Development of a Compound-Specific Carbon Isotope Analysis Method for Atmospheric Formaldehyde via NaHSO₃ and Cysteamine Derivatization

Y. X. Yu,^{†,‡} S. Wen,[‡] Y. L. Feng,[‡] X. H. Bi,[‡] X. M. Wang,[‡] P. A. Peng,[‡] G. Y. Sheng,^{†,‡} and J. M. Fu^{*,†,‡}

Research Institute of Environmental Pollution and Health, School of Environmental and Chemical Engineering, Shanghai University, Shanghai 200072, P. R. China, and State Key Laboratory of Organic Geochemistry, Guangdong Key Laboratory of Environmental Resources Utilization and Protection, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, P. R. China

A novel method has been developed for the compoundspecific carbon isotope analysis of atmospheric formaldehvde using gas chromatography/combustion/isotope ratio mass spectrometry (GC/C/IRMS). The method allows the determination of the δ^{13} C value for atmospheric formaldehyde at nanogram levels with higher precision and lower detection limit. In the present work, atmospheric formaldehyde was collected using NaHSO₃-coated Sep-Pak silica gel cartridges, washed out by water, then derivatized by cysteamine of known δ^{13} C value, and the δ^{13} C value of its derivative (thiazolidine) determined by GC/C/IRMS. Finally, the δ^{13} C value of atmospheric formaldehvde could be calculated by a simple mass balance equation between formaldehyde, cysteamine, and thiazolidine. Using three formaldehydes with different δ^{13} C values, calibration experiments were carried out over large ranges of formaldehyde concentrations. The carbon isotope analysis method achieved excellent reproducibility and high accuracy. There was no carbon isotopic fractionation throughout the derivatization processes. The differences in the carbon isotopic compositions of thiazolidine between the measured and predicted values were always <0.5%, within the specifications of the GC/C/IRMS system. The present method was also compared with the previous 2,4-dinitrophenylhydrazine derivatization method, and this method could be performed with lower analytical error and detection limit. Using this method, four 6-h ambient atmospheric formaldehyde samples were consecutively collected from 8 to 9 March 2005. The results showed that the δ^{13} C values of atmospheric formaldehyde were different during the daytime and nighttime. This method proved suitable for the routine operation and may provide additional insight on sources and sinks of atmospheric formaldehyde.

Research on atmospheric formaldehyde is important not only because of its adverse effect on human health but also because of its role in atmospheric chemistry.^{1,2} Formaldehyde constitutes the most abundant carbonyl in ambient air and is derived from direct emissions from industrial processes, vehicle exhaust emissions, and other stationary sources, and also from photochemical reactions, generally through the oxidation of hydrocarbons in the presence of nitrogen oxides, OH radicals, and ozone.^{3–6} Though many studies have been performed, there are still gaps regarding its sources and atmospheric reactions.^{1–6}

In the past decade, compound-specific carbon isotopic composition measurements have been successfully used to improve our insight into the budgets and the processes of some atmospheric trace gases, e.g., CO, CO₂, CH₄, and other trace compounds.^{7–9} Gas chromatography/combustion/isotope ratio mass spectrometry (GC/C/IRMS) has become a powerful analytical tool to infer the origin and track the fate of organic compounds in various systems.^{7–10} This technique permits continuous flow acquisition of δ^{13} C data for individual components in complex mixtures at nanogram levels. However, despite the development of improved methods for compound-specific carbon isotope analysis of CO, CO₂, CH₄, and non-methane hydrocarbons, there are few published studies concerning the stable carbon isotope analysis of atmospheric formaldehyde.^{11–13} In one of these

- Carlier, P.; Hannachi, H.; Mouvier, G. Atmos. Environ. 1986, 20, 2079– 2099.
- (2) Flores, G. E.; Andraca-Ayala, G.; Báez, A. Atmos. Environ. 2005, 39, 1027– 1034.
- (3) Takekawa, H.; Minoura, H.; Yamazaki, S. Atmos. Environ. 2003, 37, 3413– 3424.
- (4) Grutter, M.; Flores, E.; Andraca-Ayala, G.; Báez, A. Atmos. Environ. 2005, 39, 1027–1034.
- (5) Iannone, R.; Anderson, R. S.; Rudolph, J.; Huang, L.; Ernst, D. Geophys. Res. Lett. 2003, 30 (13), 1684. Doi: 10.1029/2003GL017221.
- (6) Feltham, E. J.; Almond, M. J.; Marston, G.; Ly, V. P.; Wiltshire, K. S. Spectrochim. Acta, Part A 2000, 56, 2605–2616.
- (7) Rudolph, J.; Czuba, E.; Norman, A. L.; Huang, L.; Erns, D. Atmos. Environ. 2002, 36, 1173–1181.
- (8) Mook, W. G.; Koopmans, M.; Carter, A. F.; Keeling, C. D. J. Geophys. Res. 1983, 88, 10915–10933.
- (9) Lowe, D. C.; Brenninkmeijer, C. A. M.; Brailsford, G. W.; Lassey, K. R.; Gomez, A. J. J. Geophys. Res. 1994, 99, 16913–16925.
- (10) Zwank, L.; Berg, M.; Schmidt, T. C.; Haderlein, S. B. Anal. Chem. 2003, 75, 5575–5583.

^{*} Corresponding author: (e-mail) fujm@gig.ac.cn; (fax) +86-20-85290192; (tel) +86-20-85290196.

[†] Shanghai University.

[†] Guangzhou Institute of Geochemistry, Chinese Academy of Sciences.

reports,¹¹ the carbon isotope analyses were performed as follows: the atmospheric formaldehyde was collected using a NaHSO₃-coated filter, and the product sodium hydroxymethanesulfonate (HOCH₂SO₃Na, denoted here as HMSNa) was analyzed using a conventional dual inlet isotope ratio mass spectrometry (IRMS) system. The measured carbon isotopic data were reported as pertaining to atmospheric formaldehyde. The main drawback of this method is that the analysis requires the enrichment of formaldehyde from several hundred cubic meters of air, which may take one or two days of sampling. Recently, a novel method determining the compound-specific carbon isotopic composition for atmospheric formaldehyde at ppb or sub-ppb levels by 2,4dinitrophenylhydrazine (DNPH) derivatization was developed, but its precision is poor.¹³

It is well known that formaldehyde reacts rapidly with NaHSO₃ to form the nonvolatile HMSNa.¹⁴ Other studies have shown that HMSNa decomposes to formaldehyde in strong acid and then reacts with cysteamine to form thiazolidine,^{15–20} which is much more stable and less volatile than formaldehyde. However, thiazolidine is sufficiently volatile for gas chromatographic (GC) analysis. In the present work, a novel method is described, which applies GC/C/IRMS to determine the δ^{13} C value of derivatized atmospheric formaldehyde at nanogram levels. Calibration experiments, atmospheric sampling, accuracy, and reproducibility of the method will be discussed in detail, and the stable carbon isotope effects during the procedure will be presented to demonstrate the practical utility of this method.

EXPERIMENTAL SECTION

Reagents and Materials. Acetonitrile (ACN) purchased from Merck was HPLC grade. Chloroform was purchased from Shantou XiLong Chemical Co. Ltd. and distilled three times. Water was double distilled and filtered by a Milli-Q system. Cysteamine hydrochloride (97%) purchased from Fluka was recrystallized twice in ethanol.²¹ DNPH, purchased from Fluka, was recrystallized twice in HPLC grade ACN and analyzed by HPLC. NaHSO₃ was purchased from United Research Institute of Chengdou. Standard formaldehyde (37% in water solution with 10% methanol) samples were obtained from three suppliers: Aldrich (F1), Guangzhou Second Chemical Reagent Factory (F2), and Guangzhou Chemical Reagent Factory (F3), respectively.

2,4-Dinitrophenylhydrazine was purchased from ChemService. A GV-mix standard solution containing C_{10} , C_{11} , and C_{12} *n*-alkanes and methyl decanoate with δ^{13} C values of -28.6, -26.7, -28.6, and -30.5%, respectively, was obtained from GV Corp. The standard thiazolidine was prepared in our laboratory as described

- (12) Johnson, B. J.; Dawson, G. A. Environ. Sci. Technol. 1990, 24, 898-902.
- (13) Wen, S.; Feng, Y. L.; Yu, Y. X.; Bi, X. H.; Wang, X. M.; Sheng, G. Y.; Fu, J. M. Environ. Sci. Technol. 2005, 39, 6202–6027.
- (14) Andrade, J. B.; Tanner, R. L. Atmos. Environ. 1992, 26A, 819-825.
- (15) Goldman, F. H.; Yagoda, H. Ind. Eng. Chem. 1943, 15, 377-378.
- (16) Rayner, A. C.; Jephcott, C. M. Anal. Chem. 1961, 33, 627-630.
- (17) Hayashi, T.; Reece, C. A.; Shibamoto, T. J. Assoc. Off. Anal. Chem. 1986, 69, 101–105.
- (18) Yasuhara, A.; Shibamoto, T. J. Assoc. Off. Anal. Chem. 1989, 72, 899-902.
- (19) Miyake, T.; Shibamoto, T. J. Agric. Food Chem. 1993, 41, 1968–1970.
 (20) Huang, T. C.; Huang, L. Z.; Ho, C. T. J. Agric. Food Chem. 1998, 46, 224–
- 227.
- (21) Taguchi, T.; Kojima, M.; Muro, T. J. Am. Chem. Soc. 1959, 81, 4322-4325.

below. The sampling media commercial Sep-Pak silica gel cartridges (Waters, Millipore Corp.) coated with DNPH or NaHSO₃.

Cartridge Preparation. Sep-Pak silica gel cartridges were coated with DNPH according to our previous reports.^{22,23} The cartridges were rinsed with 10 mL of ACN and were coated with 7 mL of freshly made acidified DNPH coating solution. When there was no more solution flowing out of the cartridges, they were dried with a gentle flow of high-purity nitrogen. Each cartridge was wrapped in aluminum foil and then wrapped with a piece of filter paper impregnated with DNPH coating solution to prevent contamination before use. Last, each cartridge was sealed in a Teflon bag. All the processes were carried out in a high-purity nitrogen-filled glovebox (ZKX2, 800 mm × 600 mm × 700 mm, Nanjing University Instrument Plant).²³ The prepared cartridges were stored at 4 °C until use. Three of each batch were analyzed using HPLC to test the blank compared to the EPA blank criteria.²⁴

The NaHSO₃-coated Sep-Pak silica gel cartridges were prepared similarly to the DNPH-coated cartridges. The cartridges were rinsed with 10 mL of ACN, subsequently rinsed with 7 mL of water, and then coated with 7 mL of freshly made 10% (w/v) NaHSO₃ solution. When there was no more solution flowing out, they were dried with a gentle flow of high-purity nitrogen. Each cartridge was wrapped in a piece of filter paper, impregnated with the NaHSO₃ solution to prevent contamination before use, and then sealed in a Teflon bag. All the processes were carried out in the high-purity nitrogen-filled glovebox. The NaHSO₃-coated cartridges were stored at 4 °C until use. After washing out and derivatization as described below, four cartridges were analyzed using GC/C/IRMS and the results showed no interference.

Preparation of Standard Thiazolidine. Standard thiazolidine was prepared by reacting equimolar amounts of cysteamine hydrochloride with formaldehyde in a water solution of pH 8.^{15–20} After 4 h, the solution was extracted three times with chloroform; the extract was dried over anhydrous sodium sulfate, filtered, and then concentrated by a rotary evaporator. The complete procedure was carried out at room temperature. The purity of the thiazolidine was verified using GC and GC/MS, respectively, and its δ^{13} C value was determined by GC/C/IRMS.

Measurements of δ^{13} C of Standard Formaldehyde. The method for determining the δ^{13} C value of formaldehyde in a standard stock solution was as follows:²⁵ aliquots of 37% stock formaldehyde solution were sealed in glass vials with open screw caps containing Teflon-lined silica septa. After at least 1 h to reach equilibrium, ~1 mL of headspace air containing formaldehyde was injected into the GC/C/IRMS system for analysis using a Hamilton airtight locking syringe.

Calibration Experiments for Atmospheric Sampling. Calibration experiments were performed using an airtight system (see Figure 1), consisting of a 100-L Teflon sample bag (SKC Inc.) connected to a sampling pump (Thomas). Before each experiment, the bag was washed at least three times with high-purity (99.99%)

- (24) U.S. Environment Protection Agency (US EPA). Compendium method to-11A. Active Sampling Methodology, 1999.
- (25) Wen, S.; Feng, Y. L.; Wang, X. M.; Sheng, G. Y.; Fu, J. M.; Bi, X. H. Rapid Commun. Mass Spectrom. 2004, 18, 2669–2672.

⁽¹¹⁾ Tanner, R. L.; Zielinska, B.; Uberna, E.; Harshfield, G. J. Geophys. Res. 1996, 101, 28961–28970.

⁽²²⁾ Feng, Y. L; Wen, S.; Wang, X. M.; Sheng, G. Y.; He, Q. S.; Tang, J. H.; Fu, J. M. Atmos. Environ. 2004, 38, 103–112.

⁽²³⁾ Feng, Y. L.; Wen, S.; Chen, Y. Z.; Wang, X. M.; Lü, H. X.; Bi, X. H.; Sheng, G. Y.; Fu, J. M. Atmos. Environ. 2005, 39, 1789–1800.



Figure 1. Schematic representation of the calibration experiment for atmospheric sampling (for breakthrough test).

N₂. After that, the standard formaldehyde stock solution was injected into the bag, heated to aid evaporation, and then kept for 30 min to reach equilibrium. Then the gas (containing formaldehyde) was drawn out and through the sampling cartridge (NaHSO₃-coated, DNPH-coated, or both) using the sampling pump. To test the recovery efficiency during sampling for formaldehyde, two kinds of experiments were performed: (1) for breakthrough tests, the formaldehyde was collected by drawing the gases first through a NaHSO₃-coated cartridge and then a DNPH-coated cartridge in series; and (2) for the adsorption test of the whole system, only a DNPH-coated cartridge was used to measure the formaldehyde concentration. By comparison of the measured and theoretical formaldehyde concentrations, we could determine whether the adsorption of the whole system was major or minor. In the calibration experiments for atmospheric sampling, just a NaHSO3-coated cartridge was used. The flow rate was 1 or 2 L min⁻¹ measured by a rotameter, which was calibrated with a digital flow meter (DryCal DC Lite, Bios Corp.) before use. After sampling, the DNPH-coated cartridge was eluted with ACN into 2-mL volumetric flask, and the eluate was analyzed using HPLC. The NaHSO₃-coated cartridge was treated as described below.

Sample Preparation for GC/C/IRMS. After sampling, the NaHSO₃-coated cartridge was eluted with 10 mL of water into a 25-mL beaker and the pH of the solution was adjusted to 1–2; the solution was then placed in a 60 °C water bath for 20 min to decompose the HMSNa and evaporate the SO₂, removed, and 1 mL of 19 μ g μ L⁻¹ cysteamine hydrochloride solution with known δ^{13} C value added. The final pH of the solution was adjusted to 8–9 with sodium hydroxide solution. After 4 h, the solution was extracted three times with 10 mL of chloroform, and the combined extract was dried over anhydrous sodium sulfate. Then the extract was filtered, concentrated with a rotary evaporator at 20 °C, transferred into a 2-mL vial, and blown down to ~100 μ L using a gentle flow of high-purity N₂. Finally, 1 μ l of the concentrated sample was injected into the GC/C/IRMS for analysis.

Air Sampling. The samples were collected on the roof of an office building 15 m above ground at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences located in the Tianhe District of Guangzhou, China. The Guangyuan expressway and a railway are located ~ 100 m away. All samples were collected at a height of 1 m above the floor.

Four 6-h samples were collected consecutively from 7:00 a.m. on 8 March 2005 to 7:00 a.m. on 9 March 2005. NaHSO₃-coated cartridges were used as sampling media, and air was drawn through at a flow rate of 2 L min⁻¹ by the sampling pump. After sampling, the cartridges were treated as described above, and the δ^{13} C values of the thiazolidine determined by GC/C/IRMS.

One field blank was analyzed, and the result showed no interference.

At the same time, another four samples were collected using the DNPH-coated cartridges as described earlier.^{22,23} The flow rate was 0.8–1.2 L min⁻¹ through sampling. An ozone denuder (a copper tube coil, 1.2 m × 0.5 mm i.d. coated with KI inside) was connected in front of the cartridge to avoid degradation of 2,4dinitrophenylhydrazine.^{27,28} After sampling, the cartridges were backflushed with ACN under gravity into 2-mL volumetric flasks. The sample eluates were stored at 4 °C until analysis by HPLC. One field blank was analyzed, and the result was below the EPA limit.

Analytical Systems. The concentration of formaldehyde was determined by HPLC (Hewlett-Packard model 1100) with a photodiode-array detector and UV light of 360 nm. An SB-C₁₈ reverse column (250 mm × 4.6 mm, 5 μ m, Agilent) was used. A 10- μ L aliquot was injected into the HPLC system via autosampler and analyzed as follows: mobile-phase gradient with a flow rate of 1 mL min⁻¹ from 60 to 70% ACN in water (v/v) for the first 20 min, 70 to 100% ACN for 3 min, 100% ACN isocratic elution for 4 min, 100 to 60% ACN for 1 min, and last 60% ACN 5 min isocratic.

The GC analyses were carried out with an HP 5890 system (Hewlett-Packard) equipped with an HP-5MS column (30 m \times 0.32 mm \times 0.25 μ m, Agilent) and flame ionization detector. The operating conditions were as follows: He carrier flow rate at 1.5 mL min⁻¹, splitless injection, injector and detector temperatures at 250 and 300 °C, respectively. The oven temperature was programmed from 45 °C at the rate of 3 °C min⁻¹ to 80 °C.

The GC/MS analyses were performed with an HP 5890 gas chromatograph combined with an HP 5972 mass selective detector (Hewlett-Packard) in the full scan mode for 35–350 Da. The other operating conditions were the same as those used for the GC analyses above.

The δ^{13} C value of cysteamine hydrochloride was determined with an elemental analyzer-isotope ratio mass spectrometer (EA-IRMS, Thermo Finnigan MAT, Bremen Germany, DELTA^{plus} XL mass spectrometer). The cysteamine hydrochloride samples were weighed in Sn capsules with negligible backgrounds. The weighed capsules were dropped into a CuO combustion furnace in the CE EA1112 C/N/S analyzer through an autosampler and combusted at 960 °C in an O₂ atmosphere. The combustion gases were swept through a Cu reduction oven operated at 650 °C and then passed through a GC column where CO₂ was separated from other gases. The CO₂ entered the DELTA^{plus} XL MS for measurement of its δ^{13} C value through a Conflo III interface (Finnigan). At the beginning and end of each batch of samples, carbon black standards (δ^{13} C = -36.91‰) were analyzed to evaluate the reproducibility and accuracy of the instrument.²⁹

The δ^{13} C values of formaldehyde were determined using an HP 6890 GC (Agilent) equipped with an HP-PLOT Q column (30 m × 0.32 mm × 20 μ m, Hewlett-Packard) coupled to a combustion furnace and DELTA^{plus} XL isotope ratio mass spectrometer (GC/C/IRMS). The CuO/Ni/Pt combustion furnace and Cu reduction

⁽²⁶⁾ Yu, Y. X.; Wen, S.; Feng, Y. L.; Bi, X. H.; Wang, X. M.; Sheng, G. Y.; Fu, J. M. Rapid Commun. Mass Spectrom. 2005, 19, 2469–2472.

⁽²⁷⁾ Christensen, C. S.; Skov, H.; Lohse, C. Atmos. Environ. 2000, 34, 287– 296.

⁽²⁸⁾ Müller, K.; Pelzing, M.; Gnauk, T.; Kappe, A.; Teichmann, U.; Spindler, G.; Haferkorn, S.; Jahn, Y.; Herrmann, H. Chemosphere 2002, 49, 1247–1256.

⁽²⁹⁾ Jia, G. D.; Peng, P. A. Mar. Chem. 2003, 82, 47-54.

Table 1. Sampling Efficiency and Breakthrough of Formaldehyde in Calibration Experiment for Atmospheric Sampling

total volume (L)	rate flow (L min ⁻¹)	concentrations of formaldehyde (µg m ⁻³)	formaldehyde/ cartridge ^a (μ g) (AM \pm SD) ^b
100	1	20.28-312.00 ^c	$0.07 \pm 0.02 \ (n = 6)$
100	2	20.28-312.00 ^c	0.05 ± 0.01 (n = 6)
800	2	15.6	0.06 ± 0.03 ($n = 3$)
1200	2	7.8	$0.05 \pm 0.02 \ (n = 3)$
lab blank			$0.05 \pm 0.03 \ (n=3)$

^{*a*} Amount of formaldehyde in one cartridge. ^{*b*} The arithmetic means and standard deviations. ^{*c*} Concentrations of formaldehyde in calibration experiment for atmospheric sampling at six different concentrations of 20.28, 40.56, 62.40, 99.84, 199.68, and 312.00 μ g m⁻³, respectively. *n*, number of samples analyzed by HPLC.

oven were operated at 940 and 650 °C, respectively.¹³ Split injection (~10:1) was used, and the GC oven temperature was kept at 180 °C. Standard CO₂ (δ^{13} C = -26.65‰) was used as the external reference gas. Standard CH₄ (δ^{13} C = -36.30‰) was used to evaluate the reproducibility and accuracy of the IRMS.¹³

The δ^{13} C values of thiazolidine were determined using the same GC/C/IRMS system as above. The GC was equipped with an HP-5MS column and operated as above. Over 60 ng of thiazolidine was needed for every injection to obtain data of acceptable accuracy and precision. The reproducibility and accuracy of the GC/C/IRMS system were checked daily with two isotopic standards: a GV-mix standard solution and a standard thiazolidine solution. Triplicate standard analyses yielded excellent accuracy and reproducibility. All ¹³C/¹²C ratios in this work are expressed in conventional δ notation, as per mil (‰) relative to the Vienna PDB standard.

RESULTS AND DISCUSSION

 $δ^{13}$ C Analysis of Standard Thiazolidine. The $δ^{13}$ C value of standard thiazolidine was determined from 30 measurements by GC/C/IRMS to be $-33.00 \pm 0.20\%$. The thiazolidine was stored at 4 °C as a standard stock solution and was used with the GV-mix standard solution as laboratory standards to check reproducibility and accuracy.

Efficiency of Formaldehyde Recovery in the Calibration Experiment. The results of breakthrough tests indicated that no formaldehyde appeared in the DNPH-coated cartridge (Table 1). In the adsorption test of the whole system, using different formaldehyde concentrations (similar to Table 1), the recovery efficiencies were all over 90%,³⁴ which means the loss within the system was minor. Therefore, formaldehyde was efficiently collected in the calibration experiment.

 δ^{13} C Analysis of Formaldehyde and its Derivative (Thiazoline). The reproducibility of the carbon isotope composition

- (33) Melander, L.; Saunders, W. H. Reaction Rates of Isotopic Molecules; John Wiley: NewYork 1980.
- (34) Yu Y. X. Ph.D. Thesis. The Graduate School of the Chinese Academy of Sciences, 2005; pp 41–42.

for three batches of formaldehyde (with different δ^{13} C values) was evaluated. Their δ^{13} C values and those of the corresponding thiazolidine derivatives are given in Table 2. The analytical errors (standard deviation) obtained for three or five GC/C/IRMS analyses of formaldehyde from the same supplier ranged from 0.13 to 0.40‰, with an average of 0.28 ± 0.14‰, and for thiazolidine, the analytical errors were from 0.15 to 0.26‰, with an average of 0.20 ± 0.03‰. The accuracy of these results was well within the technical specifications of the GC/C/IRMS system. The reproducibility was also excellent compared with that of the previous studies.^{7,13,25,30,31}

Storage Stability of Cartridge Samples. Different storage conditions were discussed. Samples of F3 were stored for 30 days with one batch at 4 °C and another batch at room temperature (3–26 °C) (Table 2). These samples were derivatized to thiazolidine and analyzed by GC/C/IRMS. The δ^{13} C value differences among these two batches of samples are negligible (all within instrument specifications). The results also show that the formaldehyde–NaHSO₃ adducts (HMSNa) were stable and the cartridges could be stored over long periods.

Isotope Effects of the Method. Theoretically, the substrates and products should exhibit δ^{13} C compositions that reflect the relative contributions of carbon from each component and their respective δ^{13} C values. In this method, the following reactions of occur:

$$HCHO + NaHSO_3 = HOCH_2SO_3Na$$
 (1)

$$HOCH_2SO_3Na + HCl = HCHO + NaCl + H_2O + SO_2^{\uparrow}$$
(2)

HCHO+HSCH₂CH₂NH₂=
$$\begin{bmatrix} S \\ N \\ H \end{bmatrix}$$
 +H₂O (3)

During the course of the reactions, if formaldehyde reacts quantitatively with NaHSO₃, and HMSNa discomposes completely, there should be no carbon isotopic fractionation; and if formaldehyde also quantitatively reacts with cysteamine in accordance with the stoichiometric mass balance equation, there should also be no carbon isotopic fractionation during that reaction. Thus, the stable carbon isotopic compositions of formaldehyde, HMSNa, cysteamine, and thiazolidine should comply with the following equations:

$$\delta^{13} C_{\text{HCHO}} = \delta^{13} C_{\text{HMSNa}} \tag{4}$$

$$1/3\delta^{13}C_{\rm HCHO} + 2/3\delta^{13}C_{\rm cysteamine} = \delta^{13}C_{\rm thiazolidine}$$
(5)

where 3 and 2 are the mole C numbers of thiazolidine and cysteamine, respectively. According to eq 5, the stable carbon isotopic composition of the original formaldehyde could be calculated from the known δ^{13} C values of cysteamine and thiazolidine determined by EA-IRMS and GC/C/IRMS, respectively.

According to Rieley's discussion of kinetic isotope effects,³² the primary isotope effect, whereby a bond containing the atom under consideration is changed in the rate-determining step, is the most significant.³³ If no carbon bond changed in the rate-determining step, and indeed if no carbon-containing bond is

⁽³⁰⁾ Saito, T.; Tsunogai, U.; Kawamura, K.; Nakatsuka, T.; Yoshida, N. J. Geophys. Res. 2002, 107 (D4). Doi: 10.1029/2000[D000127.

⁽³¹⁾ Abrajano, T. A.; Murphy, D. E., Jr.; Comet, P. A.; Brooks, J. Org. Geochem. 1994, 21, 611–617.

⁽³²⁾ Rieley, G. Analyst 1994, 119, 915-919.

Table 2. Stable Carbon Isotopic Compositions of	of Formaldehyde and	l Derivatives Measured	I and Calculated in the
Calibration Experiment for Atmospheric Sampli	ng		

		$\delta^{13}\mathrm{C}(\%)^a$				
suppliers	formaldehyde concn (µg m ⁻³)	measured formaldehyde ^{b,c}	measured thiazolidine $^{b-e}$	calculated formaldehyde ^f	calculated thiazolidine ^g	absolute values ^h
$F1^i$	312.0	-45.08 ± 0.40 (<i>n</i> = 5)	-32.99 ± 0.22	-44.66 ± 0.67	-33.14	0.15
	202.8		-33.39 ± 0.18	-45.86 ± 0.56		0.25
	101.4		-33.01 ± 0.18	-44.71 ± 0.53		0.13
	31.2		-32.88 ± 0.20	-44.42 ± 0.45		0.26
	7.8		-32.76 ± 0.20	-44.56 ± 0.56		0.38
$F2^i$	312.0	-42.11 ± 0.13 (<i>n</i> = 3)	-32.30 ± 0.17	-42.57 ± 0.38	-32.15	0.15
	202.8		-32.32 ± 0.26	-42.65 ± 0.78		0.17
	101.4		-32.40 ± 0.18	-42.88 ± 0.54		0.25
	31.2		-32.39 ± 0.17	-42.85 ± 0.51		0.24
	7.8		-32.30 ± 0.18	-42.59 ± 0.54		0.15
F3 ^j	312.0	-39.30 ± 0.31 (<i>n</i> = 5)	-31.44 ± 0.20	-40.01 ± 0.61	-31.21	0.23
	202.8		-31.25 ± 0.18	-39.42 ± 0.53		0.04
	101.4		-31.37 ± 0.24	-39.78 ± 0.73		0.16
$F3^k$	312.0	-39.30 ± 0.31 (<i>n</i> = 5)	-31.27 ± 0.26	-39.49 ± 0.78	-31.21	0.06
	202.8		-31.16 ± 0.24	-39.15 ± 0.71		0.05
	101.4		-31.36 ± 0.17	-39.76 ± 0.52		0.15

^{*a*} Stable carbon isotopic compositions reported in per mil relative to VPDB. ^{*b*} Determined by GC/C/IRMS. ^{*c*} The arithmetic means and standard deviations. ^{*d*} Derivatized with cysteamine hydrochloride of $\delta^{13}C = -27.16 \pm 0.02\%$, from 10 analysis determined by EA-IRMS. ^{*e*} Three times repeated in GC/C/IRMS analysis. ^{*f*} $\delta^{13}C$ values of calculated $\delta^{13}C$ values based on mass balance relationship eq 5 and standard deviations (*S*) calculated according to eq7. ^{*g*} $\delta^{13}C$ values of calculated thiazolidine based on mass balance relationship eq 5. ^{*h*} Absolute values of the difference between the $\delta^{13}C$ values of measured and calculated thiazolidine. ^{*i*} The samples were eluted and derivatized immediately after sampling. ^{*j*} The samples were stored in 4 °C for 30 days and then eluted and derivatized. ^{*k*} The samples were stored in room temperature (3–26 °C) for 30 days and then eluted and derivatized. *n*, number of analysis for each sample.

involved in the reaction, then there is not likely a primary isotope effect on δ^{13} C. In this work, during the derivatization procedure, formaldehyde reacts with cysteamine as in reaction 3. It is clear that only formaldehyde contributes a carbon atom whose bond is altered in the reaction, while the reaction positions of cysteamine are the nitrogen and sulfur atoms. So any carbon kinetic isotope effect is mostly related to the formaldehyde. In our experiments, although the formaldehyde has a carbon bond altered, the cysteamine was always used in extreme excess and the formaldehyde reacted quantitatively. Thus, no carbon isotope fractionation should be introduced. This prediction was confirmed by the results shown in Table 2: the differences between the measured and predicted (calculated according to eq 5) δ^{13} C values of thiazolidine were in the range of 0.04-0.38‰, within instrument specifications. These results imply that this method is promising for measuring the δ^{13} C of atmospheric formaldehyde.

Comparison with the DNPH Method.¹³ For both methods, the analytical error of the calculated data for underivatized formaldehyde (usually expressed as the standard deviation, *S*) should follow eqs 6 and 7, according to the propagation of random error:

$$S^{2}_{\text{formaldehyde}} = 49S^{2}_{\text{DNPH-derivative}} + 36S^{2}_{\text{DNPH}}$$
(6)

$$S^{2}_{\text{formaldehyde}} = 9S^{2}_{\text{thiazolidine}} + 4S^{2}_{\text{cysteamine}}$$
 (7)

where 49, 36, 9, and 4 are the squared numbers of carbon atoms in the respective compounds. According to eqs 6 and 7, the analytical errors (*S*) of formaldehyde δ^{13} C values are lowest for the present method (0.15–0.57 versus 1.74–2.19‰, Table 3).

Table 3. Comparison between This and the DNPHMethod

	DNPH method ^a	this method
$S^{b,c}$ (δ^{13} C, ‰) injection (ng) sampling duration (h) flow rate (L min ⁻¹) concentration (μ g m ⁻³)	$\begin{array}{c} 1.74 - 2.19 \\ > 200 \\ 20 - 24 \\ 2 \\ 14.07 - 66.97 \end{array}$	0.15-0.57 >60 6 2 4.52-10.16

 a The data were cited from ref 13. b The standard deviations were calculated with mass balance eq 6 or eq 7. c $\delta^{13}C$ reported relative to VPDB.

The detection limits for both methods are also given in Table 3. For analytical reproducibility, a minimum concentration of the formaldehyde derivative was needed for each analysis. The minimum amounts were 60 and 200 ng, respectively, for this and the DNPH methods. In addition, the sampling times were 6 and 20-24 h, respectively, where the former was at lower formaldehyde concentrations. Therefore, the detection limit of this method is much lower. Thus, it is obvious that this method has a lower detection limit and less analytical error compared to the DNPH method.

Measurements of Atmospheric Formaldehyde. Atmospheric formaldehyde samples were collected as described above. The target thiazolidine was chromatographically well resolved (Figure 2). The δ^{13} C values and concentrations of formaldehyde are summarized in Table 4. The formaldehyde was quantitatively collected by the NaHSO₃-coated cartridge at the prevalent atmospheric concentrations. The data show that the δ^{13} C values



Figure 2. Typical GC/C/IRMS chromatograms for thiazolidine. (a) Standard thiazolidine; (b) sample collected on top of an office building in Guangzhou in 2005.

Table 4. Concentrations and δ^{13} C of Atmospheric Formaldehyde Measured in Guangzhou, (8–9 March 2005)

		δ^{13} C (‰) ^a		
sampling time	formaldehyde (µg m ⁻³)	$\begin{array}{c} \text{measured} \\ \text{thiazolidine}^{b,d} \\ (\text{AM} \pm \text{SD})^c \end{array}$	calculated formaldehyde (AM± S) ^e	
7:00-13:00	10.16	-31.67 ± 0.05 (n=3)	-40.69 ± 0.15	
13:00-19:00	9.45	-31.30 ± 0.16 (n=3)	-39.58 ± 0.48	
19:00 - 1:00	4.52	-31.16 ± 0.16 (n=3)	-39.14 ± 0.48	
1:00 - 7:00	5.80	-32.10 ± 0.19 (n=3)	-41.96 ± 0.57	

^{*a*} δ^{13} C reported relative to VPDB. ^{*b*} Determined by GC/C/IRMS. ^{*c*} The arithmetic means and standard deviations for three analysis. ^{*d*} Derivatized with cysteamine hydrochloride of δ^{13} C = -27.16 ± 0.02‰, from 10 analyses determined by EA-IRMS. ^{*e*} The arithmetic means of calculated δ^{13} C values based on mass balance relationship eq 5 and standard deviations (S) calculated according to eq 7. *n*, replicate measurements by GC/C/IRMS.

of atmospheric formaldehyde were different during the daytime and nighttime, which may due to the complex reactions of this compound or its different sources.

CONCLUSIONS

A novel method for determining the compound-specific carbon isotopic compositions of atmospheric formaldehyde was developed and tested. It uses NaHSO₃-coated Sep-Pak silica gel cartridges to trap the formaldehyde, and the adduct is derivatized with cysteamine of known isotopic composition. The δ^{13} C of the resultant thiazolidine derivative is measured, and the formaldehyde δ^{13} C values are then calculated according to the mass balance equation among formaldehyde, cysteamine, and thiazolidine. Based on a calibration experiment, excellent reproducibility and accuracy for δ^{13} C are achieved without carbon isotopic fractionation. Also, a comparison between this and the previous DNPH method demonstrates the improvement of this method. The δ^{13} C values of atmospheric formaldehyde were determined with this method. The application of this method for more ambient δ^{13} C data can provide additional information on the sources and sinks of atmospheric formaldehyde.

ACKNOWLEDGMENT

This research was financially supported by the Natural Science Foundation of China (40590392), the 973 foundation (2002CB410803), Foundation of CAS (GIGCX-03-030311106 and KZCX3-SW-429031112). We sincerely thank Dr. J. Z. Liu and Dr. W. L. Jia for their help in EA-IRMS and GC/C/IRMS analysis and Dr. T. S. Xiang in GC/MS analysis.

Received for review September 9, 2005. Accepted November 30, 2005.

AC051616F