CHINESE JOURNAL OF ANALYTICAL CHEMISTRY
Volume 39, Issue 11, November 2011
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: Chin J Anal Chem, 2011, 39(11), 1653–1658.

RESEARCH PAPER

Determination of Airborne Dicarbonyls by HPLC Analysis Using Annular Denuder/Filter System Coated with 2,4-Dinitrophenylhydrazine

FENG Yan-Li[1,*], MU Cui-Cui[1], FU Zheng-Ru[1], CHEN Ying-Jun[2]

[1] Institute of Environmental Pollution and Health, School of Environmental and Chemical Engineering, Shanghai University, Shanghai 200444, China

[2] Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai 264003, China

Abstract: A HPLC method was developed using an annular denuder/filter pack sampling system coated with 2,4-dinitrophenylhydrazine (DNPH) for collecting gas- and particle-phase dicarbonyl compounds in the atmosphere. DNPH was used as a derivatizing agent to coat the denuders and the filters, when air flowed through the sampling system, the gases were absorbed and reacted with DNPH on the denuders while particles proceeded along the denuders and then analyzed by HPLC. The samples were extracted, concentrated and subjected to HPLC analysis. The sampling conditions of the system were investigated by a series of sampling experiments. The results indicated that when the coating DNPH solution was 0.47 g L^{-1}, the optimum collection efficiency was obtained at a flow rate of 4 L min^{-1} for a sampling duration of 4–5 h. The collection efficiencies of glyoxal and methylglyoxal were 82% and 85%, respectively, which were determined using Tedlar bags. The method was applied to measure dicarbonyl compounds in the atmosphere.

Key Words: Dicarbonyls; Annular denuder/filter pack system; 2,4-Dinitrophenylhydrazine; High performance liquid chromatography; Glyoxal; Methylglyoxal

1 Introduction

Dicarbonyl compounds are formed by the photooxidation of volatile organic compounds (VOCs) in the atmosphere[1]. On the one hand, free radicals are formed during further photolysis of dicarbonyl compounds, which affect the atmospheric oxidation[1]. On the other hand, dicarbonyl compounds such as glyoxal and methylglyoxal can contribute to the formation of secondary organic aerosol (SOA) by means of gas/particle partition[2]. There are two main mechanisms about SOA formation: the first is reversible partition to particles or aerosols (gas/particle partition) and the second is irreversible uptake to the particle phase and chemical reactions in the particle phase[3]. Both field and smog chamber studies have indicated the uptake of glyoxal and methylglyoxal by aerosol particles, and the heterogeneous reactions of dicarbonyls such as glyoxal and methylglyoxal can contribute significantly to SOA[4–7].

SOA is an important part of the tropospheric aerosols, which are related to climate change, atmospheric chemistry and environmental health effects, etc. SOA has been received wide attention recently[8–10]. Therefore, people show more and more concerns to dicarbonyl compounds. Because of the low concentrations of dicarbonyl compounds (10–100 ng m^{-3}, approximately two orders of magnitude lower than formaldehyde), strong polarity and high water solubility, the determination of dicarbonyl compounds is difficult. Most studies of carbonyl compounds have focused on

Received 15 March 2011; accepted 4 July 2011
* Corresponding author. Email: fengyanli@shu.edu.cn
This work was supported by the National Natural Science Foundation of China (No. 40973071) and Shanghai Rising-Star Program of China (No. 09QA142100).

DOI: 10.1016/S1872-2040(10)60481-1

monocarbonyls such as formaldehyde, acetaldehyde, and acetone[11]. However, a little is known about dicarbonyl compounds[12,13]. Furthermore, dicarbonyl compounds exist both in gas and particle phases in the atmosphere, which increase the sampling difficulties[14–16]. An annular denuder/filter pack system has good effects for gas/particle partitioning of semi-volatile organic compounds[17–19]. Bao *et al*[20] (2009) determined dicarbonyl compounds in gas and particle phases by an annular denuder/filter pack system. More and more researchers are using this sampling system to study the dicarbonyls in gas and particle phases recently[16–19].

On the basis of our previous study[21], a method was developed using an annular denuder/filter pack system combining with DNPH-HPLC for simultaneous detection of dicarbonyl compounds in gas and particle phases. The reaction of DNPH with carbonyls is quick and easy to elute, which could improve the collection efficiency in a short sampling time. In this study, the method was optimized to determine glyoxal and methylglyoxal in the atmosphere.

2 Experimental

2.1 Instruments and reagents

A Lab2000 vacuum glove box (Etelux Corp., Beijing, China) was used in the experiment. Chromatographic separations were performed on a Waters Alliance HPLC system (Waters Corp., USA) with a Waters Sunfire-C18 column (250 mm × 4.6 mm × 5.0 μm). An annular denuder/filter pack system was purchased from URG Corpotion, USA. Tedlar bag was from SKC Corporation, USA.

Acetonitrile (ACN) was purchased from Merck Corporation, Germany. Tetrahydrofuran and DNPH were from Fluka Corporation, USA. DNPH was recrystallized three times from HPLC grade ACN before use. Glyoxal (39% in water) was purchased from West Chester Corporation and Methylglyoxal (40% in water) was from sigma-Aldrich Corporation, USA. Ultrapure water was prepared using a Milli-Q system (Millipore Milford, MA, USA). Quartz fiber filters (QFF) were from Whatman Corporation, UK.

2.2 Sampling device

The sampling system consisted of an annular denuder and filter pack (as shown in Fig.1). A cyclone with a cut-off diameter of 2.5 μm was placed at the inlet of the system to remove coarse particles and was followed by a denuder impregnated with potassium iodide to eliminate ozone from the air sample to prevent oxidation during the procedure of collecting carbonyl compounds. The annular denuder (URG-2000-30, 500 mm) was a four-channel glass tube (the outermost layer was brass), the inner wall of which was coated with DNPH-ACN solution (0.47 g L^{-1} DNPH, 1.5 % HCl) to collect the carbonyls in the gaseous phase, followed by a Teflon filter pack (URG-2000-30F, #47) with three quartz fiber filters in tandem (Ø 47 mm), which were impregnated with DNPH to collect the particle-phase carbonyls. The first filter was used to collect aerosol-phase carbonyls，the second and the third filters were used to collect any dicarbonyls that may either break through from the annular denuder or evaporate from the particles collected on the first filter during sampling.

2.3 Sample preparation

2.3.1 Gas-phase samples

After sampling, the gas-phase samples were extracted in 5 mL of ACN from the annular denuders immediately. The capped denuder was rolled back and forth for 1 min within the glove box filled with high-purity nitrogen. Each denuder was extracted three times in “rolling rinse” mode[22], and then the three extracts were combined and concentrated to 200 μL under a gentle stream of nitrogen and injected into HPLC directly. The DNPH-HPLC method was described in the literature[23].

2.3.2 Particle-phase samples

After sampling, the filters were stored at −4 ºC until analysis. The filters were put into beakers with 2 mL ACN, ultrasonically extracted in an ice-bath for 15 min, and then rinsed with 3 mL of ACN, concentrated to 200 μL and analyzed by HPLC[21].

3 Results and discussion

3.1 Quality assurance and quality control

The quartz fiber filters were heated at 450 ºC for 4 h and wrapped with cleaned aluminum foil before use. The blank denuder and filter were coated with DNPH and extracted with

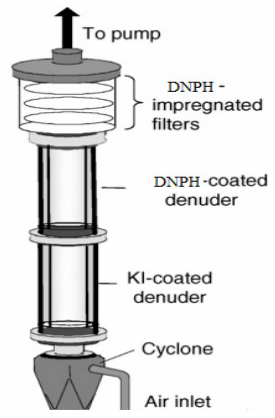

Fig.1 Annular denuder/filter pack sampling system

5 mL of ACN repeatedly, concentrated to 200 μL and analyzed by HPLC.

A series of standard samples were prepared and separated under the same chromatographic conditions. External standard method was used for quantification. Five glyoxal and methylglyoxal standards (0.02, 0.08, 0.1, 0.3 and 1 mg L^{-1}) were prepared and mixed with appropriate acidified DNPH and sealed at room temperature for 4 h. The correlation coefficients (R^2) of the standard curve were higher than 0.998. The lowest concentration of the derivatized standard was analyzed seven times by HPLC continuously. The limit of detections (LODs) of glyoxal and methylglyoxal were 2.52 and 19.3 μg L^{-1}, respectively. One blank denuder and one blank filter were analyzed during each sampling run to detect target dicarbonyls. The concentrations of glyoxal and methylglyoxal were below the detection limit in blank denuder and blank filter. The HPLC chromatograms of the blank denuder/filter sample were shown in Fig.2.

3.2 Collection efficiency

The annular denuder has four-channel glass tubes, the inner wall of which was coated with DNPH as a sink for gas-phase carbonyls. During the sampling procedure, the mixture of gas and particle flowed through the denuder at an appropriate flow rate, and the gas molecules had much greater diffusion coefficients compared with the particles. Thus, the gas molecules collided with the inner wall of the tubes with higher frequency and were absorbed onto the walls, whereas the small particles could pass through the denuder smoothly without loss and collected by the filters[24]. To test the collecting efficiency, the standard gas was introduced into the Tedlar bag (100 L) and then collected by the annular denuder and the silica-gel Sep-Pak cartridge, respectively.

The bag was flushed at least three times with high-purity nitrogen (N_2) before use. When the bag was filled to about 60 L of N_2, a mixed standard of glyoxal and methylglyoxal (50 μL, 10 μg m^{-3}) was injected into the bag with a gas-tight syringe through a septum. Liquid vaporization was assisted by gently heating the bag with a hair dryer. The bag was also gently shaken to facilitate uniform distribution of carbonyls.

The collection efficiency was investigated with testing atmospheres generated from liquid vaporization in the Tedlar bag. The wall loss was characterized by measuring the carbonyl content in the bag using the well-established DNPH/HPLC method. Three aliquots of carbonyl standard mixture were prepared, two of which were injected into the Tedlar bag to produce test atmosphere and collected by the DNPH-coated silica cartridge and the annular denuder respectively, and the other one was directly mixed with the DNPH solution. The collection efficiencies of glyoxal and methylglyoxal were found to be 82% and 85%, respectively, considering the adsorption of the bag wall.

3.3 Elution efficiency and recoveries

To determine the elution efficiency of solvent, the denuder was eluted five times with an appropriate amount of ACN, and then concentrated to 200 μL by nitrogen separately and analyzed by HPLC. The results showed that the first three elution concentrations of glyoxal and methylglyoxal accounted for 75%, 23% and 2%, respectively, and the fourth and fifth were below the detection limit. Therefore, the annular denuder samples were washed three times with 5 mL of ACN separately and combined together to attain good extraction efficiency.

The filter samples were put into the beaker with addition of 2.0 mL ACN, then extracted in an ice-bath by ultrasonic vibration for 15 min, and rinsed with 3 mL of ACN for three times. The extracts were mixed and concentrated to 200 μL, and then analyzed by HPLC. Then 2 mL of ACN was added to re-extract the filter again and the detected target carbonyls were all found to be below the detection limit. Therefore, it is enough to efficiently elute the target carbonyls by the following steps: after ultrasonic extraction with 2.0 mL of ACN, the filter samples were washed three times with 1.0 mL of ACN.

To test the recovery solvent of elution, the underived standard solution of target carbonyls was added to the annular

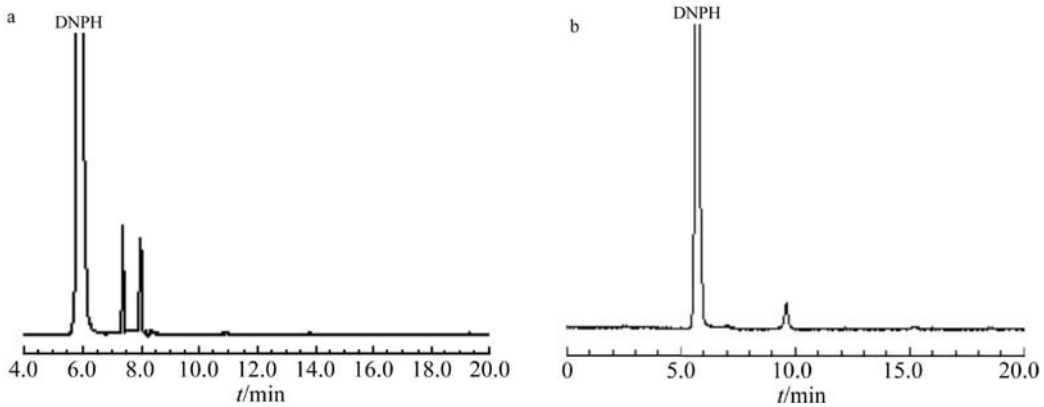

Fig.2 HPLC chromatograms for blank denuder (a) and filter (b)

denuder and filter coated with DNPH in the experiment. After evaporating to dryness, the annular denuders and filters were extracted separately by the method described earlier and detected. The experiment was repeated three times, and the recoveries of glyoxal and methylglyoxal were found to be 78% and 82%, respectively.

3.4 Annular denuder system sampling conditions

Sampling at higher flow rates may reduce the collection efficiency of carbonyls, and the gaseous carbonyls do not have enough time to react with the DNPH on the inner wall of the annular denuder and to be collected on the filters. Moreover, the high flow rate would increase the deposition of particulate matter and make the third filter break through. In order to ensure the collection efficiency of the annular denuder/filter pack system, the denuders were coated with 0.47 g L^{-1} and the sampling flows were conducted at 2, 3, 4, 5 and 6 L min^{-1} with the sampling time of 3, 4, 5, 6, 8, 12 and 24 h, respectively. The third filters were detected to check the breakthrough. The results are listed in Table 1. At all these sampling flow rates, when the sampling time was more than 8 h, the breakthrough was detected. The breakthrough happened when the sampling time was more than 4 h at flow rates of 5 and 6 L min^{-1} and when the sampling time was more than 6 h at a flow rate of 4 L min^{-1}.

As shown in Fig.3, when DNPH concentration was 0.47 g L^{-1}, the concentration of glyoxal was higher at a flow rate of 4 L min^{-1}, though the concentrations of methylglyoxal varied irregularly, which could still indicate the effect of the sampling time and flow rate on the collecting efficiency. Therefore, 4 L min^{-1} was chosen as the sampling flow rate, and the sampling time was 4 h to 5 h for the annular denuder/filter pack system in this experiment.

3.5 Field sampling and analysis

The developed method was employed in a field study at the roof of buildings D, Baoshan Campus, Shanghai University, during July 31 to August 3, 2010. The samples were collected at 4 L min^{-1}, the sampling time was 5 h, and the sampling periods were 6:30–11:30, 11:30–16:30 and 16:30–21:30, respectively. A total of 10 samples were collected. The HPLC chromatograms are shown in Fig.4.

Five-field blank samples were also processed in the same way as real samples according to the aforementioned method. No target dicarbonyls were detected for field blanks. The average concentrations of gas- and particle-phase glyoxal in the ambient air were 1.30 and 0.39 μg m^{-3}, respectively; the average concentrations of gas- and particle-phase methylglyoxal

Table 1 Concentrations of glyoxal and methylglyoxal at different sampling times and flow rates

Sampling flow rate (L min^{-1})	Glyoxal (μg m^{-3})							Methylglyoxal (μg m^{-3})						
	Sampling time (h)							Sampling time (h)						
	3	4	5	6	8	12	24	3	4	5	6	8	12	24
2.00	0.23	0.51	0.39	0.47	0.64*	0.43*	0.29*	0.70	0.58	0.51	0.41	0.34*	0.17*	0.14*
3.00	0.21	0.47	0.31	0.32	0.42*	0.30*	0.21*	1.70	1.02	0.49	0.59*	0.21*	0.14*	0.10*
4.00	0.34	0.58	0.41	0.30*	0.29*	0.21*	0.20*	1.31	1.06	0.52	0.52*	0.31*	0.18*	0.10*
5.00	0.15	0.31	0.29*	0.24*	0.29*	0.19*	0.16*	0.43	0.76	0.38*	0.40*	0.18*	0.12*	0.06*
6.00	0.12	0.24	0.21*	0.18*	0.28*	0.20*	0.15*	0.54	0.66	0.34*	0.29*	0.12*	0.09*	0.06*

* Breakthrough.

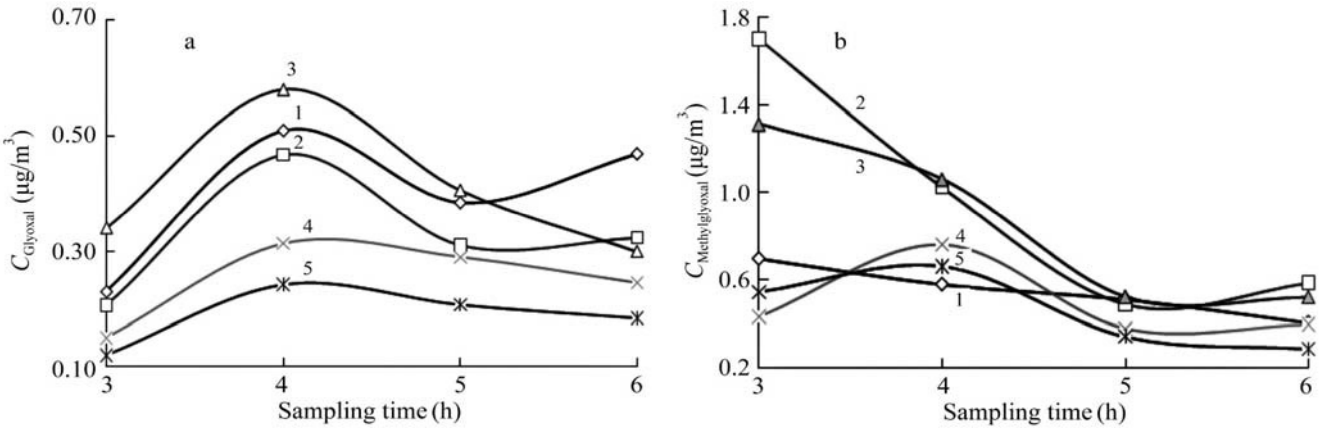

Fig.3 Impact of sampling time and sampling flow rate on the concentrations of dicarbonyls (a: Glyoxal, b: Methylglyoxal)

Sampling flow rates for 1–5 are 2, 3, 4, 5 and 6 L min^{-1}, respectively

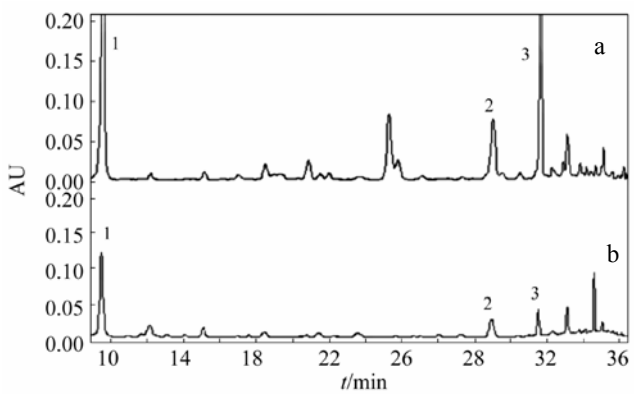

Fig.4 HPLC chromatogram of carbonyl compounds of annular denuder (a) and filter samples (b)

1. DNPH; 2. Glyoxal; 3. Methylglyoxal

were 0.91 and 0.30 μg m^{-3}, respectively. As shown in Fig.5, the average concentrations of glyoxal were higher than those of methylglyoxal. What is more, the gas-phase concentrations of both compounds were higher than those of the particle phase.

As shown in Fig.6, the gas/particle partitioning values of the two dicarbonyls have a common trend. The gas/particle partitioning ratio was lower in the evening than during the day. The reason was that dicarbonyls would exist in the particle phase at lower temperatures. This was similar to the result in the literature[13]. The gas/particle partitioning ratio of glyoxal was larger than that of methylglyoxal. But the gas/particle partitioning value of glyoxal was higher at noon than in the morning; in contrast, the gas/particle partitioning ratio of methylglyoxal was higher in the morning.

4 Conclusions

A method was developed to collect and extract dicarbonyl compounds (glyoxal, methylglyoxal) in gas and particle samples with an annular denuder/filter-pack system coupled with DNPH-HPLC. When the coating DNPH was 0.47 g L^{-1} for the annular denuder/filter pack system, the concentrations of the two dicarbonyls were higher at a sampling time of 4–5 h and a sampling flow rate of 4 L min^{-1}. The extraction solvents were 15 and 5 mL ACN, respectively, for the annular denuder and the filter. The method was applied to determine the dicarbonyl compounds in the atmosphere. Both glyoxal and methylglyoxal were detected in all the 10 samples. The average glyoxal concentrations of gas and particle phases were 1.30 and 0.39 μg m^{-3}, respectively, and the average methylglyoxal concentrations of gas and particle phases were 0.91 and 0.30 μg m^{-3}, respectively. By this method, it is feasible to predict the gas/particle partitioning behavior of dicarbonyl compounds, which is helpful in understanding their potential contribution to SOA formation.

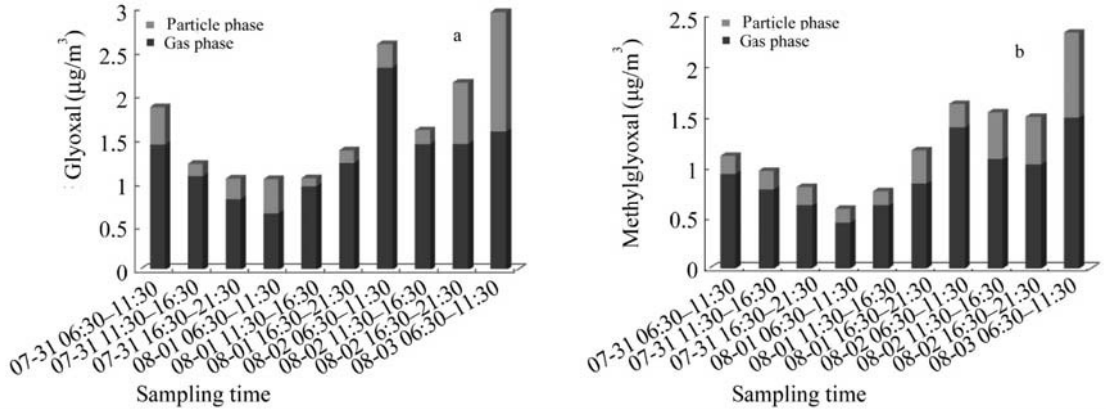

Fig.5 Comparison of glyoxal and methylglyoxal concentrations with gas and particle phases (a: Glyoxal, b: Methylglyoxal)

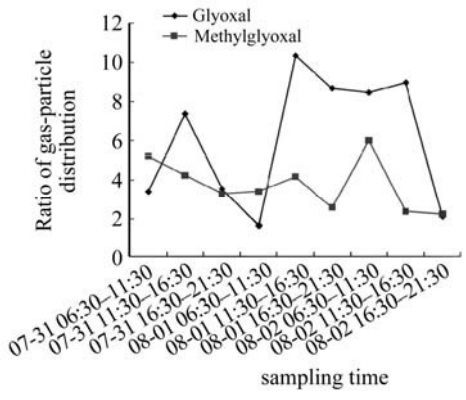

Fig.6 Trends of gas-particle partition ratio with time

References

[1] Spaulding R S, Schade G W, Goldstein A H, Charles M J. *J. Geophy. Res.,* **2003**, 108 (D8): 4247

[2] Healy R M, Wenger J C, Metzger A, Duplissy J, Kalberer M, Dommen J. *Atmos. Chem. Phys.,* **2008**, 8(12): 3215–3230

[3] Volkamer R, Martini F S, Molina L T, Salcedo D. *Geophys. Res. Lett.,* **2007**, 34(19): L19807

[4] Jang M, Czoschke N M, Lee S, Kamens R M. *Science,* **2002**, 298(5594): 814–817

[5] Jang M, Czoschke N M, Northcross A, Cao G, Shaof D. *Environ. Sci. Technol.,* **2006**, 40(9): 3013–3022

[6] Liggio J, Li S M, McLaren R. *J. Geophys. Res.,* **2005**, 110: D10304

[7] De Hann D O, Corrigan A L, Smith K W, Stroik D R, Turley J J. *Environ. Sci. Technol.,* **2009**, 43(8): 2818–2824

[8] Bai Z P, Li W F. *Chinese Journal of Process Engineering,* **2008**, 8(1): 202–208

[9] Xie S D, Tian X X. *Progress in Chemistry,* **2010**, 22(4): 727–733

[10] Ye X N, Chen J M. *Progress in Chemistry,* **2009**, 21(2): 288–296

[11] Grosjean D, Grosjean E, Moreira L F R. *Environ. Sci. Technol.,* **2002**, 36(7): 1389–1395

[12] Matsunaga S, Mochida M, Kawamura K. *J. Geophys. Res.,* **2004**, 109: D04302

[13] Matsunaga S, Kato S, Yoshino A, Greenberg J P, Kajii Y, Guenther A B. *Geophys. Res. Lett.,* **2005**, 32: L11805

[14] Murata-Kamiya N, Kamiya H. *Nucleic Acids Research,* **2001**, 29(16): 3433–3438

[15] Grosjean D, Grosjean E, Gertler A W. *Environ. Sci. Technol.,* **2001**, 35(1): 45–53

[16] Ortiz R, Hagino H, Sekiguchi K, Wang Q, Sakamoto K. *Atmos. Res.,* **2006**, 82(3-4): 709–718

[17] Matsunaga S, Mochida M, Kawamura K. *Atmos. Environ.,* **2003**, 37(15): 2045–2050

[18] Ortiz R, Enya K, Sekiguchi K, Sakamoto K. *Atmos. Environ.,* **2009**, 43(2): 382–388

[19] Temime B, Healy R M, Wenger J C. *Environ. Sci. Technol.,* **2007**, 41(18): 6514–6520

[20] Bao L, Matsumoto M, Kubota T, Kazuhiko S, Wang Q, Sakamoto K. *Atmos. Environ.,* **2009**, doi: 10.1016/j.atmosenv. 2009.09.014

[21] Mu C C, Feng Y L, Zhai J Q, Zou T, *Chinese J. Anal. Chem.,* **2010**, 38(11): 1573–1577

[22] Swartz E, Stockburger L. *Environ. Sci. Technol.,* **2003**, 37(3): 597–605

[23] Huang J, Feng Y, Li J, Xiong B, Feng J, Wen S, Sheng G, Fu J, Wu M. *J. Atmos. Chem.*, **2008,** 61(1): 1–20

[24] Berg J M, James D L, Berg C F, Toda K, Dasgupta P K. *Anal. Chim. Acta,* **2010**, 664(1): 56–61