration signal to decay to 10% of the initial value when the source is removed, was approximately 90 s for the LI-COR compared to over 300 s for the Beckman analyzer. The detection limit for the compounds investigated in this study was determined from a signal-to-noise ratio of 2 as twice the standard deviation in the background. The LI-COR detection limit of 5 ppbv was significantly lower than that of the Beckman analyzer, 150 ppbv. The precision in LI-COR CO_2 measurements through the calibrated concentration range is ±1% of the measurement +1 ppbv. The accuracy of LI-COR CO_2 measurements through the 2 ppmv to 50 ppmv concentration range is ±1% of the measurement +80 ppbv. In addition to improvements in precision, accuracy and detection limit, the overall error from the average of multiple TOC cycles is also reduced from 5% of the measurement to 1% when using the LI-COR analyzer. These improvements from use of the LI-COR analyzer compared to the Beckman NDIR analyzer are significant and show that the accuracy of this technique is highly dependent on the type of CO_2 analyzer used.

4 Conclusions

A portable system for the dynamic production and calibration of gas phase VOCs has been developed. We use a combination of catalytic reduction of VOCs to CO_2 and the subsequent measurement of the CO_2 produced by an NDIR analyzer to standardize calibration sources. We have validated the TOC measurement technique through total carbon analysis of two high accuracy methane standards showing excellent agreement with 3% absolute error. MOCCS was validated further by the production and subsequent calibration of a benzene standard by GC-MS and TOC with excellent agreement (<4% relative difference). Four laboratory prepared mixed VOC gas-phase standards were analyzed for TOC and shown to be accurate to within 15%. The MOCCS system is relatively inexpensive to develop in laboratory. It allows for dynamic generation and calibration of pure compounds, such as acids, which are not well suited for other commonly used standard generation processes. Additionally, MOCCS is particularly well suited for field deployment, as it is completely mobile. This technique represents a novel advancement in gas phase standard production and calibration for both VOCs and potentially SVOCs.

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Table 1. Standard Gas Mixtures.

Standard Name	Contents	Concentration (ppmv, ±20%[a])	[Carbon] (ppmv)
VOC Mix 1	2-methylfuran	10.01	413.21
	Methyl vinyl ketone	7.53	
	Benzene	10.53	
	Furfural (2-furanaldehyde)	10.68	
	a-methyl styrene	12.44	
	p-cymene	10.44	
VOC Mix 2	Acetaldehyde	2.01	89.76
	Methanol	1.96	
	Isoprene	1.97	
	Acetone	1.89	
	Acetonitile	2.01	
	Methacrolein	2.09	
	2-butanone	1.92	
	Benzene	1.97	
	b-pinene	1.91	
	1,3,5-Trimethylbenzene	1.90	
VOC Mix 3	MBO	10.73	463.81
	2,3-Butanedione	5.82	
	2-Butenal	8.56	
	Toluene	10.62	
	Decene	8.69	
	Benzofuran	11.01	
	Indene	11.46	

[a]The error in the concentration of the species listed is assumed to be 20% unless otherwise stated.

Table 1. Continued.

Standard Name	Contents	Concentration (ppmv, ±20%[a])	[Carbon] (ppmv)
VOC Mix 4	Acetylene	13.41	274.95
	Propene	11.30	
	1,3-Butadiene	10.54	
	MTBE	9.50	
	Benzene	9.41	
	Benzaldehyde	9.73	
CH_4 (a)	Methane 5.752	± 0.11	5.75
CH_4 (b)	Methane 10.79	± 0.22	10.79

[a]The error in the concentration of the species listed is assumed to be 20% unless otherwise stated.

Table 2. Performance of MOCCS with the Beckman Industrial Model 870 NDIR and the LI-COR LI-6252.

	Beckman 870	LI-6252
Response time[*]	300 s	90 s
TOC Detection Limit	150 ppbv	5 ppbv
TOC Accuracy	±4% of the measurement +400 ppbv	±1% of the measurement +80 ppbv
TOC Precision	±1% of the measurement +30 ppbv	±1% of the measurement +1 ppbv
Error on replicate TOC cycles	5%	1%

[*]Response times are listed for a formic acid permeation source.
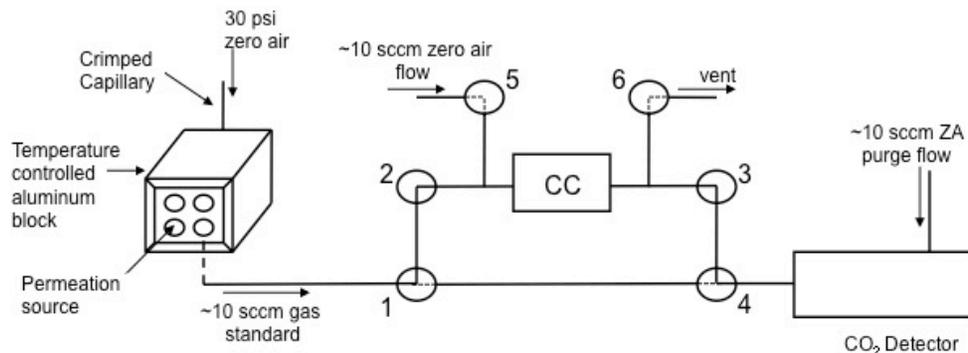
Fig. 1. A schematic diagram of the TOC calibration system. Gas standards are selectively passed over a palladium catalyst (CC). The CO_2 generated via oxidation of a standard is then measured using NDIR. During a background measurement, valves 1 and 4 open to allow flow to bypass the catalyst. At this time, valves 2 and 3 are closed shut and valves 5 and 6 are opened to flush the catalyst with zero air. To make a total carbon measurement, valves 2 and 3 opened, 5 and 6 closed, and valves 1 and 4 are switched to allow the sample to flow through the catalyst with the outflow to the CO_2 detector.

Standard generation and calibration system for volatile organic compounds

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Plot details: y-axis "Beckman 870 NDIR Output (Volts)" ranging 0.05 to 0.35; x-axis "CO_2 Concentration (ppmv)" ranging 10 to 50. Text box: slope = 0.0070 ± 0.0001 Volts/ppmv; intercept = 0.002 ± 0.002 ppmv; R^2 = 0.99.
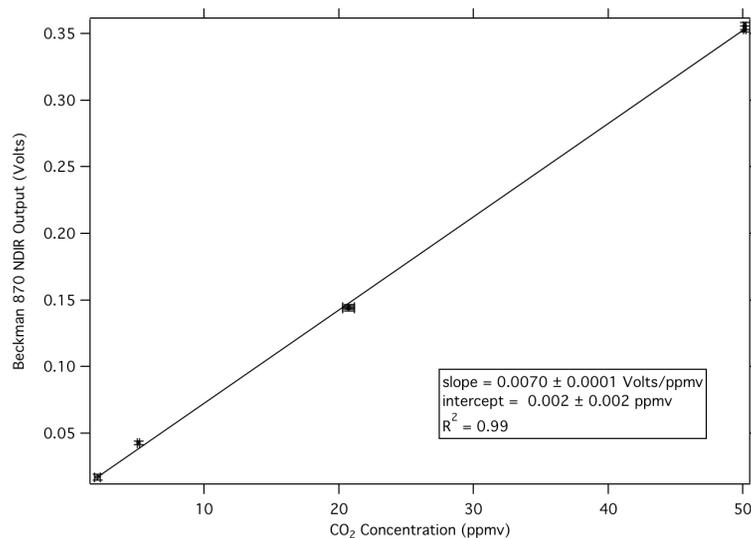
Fig. 2. Calibration of the Beckman 870 NDIR CO_2 analyzer. Four CO_2 gas standards were used: 2.065 (±0.207) ppmv, 5.12 (±0.10) ppmv, 20.07 (±0.40) ppmv, and 50.1 (±0.5) ppmv.
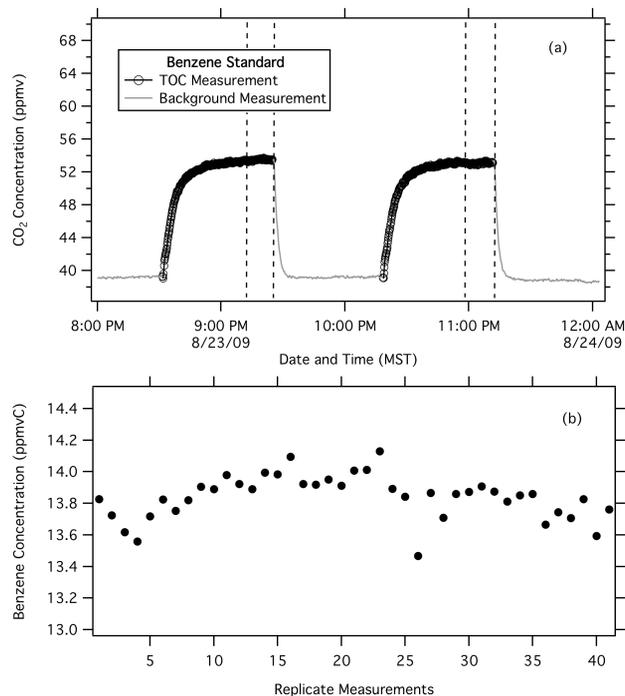
Fig. 3. CO_2 measurements showing two complete cycles of background and TOC measurement of a benzene standard generated by MOCCS, **(a)** The TOC measurements are shown in black with open circles and the background measurements are shown in grey. Subtracting the interpolated background and dividing the result by the number of carbon atoms in a benzene molecule (6) gives the benzene concentration from the permeation source. After the signal stabilizes, an average of the measured signal minus background is taken (shown as the data between the dashed line). Shown in **(b)** are replicate measurements of the benzene concentration made over the course of five days. The average concentration over this time period (38 cycles) was determined to be 13.8±0.1 ppmv of carbon (ppmvC).

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Interactive Discussion
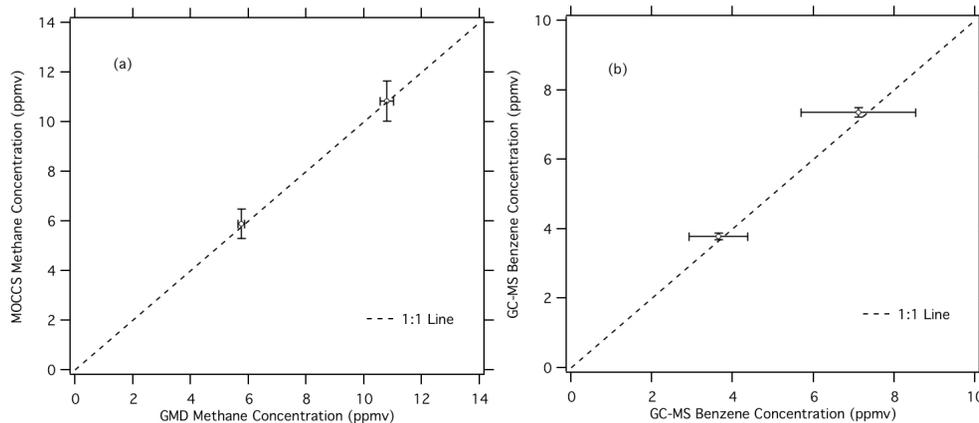
Fig. 4. Results of MOCCS determined methane concentration compared to GMD determined methane concentration of two standards, **(a)**. The relative difference between the two measurements is 3%.The results of GC-MS/TOC measurements of two benzene standards generated using MOCCS, **b)**. The relative difference between the two measurements is less than 4%.
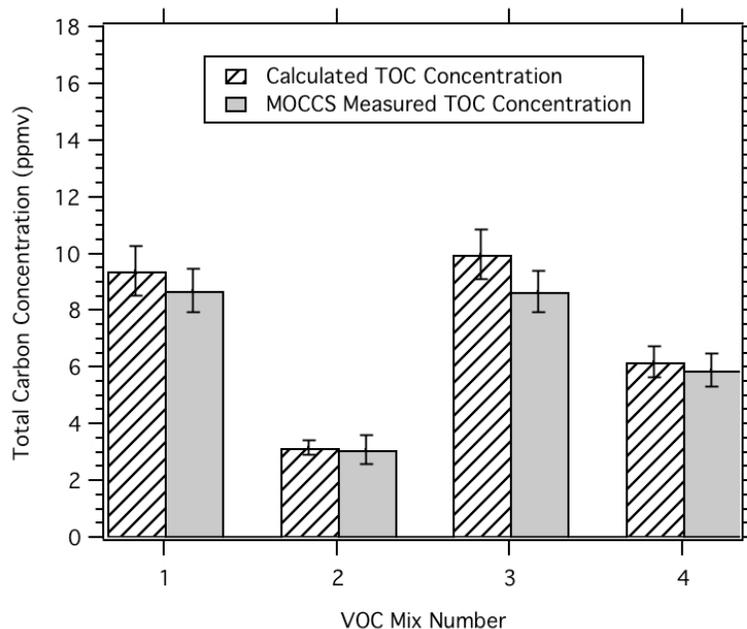
Fig. 5. The results of a total carbon analysis of 4 gas phase VOC standards. The contents of each mixture are detailed in Table 1. An uncertainty of 20% was assumed for each component in the laboratory-generated VOC standards.
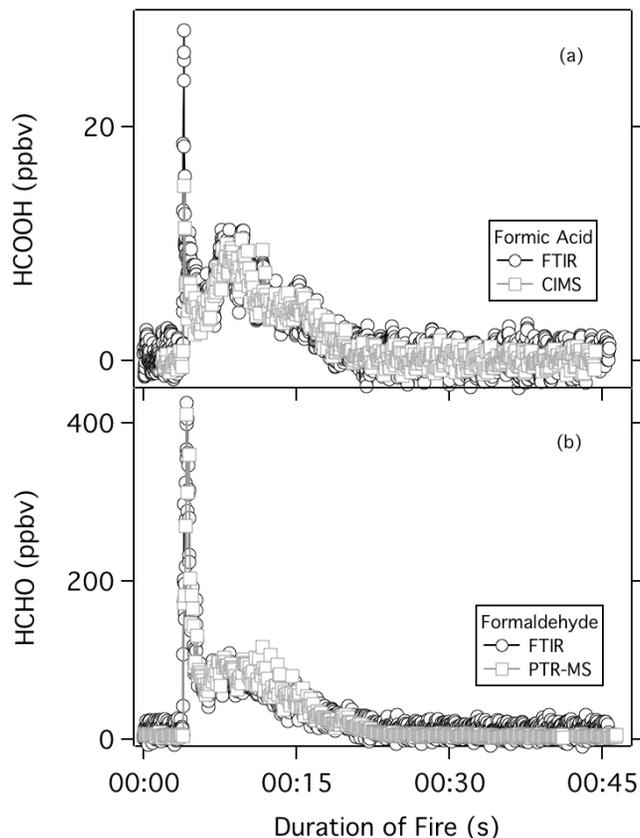
Fig. 6. A comparison of NI-PT-CIMS formic acid and PTR-MS formaldehyde measurements to simultaneous measurement of OP-FTIR formic acid and formaldehyde. NI-PT-CIMS was calibrated using a formic acid permeation source that was standardized using MOCCS. PTR-MS was calibrated for formaldehyde measurement with a permeation source that was standardized using MOCCS.
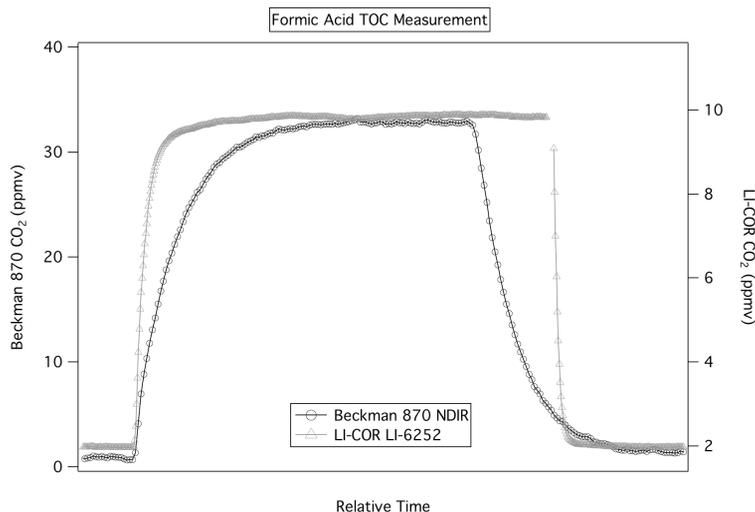
Fig. 7. Formic acid measurement comparison using MOCCS with the Beckman model 870 NDIR CO_2 analyzer and the LI-COR LI-6252 CO_2 analyzer. The TOC system was set to a 1-hour cycle between CO_2 catalysis measurements and background measurement. Significant improvements in both CO_2 detection limit and instrument response times are achieved with the LI-COR LI-6252 analyzer. It is important to note that the two CO_2 measurements are not of the same formic acid standard, which explains the difference in left and right axes.