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Technical Note: Concerns on the Use of Ozone Scrubbers for Gaseous Carbonyl Measurement by DNPH-Coated Silica Gel Cartridge

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ABSTRACT

2,4-Dinitrophenylhydrazine (DNPH) is a typical derivatizing agent coated on sorbent cartridges for detection of carbonyl compounds at ambient levels. However, airborne oxidant of ozone (O_3) can react with DNPH to form side products that can interfere with the accurate detection of carbonyls. It is the most critical interferer degrading carbonyl-DNP-hydrazone formed on the cartridge during sampling, resulting in underestimation of carbonyl concentrations; this strong oxidant can be removed by installing a denuder or scrubber coated or filled with potassium iodide (KI) upstream. The purpose of this study is to demonstrate and discuss the usage of novel KI-filled ozone traps in affecting carbonyl collection efficiency of DNPH-coated silica gel cartridges in field and laboratory settings. Results of the study showed that measured carbonyls concentrations were 4.9–13.5% lower in samples collected without any ozone traps compared to those collected with a commercially available ozone scrubber or KI denuder. Although ozone can be reduced efficiently by KI, both environmental relative humidity (RH) and byproducts formed from the oxidation of KI with ozone, namely iodine (I_2) and hydroxyl ion (OH^-), can inhibit derivatization kinetics and contribute to degradation of the carbonyl-DNP-hydrazones formed during sampling. Placement of an acid-permeated polyethylene filter between the ozone scrubbers and the DNPH-coated cartridge notably improved carbonyl collection efficiency by neutralizing the byproduct OH^-. End-users of the DNPH method should consider these findings and evaluate the performance of ozone scrubbers accordingly during sampling events.

Keywords: Carbonyls; DNPH; Ozone; Relative humidity; Potassium iodide.

INTRODUCTION

Method TO-11A specified by the United States Environmental Protection Agency (U.S. EPA) in the Compendium of Methods is the international standard for determination of aldehydes and ketones in air using active sampling onto 2,4-dinitrophenylhydrazine (DNPH)-coated solid sorbent cartridges (USEPA, 1999). Nonetheless, its potential shortcomings in measurement have been reported in published studies. Nitrogen dioxide (NO_2) can react with DNPH to form 2,4-dinitrophenylazide (DNPA) which has chromatographic properties similar to those of formaldehyde-DNP-hydrazone (or co-called formaldehyde-DNPH derivative), leading to co-elution problems (Grömping *et al.*, 1993; Karst *et al.*, 1993; Grömping and Cammann, 1996; Ban-Weiss *et al.*, 2008). Tang *et al.* (2004) further suggested that ambient nitrogen monoxide (NO) can oxidize to NO_2 while an ozone scrubber is installed upstream. Another identified interferer to formaldehyde-DNP-hydrazone formation is 2,4-dinitrochlorobenzene (DNCB), originating from reaction of hydrochloric acid with DNPH (Pötter and Karst, 1996). Furthermore, unsaturated carbonyls such as acrolein and crotonaldehyde cannot be accurately quantified using the DNPH method (Schulte-Ladbeck *et al.*, 2003; Ho *et al.*, 2011).The double-bond-containing derivatives eventually undergo polymerizations with DNPH, causing negative or positive artifacts in the carbonyl quantifications (Ho *et al.*, 2011).

The most critical interferer to the DNPH is ozone (Arnts and Tejada, 1989; Sirju and Shepson, 1995; Achatz *et al.*, 1999). Ozone can degrade carbonyl-DNP-hydrazone formed on the cartridge during sampling, resulting in underestimation of carbonyl concentrations. The degradation products, however, potentially co-elute with the target carbonyl-DNP-hydrazone causing misidentification and inaccurate results. Ozone can also react with DNPH simultaneously,

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leading to less availability of DNPH for derivatization and thus decreasing collection efficiency of the cartridge. Such artifacts, either negative or positive, may be eliminated by installing a copper oxide-coated and a potassium iodide (KI)-coated denuder or KI-filled ozone scrubber upstream; under atmospheric conditions, the oxidants at ambient level can be removed efficiently (Helmig, 1997; Possanzini and Di Palo, 1999).

Even though the shortcomings have been demonstrated in published literature (Ho *et al.*, 2011; Herrington and Hays, 2012), many end-users who are currently applying the DNPH-coated sorbent cartridge method are unaware all of them. Lack of awareness for such issues can lead to inaccurate carbonyl concentration measurements and consequently defraud relative atmospheric studies or computational models based on the data set. The focus of this study is to analyze the utilization and applicability of ozone scrubber in carbonyl measurement using DNPH-coated silica gel cartridges.

METHODS

Sample Collection

24-hour integrated samples were collected at two sites from February 1, 2010, to February 14, 2010. The air samples were collected into silica cartridges impregnated with acidified DNPH (Sep-Pak DNPH-silica, 55–105 µm particle size, 125Å pore size, Waters Corporation in Milford, MA, USA) at a flow rate of 0.7 L/min. The flow rates were checked in the field in the beginning and at the end of each sampling period using a calibrated flow meter (Gilibrator Calibrator, Gilian Instrument Corp., West Caldwell, NJ, USA). A Teflon filter assembly (Whatman Inc., Clifton, NJ, USA) was installed in front of the air sampling stream to remove any particulate matters. A cartridge was designated as a field blank on each sampling trip and was handled the same way as the sample cartridges. When computing air concentrations of carbonyl, the measured amounts of carbonyls detected in the cartridges were corrected based on the field blank cartridge. The DNPH-coated cartridges were stored in a refrigerator at < 4°C after sampling and before analysis. Meteorological parameters, including temperature, air pressure, relative humidity (RH), and rainfall were recorded during the sampling period.

Preparation of Ozone Traps

In order to investigate the oxidant removal efficiency of an ozone scrubber, three sets of co-located samples were collected: one set without any oxidant-removing device; one set with a commercially available ozone scrubber (Sep-Pak, Waters Corporation); and one set with a KI-filled denuder that is one meter in length, 3/8 inch in outer diameter, and 1/4 inch in inner diameter (Spaulding *et al.*, 1999).The commercial ozone scrubber was kept at 35°C to prevent water condensation during sampling (USEPA, 1998). The KI-coated denuder was prepared according to Method TO-11A detailed in the U.S.EPA. Compendium of Methods; it consisted of a copper tube coated internally with a saturated solution of KI (solubility = 1.40 g/L at 20°C) and in water (Lide, 1990). The tube was dried, coiled, and housed at 66°C during sample collection (USEPA, 1998).

Determination of Collection Efficiency

Collection efficiencies were measured under field and laboratory conditions by sampling carbonyls with two identical cartridges connected in series. Liquid vaporization to a bag was used in preparing gaseous standards for method characterization. (Ho and Yu, 2002, 2004). Gas phase standards of carbonyls at 5 parts per billion by volume (ppbv) were prepared in a 100-liter Tedlar bag (SKC Inc. Eighty Four, PA, USA) by injection of known amounts of liquid standards (GC grade, Sigma, St. Louis, MO, USA) in methanol (HPLC grade, Alltech, Dearfield, IL, USA). The bag was cleaned by filling it with high purity nitrogen gas and evacuating it with a pump for at least three times before use. The air volume in the bag was determined by filling the bag at a set flow rate controlled by a rotor meter, which was calibrated with a flow calibrator (Gilibrator Calibrator, Gilian Instrument Corp.). The bag was filled to about 80 liters. Then a mixture containing known amounts of carbonyls in methanol 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 the uniform distribution of carbonyls in the bag. The test atmosphere generated in this manner had a RH less than 1%. Test atmospheres of 75% RH were generated by injecting the amount of water required to achieve this RH under experimental conditions. Ozone in the testing atmospheres was produced by an ozone generator (Model 2000, Jelight Company Inc., Irvine, CA, USA). For safety precautions, the preparation of the carbonyl standards in methanol was carried out in a fume hood and the sampling pump exhaust was discharged to the fume hood as well.

Sample Analysis

Each DNPH-coated cartridge was eluted with 2.0 mL of acetonitrile (HPLC/GCMS grade, J&K Scientific Ltd., Ontario, Canada) to a volumetric flask. Testing has been done to demonstrate that DNPH and its derivatives in the cartridge after the 2.0 mL elution were undetectable (Ho *et al.*, 2007). Certified calibration standards were purchased from Supelco (Bellefonte, PA, USA) and diluted into concentration ranges of 0.015–3.0 mg/mL. The cartridge extracts and calibration standards were analyzed by injecting 20 µL of the samples to a high-performance liquid chromatography system (Series 1200, Agilent Technology, Santa Clara, CA, USA) equipped with a photodiode array detector (PAD). The column for separation was a 4.6 × 250 mm Spheri-5 ODS 5 µm C-18 reversed-phase column (PerkinElmer, Norwalk, CT, USA) operated at room temperature. The mobile phase consisted of three solvent mixtures: (A) 6:3:1 (vol./vol./vol.) of water, acetonitrile, and tetrahydrofuran, respectively; (B) 4:6 (vol./vol.) of water and acetonitrile, respectively; and (C) acetonitrile. The gradient program was set at 80% A/20% B for 1 minute, followed by linear gradients to 50% A/50% B for 8 minutes, 100% B for 10 minutes, 100% C for 6 minutes, and finally held at

100% C for 5 minutes. The flow rate was 2.0 mL/min throughout the run. The absorbance at 360 nm and 390 nm were used for identification of the aliphatic and aromatic carbonyls, respectively. Identification and quantification of carbonyl compounds were based on retention times and peak areas of the corresponding calibration standards, respectively. The limit of detection (LOD) was calculated by analyzing a minimum of seven replicates of a standard solution containing the analytes at a concentration of 0.015 µg/mL. It is estimated using the equation LOD = $t_{(n-1,\ 1-\alpha=99\%)} \times S$, where $t_{(n-1,\ 1-\alpha=99\%)}$ is the t-distribution value at $n - 1$ degrees of freedom and S is the standard deviation of the replicates. The LODs of the target carbonyls ranged from 0.002–0.010 µg/mL, which can be converted to 0.032–0.18 µg/m^3, with a sampling volume of 1.01 m^3. The chromatographic peaks were further confirmed by a liquid chromatography/mass spectrometry system (Series 6100, Agilent Technologies) for electrospray ionization (ESI) analysis.

RESULTS AND DISCUSSION

Field Carbonyl Measurement

Two sampling locations were selected in this study to represent urban and rural areas in Hong Kong. The average concentrations and collection efficiencies for 16 carbonyls, defined by USEPA. Method TO-11A as target compounds, are shown in Table 1. The collection efficiencies were calculated as 100% × $(1 - A_b/A_f)$, where A_f and A_b were the amounts of carbonyl collected on the front and the back sampling tubes, respectively. Formaldehyde was the most abundant carbonyl in the sampling sites. Without correcting the concentration values by the measured collection efficiencies, the next abundant carbonyl species were acetaldehyde and acetone. Higher carbonyl concentrations were observed at the urban sampling location compared to those measured at the rural location, suggesting the dominance of anthropogenic sources (e.g., vehicular and cooking emissions) in local carbonyl emissions (Ho and Yu, 2002; Ho *et al.*, 2006; Hwang *et al.*, 2011; Panagopoulos *et al.*, 2011; Han *et al.*, 2012; Ho *et al.*, 2012; Wang *et al.*, 2012). Unsaturated carbonyls including acrolein and crotonaldehyde were detected but their abundances were uncertain or inaccurate. The unsaturated carbonyl DNP-hydrazones can react with excess reagent to form adducts, which could not be quantified accurately due to chromatographic and response factor issues (Schulte-Ladbeck *et al.*, 2003; Ho *et al.*, 2011).

Ozone Influence

The measured carbonyls concentrations were 4.9–13.5% lower for the samples collected without any ozone traps compared to those collected with a commercially available ozone scrubber or KI denuder upstream (see Table 1). For formaldehyde, the decrease was in the range of 5.6–7.7% at the two sites, slightly larger than the value reported by Kleindienst *et al.* (1998) who found a 5% decrease in the reference standard for a DNPH-coated silica gel cartridge in the presence of ozone. The degradation of formaldehyde-DNP-hydrazone is much more significant (20%) on the C_{18} cartridge (Kleindienst *et al.*, 1998). Fig. 1 is a plot of the concentrations of carbonyls having concentrations above the detection limits when a commercially available ozone scrubber and KI denuder are in use. In general, the two ozone traps yielded comparable concentration measurements, and the difference in individual pairs of measurements did not exceed 25%. Each commercially available ozone scrubber contains 1.4 grams of granular KI, having optimum particle size for good mass transfer and flow characteristics (Waters, 2007). The manufacturer notes that the theoretical capacity of an ozone scrubber is 4.2 mmoles of ozone (200 µg), equivalent to the amount in the air at 200 ppbv sampled for 48 hours. A new scrubber was installed for every 24-hour sampling period. The KI denuder is expected to last for six months when a 24-hour sampling of air (with an average ozone concentration of 120 ppbv) is being done once every six days (USEPA, 1998). However, its ozone removal efficiency actually depends on the amount of saturated KI coated internally on the tube. There is no recommended or standard guideline on such amount, thus the lifetime for the KI tube in removal of ozone can vary from laboratory to laboratory or even from batch to batch. In this experiment, the tube was coated with > 20 grams of KI after drying and replaced weekly; therefore it should be noted that its ozone removal efficiency was estimated to be > 99% during sample collections (Possanzini and Di Palo, 1999). We here remind the method end-users that it is critical to test and track the ozone removal efficiency if home-made KI denuder is applied in field samplings.

Collection Efficiency

The collection efficiencies for formaldehyde were ≥ 97% (refer to Table 1), consistent with the report from USEPA, which showed > 95% at sampling rates up to 2.0 L/min (USEPA, 1999). Acetaldehyde had collection efficiencies ranging from 87% to 90%, slightly lower than an examined value of > 95% for all aldehydes at < 1.0 L/min suggested by the cartridge manufacturer (Waters, 2007). A relative low collection efficiency of 80% for acetaldehyde also found by (Lazarus, 1999). Herrington *et al.* (2007) even found that 24-hour acetaldehyde sampling collection efficiencies ranged from 1 to 62%. Except ketones, the collection efficiencies for other monocarbonyls and dicarbonyls were close to 100% as their ambient levels were a magnitude lower than formaldehyde and acetaldehyde. Lower collection efficiencies in the field were observed for acetone and methyl ethyl ketone (MEK), ranging from 90 to 95% and 89 to 94%, respectively. The reaction between DNPH and carbonyl is known as an addition-elimination reaction, beginning with the nucleophilic addition of the -NH_2 group to the C = O group and followed by the removal of a H_2O molecule. The reaction is essentially a two-step reaction of a vapor-solid derivatization (see Fig. 2). In the first step, gaseous carbonyl molecules diffuse onto the solid sorbent surface on which DNPH is immobilized and react with DNPH to form a tetrahedral carbinolamine intermediate. The reaction rate for this reversible step is expected to play a key role in the collection efficiency of carbonyls. In the second step, the carbinolamine intermediate loses a molecule

Table 1. Average concentrations and collection efficiencies for 16 carbonyls defined in U.S.EPA TO-11A method in field.

Symbol	Carbonyls	Urban (temp[a] = 16°C; RH[b] = 58%; O_3[c] = 57 μg/m^3)						Rural (temp = 17°C; RH = 64%; O_3 = 73 μg/m^3)					
		with commercial ozone scrubber		with KI-filled denuder		without ozone trap		with commercial ozone scrubber		with KI-filled denuder		without ozone trap	
		Conc[d]	CE[e]	Conc	CE	Conc	CE	Conc	CE	Conc	CE	Conc	CE
aliphatic aldehydes													
C1	Formaldehyde	9.25	99%	8.89	99%	8.54	97%	2.82	98%	2.87	97%	2.71	93%
C2	Acetaldehyde	3.87	90%	3.67	89%	3.51	83%	1.47	88%	1.38	87%	1.25	81%
nC3	Propionaldehyde	0.41	100%	0.40	100%	0.38	93%	0.23	100%	0.22	100%	0.21	92%
C4n+1	butyraldehyde/isobutyraldehyde	0.27	100%	0.25	100%	0.25	92%	0.13	100%	0.11	100%	0.10	91%
i-C5	Isovaleraldehyde	0.88	100%	0.85	100%	0.82	93%	0.32	100%	0.32	100%	0.29	95%
n-C5	Valeraldehyde	0.28	100%	0.29	100%	0.26	95%	0.067	100%	0.062	100%	0.057	93%
C6	hexaldehyde	0.41	100%	0.42	100%	0.39	96%	0.076	100%	0.072	100%	0.068	95%
aromatic aldehydes													
benz	benzaldehyde	0.32	100%	0.34	100%	0.30	92%	0.21	100%	0.20	100%	0.19	93%
o-tol	o-tolualdehyde	0.11	100%	0.092	100%	0.090	94%	nd	-	nd	-	nd	-
m-tol	m-tolualdehyde	0.17	100%	0.19	100%	0.16	94%	0.081	100%	0.078	100%	0.071	92%
p-tol	p-tolualdehyde	nd[f]	-[g]	nd	-	nd	-	nd	-	nd	-	nd	-
2,5-C6	2,5-dimethylbenzaldehyde	0.08	100%	0.076	100%	0.069	93%	nd	-	nd	-	nd	-
unsaturated aldehydes													
ACRO	acrolein	0.075	100%	0.071	100%	0.068	95%	0.05	100%	0.052	100%	0.045	97%
CROT	crotonaldehyde	0.22	100%	0.21	100%	0.20	93%	0.13	100%	0.11	100%	0.098	95%
ketones													
ACET	acetone	1.27	95%	1.22	93%	1.16	87%	0.65	94%	0.62	90%	0.55	86%
MEK	methyl ethyl ketone	0.42	94%	0.41	93%	0.39	88%	0.36	93%	0.35	89%	0.31	84%

Note:

[a] average temperature; [b] average relative humidity; [c] average ozone concentration; [c] average concentration of carbonyl in unit of μg/m^3

[e] average collection efficiency

[f] below detection limit

[g] no collection efficiency was reported as carbonyl concentration was below detection limit

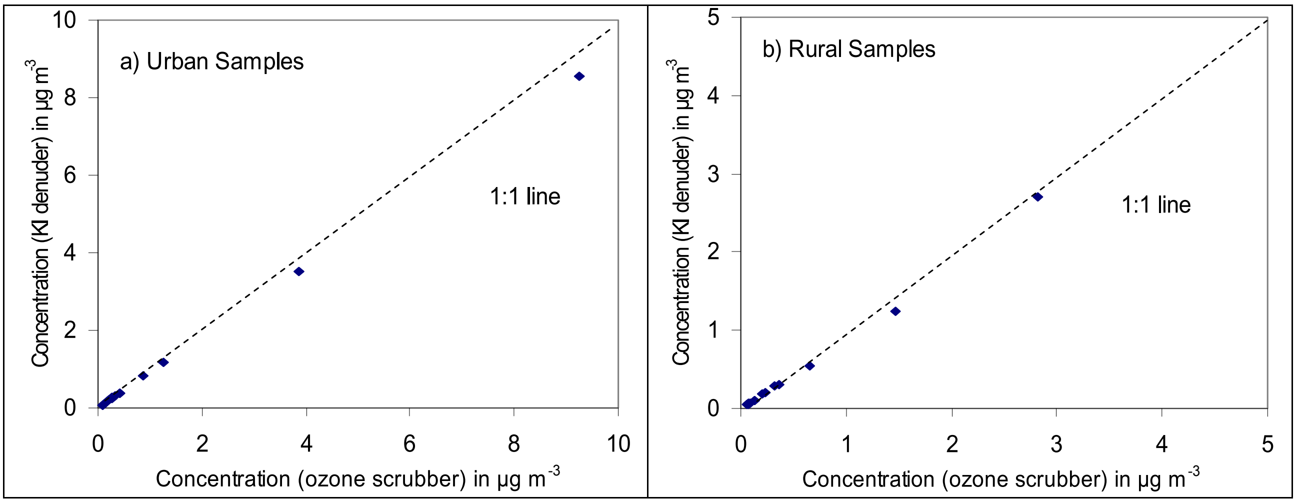

Fig. 1. Comparison of carbonyl concentrations determined with the ozone scrubber and KI-filled denuder: (a) urban samples; (b) rural samples.

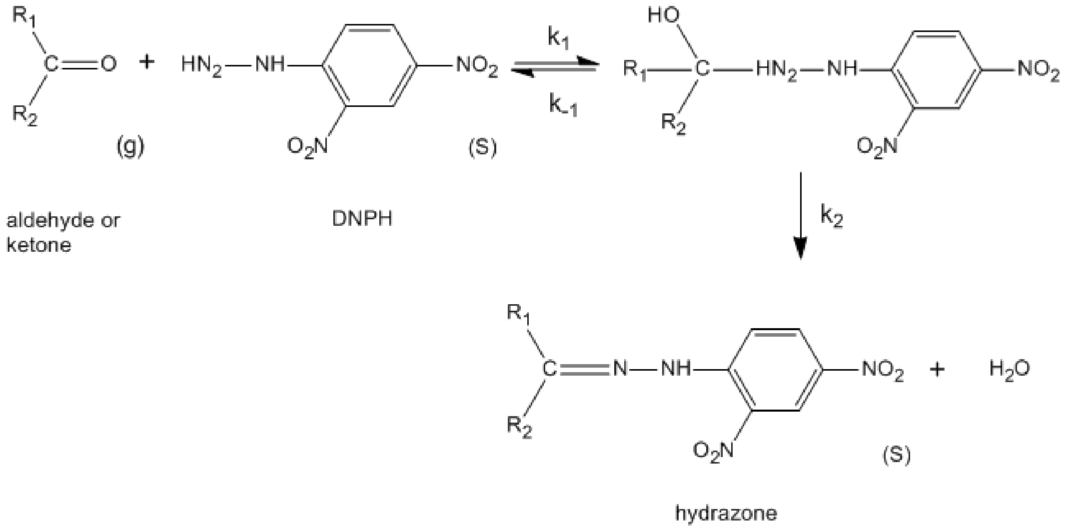

Fig. 2. Bidirectional derivatization reaction of carbonyls with DNPH.

of water to form the hydrazone derivative. In regards to low ketone collection efficiency, the phenomenon may be explained using pure chemistry theories associated with reactivity differences between ketones and aldehydes, and the bidirectional nature of the derivatization reaction. Since water is a product of the reaction, the backward reaction becomes increasingly prominent under humid conditions and becomes more competitive compared to the forward reaction given the lower reactivity of carbonyls (Grosjean and Grosjean, 1996). The results proved that ketone concentrations were undoubtedly underestimated in real sampling. Given a condition of > 90% RH, the actual carbonyl concentrations could possibly be at least 10% less than the measured values. Unfortunately, correction for the measured values based on collection efficiencies is rarely shown explicitly in publications; furthermore, the significance of collection efficiency has not been thoroughly examined in most studies, indicating an imminent need to increase awareness of such circumstance among end-users of the DNPH method.

Ozone Scrubber Affecting Collection Efficiency

Fig. 3 illustrates the effects of ozone and RH on sample collections and measurements, comparing theoretical amounts of standard carbonyls passing through the DNPH-coated cartridge with the experimental values. In the absence of ozone, > 92% of individual carbonyls can be collected efficiently on the cartridge at < 10% RH. However, these values decreased by 3–7% at ozone concentration of 100 ppbv, within the episode levels in Hong Kong (Zhang *et al.*, 2007). The commercially available ozone scrubber was installed upstream during sampling, thus the direct degradation of carbonyl-DNP-hydrazone by ozone should be neglected. Ozone in the gas stream passing through the scrubber or denuder would oxide iodide (I^-) to iodine (I_2) according to Eq. (1):

$$O_{3(g)} + 2I^- + H_2O \rightarrow I_2 + O_{2(g)} + 2OH^- \quad (1)$$

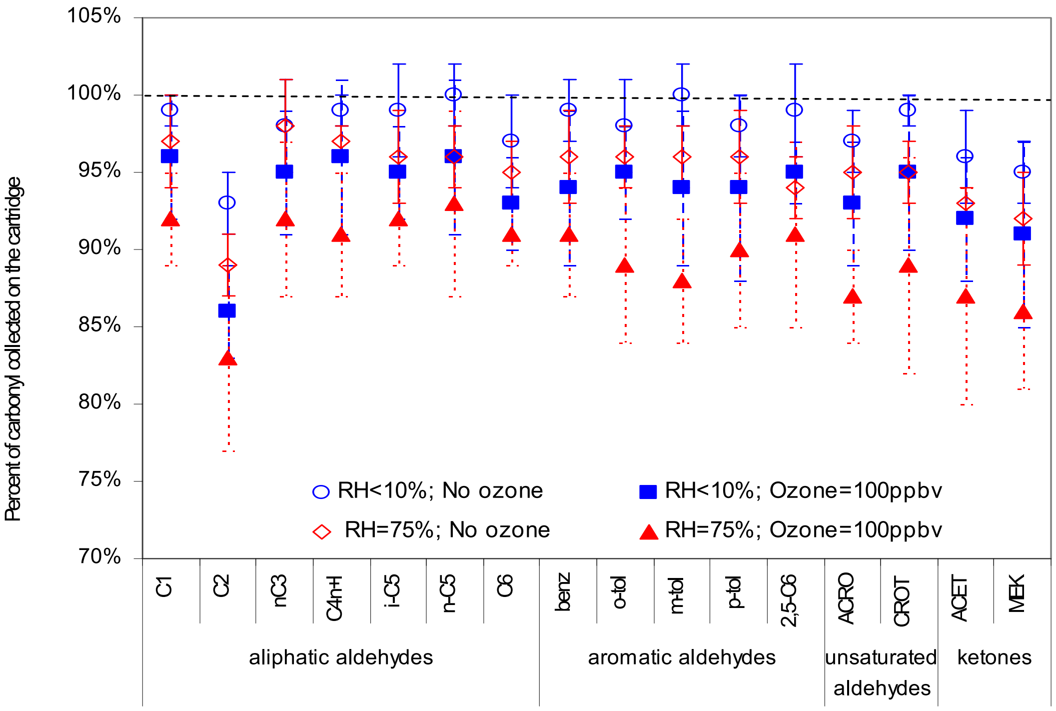

Fig. 3. Carbonyl collections at ozone concentration of 0 and 100 ppbv under RH of < 10% and 75%.

It is noted that the oxidation of KI to form KIO_3 (as shown in Eq. (2) is unlikely to occur during the sampling period because its progression requires a relatively dry environment (Brown *et al.*, 2008).

$$KI_{(s)} + 3O_{3(g)} \rightarrow KIO_{3(s)} + 3O_{2(g)} \qquad (2)$$

With reference to Eq. (1), Helmig and Greenberg (1995) claimed that the use of KI ozone traps may lead to formation of few organic iodine compounds arising from the reaction between sampled organic gases and reactive I_2 or hypoiodite released from reaction of ozone, but no losses of the individual organic trace gases were seen as a result of this mechanism. However, wet KI may potentially react with I_2 to form potassium iodate (KI_3), which is an oxidizing reagent that is in contact with the DNPH-coated cartridge and has the potential to destroy DNPH and carbonyl-DNP-hydrazones (Uchiyama *et al.*, 2012).

The DNPH cartridge had a performance drop (< 10%) for the aldehydes when RH rose from < 10% to 75%, a typical RH level in Hong Kong (Ho and Yu, 2002), in the absence of ozone (see Fig. 3). For the ketones, RH becomes a dominated parameter in controlling derivatization kinetics. The actual amount of acetone and MEK collected on the DNPH-coated cartridge were only 87% and 86%, respectively, of the theoretical values. It is reasonable to conclude that water molecules in the sampled air stream could retain on the polar-based silica gel, resulting in a condition that is more favorable to the backward reaction (k_{-1}) compared to the forward reaction driven by the less reactive ketones (see Fig. 2). The least amounts of carbonyls collected on the cartridges were found at ozone concentration of 100 ppbv at 75% RH. When more ozone is reduced by KI, more KI_3 can possibly be formed. It should also be noted that moist KI in the ozone scrubber can even trap carbonyls before they come into contact with the DNPH-coated cartridge (Uchiyama *et al.*, 2012).

Improvement of Collection Efficiency

The oxidative product of KI_3 cannot be eliminated from the ozone scrubber during sampling. In contrast, it is proposed that the hydroxyl ion (OH^-) formed during the reaction of ozone with KI (Eq. (1)) can move to the DNPH-coated cartridge as well. The alkaline ion increases the pH level on the silica gel, prohibiting the formation of an acidic environment favorable to the forward reaction (k_1) between carbonyls and DNPH; this phenomenon may be classified as the rate-limiting step of the derivatization reaction (see Fig. 2). An improvement was thus proposed to neutralize the OH^- by placing an acid-permeated polyethylene filter between the ozone scrubber and the DNPH-coated cartridge. Fig. 4 shows the schematic diagram of the sampling stream. The filter was permeated in 5% sulfuric acid (weight/weight) and dried in an oven at 90°C to evaporate excessive water. It was then installed in a blank cartridge with the same dimension and connection fittings as the ozone scrubber and DNPH-coated cartridge. Table 2 compares the collection efficiencies for the carbonyls collected in the testing atmospheres. After the acid-permeated filter was installed, collection efficiencies increased significantly in a range of 3–10% in the presence of ozone at 100 ppbv. Under an ozone-free environment, no significant differences (± 3%) in the collection efficiencies were seen between samplings with and without an acid-permeated filter, demonstrating the implausibility of non-polar polyethylene taking up carbonyls in the collection process. The acid-permeated

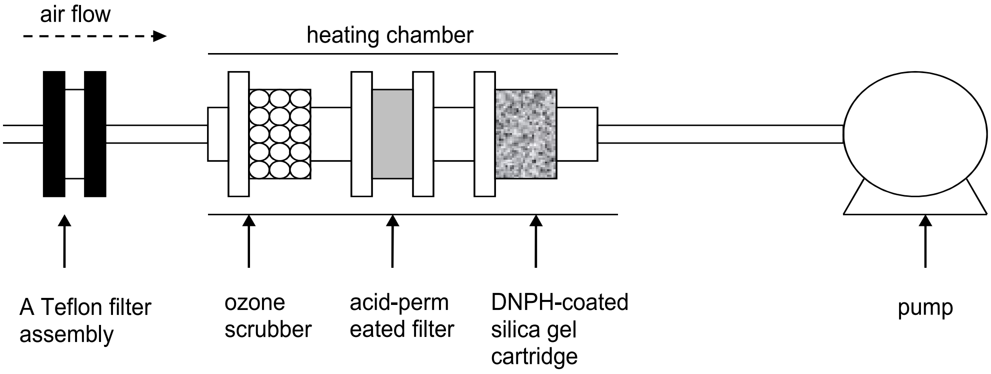

Fig. 4. Schematic diagram of the sampling stream.

Table 2. Collection efficiencies for 16 carbonyls demonstrated in test atmospheres.

		Collection Efficiency			
	Ozone concentration	ND[a]		100 ppbv	
	Acid-permeated filter installed	Equipped	Not equipped	Equipped	Not equipped
aliphatic aldehydes	formaldehyde	100 ± 1%	100 ± 2%	98 ± 3%	91 ± 4%
	acetaldehyde	93 ± 3%	92 ± 2%	91 ± 3%	84 ± 4%
	propionaldehyde	100 ± 2%	99 ± 3%	98 ± 2%	90 ± 5%
	butyraldehyde/isobutyraldehyde	100 ± 2%	98 ± 3%	98 ± 4%	89 ± 6%
	isovaleraldehyde	100 ± 1%	98 ± 3%	97 ± 4%	90 ± 3%
	valeraldehyde	98 ± 3%	99 ± 2%	96 ± 3%	90 ± 2%
	hexaldehyde	99 ± 2%	98 ± 3%	96 ± 3%	88 ± 4%
aromatic aldehydes	benzaldehyde	99 ± 3%	98 ± 3%	97 ± 2%	88 ± 2%
	o-tolualdehyde	100 ± 2%	97 ± 2%	97 ± 2%	87 ± 4%
	m-tolualdehyde	99 ± 2%	99 ± 2%	96 ± 3%	91 ± 5%
	p-tolualdehyde	100 ± 2%	99 ± 1%	95 ± 3%	92 ± 4%
	2,5-dimethylbenzaldehyde	99 ± 2%	100 ± 1%	96 ± 4%	90 ± 3%
unsaturated aldehydes	acrolein	97 ± 1%	97 ± 2%	96 ± 2%	91 ± 3%
	crotonaldehyde	98 ± 3%	96 ± 3%	97 ± 3%	90 ± 2%
ketones	acetone	94 ± 3%	92 ± 2%	92 ± 2%	88 ± 4%
	methyl ethyl ketone	93 ± 2%	91 ± 2%	92 ± 3%	87 ± 5%

[a] below detection limit.

filter offered a thin film to neutralize the OH^- even though water is an end product that potentially increases moisture level in the sampling stream. Persistency of the acid-permeated filter was also examined in ambient environment. Fig. 5 compares the collection efficiencies for the four carbonyls in the daily samples collected with an acid-permeated filter being used for five consecutive sampling days. The results demonstrate that the efficiency of a fresh acid-permeated filter can last for 72 hours with a flow rate of < 1 L/min. It is thus recommended to replace the filter after two consecutive 24-hour sampling periods. The acid-permeated filters should be stored in a organic-free desiccator to prevent absorb any carbonyls and moisture.

Substitutes Used in Ozone Trap

In recent researches, due to shortcomings of KI, chemicals such as trans-1,2-bis-(4-pyridyl)ethylene (4-BPE), trans-1,2-bis-(2-pyridyl)ethylene (2-BPE), and hydroquinone (HQ) have been utilized as ozone scrubber for sampling (Uchiyama and Otsubo, 2008; Uchiyama *et al.*, 2009, 2012). BPE reacts with ozone to form pyridine aldehyde, which can also be derivatized by DNPH; HQ reacts with ozone to form benzoquinone, allowing simultaneous quantifications of ozone as well. However, the reactions between BPE and ozone are highly dependent on RH conditions. 2-BPE exhibits a maximum reaction efficiency of 84% at 32% RH, while 4-BPE attains a maximum reaction efficiency of 82% at 49% RH. The fair reaction efficiencies of these chemicals, compared to 99% efficiency of KI, may still result in the degradation of carbonyl-DNP-hydrazone formed on the DNPH-coated cartridge during sampling, particularly in humid (RH > 80%) areas such as Southern Asian countries; given these observational and experimental results, it is justifiable to replace these chemicals with KI which demonstrates a significantly higher level of efficiency.

CONSLUSIONS

Ozone would degrade carbonyl-DNP hydrazones and also decrease collection efficiency during carbonyl sampling with DNPH-coated cartridge. Either commercial ozone scrubber or home-made KI tube can remove ozone efficiently

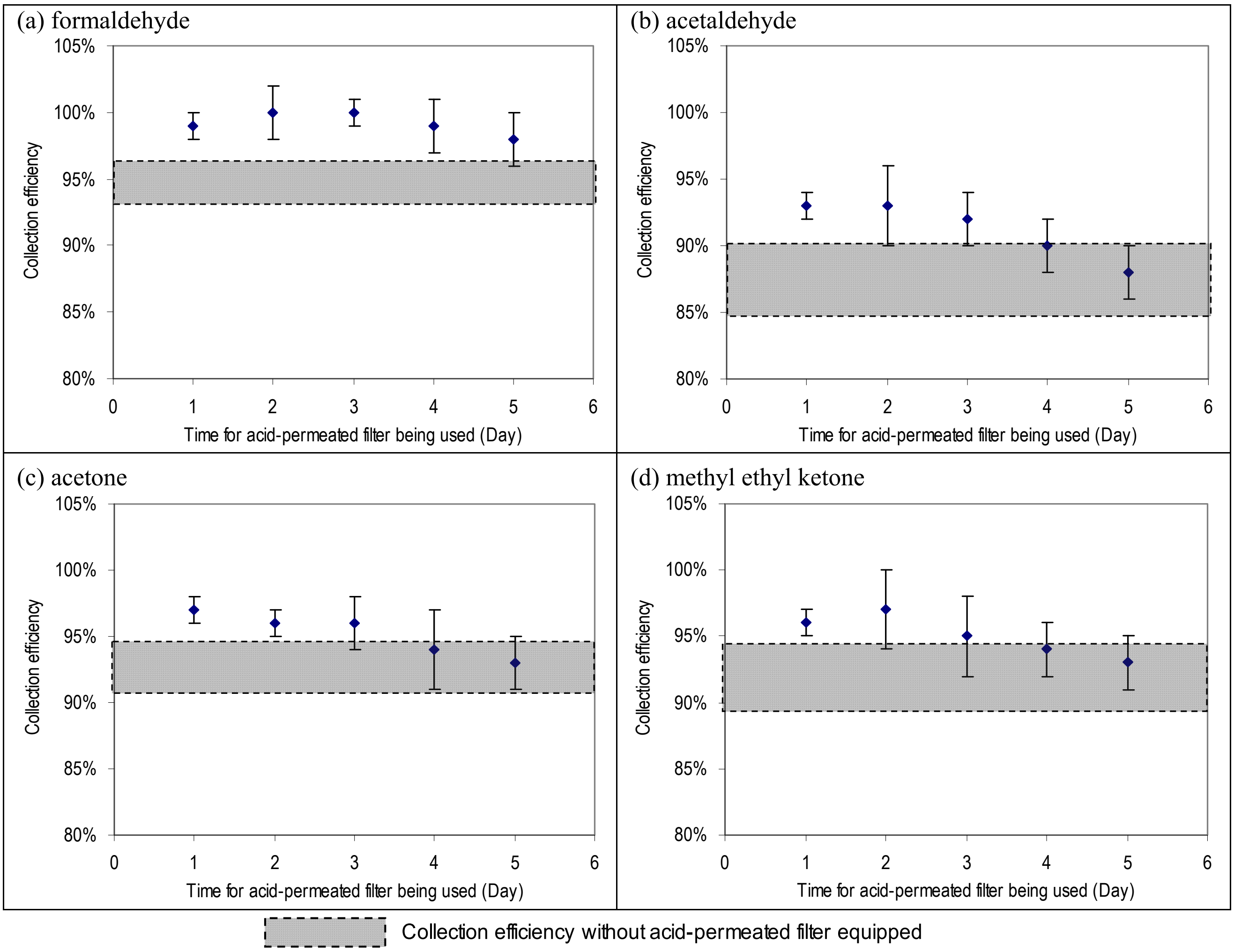

Fig. 5. Persistency test for the acid-permeated filter equipped in carbonyl sampling (temp ranged from 26–32°C; RH ranged from 53–68%; O_3 ranged from 26–57 ppbv; and no raining fall in the sampling dates).

from air stream but may not be sufficient. In-laboratory and ambient sampling tests show that placement of proposed acid-permeated polyethylene filter between the ozone scrubbers and the DNPH-coated cartridge improved carbonyl collection efficiency. The technical approach is essential to advance the collection efficiency for target carbonyls especially ketones.

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