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Biases in Ketone Measurements using DNPH-coated Solid Sorbent Cartridges

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Abstract

Biases associated with carbonyl measurement using active air sampling through a 2,4-dinitrophenylhydrazine (DNPH)-coated solid sorbent cartridge following the U.S. EPA Method TO-11A are known but have not been fully investigated. Ketones are less reactive than aldehydes in the derivatization with DNPH, resulting in poor collection efficiency. Field studies and laboratory experiments demonstrate the uncertainties associated with two ketones (i.e., acetone and methyl ethyl ketone [MEK]). Ketone collection efficiencies are inversely related to relative humidity (RH), sample flow rate, and sample duration. Since water is a product in the bidirectional derivatization of carbonyls, the reverse reaction competes with the forward reaction as RH increases. Laboratory experiments demonstrate that ~35–80% of the ketones can be lost for RH > 50% with a single DNPH cartridge at a temperature of 22±2 °C. Optimal sampling flow rates and sampling durations under high RH need to be determined in various environments to ensure tolerable collection efficiencies.

Keywords:

Ketones, DNPH, relative humidity, and collection efficiencies

1. Introduction

Acetone and methyl ethyl ketone (MEK) are the two most abundant atmospheric ketones in carbonyls. Acetone, a precursor of methylglyoxal that forms secondary organic aerosols,[1-3] has been used as a solvent for paints, varnishes, lacquers, fats, oils, waxes, resins, printing inks, plastics, and glues.[4] Acetone levels of 5.1 μg m^{-3} were reported in Guiyang[5] and 17.8 μg m^{-3} in Guangzhou, China.[6-7] Excessive acetone exposure can cause eye irritation, respiratory distress (e.g., nose, throat, and lung), and ultimately unconsciousness, seizures, coma, and even death. MEK is naturally emitted by volcanoes, forest fires, and biological degradation; and is also a natural component of food.[8] In 2005, the United States Environmental Protection Agency (U.S. EPA) removed MEK from the list of hazardous air pollutants (HAPs), since there was insufficient evidence that manmade MEK caused adverse health or other environmental effects[9]. However, MEK is still being monitored due to its participation in tropospheric ozone (O_3) chemistry. Ambient MEK concentrations range from 0.16–3.45 μg m^{-3} in Guangzhou, China[10-11] to 20 μg m^{-3} in the industrial city of Gumi, Korea.[12]

Real-time analyzers have been developed to measure ambient concentrations of the most abundant carbonyl species such as formaldehyde.[13,14] Solid phase approaches combine ambient sampling and derivatization into a single step to determine carbonyls, including aldehydes and ketones.[15-17] The most commonly used method for simultaneous determination of multiple carbonyls is U.S. EPA Method TO-11A which calls for sampling onto a 2,4-dinitrophenylhydrazine (DNPH)-coated solid sorbent (i.e., silicon gel) cartridge at a flow rate of 0.7 L min^{-1}, followed by solvent elution and high-pressure liquid chromatographic (HPLC) analysis.[18] The DNPH-coated cartridge method has been globally applied for research and in compliance networks. This method has potential interferences, since oxidants (e.g., nitrogen oxide [NO], nitrogen dioxide [NO_2], and O_3) react with the DNPH, forming side-products that bias carbonyl quantification.[19-21] Uncertainties in the determination of unsaturated carbonyls such as acrolein and crotonaldehyde have also been reported,[22,23] owing to double-bond-containing carbonyls that react further with DNPH to form larger molecules.[23]

Collection efficiencies (CEs) for aldehydes have been reported by Herrington et al.[24] and Herrington and Hays.[25] Ketones are less reactive than aldehydes in the derivatization with DNPH and they are affected by sampling conditions. This paper examines the CEs of acetone and MEK under different relative humidities (RHs), flow rates, and sample durations, for ambient sampling and laboratory experiments.

2. Materials and Methods

2.1 Field and Laboratory Sample Collection

Twenty-four hour duration (midnight to midnight) samples were collected at three sites representing urban (Tsim Sha Tsui), suburban (Sai Kung West Country Park), and coastal (Tai Tam Bay) areas in Hong Kong from 10th – 23rd January 2010 (winter) and from 13th – 26th July, 2011 (summer). Ambient samples were collected on silica gel cartridges impregnated with acidified 2,4-DNPH (Sep-Pak DNPH-silica, 55-105 μm particle size, 125Å pore size; Waters Corporation, Milford, MA, USA) using an automatic carbonyl sampler (Model 8000, ATEC, Malibu, CA, USA) at a flow rate of 0.7 L min^{-1}.[18] The sampling system employs a heated inlet maintained at 50 °C to minimize liquid water interferences with the DNPH-coated cartridge. The selected 24-hr sample duration ensures that the collected carbonyls do not consume >30% of the derivatizating agent coated on the cartridge. Two DNPH cartridges in series were collected at the three sites with an inlet height of 1.2–1.5 m above ground level. Past studies show no appreciable breakthrough at such sampling flow rates and durations.[18,26,27]

Flow rates were verified in the field at the beginning and end of each sampling period using a calibrated flow meter (Gilibrator Calibrator; Gilian Instruments, W. Caldwell, NJ, USA). A Teflon-membrane filter assembly (Whatman, Clifton, NJ, USA) and an O_3 scrubber (Sep-Pak; Waters Corporation, Milford, MA, USA) were installed in front of the DNPH-coated cartridge in order to remove particulate matter and prevent possible O_3 interference, respectively[27]. The recovery of carbonyls collected in the process should not be affected by the O_3 trap[28]. Collocated samples were acquired to determine reproducibility, with correlation coefficient (r) >0.98 in the field. One cartridge was designated as a field blank on each sampling trip for the three sites and was handled the same way as the sample cartridges. Fourteen field blanks were collected at each site during each season. The amounts of carbonyls detected in each cartridge were corrected by subtracting averaged field blanks. The DNPH-coated cartridges were stored in a refrigerator at <4 °C after sampling and before chemical analyses. Samples were analyzed within two weeks after sampling to minimize sample degradation during cold storage. Meteorological parameters, including temperature, RH, air pressure, and rainfall, were recorded during each sampling period.

Liquid vaporization to a Tedlar® gas sampling bag (Sigma-Aldrich, St. Louis, MO, USA) was used to examine the stability of gaseous carbonyl standards in methanol under a vented fume hood for different RH.[15,16] High CEs (>93±5%) were achieved, suggesting negligible wall losses and high stabilities, similar to those found in prior experiments[15,16]. As RH inside the bag was <1% during calibration, carbonyl concentrations varied by <10% after 24 hr storage. Various amounts of water were injected into the bag to simulate different atmospheric RH.

2.2 Chemical Analysis

Target carbonyls were quantified as shown in Table 1. Since unsaturated carbonyls may react with excess reagent to form adducts, these compounds were not accurately quantified due to co-elution and changing response factors[22,23].

Each DNPH-coated cartridge was eluted with 2.0 mL of acetone-free acetonitrile (HPLC-grade; Mallinckrodt Laboratory Chemicals, Phillipsburg, NJ, USA) to a volumetric flask. Prior tests demonstrate that neither DNPH nor its derivatives remaining in the cartridge are detectable after the 2.0 mL elution[29]. Certified calibration standards of monocarbonyl DNP-hydrazones (Supelco; Bellefonte, PA, USA) were diluted into concentration ranges of 0.015-3.0 mg mL^{-1} for instrument calibration. The final volume of each calibration mixture was set at 2.0 mL with 8:2 (volume/volume) of acetonitrile/pyridine (HPLC grade; Sigma-Aldrich, St. Louis, MO, USA). Concentrations of the dicarbonyl DNP-hydrazones in the calibration standards ranged from 0.01-2.0 μg mL^{-1}. Instrument response was linear with concentration ($r > 0.999$). The cartridge extracts and calibration standards were analyzed by injecting 20 μL of the extract into an HPLC system (Series 1200; Agilent Technology, Santa Clara, CA, USA) equipped with a photodiode array detector (PAD). The separation column (i.e., 4.6×250 mm Spheri-5 ODS 5μm C-18 reverse-phase column; PerkinElmer, Norwalk, CT, USA) was operated at room temperature (22±2 °C).

The mobile phase consisted of three solvent mixtures: (A) 6:3:1 (v/v) of water, acetonitrile, and tetrahydrofuran, respectively; (B) 4:6 (v/v) of water and acetonitrile, respectively; and (C) acetonitrile. The gradient program was 80% A/20% B for 1 minute, followed by linear gradients to 50% A/50% B for 8 minutes, 100% B for 10 minutes, transition from 100% B to 100% C over 6 minutes, and 100% C for 5 minutes. The flow rate was 2.0 mL min^{-1} throughout the run. Absorbances at 360 nm and 390 nm were used to identify the aliphatic and aromatic (e.g., benzaldehyde, tolualdehydes, and 2,5-dimethylbenzaldehyde) carbonyls, respectively.

Identification and quantification of carbonyl compounds were based on retention times and peak areas compared with the corresponding calibration standards, respectively. The minimum detection limits (MDLs) in Table 1 were obtained by analyzing ≥7 replicates for each standard solution containing the analytes at a concentration of 0.015 μg mL^{-1}. The MDLs of the target carbonyls ranged from 0.002–0.010 μg mL^{-1}, which can be converted to 0.032–0.18 μg m^{-3} based on a sampling volume of 1.01 m^3. Measurement precision, derived from replicate analyses, ranges from 0.5–3.2% for the target carbonyls. The chromatographic peaks were further confirmed as an independent quality assurance/quality control (QA/QC) by a liquid chromatograph (LC)/mass spectrometry (MS) system (Series 6100, Agilent Technology, Santa Clara, CA, USA) for electrospray ionization (ESI) analysis.

2.3 Determination of Collection Efficiency (CE)

Carbonyl CEs were determined by connecting two or three cartridges in series for field and laboratory samples. CEs were calculated as $(1-A_b/A_f)\times100\%$ where A_b and A_f were the amounts of a carbonyl collected on the back and front cartridges, respectively. Additional uncertainties may be introduced owing to differences between standards generated by vaporization to the Tedlar® bag and liquid injection to the HPLC. Laboratory experiments show a standard recovery of 87–98% with the liquid vaporization method; this was normalized to obtain absolute CEs.

3. Results and Discussion

3.1 Ambient Collection Efficiencies

Average concentrations and CEs for field measurements are shown in Table 2. Carbonyl concentrations were ~3 to 10 times higher at the urban than the coastal sites, indicating that anthropogenic sources (e.g., vehicular and cooking emissions) dominated urban carbonyl production. Formaldehyde was the most abundant carbonyl, on average ranging from 1.46 to 8.77 µg m^{-3}. Acetaldehyde (0.5–3.37 µg m^{-3}) and acetone (0.06–1.09 µg m^{-3}) were the next most abundant carbonyls.

High CEs (96–99%) were achieved for formaldehyde, consistent with >95% CE specified by U.S. EPA.[18] More variable CEs (83–98%) were found for acetaldehyde, deviating from the >95% CEs specified by the cartridge supplier,[21] but comparable with the 80% CE reported by Lazarus.[30] The CEs for other mono- and di-carbonyls were either close to >99% or undetectable (below the MDLs in Table 1), as their concentration levels were one to two orders of magnitude lower than those of formaldehyde, acetaldehyde, and acetone.

Lower CEs were found for acetone and MEK, ranging from -240% to 23% and -273% to 18%, respectively. More negative CEs were found for samples collected at the more humid coastal site. Negative CEs indicate higher ketone concentrations on the back compared to the front cartridge. Fig. 1 compares front and back chromatograms from the urban Tsim Sha Tsui site, showing acetone and MEK peaks (ID# 3 and 7, respectively) were higher on the back than front cartridges. Similar results are observed for aldehyde compounds. Gaseous carbonyl molecules diffuse onto the solid sorbent surface where DNPH is immobilized (i.e., the addition of the -NH_2 group to the -C=O group) and form a tetrahedral carbinolamine intermediate.[31] The reaction rate for this reversible step is expected to play a key role in determining the CEs of carbonyls. In the second step, the carbinolamine intermediate loses a molecule of water (H_2O) to form the hydrazone derivative. Water is a product of the reaction and, when the water mixing ratio is high (corresponding to RH at typical ambient temperatures), the backward (i.e., reverse) reaction becomes prominent and competes with the forward reaction for the carbonyls of lower reactivity.

For carbonyls, the $>C^{\delta+}=O^{\delta-}$ bond is highly polarized because of the differences in electronegativity between carbon and oxygen. However, such polarization is much stronger for aldehydes than ketones, since aldehydes consist of a strong electron withdrawing group of –H attached to the polarized carbon. The nucleophilic –NH_2 tends to attack the aldehydes quickly, resulting in a faster reaction rate than that for ketones. Therefore, less reactive ketones re-entrain from the front cartridge and re-react on the back cartridges. Since >90% of the aldehydes have been collected by the front cartridge, re-entrained ketones can be retrieved from the back cartridge. Fujita et al.[32] reported "unsatisfactory" CEs for acetone, but no values were provided for comparison.

3.2 Relative Humidity Effect

Table 2 shows larger seasonal variations in CEs for ketones than aldehydes. Ketone CEs varied from –67 to –273% during summer under higher RH (87–91%) and temperatures (32-33 °C), with higher CEs (–29 to 23%) during winter under lower RH (56–80%) and temperatures (14–15 °C). Poorer efficiencies during summer could be caused by water vapor interferences, as H_2O mixing ratios increase with temperature for a given RH. Grosjean and Grosjean[33] observed opposite effects with a C_{18}-based cartridge. Aldehydes and ketones had good agreements (r >0.8) between measured and nominal concentrations at 55±10% RH for temperatures similar to those of Hong Kong, while poor agreement (r<0.8) was found for heavier aldehydes (C_4-C_9) at 3-7% RH. It is expected that moisture can have dissimilar influences on C_{18}- and silica gel-based cartridges. Pires and Carvalho[34] also demonstrated that oxidants in air can react differently with DNPH on C_{18}-based cartridges in generating a wide variety of compounds.

Laboratory experiments were carried out to examine CEs at five RH levels with temperatures of 22±2 °C. Experimental CEs in the laboratory are expected to be higher than those determined in ambient air because there are fewer competitors (e.g., organic acids or nitrogen oxides) for reactions with DNPH. Fig. 2 illustrates the relative distribution of acetone and MEK collected from a standard gas stream with a series of three cartridges. The CEs for the front cartridge decreased from 90% at <10% RH to ~20% at ~100% RH. At low (<10%) RH, average CEs for acetone and MEK were comparable, at 91±8% and 89±9%, respectively, and nondetectable (0%) on the third cartridge. CEs decreased to -47±15% for acetone and -79±18% for MEK at 75% RH (representing typical RH in Hong Kong[15]). These results demonstrate that under high RH (>50%) and at temperature of 22±2 °C, ketone concentrations from single-cartridge sampling could be underestimated by ~35–80%. At 1 µg m^{-3} concentrations, a dual-cartridge sampler (i.e., single front-and-back) may not be adequate for ambient RH >50%, as 2–10% of the ketones were found on the third cartridge as shown in Fig. 2. The sum of ketones collected by the three cartridges in series was close to unity (>97%) as compared to the laboratory-generated standards. However, it may not be practical or cost-effective to sample three cartridges in series in the field.

3.3 Sampling Flow Rate Effect

The CEs of the two ketones collected at flow rates ranging from 0.1 to 1.0 L min^{-1} were examined. Although the concentrations were correlated (r >0.91), a progressive reduction in CEs for ketones by two- to three-fold was found as flow rate increases (Fig. 3). With longer residence times at lower flow rates, most of the carbonyls are expected to be retained in the cartridge and react with

DNPH. However, the two ketones still exhibited negative CEs at the lowest flow rate of 0.1 L min^{-1}, reconfirming the inadequacy of using single-cartridge sampling at 90% RH.

3.4 Sampling Duration Effect

Fig. 4 shows that higher CEs (>55±12%) were obtained for 6 hr as compared to 24 hr sample durations. At 75% RH, water molecules in the sampled air stream can accumulate and retain on the polar-based silica gel, influencing the kinetics of derivatization and leading to decreases in CE. Apel et al.[35] reported an average CE of 79% for acetone using C_{18}-based cartridge measurements for six hr duration at an average of ~50% RH; lower CEs (45–65%) were found for nighttime samples.[35] The suitability of quantifying daily or diurnal ketone variations using DNPH-coated cartridges under high RH needs to be further investigated.

4. Conclusion

Both field observations and laboratory experiments demonstrate CE changes for carbonyls depending on RH, sample flow rates, sample durations, and concentration levels.[36] Commercially available carbonyl samplers with inlets heated to 50 °C can remove water droplets (i.e., rainfall) from the air stream, but elevated RH affects CEs. Table 3 summarizes the interferences and solutions related to the DNPH-coated cartridge method. Even though the potential effects from NO, NO_2, and O_3 can be minimized by upstream denuders/absorbents, the method shows negative biases for the determination of unsaturated aldehydes and ketones. The current DNPH method is adequate for determination of species such as formaldehyde by HPLC. Larger molecular weight carbonyls (e.g., MEK) can be measured more reliably by gas chromatography with flame ionization detector (GC-FID) than HPLC with PAD.[37,38]

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Table 1. Minimum detection limit (MDL) for the target carbonyls.

Anonym	Carbonyl	CAS#	MW[b]	Class	MDL (μg m^{-3}) [c]
C1	formaldehyde	50-00-0	30	aliphatic	0.045
C2	acetaldehyde	75-07-0	44	aliphatic	0.075
ACE	acetone	67-64-1	58	aliphatic	0.086
ACRO	acrolein	107-02-8	56	aliphatic	0.091
nC3	propionaldehyde	123-38-6	58	aliphatic	0.032
CROT	crotonaldehyde	123-73-9	70	aliphatic	0.087
MEK	methyl ethyl ketone	78-93-3	72	aliphatic	0.092
i-C4	iso-butyraldehyde [a]	78-84-2	72	aliphatic	0.11
nC4	n-butyraldehyde [a]	123-72-8	72	aliphatic	0.11
benz	benzaldehyde	100-52-7	106	aromatic	0.081
iC5	iso-valeraldehyde	590-86-3	86	aliphatic	0.11
nC5	n-valeraldehyde	110-62-3	86	aliphatic	0.14
o-tol	o-tolualdehyde	529-20-4	120	aromatic	0.12
m-tol	m-tolualdehyde	620-23-5	120	aromatic	0.13
p-tol	p-tolualdehyde	104-87-0	120	aromatic	0.13
C6	hexaldehyde	66-25-1	100	aliphatic	0.15
2,5-DB	2,5-dimethylbenzaldehyde	5779-94-2	134	aromatic	0.18

[a] iso-Butyraldehyde and n-butyraldehyde were co-eluted in the HPLC analysis.

[b] Molecular Weight

[c] The MDL is the minimum detection limit of a carbonyl determined by analyzing $\geq$7 replicates of a standard solution containing an analyte at 0.015 μg mL^{-1}. MDL is expressed as μg m^{-3}, calculated using a sampled air volume of 1.01 m^3 (at a flow rate of 0.7 L min^{-1} for 24 hr).

Table 2. Average concentrations and collection efficiency for 16 carbonyls measured by U.S. EPA method TO-11A.

		Urban (Tsim Sha Tsui)				Suburban (Sai Kung West Country Park)				Coastal (Tai Tam Bay)			
		Winter		Summer		Winter		Summer		Winter		Summer	
		Temp[a] = 14°C (9-16°C) RH[b] = 56% (44-65%)		Temp = 32°C (30-33°C) RH = 87% (81-98%)		Temp = 15°C (10-16°C) RH = 67% (48-71%)		Temp = 33°C (29-34°C) RH = 88% (78-97%)		Temp = 15°C (10-17°C) RH = 80% (62-85%)		Temp = 33°C (28-34°C) RH = 91% (85-99%)	
Symbol	**Carbonyls**	**Conc[c]**	**CE[d]**	**Conc**	**CE**	**Conc**	**CE**	**Conc**	**CE**	**Conc**	**CE**	**Conc**	**CE**
aliphatic aldehydes													
C1	formaldehyde	7.36	99%	8.77	97%	2.52	97%	2.71	97%	2.02	98%	1.46	96%
C2	acetaldehyde	2.97	97%	3.37	90%	1.28	98%	0.91	87%	1.04	96%	0.50	83%
nC3	propionaldehyde	0.36	>99%[e]	0.61	99%	0.18	>99%	0.19	99%	0.19	98%	0.12	99%
C4n+l	n-butyraldehyde/isobutyraldehyde	0.23	>99%	0.45	>99%	0.10	>99%	0.22	>99%	0.05	>99%	0.23	>99%
i-C5	isovaleraldehyde	0.73	>99%	0.82	>99%	0.31	>99%	0.23	>99%	0.25	>99%	0.06	>99%
n-C5	valeraldehyde	0.13	>99%	0.11	>99%	0.04	>99%	0.06	>99%	0.04	>99%	0.05	>99%
C6	hexaldehyde	0.38	>99%	0.33	>99%	0.06	>99%	0.15	>99%	0.06	>99%	0.07	>99%
aromatic aldehydes													
benz	benzaldehyde	0.35	>99%	0.49	>99%	0.19	>99%	0.16	>99%	0.13	>99%	0.15	>99%
o-tol	o-tolualdehyde	0.08	>99%	0.06	>99%	ND	-	ND	-	ND	-	ND	-
m-tol	m-tolualdehyde	0.18	>99%	0.14	>99%	0.06	>99%	ND	-	0.03	>99%	0.03	>99%
p-tol	p-tolualdehyde	ND[f]	-[g]	ND	-	ND	-	ND	-	ND	-	ND	-
2,5-C6	2,5-dimethylbenzaldehyde	0.07	>99%	ND	-	ND	-	ND	-	ND	-	ND	-
unsaturated aldehydes													
ACRO	acrolein[h]	0.05	>99%	0.67	>99%	0.04	>99%	0.45	>99%	3.49	>99%	1.89	>99%
CROT	crotonaldehyde[h]	0.14	>99%	0.23	>99%	0.12	>99%	0.27	>99%	0.11	>99%	0.29	>99%
ketones													
ACET	acetone	1.09	23%	0.78	-50%	0.63	-12%	0.05	-133%	0.38	-10%	0.06	-240%
MEK	methyl ethyl ketone	0.38	18%	0.31	-67%	0.34	-20%	0.22	-244%	0.18	-29%	0.20	-273%

[a] Average temperature during winter (10th to 23rd January 2010) and summer (13th to 26th July 2011); [b] Average relative humidity; [c] Average concentration in µg m^{-3} derived from front cartridge only, for 14 samples each during winter and summer; [d] Average collection efficiency, defined as $(1–A_b/A_f)\times100\%$ where A_b and A_f represent carbonyls collected on backup and front cartridges, respectively ;[e] Carbonyl might exist slight amount in the backup cartridge but was below minimum detection limit (MDL), see MDLs in Table 1, expressed CE as >99%; [f] Not detectable, below MDL; [g] No collection efficiency is reported as carbonyl concentration was below MDLs; [h] Unsaturated carbonyl DNP-hydrazones may react with excess reagent to form adducts, which is subject to high uncertainties due to chromatographic and response factor issues[10,11].

Table 3. Summary of interferences and remedies on DNPH-coated solid sorbent cartridge method in determination of carbonyls

Parameters	Influenced species	Interference	Remedy	References
O_3	all carbonyls	positive and negative artifacts on the carbonyl derivatives	sampling with an upstream ozone scrubber	19,39
NO and NO_2	formaldehyde and acetaldehyde	NO and NO_2 react with DNPH, forming side-products which overlap with formaldehyde and acetaldehyde derivatives peaks	better chromatographic separation	20,21
-	unsaturated carbonyls	derivatives undergo polymerization	None	22,23
Relative Humidity (RH)	mostly ketones	Poor collection efficiencies at nominal sampling flow rates, leading to large underestimation of ketone concentrations	Use alternative derivatization agent; quantify ketones with GC-FID[a]	This study

[a] GC-FID: Gas chromatography-flame ionization detection

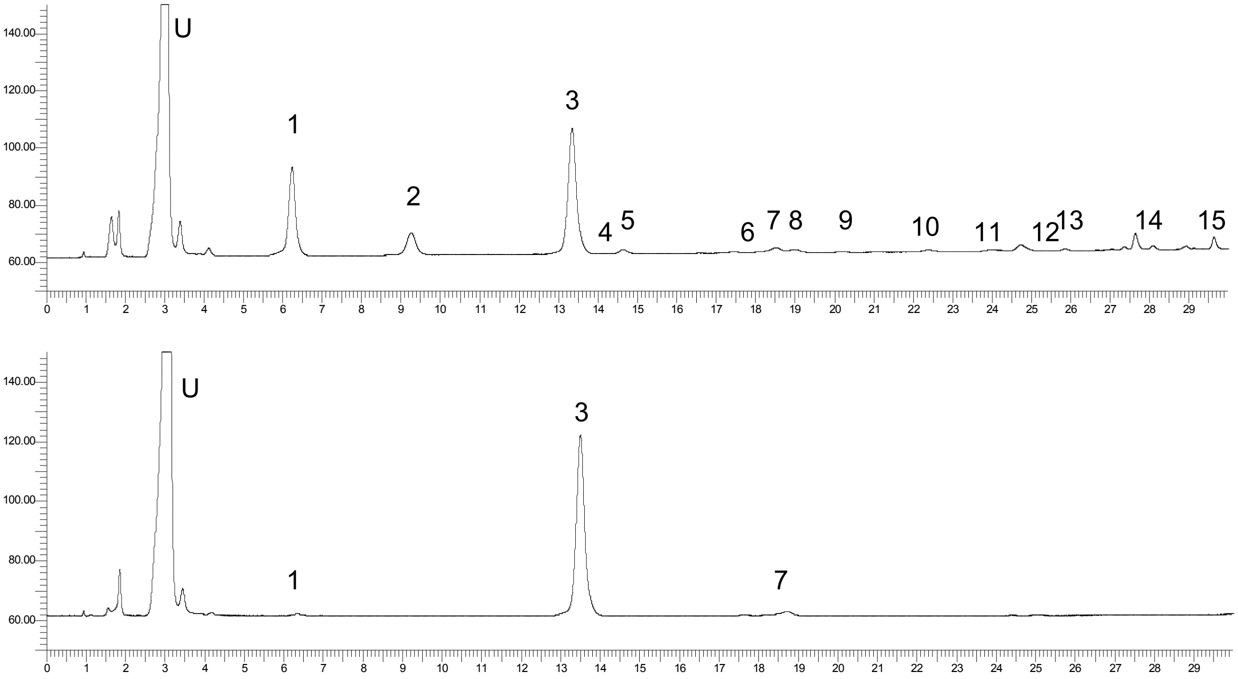
FIGURE CAPTIONS

Fig. 1. Chromatograms for a pair of front (upper) and back (lower) cartridges for a sample collected at the urban Tsim Sha Tsui site in Hong Kong on 15th January 2010.

Fig. 2. Three-stage collection efficiencies (CEs) for acetone and methyl ethyl ketone (MEK) under five different relative humidities (RHs) at room temperature (22±2°C). Distribution of the standard concentrations is expressed in percent of total ketone injected (Gaseous concentrations were 1 μg m^{-3} for acetone and MEK. Averages are shown based on a total of 30 sample-sets tested.)

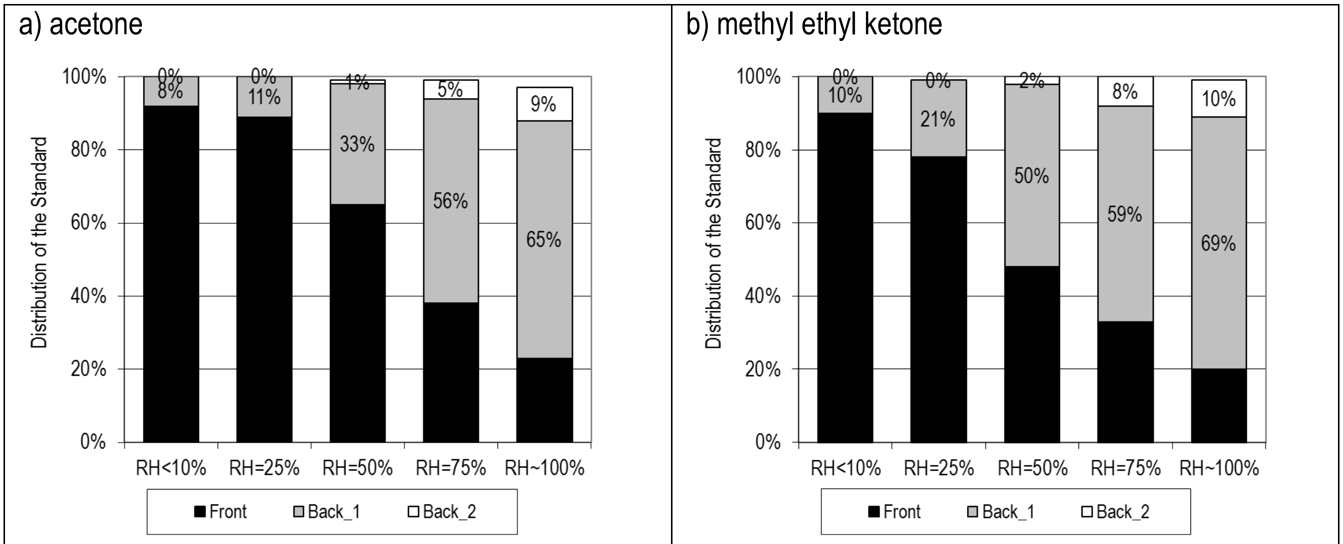
Fig. 3. Collection efficiencies at laboratory temperatures of 22±2 °C for 24-hr ketones at sampling flow rates ranging from 0.1 to 1.0 L min^{-1} in 90% relative humidity (RH), representing summertime RH in Hong Kong. (Gaseous concentrations were 2 μg m^{-3} for acetone and methyl ethyl ketone (MEK). Averages are shown on a total of 22 dual-cartridge sample-sets tested.)

Fig. 4. Collection efficiencies at laboratory temperatures of 22±2 °C for ketones at a flow rate of 0.7 L min^{-1} for sample durations ranging from 6 to 24 hr at a relative humidity (RH) of 75%, representing typical RH in Hong Kong. Vertical uncertainty bars represent the measurement precision based on collocated sampling. (Gas concentrations were 2 μg m^{-3} for acetone and MEK. Averages are shown on a total of 20 dual-cartridge sample-sets tested.)



Peak Identification
Carbonyl-DNP-hydrazone: 1: formaldehyde; 2: acetaldehyde; 3: acetone; 4: acrolein; 5: propionaldehyde; 6 : crotonaldehyde; 7 : methyl ethyl ketone (MEK); 8: *iso*+ *n*-butyraldehyde; 9 : benzaldehyde; 10 : isovaleraldehyde; 11 : *n*-valeraldehyde; 12 : *o*-tolualdehyde; 13 : *m*-tolualdehyde; 14 : *n*-hexaldehyde; 15: 2,5-dimethylbezaldehyde
U: Unreacted DNPH

Fig. 1. Chromatograms for a pair of front (upper) and back (lower) cartridges for a sample collected at the urban Tsim Sha Tsui site in Hong Kong on 15th January 2010.



a) acetone

	Collection efficiencies (CEs)	
	100%(1-Back_1/Front)[a]	100% (1-Back_2/Back_1)[b]
RH<10%	91%	100%
RH=25%	88%	100%
RH=50%	49%	97%
RH=75%	-47%	91%
RH~100%	-183%	86%

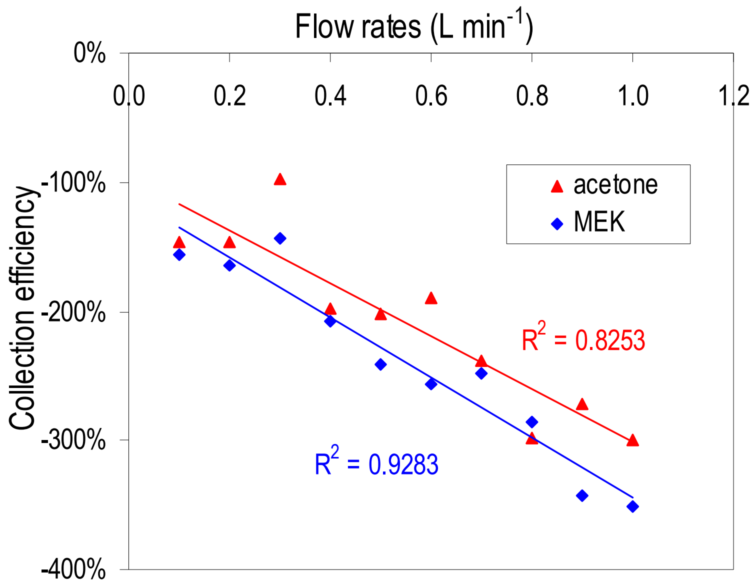
b) methyl ethyl ketone

	Collection efficiencies (CEs)	
	100%(1-Back_1/Front)[a]	100% (1-Back_2/Back_1)[b]
RH<10%	89%	100%
RH=25%	73%	100%
RH=50%	-4%	96%
RH=75%	-79%	86%
RH~100%	-245%	86%

[a] The collection efficiencies are calculated as 100% (1-A_{Back_1}/A_{Front}), where A_{Back_1} and A_{Front} were the amounts of a carbonyl collected on the Back_1 (i.e., second) and Front cartridges, respectively.

[b] The collection efficiencies are calculated as 100% (1-A_{Back_2}/A_{Back_1}), where A_{Back_2} and A_{Back_1} were the amounts of a carbonyl collected on Back_2 (i.e., third) and Back 1 (i.e., second) cartridges, respectively.

Fig. 2. Three-stage collection efficiencies (CEs) for acetone and methyl ethyl ketone (MEK) under five different relative humidities (RHs) at room temperature (22±2°C). Distribution of the standard concentrations is expressed in percent of total ketone injected (Gaseous concentrations were 1 µg m^{-3} for acetone and MEK. Averages are shown based on a total of 30 sample-sets tested.)



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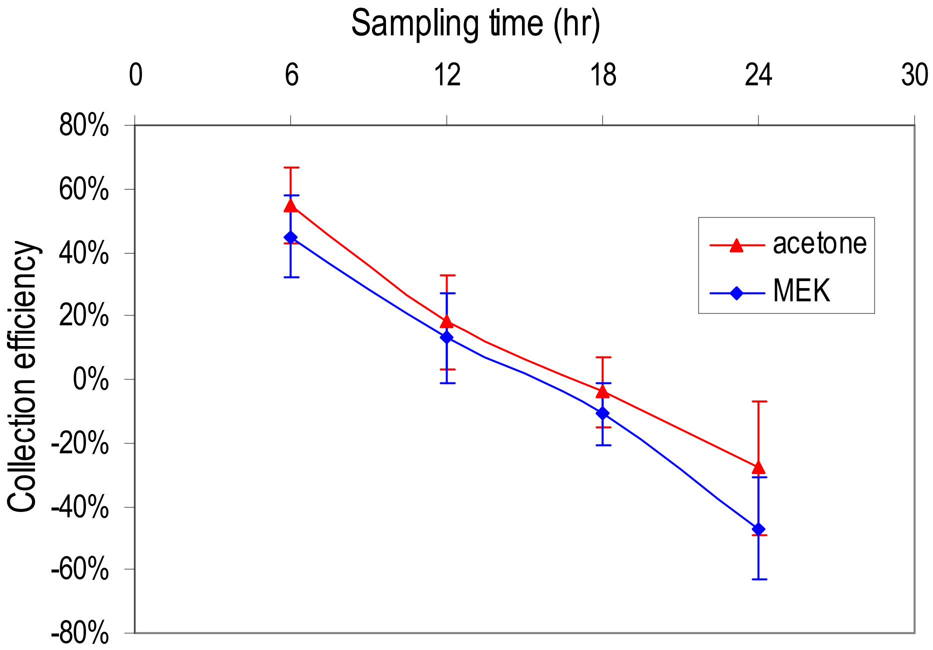

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