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Letter to the Editor

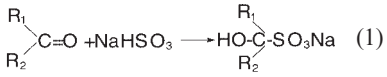
To the Editor-in-Chief
Sir,

Carbon isotope analysis of acetaldehyde and acetone by cysteamine derivatization

There is growing concern about atmospheric carbonyl compounds[1–3] due to their potential health hazard, and to their roles as intermediate products in photochemical processes and precursors of secondary pollutants.[4–7] The most important carbonyls in the atmosphere are formaldehyde, acetaldehyde and acetone, with concentrations ranging from tens to thousands of parts per trillion (ppt).[1–3] The formaldehyde, acetaldehyde and acetone could be derived from different sources, including direct anthropogenic (especially auto exhausts) and biogenic emissions,[8–11] and secondary formation from photochemical oxidation of volatile organic compounds in the atmosphere.[5–7,12,13] Although many studies have been conducted, there is still much uncertainty as to their sources.

Recently, studies of isotope compositions of trace atmospheric species (such as CO, CO_2, CH_4, non-methane hydrocarbons (NMHC)) have proved valuable in providing insights into their budgets and processes.[14–16] Capillary gas chromatography with on-line combustion coupling to isotope ratio mass spectrometry (GC/C/IRMS) has been developed to allow the determination of $\delta^{13}C$ values for organic substances at the nanomole level. Due to its ability to measure isotope ratios at natural abundance levels with great accuracy and high precision, GC/C/IRMS has become a very powerful tool for elucidating the source and fate of trace atmospheric species,[17,18] e.g. carbonyls such as formaldehyde, acetaldehyde and acetone.[19,20] However, until recently, only a few studies were available on the carbon isotopes of atmospheric carbonyls.[19,20]

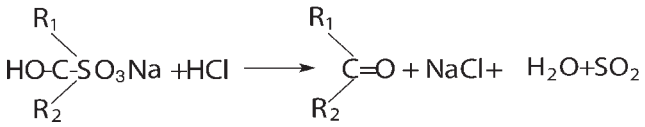
Formaldehyde, acetaldehyde and acetone may react quickly with sodium bisulfite ($NaHSO_3$) to form the respective non-volatile derivatives ($HOCR_1R_2SO_3Na$),[21–23] as described in Eqn. (1):



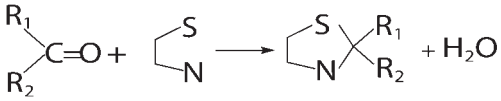
(1)

where R_1 and $R_2 = H$ or CH_3. In one study, $NaHSO_3$ was used to gather atmospheric formaldehyde and the non-volatile sodium formaldehyde-bisulfite derivative ($HOCH_2SO_3Na$) thus formed was then analyzed by conventional dual-inlet isotope ratio mass spectrometry (IRMS).[24] In that study, it took about one day of sampling, which meant hundreds of cubic meters of air, to obtain sufficient formaldehyde for analysis.

Previous studies have shown that the sodium carbonyl-bisulfite compounds ($HOCR_1R_2SO_3Na$) could be decomposed back to carbonyl,[21,25] and the respective carbonyl compounds then reacted with cysteamine ($HS–CH_2\ CH_2–\ NH_2$) at ambient temperature to form the respective cysteamine derivative, as described in Eqns. (2) and (3):



(2)



(3)

where R_1 and $R_2 = H$ or CH_3. The resulting respective cysteamine derivatives could then be measured by gas chromatography (GC).[26,27]

We have previously reported successfully obtaining carbon isotope data for atmospheric formaldehyde via the $NaHSO_3$ and cysteamine derivatization described above.[28] In this paper, the stable carbon isotope effects during the production of $HOCR_1R_2SO_3Na$, the decomposition of $HOCR_1R_2SO_3Na$, and the derivatization of carbonyls with cysteamine were evaluated. This report gives examples of this novel method for determining the carbon isotope values of acetaldehyde and acetone in standards and in the atmosphere.

The methods used were as follow. Water was double distilled. Chloroform was purchased from Shantou Xilong Chemical Co. Ltd. (Shantou, China) and distilled twice. Cysteamine hydrochloride (97%) was purchased from Fluka (Buchs, Switzerland), and recrystallized twice in ethanol.

Acetaldehyde and acetone from four suppliers were used. Acetaldehyde (37–40% aqueous solution) was supplied by the Kemiou Chemical Reagent Centre (Tianjin, China) (S1) and the Xilong Chemical Factory (Shantou, China) (S2). Acetone of HPLC grade was supplied by the Chemical Reagent Factory of Hubei University (Hubei, China) (S3) and the Guangzhou Chemical Reagent Factory (Guangzhou, China) (S4). Sodium bisulfite ($NaHSO_3$) was purchased from the United Research Institute of Chengdou (Chengdou, China).

Carbonyl-$NaHSO_3$ was prepared similarly to the previous study.[21] Sodium bisulfite (32.4 g) was dissolved in distilled water (for acetaldehyde and acetone, the volumes were 62 and 80 mL, respectively), and the solution was reacted with sufficient carbonyl compound (acetaldehyde, 50 mL; acetone, 25 mL) for 24 h in a 300 mL beaker. The solutions were then stirred for 5 h and stored in a refrigerator at 4°C for 24 h. About 110 mL of anhydrous ethanol was then added to the solutions, and the carbonyl-$NaHSO_3$ crystals formed were grown in the reaction beakers after 3 days of evaporation. The crystals were removed by

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filtration and washed with the minimum amount of ethanol. The crystals were dried in an aerator at ambient temperature.

The decomposition of carbonyl-$NaHSO_3$ compounds back to carbonyls, and subsequent derivatization with cysteamine, were carried out as follows. HCl solution (2 mL; pH 2) and a solution of about 20 μg/μL of the carbonyl-$NaHSO_3$ compounds (5 μL) were mixed in a 5 mL cuvette, placed in a water bath at 60°C for 20 min, and then cysteamine aqueous solution (20 μL; 150 μg/μL) was added. The final pH of the solution was adjusted to 8–9 by adding about 100 μL of sodium hydroxide solution (200 μg/μL). After being held at room temperature for 24 h, the solutions were extracted with chloroform (3 × 2 mL) and dried over anhydrous sodium sulfate. The extracts were concentrated to about 200 μL with a gentle flow of high-purity N_2. The samples were stored in a refrigerator at 4°C until analysis.

A standard acetaldehyde (acetone)-cysteamine derivative was prepared by reacting equimolar amounts of cysteamine hydrochloride with the required carbonyl compound in an aqueous solution of pH 8–9 for 24 h. The solution was then extracted once with chloroform and the extract was dried over anhydrous sodium sulfate, filtered and concentrated using a rotary evaporator until all the chloroform had evaporated. The structure of the derivatives was confirmed by GC/MS. The $\delta^{13}C$ value of the derivative was determined by GC/C/IRMS.

GC/MS analysis were accomplished using an HP 5890 gas chromatograph (Hewlett-Packard – now Agilent Technologies, Palo Alto, CA, USA) equipped with a DB-5 column (30 m × 0.32 mm × 0.25 μm; J & W Scientific, Folsom, CA, USA), connected to an HP 5972 mass-selective detector (Hewlett-Packard) operated in scan mode in the range *m/z* 35–250. The analytical conditions were as follows: the injector temperature was set at 200°C and splitless mode was used; ultrapure helium was used as carrier gas at 1.5 mL/min; the oven temperature programme was set at 50°C for 2 min at the start, and then increased at 3°C/min to 85°C.

The $\delta^{13}C$ value of cysteamine hydrochloride was measured by using an elemental analyzer/isotope ratio mass spectrometer combination (EA/IRMS, Thermo Finnigan, Bremen, Germany, DELTA^{plus}XL mass spectrometer). The method was the same as that used in our previous studies.[19,29]

The conditions for the analysis of acetaldehyde and acetone were the same as those used in our previous studies.[19,29] Aliquots of stock acetaldehyde solution were sealed in glass vials with screw caps containing Teflon-lined silicone septa. After allowing 1 h for the samples to reach equilibrium, about 10 μL of headspace air containing acetaldehyde was injected into the GC/C/IRMS system (for acetone, less than 0.1 μL of solution was injected directly). The $\delta^{13}C$ values of acetaldehyde and acetone were measured by using an Agilent 6890 gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) equipped with a HP-PLOT Q column (30 m × 0.32 mm × 20 μm; Hewlett-Packard) coupled to a combustion furnace and an isotope ratio mass spectrometer (GC/C/IRMS) (Isoprime, GV Instruments, Manchester, UK). Ten laboratory isotopic standards (C_{12}, C_{14}, C_{16}, C_{18}, C_{20}, C_{22}, C_{25}, C_{28}, C_{30} and C_{32} n-alkanes supplied by Indiana University; Bloomington, IN, USA) with predetermined isotopic values (−31.89, −30.67, −30.53, −31.02, −32.24, −32.77, −28.94, −32.11, −33.05 and −29.41‰, respectively) and standard CH_4 ($\delta^{13}C = -36.30$‰) were used to evaluate the accuracy of the IRMS system.[28] The injector temperature was 200°C and the split mode was used (split ratios 20:1 and 250:1 for acetaldehyde and acetone, respectively); the GC oven temperature was 180°C. The other operating GC/C/IRMS system conditions were the same as those used in the GC/C/IRMS analysis described below.

The $\delta^{13}C$ value of the carbonyl-cysteamine derivative was measured using an Agilent 6890 GC system with a HP-5MS column (30 m × 0.32 mm × 0.25 μm; J & W Scientific) coupled to an isotope ratio mass spectrometer (GC/C/IRMS) (Isoprime, GV Instruments). CO_2 of known $\delta^{13}C$ value (−26.65‰) was used as the external reference gas. The temperature of the interface between the gas chromatograph and the combustion furnace was set at 200°C. The combustion furnace containing CuO catalyst and the reduction oven containing Cu catalyst were set at 880°C and 580°C, respectively. The splitless mode was used. Other GC conditions were the same as those used in the GC/MS analysis described above. Over 60 ng of carbonyl-cysteamine derivative was needed for every injection to obtain data of acceptable accuracy and precision. Ten laboratory isotopic standards (C_{12}, C_{14}, C_{16}, C_{18}, C_{20}, C_{22}, C_{25}, C_{28}, C_{30} and C_{32} n-alkanes supplied by Indiana University) with predetermined isotopic values (−31.89, −30.67, −30.53, −31.02, −32.24, −32.77, −28.94, −32.11, −33.05 and −29.41‰, respectively) and the laboratory standard GV-mix standard solution (GV Instruments) contained C_{10}, C_{11}, C_{12} n-alkanes and a C_{13} compound (methyl decanoate) with $\delta^{13}C$ values of −28.6, −26.7, −28.6 and −30.5‰, respectively, were used for routine analysis to evaluate the reproducibility and accuracy of the analytical system. The $\delta^{13}C$ value of the acetaldehyde-cysteamine derivative, prepared as described above, was measured 30 times by GC/C/IRMS to obtain the value of −25.85‰ with a standard deviation of 0.06‰. This sample was also used as the laboratory standard to evaluate the reproducibility and accuracy of the analytical system during GC/C/IRMS analysis of experimental samples.

All $^{13}C/^{12}C$ ratios are expressed in conventional delta (δ) notation, which is the per mil (‰) deviation from the standard Pee Dee Belemnite (PDB).

The reproducibility of the carbon isotopic measurement was evaluated. The $\delta^{13}C$ values of acetaldehyde and acetone (each from two independent suppliers), their respective derivatives and cysteamine hydrochloride were measured by GC/C/IRMS, GC/C/IRMS and EA/IRMS, respectively (Table 1). The five replicated analyses of each acetaldehyde and acetone sample from the different suppliers gave a reproducibility of less than 0.12‰ (ranging from 0.05–0.12‰). Two cysteamine hydrochlorides with different $\delta^{13}C$ values were used. The analytical error obtained for five EA/IRMS measurements of the different cysteamine hydrochlorides was less than 0.11‰ (ranging from 0.08–0.11‰). The analytical error obtained for three

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Table 1. Measured and predicted stable carbon isotopic compositions of carbonyls and their respective cysteamine derivatives

		$\delta^{13}C$ (‰)[a]						
Carbonyl	Sample	Measured underivatized carbonyl[b,c,d]	Measured cysteamine hydrochloride[c,d,e]	Measured carbonyl-cysteamine derivatives[b,c,f]	Predicted carbonyl-cysteamine derivatives[g]	Calculated underivatized carbonyl[h]	Δ^i	Δ^j
Acetaldehyde	S1	-25.92 ± 0.12	-27.05 ± 0.08	-26.62 ± 0.03	-26.49	-26.19 ± 0.10	0.13	0.27
	S1	-25.92 ± 0.12	-25.97 ± 0.11	-26.12 ± 0.08	-25.95	-26.27 ± 0.19	0.17	0.35
	S2	-29.69 ± 0.05	-27.05 ± 0.08	-28.65 ± 0.12	-28.37	-30.25 ± 0.25	0.28	0.56
Acetone	S3	-21.35 ± 0.05	-27.05 ± 0.08	-23.63 ± 0.11	-23.63	-21.35 ± 0.19	0	0
	S4	-28.97 ± 0.06	-27.05 ± 0.08	-28.46 ± 0.11	-28.20	-29.40 ± 0.19	0.26	0.43

[a] Stable carbon isotopic compositions reported in per mil relative to PDB.
[b] $\delta^{13}C$ values determined by GC/C/IRMS analysis.
[c] The arithmetic means and standard deviations.
[d] Five replicate analysis for each sample.
[e] $\delta^{13}C$ values determined by EA/IRMS analysis.
[f] Three replicate analysis for each sample.
[g] Predicted $\delta^{13}C$ values of carbonyl-cysteamine derivative based on mass balance relationship (Eqn. (5)).
[h] $\delta^{13}C$ values of calculated underivatized carbonyl based on mass balance relationship (Eqn. (5)); and standard deviations was according to Eqn. (6).
[i] Absolute values of the difference between the predicted and measured $\delta^{13}C$ values of carbonyl-cysteamine derivatives.
[j] Absolute $\delta^{13}C$ values of the difference between the calculated and measured underivatized carbonyl.

GC/C/IRMS measurements of the derivatives formed ranged from 0.00–0.28‰, with an average of 0.17 ± 0.11‰. These reproducibilities are within the error reported for previous GC/C/IRMS $\delta^{13}C$ determinations.[28] The analysis of the laboratory standards (GV-mix standard solution and the standard acetaldehyde-cysteamine derivative) also yielded excellent accuracy and precision.

Theoretically, the carbonyl, cysteamine and the carbonyl-cysteamine derivative should give $\delta^{13}C$ compositions that reflect the relative contributions of carbon from each component and their respective $\delta^{13}C$ values. If no carbon isotopic fractionation occurred during these processes, the carbon isotopic compositions of carbonyl, cysteamine and the carbonyl-cysteamine derivative should comply with the following equations:

$$\delta^{13}C_{HOCR1R2SO3Na} = \delta^{13}C_{carbonyl} \quad (4)$$

$$\delta^{13}C_{carbonyl-cysteamine\ derivative} = f_{carbonyl}\ \delta^{13}C_{carbonyl} + f_{cysteamine}\ \delta^{13}C_{cysteamine} \quad (5)$$

where R_1 and $R_2 = H$ or CH_3; $f_{carbonyl}$ and $f_{cysteamine}$ are the mole fractions of carbon in the carbonyl-cysteamine derivatives arising from the underivatized carbonyl and cysteamine reagent, respectively, and $f_{carbonyl} + f_{cysteamine} = 1$. For example, $f_{carbonyl}$ has the value of 1/2 for the derivatization of acetaldehyde and 3/5 for the derivatization of acetone. The analytical errors of the calculated date for underivatized carbonyl (usually expressed as the standard deviation, S), which were calculated by Eqn. (6) listed below, were 0.10–0.25‰, and the analytical errors (S) of the acetaldehyde and acetone $\delta^{13}C$ values were lower than that of formaldehyde.[28]

$$S^2_{carbonyl} = (1/f_{carbony})^2\ S^2_{carbonyl-cysteamine\ derivative} + (f_{cysteamine}/f_{carbonyl})^2\ S^2_{cysteamine} \quad (6)$$

The standard carbonyl-cysteamine derivatives were separated as shown in Fig. 1. The differences between the calculated (according to Eqn. (5)) and measured $\delta^{13}C$ values of the derivatives and the underivatized carbonyls were in the range of 0.00–0.28‰ and 0.00–0.56‰ (Table 1). These $\delta^{13}C$ values agreed well within the precision limits of the GC/C/IRMS system. The differences are thus so small that they can be ignored, and no carbon isotope fractionation occurred during all experimental processes. According to Rieley's discussion on kinetic isotope effects,[30] fractionations are generally caused by kinetic isotope effects during the derivatization processes. Rieley described several possible kinetic isotope effects in his study. The primary isotope effect, where a bond containing the atom under consideration is changed in the rate-determining step, is the most important. In the present work, if the $HOCR_1R_2SO_3Na$ decomposed completely, no carbon isotope fractionation should be introduced. When the free carbonyl reacts with cysteamine as described in Eqn. (3), only the carbonyl group contributes a carbon atom whose bonds are altered in the rate-determining step, and thus the carbon kinetic isotope effect is mostly related to the carbonyl. As a great excess of cysteamine is used in the derivatization reaction, although the carbonyl has a carbon bond altered, it reacts quantitatively and thus introduces no carbon isotope fractionation effect. Thus, no carbon isotope fractionation should occur during the synthesis of the cysteamine derivatives under our conditions. This is confirmed by our results.

Concentrations of acetaldehyde and acetone in Guangzhou city range from several $\mu g/m^3$ to tens of $\mu g/m^3$.[2] About 100 ng of cysteamine derivative was required for each injection to obtain accurate and precise data, i.e. acetaldehyde and acetone contained in a volume of air of tens to hundreds of liters may be sufficient for GC/C/IRMS analysis, which means a much shorter sampling time.

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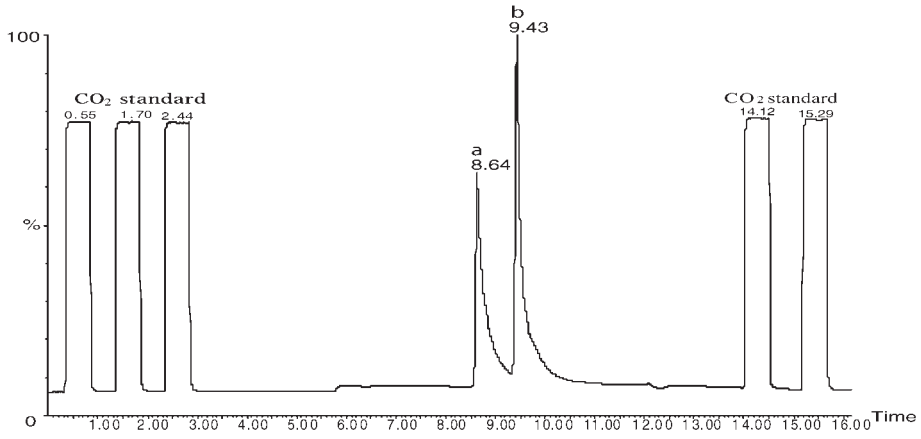

Figure 1. Typical GC/C/IRMS chromatograms for standard carbonyl-cysteamine derivatives. (a) acetaldehyde-cysteamine derivative; (b) acetone-cysteamine derivative.

No carbon isotopic fractionation occurred under our study conditions, and the carbon isotope data for acetaldehyde and acetone could be determined via the mass balance equations with excellent reproducibility (precision). In conclusion, the carbon isotope data were reproducible and no isotopic fractionation occurred during the processes of the formation and decomposition of carbonyl-$NaHSO_3$ and derivatization with cysteamine. The results allow the calculation of the $\delta^{13}C$ values of acetaldehyde and acetone. Using this method, it is possible to obtain the carbon isotope data of atmospheric acetaldehyde and acetone.

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