δ^{13}C Stable Isotope Analysis of Atmospheric Oxygenated Volatile Organic Compounds by Gas Chromatography-Isotope Ratio Mass Spectrometry

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We present a new method for analyzing the δ^{13}C isotopic composition of several oxygenated volatile organic compounds (OVOCs) from direct sources and ambient atmospheric samples. Guided by the requirements for analysis of trace components in air, a gas chromatograph isotope ratio mass spectrometer (GC-IRMS) system was developed with the goal of increasing sensitivity, reducing dead-volume and peak band broadening, optimizing combustion and water removal, and decreasing the split ratio to the isotope ratio mass spectrometer (IRMS). The technique relies on a two-stage preconcentration system, a low-volume capillary reactor and water trap, and a balanced reference gas delivery system. The instrument's measurement precision is 0.6 to 2.9‰ (1σ), and results indicate that negligible sample fractionation occurs during gas sampling. Measured δ^{13}C values have a minor dependence on sample size; linearity for acetone was 0.06‰ ng C^{-1} and was best over $1-10$ ng C. Sensitivity is ~10 times greater than similar instrumentation designs, incorporates the use of a diluted working reference gas (0.1% CO_2), and requires collection of >0.7 ng C to produce accurate and precise results. With this detection limit, a 1.0 L sample of ambient air provides sufficient carbon for isotopic analysis. Emissions from vegetation and vehicle exhaust are compared and show clear differences in isotopic signatures. Ambient samples collected in metropolitan Miami and the Everglades National Park can be differentiated and reflect multiple sources and sinks affecting a single sampling location. Vehicle exhaust emissions of ethanol, and those collected in metropolitan Miami, have anomalously enriched δ^{13}C values ranging from -5.0 to -17.2‰; we attribute this result to ethanol's origin from corn and use as an additive in automotive fuels.

Oxygenated volatile organic compounds (OVOCs) such as methanol, ethanol, acetaldehyde, and acetone are gases found throughout the troposphere that influence atmospheric chemistry in many ways. These compounds act as a source of radicals and a sink for the hydroxyl radical (OH), participate in tropospheric ozone formation, and are precursors to formaldehyde and CO.[1] Mixing ratios for OVOCs are typically at the low parts per billion by volume (ppbv) level and depend on sampling location and season.[2–5] Most atmospheric OVOC measurements have reported information on ambient levels, source emission strengths, and flux rates,[2,3,5–9] with two individual OVOCs, methanol and acetone, receiving the majority of focus thus far.

Methanol is the second most abundant organic gas in the atmosphere after methane and its global budget has been studied extensively.[3,10–12] Emissions from vegetation are the single largest source to the atmosphere and are estimated between $75-312$ Tg year^{-1}. Other sources of methanol exist, including fossil fuel combustion, biomass burning, plant decay, and *in situ* atmospheric production via oxidation of methane. Combined, these sources are estimated at <100 Tg year^{-1}. The primary sink for methanol is reaction with OH, and the estimated lifetime for methanol against OH is 12 days.[13]

Acetone has many sources and, as with methanol, substantial uncertainty is associated with its global budget.[3,7,14] With an

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estimated source strength of 40−95 Tg year^{-1}, primary biogenic emissions comprise 22%−40% of acetone's presence in the atmosphere.[15] Whereas secondary sources, such as the photooxidation of nonmethane hydrocarbons (NMHCs), contribute the largest fraction and are estimated to account for 24%−96% of acetone's total source strength.[10,14,15] Sinks for acetone consist of an oxidation mechanism by OH and direct photolysis, and acetone's estimated atmospheric lifetime against each of these loss pathways is 60 days.[13,14]

The value of stable isotope measurements in the unique isotopic compositions which exist for individual sources and in the fractionation associated with atmospheric removal. The distinctions arise from isotope fractionation effects which occur during chemical and physical processes. There are two types of fractionation effects, kinetic effects and equilibrium effects. Both kinetic and equilibrium effects influence the isotopic composition of gas phase products produced during photosynthesis, fermentation, and secondary metabolic processes within vegetation. Kinetic effects, however, are principally responsible for isotopic compositions resulting from unidirectional removal processes where equilibrium is not achieved, as is the case of *in situ* chemical oxidation by OH or photolysis. The use of stable isotopes of carbon, oxygen, and hydrogen is a valuable tool to enhance our understanding of global patterns for OVOCs, a unique class of hydrocarbons that originate from not only primary biogenic and anthropogenic sources but also secondary sources. Collectively, the measured average isotopic composition of an OVOC in the atmosphere, coupled with isotopic characterization of its major sources and sinks, can be used as a means to elucidate the chemistry of these compounds within the atmosphere, their formation pathways, and reduce uncertainty in their budgets. An excellent review by Goldstein and Shaw contains more details on the use of stable isotopic data and its application to atmospheric budgets of VOCs.[16]

Herein, we restrict the discussion to variations in the stable isotopes of carbon, ^{13}C and ^{12}C. The stable isotopic composition of a sample is expressed as a ratio (R) of ^{13}C to ^{12}C. During analysis, the ratio of a sample is compared to that of Vienna Pee Dee Belemnite (V-PDB) by way of a working reference gas using an isotope ratio mass spectrometer (IRMS). The ratio of the sample is reported in delta (δ) notation as a per mil (‰) difference of the sample compared to the reference: δ^{13}C (‰) $= ((R_{SAMPLE}/R_{STANDARD}) - 1) \times 10^3$. If a compound has a negative value, then it contains less ^{13}C than the standard and is said to be isotopically light (or depleted); if a compound has a positive value then it is isotopically heavy (or enriched).

Application of stable isotopic techniques in atmospheric chemistry has focused on more abundant components of the atmosphere, notably, CO_2, CH_4, and CO. The use of isotopes led to an increased understanding of sources, sinks, and seasonal cycling of these compounds.[17−24] Rudolph and his colleagues are credited as the first to use gas chromatography-isotope ratio mass spectrometry (GC-IRMS) to analyze NMHCs in atmospheric gases.[25] These compounds are difficult to measure because their mixing ratios are low; they require separation from the atmospheric matrix and need to be combusted to CO_2 before transfer to the IRMS. For this reason, analyses are performed using a gas chromatograph and combustion oven coupled to an IRMS operating under continuous flow conditions. Rudolph et al. sampled a variety of locales, ranging from pristine noncontaminated air to heavily contaminated air dominated by automobile emissions.[27] Results from their work showed clear distinctions between the δ^{13}C signatures of NMHCs sampled at each location. The signatures reflected the local sources, meteorological conditions, and fractionation mechanisms acting at each site. Additional studies of NMHCs include studying specific sources, oxidation processes, and other locations.[26−28]

Applications of GC-IRMS techniques for analysis of OVOCs are restricted in scope and focus on one or two compounds.[29−39] This is due to additional difficulties associated with sampling and analyzing OVOCs, including low mixing ratios, tendency for sample to become lost on sampling surfaces caused by OVOCs' polar nature, difficulty in selectively removing water and CO_2 from the sample matrix without perturbing the OVOCs, and optimizing chromatographic separation in the presence of associated NMHCs. To circumvent some of these difficulties, derivatization has been used as a technique to make the polar compounds amenable to analysis.[29−31,36,37] Four studies of OVOCs using direct GC-IRMS are available, two for formaldehyde[34,35] and two for acetaldehyde.[32,39]

The technique presented here allows for direct conversion of several OVOCs to CO_2 for measurement of δ^{13}C from small sample volumes and a range of sample types, including

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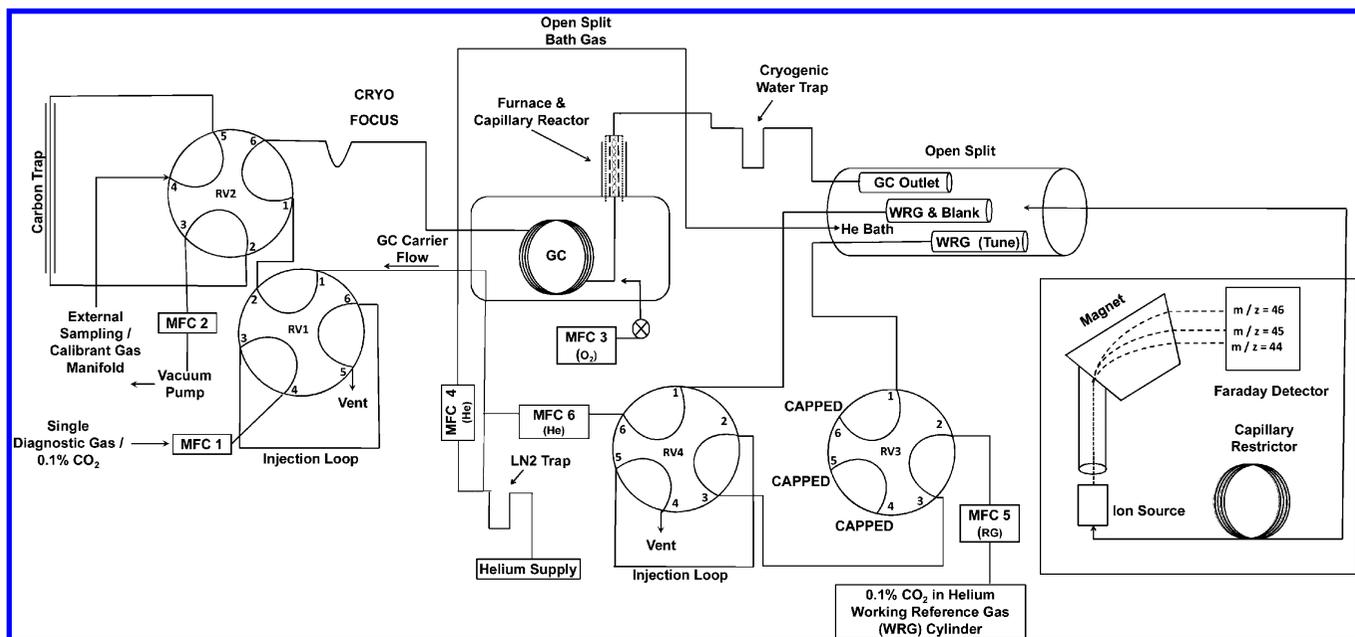
Figure 1. Schematic view of the preconcentration system and GC-IRMS. The GC-IRMS relied on a low-volume capillary reactor, water trap, and a balanced reference gas delivery system (WRG, working reference gas).

emissions from vegetation and automobiles and rural and urban ambient air. The system consists of a two-stage trapping procedure using a carbon sorbent followed by cryofocusing. A low-volume capillary reactor, water trap, and open split combined with high-speed chromatography enhance sensitivity and improve peak resolution.

EXPERIMENTAL SECTION

Reference and Calibrant Gases. A working CO_2 reference gas calibrated against the V-PDB carbonate standard was used for determination of the $^{13}C/^{12}C$ ratio of OVOCs using IRMS. To achieve proper instrument response, a 0.1% CO_2 working reference was prepared and calibrated. A cylinder of research grade CO_2 was used to create a gas phase subsample, from which, a dilution of 0.1% CO_2 was made in helium. The isotopic values for pure CO_2, its subsample, and the 0.1% CO_2 dilution were measured using a Finnigan MAT 251 IRMS with conventional dual inlet and a Europa Scientific 20-20 IRMS linked to an automated nitrogen carbon analyzer (ANCA) under continuous flow. Henceforth, the 0.1% CO_2 gas will be referred to as working reference gas.

The primary calibrant gas mixture used for testing and development was prepared gravimetrically.[40] Liquid compounds with purity ≥98% were obtained from Sigma-Aldrich and included methanol, ethanol, propanal, acetone, methyl ethyl ketone, 2-pentanone, and 3-pentanone. Microliter volumes of the compounds were discharged directly into a clean, evacuated aluminum cylinder (Luxfer Gas Cylinders, Riverside, CA) with a stainless steel valve (Ceoedux, Mount Pleasant, PA). The cylinder was pressurized with high-purity BIP Technology N_2 gas (all compressed gases utilized in this work were obtained from Airgas South, Keenesaw, GA) to achieve desired mixing ratios for all components. The mixing ratio and purity of the mixture were

verified via GC-flame ionization detector (FID) and GC/mass spectrometry (MS). Final mixing ratios for each individual component fell between 365 ppbv (2-pentanone) and 931 ppbv (methanol) with an associated error of 5% for each component. The calibration gas mixture was diluted further by dynamic dilution into moist zero air when needed.[41]

Low-pressure single and multicomponent gases were made similarly to the calibrant gas mixture except an evacuated electropolished stainless steel canister (Entech Instruments, Simi Valley, CA) was used and pressurized with 55 pounds per square inch absolute (psia) UHP helium for dilution. Mixing ratios for the single mixed gases were selected to equal that of the working reference gas.

Elemental Analyzer. A Europa Scientific 20-20 IRMS linked to an automated nitrogen carbon analyzer (ANCA) was used to obtain the $\delta^{13}C$ signature of each raw liquid compound used to prepare the calibrant gas mixture. Microliter volumes of liquid reagents were loaded on a sorbent (Chromosorb W, Advanced Minerals, Goleta, CA) contained within a small tin capsule. The capsule was folded over itself to prevent sample loss and quickly dropped into the furnace to begin the analysis. Raw compounds were compared against a working lab standard of pure CO_2 calibrated against V-PDB.

Preconcentration System. A custom preconcentration system was installed on the inlet of the gas chromatograph and included two manual stainless steel six-port rotary valves (1/16 in. fitting, 0.40 mm i.d.; all rotary valves in this work were obtained from Vici Valco Instruments, Houston, TX) connected in series. Fused silica-lined stainless steel tubing joined the entire precononcentration system (1.59 mm o.d., 0.51 mm i.d.; Silcosteel tubing, all Silcosteel tubing in this work were obtained from Restek, Bellefonte, PA). A schematic of the complete analytical design appears in Figure 1.

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The first rotary valve (RV1) used an injection loop (14.3 cm × 1.6 mm o.d. × 1.02 mm i.d.; Silcosteel tubing) yielding a volume of 0.12 cm^3. Rotary valve 1 allowed for analysis of working reference gas for leak check purposes and single-component gases in helium to test the system with individual OVOCs. Sample flow rates through RV1 were set at 3 cm^3 min^{-1} and regulated upstream by a 0−100 standard cubic centimeters per minute (sccm) mass flow controller (MFC, no. 1) (all MFCs used in this work were obtained from Unit/Celerity, San Jose, CA).

The second valve (RV2) allowed for loading of the multicomponent calibrant gas during development tests and samples for analysis. The calibrant gas or samples connected to a simple valve system giving the operator ease of on/off control and an additional helium input used to purge the sample loop. Flow rates through RV2 were 50 cm^3 min^{-1} and controlled by an oil pump (Alcatel Vacuum Products, Smyrna, GA) with a liquid nitrogen vapor trap and a 0−200 sccm MFC (no. 2) located downstream. The sampling loop of RV2 included a carbon adsorbent trap which is nonretentive for the major components of air (N_2, O_2, CO_2, and H_2O) while trapping OVOCs. The carbon adsorbent trap consisted of a section of Silcosteel (30.5 cm × 3.2 mm o.d. × 2.1 mm i.d) packed with 24.6 cm of Carboxen 1016 (Supleco, St. Louis, MO). Carboxen 1016 retained all the analytes of interest, completely desorbed them when heated, and contributed negligible amounts of CO_2 during the desorption process.

Typically, 1.0 L volumes were sampled over 20 min. Helium purged the sampling loop and adsorbent trap (50 cm^3 min^{-1}) for 5 min to remove unwanted gases and water that may remain after loading. After the purge procedure, RV2 was manually switched allowing carrier gas (0.7 cm^3 min^{-1}) from the GC to back flush the adsorbent trap for 10 min. During this step, the adsorbent trap was desorbed with resistive heating at 200 °C using high temperature heater tape, thermocouple, and a CN76000 temperature controller (Omega Engineering, Stamford, CT).

Desorbed material was cryo-focused as it passed through an open loop trap (46 cm, 0.56 mm o.d., 0.28 mm i.d., Siltek/Sulfinert tubing, Restek, Bellefonte, PA) contained in liquid nitrogen. Before injection, RV2 was switched to remove the carbon adsorbent trap from the carrier gas flow path. The cryo-focuser was heated with boiling water to inject the compounds onto the GC column.

GC-IRMS System. An Agilent 6890 gas chromatograph was fitted with a DB-624 capillary chromatography column (20 m × 0.18 mm i.d. × 1 μm film thickness, 6% cyanopropylphenyl/94% dimethyl polysiloxane, Agilent Technologies, Santa Clara, CA). Ultrahigh purity helium entering the GC and IRMS passed through liquid nitrogen as a final measure to scrub it of possible contaminants, including trace CO_2. The GC operated in constant flow mode with a nominal carrier flow rate set to 0.7 cm^3 min^{-1}. Carrier flow was measured at the open split located immediately upstream of the IRMS ion source. Temperature programming for the GC oven started at 30 °C for 3 min followed by a ramp of 10 °C min^{-1} and held at a final temperature of 125 °C for 7.5 min. The total GC run time was 23 min.

A capillary reactor used for combusting OVOCs to CO_2 was constructed of fused silica tubing and contained two catalytic wires. One was an alloy blend consisting of Cu/Mn/Ni (84%/

12%/4%, 0.1 mm diameter, Alfa-Aesar, Ward Hill, MA), the other is Pt (99.99%, 0.1 mm diameter, Sigma-Aldrich, St. Louis, MO). Details about the fabrication and conditioning of the reactor are provided in the Supporting Information.

Trace amounts of H_2O, created with CO_2 during the combustion process, can interfere by contributing signal at m/z −45 and −46 due to protonation of CO_2 within the ion source. A continuous length of deactivated fused silica (~1.5 m × 0.36 mm o.d. × 0.25 mm i.d., Supelco, St. Louis, MO) was connected to the downstream end of the capillary reactor and served as a transfer line, water trap, and link to the open split. At the midpoint of the transfer line a single loop (~10−15 cm in length) created a water trap when immersed in a dry ice−ethanol slurry (−55 to −65 °C) and prevented water from reaching the ion source. Sample derived CO_2 continued to the outlet located in the open split. The looped trap was removed from the slurry after every run, and condensed water was driven off with helium carrier gas and by warming the loop to 100 °C for several minutes.

A custom designed open split (Figure 1) was positioned adjacent to the ion source of a Europa Scientific GEO 20-20 IRMS.[42] The open split resided within a chamber that housed four distinct outlets: two primary outlets for (1) the GC effluent and (2) the helium blank/0.1% CO_2 reference gas; two secondary outlets for (1) tuning the IRMS ion beams and (2) supplying the chamber assembly with an inert atmosphere of helium (MFC no. 4, 10 cm^3 min^{-1}). Details of the open split and working reference gas delivery system are contained in the Supporting Information. A length of deactivated fused silica (~3 m × 0.36 mm o.d., 0.10 mm i.d. SGE, Austin, TX) produced a capillary leak to the ion source and was manually moved between the various outlets located in the open split as needed.

Europa Scientific GEO 20-20 IRMS. The IRMS was tuned daily with working reference gas and operated with an accelerating voltage of 2.5 kV. The ion trap and filament emission currents were set to approximately 600 and 1300 μA, respectively. The vacuum system of the IRMS created a 0.2 cm^3 min^{-1} flow rate through the restriction capillary leading to the ion source while maintaining an operating source pressure of 4.5×10^{-6} Torr. When combined, the carrier flow rate (0.7 cm^3 min^{-1}) exiting the GC outlet and the ion source flow (0.2 cm^3 min^{-1}) resulting from the capillary leak produced a split ratio of 3.5 and reduced the amount of carbon transferred to the IRMS by approximately 70%.

Data Collection and Analysis. Data for time (t) and mass to charge ratios (m/z) 44, 45, and 46 were recorded at 1.0 Hz to a PC using acquisition software provided by the IRMS manufacturer. Three separate third party software packages were used (i.e., Thermo Grams AI/8.0, Origin Lab Origin Pro 8, and Microsoft Excel 2007) for data analysis. Details of the data manipulation are described in the Supporting Information.

Source and Ambient Sampling. Two types of sources were investigated in this study, natural emissions released from five tropical plants and exhaust from an automobile without a catalytic converter. Plant emissions were studied using static enclosure methods with (1) clipped and (2) intact vegetation. For the (1) clipped vegetation experiments, a branch was physically removed

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from the specimen and enclosed in a Teflon sampling bag with a Nupro valve fitting (SS-4H, Swagelok Co., Solon, OH). Hydrocarbon-free zero-air flushed the enclosed branch before being zip-tied shut and returned to direct sunlight for a period of 20−60 min. After this period, the bag and branch were brought into the lab and connected to the preconcentration system via the gas manifold. Sample volumes between 100−200 cm³ were loaded using the RV2 loop and carbon sorbent. For (2) intact branch experiments, a single branch on the specimen was enclosed with the Teflon bag assembly and flushed with zero-air before being zip-tied shut and left in ambient light for a period 20−60 min. Instead of clipping the branch and returning the bag to the laboratory, an evacuated canister was connected to the bag's valve and its contents were removed. As with the clipped branch, sample volumes between 100−200 cm³ were loaded for analysis.

Automobile emissions from the right exhaust bank of a 1972 International Scout were collected. The Scout lacks a catalytic converter and was operated at constant cruising and load conditions (∼2000 rpm, ∼80 kph) during sample collection. A piece of stainless steel tubing (∼1.5 m length) was secured to the inside of the passenger side exhaust and brought to the inside of the passenger compartment for connection to an evacuated canister. Samples were at atmospheric pressure after collection.

Ambient whole air samples were collected at three locations in South Florida. Everglades National Park was chosen to represent a rural atmosphere dominated more by biogenic sources than anthropogenic sources. A partially enclosed lower roadway of Miami International Airport was sampled to ascertain a collective measure of concentrated and fresh vehicular emissions; Miami's Financial District represented a more semiurban environment. Samples from the Everglades were pressurized to approximately 30 pounds per square inch gauge (psig) by a DC powered metal bellows pump (MB-302, Senior Flexonics, Sharon, MA) into an evacuated canister; airport and financial district samples were collected at atmospheric pressure. Sample volumes for analysis ranged between 100−200 cm³ for the airport and financial district to 1.0 L for Everglades National Park.

RESULTS AND DISCUSSION

Guided by the requirements for analysis of trace components in air, a GC-IRMS system was developed with the goal of analyzing OVOCs in ambient air. This included developing a preconcentration stage, increasing sensitivity, reducing dead-volume and peak band broadening, optimizing combustion and water removal, and decreasing the split ratio to the IRMS. An extended discussion focusing on these developments, including images of the working reference gas delivery system and open split, are available in the Supporting Information. These developments allowed for analysis of several OVOCs in ambient air at mixing ratios representative of a large portion of the troposphere ranging from urban to remote. Figure 2 shows the range of mixing ratios present in the atmosphere for methanol, ethanol, acetone, and MEK and the corresponding nanograms of C transmitted to the ion source with this analytical technique.[3,6,9,12,14,43] All but the most remote portions of the atmosphere can be investigated using this method.

Reference Gas Analyses. *Working Reference Gas.* The diluted working reference gas was prepared carefully in a series of steps in order to monitor possible fractionation during the dilution
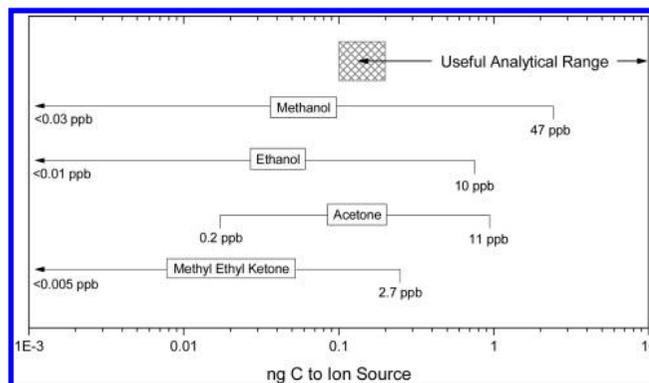
Figure 2. Range of atmospheric OVOC mixing ratios expected in large portions of the troposphere and their relation to carbon transmitted to the IRMS ion source. The shaded area corresponds to the method detection limit.

process. Results and further discussion of the preparation procedure, including an interlab comparison performed with Stony Brook University, can be found in the Supporting Information (Working Reference Gas Analyses and Table S-1).

System Diagnostic Leak Assessments. Rotary Valve 1 (RV1) was used for various diagnostics tests. One test evaluated the leak tightness of the complete sample path through the preconcentration system, gas chromatograph, reactor assembly, water trap, and open split delivery to the IRMS. We compared working reference gas injected at the preconcentration system to that of its normal injection site at the open split. In the absence of detectable leaks in the sample path, daily offsets of 0.3−0.5‰ were routinely observed. On occasions when a microcrack was suspected of breaching the capillary reactor, offsets >2‰ were observed. This test was performed daily to evaluate the integrity of the instrumentation. If the offsets were 0.3−0.5‰, the concurrent data for the day were corrected by the appropriate amount. If the offset exceeded 0.5‰, the capillary reactor was replaced.

Dynamic Range and Linearity. A 6 L electropolished stainless steel bulb with a dip tube assembly served as an exponential dilution flask to test the dynamic range and linearity of the method and IRMS in the absence of combustion. The bulb contained a 1% CO_2 mixture in helium made from the same subsampled CO_2 used in the production of working reference gas. A diluant flow of helium entered the steel bulb through the dip tube at a rate of ∼125 cm³ min⁻¹ and the outflow was plumbed to RV1. The total analysis occurred over a 5.5 h period broken into 9 segments with the introduction of working reference gas. The amount of carbon reaching the ion source was ∼0.1−80 ng. The $\delta^{13}C$ values over this range are expressed as a difference of the measured (and corrected) exponentially diluted CO_2 from the working reference gas' accepted value and are displayed in Figure 3a. Of particular interest is the appearance of a positive offset, ∼0.46‰, from zero. Efforts were made to minimize fractionations during the gas transfers, and the gases were made from the same stock. Despite this effort, the offset still persisted.

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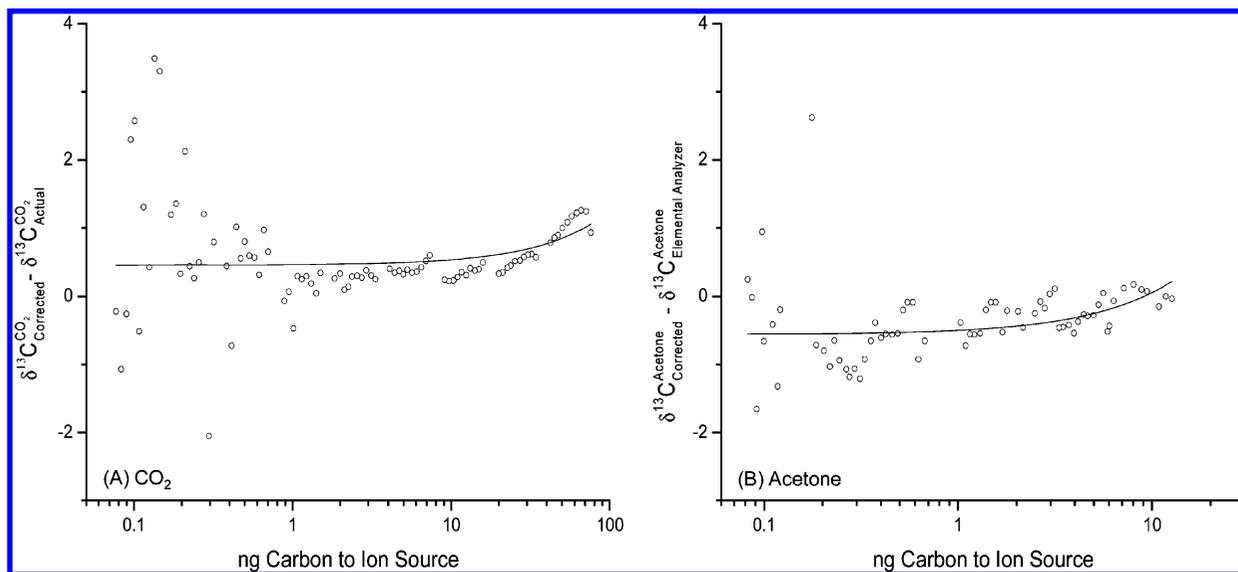
Figure 3. (A,B) Results for exponentially diluted (A) CO_2 and (B) acetone samples. $\delta^{13}C$ values are expressed as a difference of the diluted CO_2 and acetone from the accepted value of the 0.1% working reference gas and acetone value obtained on the elemental analyzer. An offset, opposite in sign but almost equal magnitude, exists for CO_2 ($\sim 0.5‰$) and acetone ($\sim -0.6‰$). For CO_2, this is thought to be the result of an ambient leak whereby atmospheric CO_2 enters the system. For acetone, incomplete combustion within the capillary reactor may contribute to the observed negative offset.

Table 1. Tabulated $\delta^{13}C$ Values for OVOCs Used in This Work[a]

	elemental analyzer liquid compounds	GC-IRMS single-component gas			GC-IRMS low-pressure 7-component			GC-IRMS high-pressure 7-component			pooled GC-IRMS		
	mean $\pm 1\sigma$ (‰)	mean $\pm 1\sigma$ (‰)	95% confidence ($\pm‰$)	% error	mean $\pm 1\sigma$ (‰)	95% confidence ($\pm‰$)	% error	mean $\pm 1\sigma$ (‰)	95% confidence ($\pm‰$)	% error	mean $\pm 1\sigma$ (‰)	95% confidence ($\pm‰$)	% error
methanol	−35.3 ± 0.1	−34.1 ± 0.1	0.1	3.5	−33.0 ± 0.1	0.1	6.5	−34.4 ± 2.8	2.1	2.5	−34.0 ± 1.6	0.7	3.7
ethanol	−29.2 ± 0.2	−27.8 ± 0.8	0.6	4.8	−26.2 ± 0.8	1.3	10.2	−26.5 ± 0.5	0.4	9.2	−26.6 ± 1.4	0.6	8.7
propanal	−32.8 ± 0.1	−31.9 ± 0.2	0.1	2.7	−35.0 ± 0.6	1.0	−6.9	−27.4 ± 0.8	0.6	16.5	−30.5 ± 2.9	1.2	6.9
acetone	−27.5 ± 0.2	−28.5 ± 0.7	0.5	−3.7	−27.9 ± 0.2	0.3	−1.4	−27.6 ± 0.2	0.1	−0.4	−28.0 ± 0.6	0.2	−1.7
MEK	−23.2 ± 0.2	−23.5 ± 0.9	0.6	−1.3	−25.5 ± 0.7	1.1	−10.1	−22.5 ± 0.3	0.2	−3.0	−23.5 ± 1.2	0.5	−1.2
2-pentanone	−25.0 ± 0.3	−26.1 ± 0.2	0.1	−4.3	−33.7 ± 1.1	1.8	−34.8	−28.4 ± 0.6	0.5	−13.6	−28.6 ± 2.8	1.1	−14.3
3-pentanone	−30.7 ± 0.2	−30.7 ± 0.6	0.4	−0.1	−34.3 ± 0.3	0.5	−11.6	−32.7 ± 0.7	0.5	−6.5	−32.3 ± 1.5	0.6	−5.1
sample number	$n = 3$	$n = 10$			$n = 4$			$n = 9$			$n = 23$		
					Instrument Variables								
diluent		He			He			N$_2$					
sample loop		RV1			RV1			RV2					
cryo-focus		no			yes			yes					
carbon sorbent		no			no			yes					
zero air dilution		no			no			yes					

[a] Accuracy and precision is traced from the elemental analyzer through the final design of the GC-IRMS system. Different variables tested during each phase are listed. The system's total precision was calculated between 0.6 and 2.9‰ when compared to the values obtained on the elemental analyzer.

The positive offset for CO_2 was likely a result of small amounts of ambient CO_2 becoming entrained in the system and thereby enriching the measured $\delta^{13}C$ value. For large sample sizes this appeared to have a minimal effect. However, the effect became magnified for sample sizes below 1 ng C, where deviations up to 2‰ are observed. The linearity over this range, determined by ordinary linear regression, was 0.01‰ ng C^{-1}. This suggests that variation of the $\delta^{13}C$ signature with sample size is negligible and requires 10 ng C to induce a change of 0.1‰. Accuracy and precision were best over the range of ~0.2 to ~20 ng C. Samples containing more than 20 ng C and less that 0.2 ng C were enriched in ^{13}C.

Liquid Compounds and Single-Component Gases. Low-pressure single-component gas samples entered RV1 at a rate of 3 cm^3 min^{-1} and were loop injected onto the GC-IRMS with no cryo-focusing before the chromatographic column. Ten injec-

tions of each gas were compared to six injections of working reference gas. Single-component gases tested the GC-IRMS instrumentation by comparison to the isotopic values obtained for the raw liquids on the elemental analyzer (ANCA). The values for the raw liquids served as the basis of all our comparisons. The calculated percent difference between the two measurements ranged between −0.1 and 4.8%, and the results are listed in Table 1.

Acetone was suitable to test the dynamic range and linear response of the IRMS with the added step of combustion. Acetone was chosen as the analyte because it showed consistent and excellent reproducibility across all aspects of this study. The experimental design was identical to that of the CO_2 experiment described previously but with one exception, the acetone mixture had a starting carbon equivalent of 0.1% before the diluent flow of helium was added. A 1% mixture of acetone was
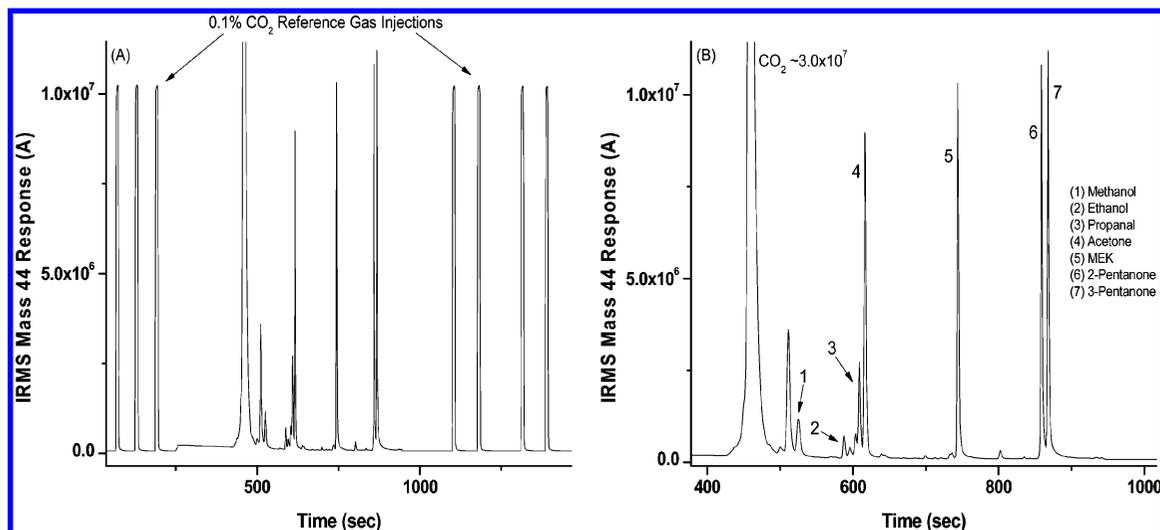
Figure 4. (A) IRMS mass-44 chromatographic response for the high-pressure, seven-component gas. (B) An enlarged plot shows reasonable separation for all seven components. The first peak observed in part B is a combination of CO_2 collected during the zero-air dilution of the calibrant gas and CO_2 created by Carboxen 1016 during the desorption process. The peak immediately preceding methanol was identified as the OVOC acetaldehyde and is an artifact background from the adsorption trap.

avoided for two reasons. First, ambient samples are not expected to be greater than 0.1%, and second, there is more concern for what happens to measured isotopic signatures as smaller sample concentrations are approached. The amount of carbon reaching the ion source was determined similarly to the CO_2 test and ranged between ~0.8 and 12 ng. The $\delta^{13}C$ values over this range are expressed as a difference of the measured and corrected exponentially diluted acetone from the value obtained on the elemental analyzer (Figure 3b). The linearity over this range, determined by ordinary linear regression, was 0.06 ‰ ng C^{-1}. For acetone, this indicates that sample size can influence measured $\delta^{13}C$ and that a change between 1 and 10 ng C can induce a noticeable shift of 0.6‰ in measured $\delta^{13}C$. Accuracy and precision were best over the range of 0.2−10 ng C.

Also worth noting is the apparent negative offset for acetone, ~−0.56‰, compared to the positive offset for CO_2, ~0.46‰. Raw data for both experiments were corrected by 0.5‰ and 0.4‰ for acetone and CO_2, respectively. However, the offsets still exist. Entrainment of ambient CO_2 did not appear to affect acetone because of its separation on the chromatographic column. The negative offset for acetone was likely related to incomplete combustion within the capillary reactor. Thermodynamic principles support ^{12}C being combusted before ^{13}C; thus, if combustion was incomplete, we would observe a lighter $\delta^{13}C$ value.

Calibrant Gas Analyses. *Low-Pressure Seven-Component Gas Mixture.* A low-pressure seven-component gas mixture in helium was used preliminarily to test chromatographic conditions in the absence of the carbon sorbent by using the RV1 loop (Table 1). This was a logical step between the use of single-component gases and a gravimetrically prepared, high-pressure, seven-component calibration gas in nitrogen. The low-pressure seven-component gas mixture flowed through the RV1 loop for 5 min prior to starting the analysis. The flow rate (3 cm³ min^{-1}) was maintained by MFC (no. 1) upstream of RV1. After the initial 5 min purge period, RV1 was manually switched and the gas within the injection loop was diverted through RV2 and cryogenically

focused in liquid nitrogen for an additional 5 min before injection into the chromatographic column. Of particular note are the values obtained for 2- and 3-pentanone, which are depleted in ^{13}C compared to both the liquid compounds and the single component gas mixtures. This may indicate an unknown effect resulting from the analytical column. The percent error between this measurement technique and that performed on the elemental analyzer for the pure liquid compounds ranges between 1.4 and 35%.

Gravimetric Seven-Component Gas Mixture. One of the main goals of this work was to develop a GC-IRMS system capable of measuring OVOCs over the dynamic range found in the atmosphere. To mimic ambient levels of these compounds in the atmosphere, the high-pressure calibrant gas was diluted into moist zero-air using a dynamic dilution system. Dilution produced mixing ratios between ~18.6 ppbv (methanol) and 7.3 ppbv (2-pentanone) for all components. The diluted calibrant was connected directly to the gas manifold (Figure 1). Using the range of mixing ratios produced after the high-pressure calibrant gas was diluted in zero-air (7.3−18.6 ppbv), the volume of air concentrated (1.0 L), and the open split dilution (~30%), we calculated ~2.5−5 ng C were delivered to the ion source for all components. Results for nine replicate analyses are presented in Table 1, and an example of the chromatographic response appears in Figure 4. Reasonable agreement exists for all seven components compared to the liquid reagents analyzed on the elemental analyzer; the margin of error between these two measurements ranged between 0.4 and 16.5%. The components with the two largest errors were propanal (16.5%) and 2-pentanone (13.6%). Both of these peaks are the leading peak in a pair (propanal/acetone and 2-penatnone/3-penatanone), and perhaps the later eluting compounds influence the measured $\delta^{13}C$ values of the earlier compounds. This is supported by the observation that analysis of the single-component gases for the same compounds on the GC-IRMS had a lower error (<5%).

We pooled all data ($n = 23$) collected on the GC-IRMS for each test series and compared them to results obtained on the elemental analyzer. The pooled data were evaluated using a

Table 2. $\delta^{13}C$ Values for Compounds Emitted from Various Tropical Plants and a Fossil Fuel Combustion Source[a]

	sand live oak *Quercus geminata*	orange *Citrus sinensis*	lemon *Citrus limon*	philodendron *Philodendron selloum*		sea grape *Coccoloba uvifera*		Keppler et al.[33]	fossil fuel combustion
				plant type					
acetaldehyde	−29.9 (2.3)	−25.7 (0.1)			−22.4 (1.4)*	−17.5 (0.5)	−30.7 (1.1)*	−24.9 (2.2)	−20.9 (0.4)
methanol	−41.9 (3.1)	−59.7 (2.9)			−37.8 (2.6)*	−27.5 (0.5)	−30.7 (1.0)*	−68.2 (11.2)	−16.9 (1.3)
ethanol			−41.5 (0.8)	−37.5 (0.3)		−30.6 (0.2)	−36.5 (0.2)*	−29.4 (2.6)	−5.0 (0.4)
propanal									−25.6 (2.7)
isoprene	off scale[b]	−26.9 (3.7)	−35.2 (3.5)	−33.8 (2.6)	−23.0 (2.6)*	−16.7 (1.2)	−32.6 (0.9)*		
acetone	−35.7 (4.1)	−37.4 (2.4)	−32.8 (1.2)	−38.8 (1.1)	−29.3 (1.5)*	−33.8 (0.8)	−31.3 (0.8)*	−28.1 (2.5)	−25.6 (0.5)
2-pentanone									−35.2 (1.4)
benzene									−26.9 (0.3)
toluene									−27.5 (0.6)

[a] Also included are values for prepped and incubated biogenic samples from Keppler et al..[33] All values are reported as the average (standard deviation). All samples $n = 5$, except the fossil fuel source where $n = 3$. All biogenic samples are wounded/clipped branches, except where noted (*), which represents an intact branch on the sample specimen. The fossil fuel source was collected from a 1972 Scout International with no catalytic converter at a constant cruise. [b] Isoprene was present; however, it saturated the detectors and the signal response was off scale and the $\delta^{13}C$ value could not be calculated.

Students' *t* test, and the results show that differences between the raw material on the elemental analyzer and the gases on the GC-IRMS system are significant. However, the percent difference between the two procedures is small; less than 9% error exists between the pooled results and those of the raw liquid compounds for all compounds except 2-pentanone, which has an associated error of 14.3%.

Source Measurement Results. The $\delta^{13}C$ results from the automotive exhaust and tropical plants are presented in Table 2. A representative chromatogram from the automotive exhaust sample is shown in the Supporting Information (Figure S-1) and serves as a good example of a complex sample matrix and the system's peak resolution. We have also incorporated, in some instances, for both source and ambient samples, results for the OVOC acetaldehyde even though analysis of this compound is influenced by a variable artifact background.[9,41] Data for NMHCs, isoprene, benzene, and toluene are made known because they were easily identifiable in the chromatograms and offer a comparison to previously measured NMHCs $\delta^{13}C$ values.[44−46] In general, a clear distinction exists between plant and fossil fuel emissions, and as would be expected based on the range of $\delta^{13}C$ values for oils and fuels worldwide,[16,46] fossil fuel derived OVOC emissions were more enriched in ^{13}C compared to the plant results.

Of particular note are the substantially enriched $\delta^{13}C$ values (−5.0 ± 0.4‰) for ethanol, compared to the other compounds in the fossil fuel combustion experiments. Ethanol, derived from corn, is currently being blended into gasoline in mixtures ≥10% (v/v). It has been reported that biofuels consume >25% of U.S. corn production and that ethanol constitutes 99% of all biofuels in the United States.[47,48] Utilizing C4 photosynthesis, which discriminates less against ^{13}C, corn and other C4 plants are generally enriched in the isotope compared to C3 plants.

Bulk carbohydrate analyses between the two plant types show an enrichment of ∼15‰ in carbohydrates extracted from C4 plant material.[49] Investigations of industrially produced ethanol originating from corn have been shown to have $\delta^{13}C$ values of −10.71 ± 0.31‰.[49] The values we observed in the Scout samples are ∼5‰ heavier and, considering the widespread use of ethanol (7.5 billion gallons are expected to be used in fuel by 2012[48]), may serve as a tracer for transportation related sources to the atmosphere.

Some biogenic samples in this study, such as sand live oak and orange citrus, had substantially depleted values for methanol and agree with incubated emissions from various deciduous trees and grasses made by Keppler et al.[33] (Table 2). However, this observation is not consistent across all samples and suggest that variations in $\delta^{13}C$ values may result from interspecies differences, microbe interaction on the leaf's surface, prey/injury response, the potential presence of a methanol utilization pathway which oxidizes methanol to formaldehyde and formic acid/formate,[50,51] and other lesser known metabolic, formation, and loss pathways within plants.[52] Finally, a wound response may be observed between the clipped and intact philodendron and sea grape samples. In one distinct case, acetaldehyde emitted from clipped sea grape specimens were enriched by ∼4‰ compared to the fossil fuel emissions.

Ambient Measurement Results. Considerable differences in $\delta^{13}C$ are observed between ambient sampling locations (Table 3). Results from Miami International Airport are reflective of an averaged value for fresh vehicular sources. The measured $\delta^{13}C$ range for airport samples is between −12.3 ± 3.7‰ (ethanol) to −35.3 ± 1.7‰ (3-pentanone). With the exception of ethanol, which has a $\delta^{13}C$ value consistent with its C4 plant source, and 2- and 3-pentanone, the measured range at the airport agrees with that established for NMHCs from transportation-related sources by Rudolph, namely, −21.9 to −31.3‰.[25] Our acetaldehyde value is consistent with the range

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Table 3. Ambient Measurement Results for Samples Collected from Metropolitan Miami and Everglades National Park[a]

	$\delta^{13}C \pm 1\sigma$ (‰)		
	Miami International Airport	Miami Financial District	Everglades National Park
acetaldehyde	−26.7 ± 0.7	−26.8 ± 1.2	−19.0 ± 2.7
methanol			−36.3 ± 3.7
ethanol	−12.3 ± 3.7	−17.2 ± 4.1	
isoprene			−30.3 ± 2.1
propanal	−28.4 ± 1.5	−26.2 ± 2.4	
acetone	−31.0 ± 3.5	−26.6 ± 0.4	−23.7 ± 0.4
MEK	−28.3 ± 2.1	−25.9 ± 1.9	
2-pentanone	−34.8 ± 6.5	−29.4 ± 0.1	
3-pentanone	−35.3 ± 1.7	−37.8 ± 1.8	
toluene		−33.7 ± 2.0	

[a] Miami International Airport, $n = 5$; Miami financial district, $n = 4$; Everglades National Park, $n = 3$.

presented by Wen et al. who measured values via a derivatization procedure of ∼−21.0‰ and ∼−29.2‰ for samples collected at a bus station and petrochemical refinery, respectively.[36]

Some observations at Miami's Financial District are between 2.2 and 4.4‰ enriched in ^{13}C compared to the same compounds at Miami International Airport, and again we observe an anomalously enriched value for ethanol (−17.2 ± 4.1‰). Samples from the airport are general $\delta^{13}C$ values we can expect for OVOCs from transportation related sources without addition from other sources and losses caused by solar radiation and reaction with OH. Miami's Financial District is located within 0.1 mile of Biscayne Bay and 1 mile of the Port of Miami and was dominated by an onshore breeze during the sample collection. Therefore, we can expect values from the financial district to be enriched since the $\delta^{13}C$ signature for each compound will reflect a combination of vehicular, biogenic, and possibly marine sources and, additionally, losses attributable to reactivity with OH and photolysis. Isotopic values for samples from the financial district are bound within the reported range of −15.8 to −37.4‰ for NMHCs sampled at a moderately polluted waterfront in Wellington, New Zealand.[25]

In comparison with automobile exhaust (Table 2), the mean values observed at Miami International Airport and Miami's financial district are generally depleted in [13]C. The two most obvious differences among these samples that may influence the observations are the fuel source and the presence of a catalytic converter. Emissions collected at the airport are a mix of refined petroleum and diesel, whereas the Scout International was fueled by unleaded gasoline. Furthermore, vehicle emissions at the airport are assumed to be produced by engines having a catalytic converter. However, the Scout lacked a converter, and the speeds of the engines producing the emissions were very different. Traffic through the airport's lower roadway moved at an idle pace and rarely exceeded 15 mph. The Scout samples were obtained with the engine under significant load and at a constant revolution per minute (2000 rpm) and cruise speed (80 kph). To our knowledge, no studies exist showing how the presence of a catalytic converter or engine speed may influence the $\delta^{13}C$ of emitted hydrocarbons.

Samples from Everglades National Park spanned a large range from −19.0 to −36.3‰. Measured methanol from within the National Park was −36.3 ± 3.7‰, considerably depleted and consistent with other values obtained in the tropical plant enclosure studies (i.e., sand live oak $\delta^{13}C_{Methanol} = -41.9 \pm 3.1‰$) and with the results presented earlier from Keppler et al.[33] Similarly, $\delta^{13}C$ values for isoprene released from C3 plants range from −26 to −29‰.[45] Isoprene values at the National Park are lighter (−30.3 ± 2.1‰) than the range presented by Rudolph et al. However, when the precision of the measurement is considered, the isoprene values measured from the Everglades' samples overlap the range observed with that previous work. Acetone and acetaldehyde values from within the National Park are more enriched than anticipated. The mean $\delta^{13}C$ values for these compounds are −23.7‰ and −19.0‰, respectively. Each are enriched approximately 7.5‰ compared to samples collected at Miami International Airport and are fairly consistent with samples from Miami's financial district and fossil fuel combustion.

When estimated atmospheric lifetimes (τ) are considered for these compounds in the troposphere for losses caused by reactivity with OH ($\tau_{acetone}^{OH} = 66$ days; $\tau_{acetaldehyde}^{OH} = 11$ h) and photolysis ($\tau_{acetone}^{hv} = 38$ days; $\tau_{acetaldehyde}^{hv} = 5$ days), these observations can be explained, especially for the enrichment of acetaldehyde over acetone (∼5‰). Few studies of ambient $\delta^{13}C$ for acetaldehyde exist,[29,36] and only one exists for acetone.[37] For samples collected within a biosphere reserve in China, Guo et al. measured acetaldehyde values between −31.6 and −34.9‰. These values are depleted in ^{13}C compared to our measurements. However, they report weak photolytic loss of formaldehyde in the same study, and considering formaldehyde's lifetime against photolysis is shorter (4 h) compared to acetaldehyde (5 days), we assume this to be true for acetaldehyde at the same location.

Guo et al. used a derivatization method to calculate $\delta^{13}C$ values for acetone collected at a forested site (∼−31‰) and at the top of a 10 m building influenced by vehicle emissions (∼−26‰). The acetone values from Everglades National Park are enriched by 2−7‰ compared to the values presented by Guo et al. Isotopic values obtained from the forest may reflect the signature of fresh acetone emissions from biomass, while values for Everglades National Park samples may be more strongly influenced by photochemistry. The measured values for acetone and acetaldehyde from within the Everglades may also indicate contributions from *in situ* atmospheric production via oxidation and photolysis of higher order hydrocarbons. An exact assessment to separate direct emissions from photochemical production and loss is not possible at this time since fractionations associated with these pathways are not known.

CONCLUSIONS

A new method for measuring $\delta^{13}C$ values of low-molecular weight OVOCs from direct sources and ambient samples was developed. The method incorporated a carbon sorbent, a low-volume capillary reactor, water trap, and balanced working reference gas delivery system. The method's total precision ranged between 0.6 and 2.9‰, and negligible sample fractionation occurred while sampling and trapping gases. Further testing showed that measured $\delta^{13}C$ values had little dependence

on sample size (0.06 ‰ ng C^{1-}), and linearity was best over the range of 1−10 ng C. The method was sensitive, requiring >0.2 ng C into the ion source to produce accurate and precise results. The analysis of ambient samples required small sample volumes, with ∼1.0 L of gas providing sufficient carbon for analysis.

Clear distinctions in δ^{13}C were observed between emissions released from plants and automobiles. In particular, ethanol emissions from automotive exhaust and metropolitan Miami were significantly enriched in ^{13}C. This is related to ethanol's C4 plant origin and use as a fuel additive. Ambient samples can be differentiated, but the variation in δ^{13}C values was not as great as for the source samples. Ambient samples suffer from additional complexity with multiple sources and sinks affecting single sampling locations. Clearly, more studies of sources and ambient sampling are required to define and characterize OVOCs in the troposphere along with laboratory studies to determine the kinetic isotope effects associated with OVOCs' *in situ* production and loss from reaction with OH and photolysis. As it stands now, this technique can be used to differentiate OVOC sources and to assess the carbon isotopic values for OVOCs in ambient air. It should serve as a useful way to investigate transformations of organic gases in the atmosphere.

SUPPORTING INFORMATION AVAILABLE

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.