

Determination of carbonyl compounds in the atmosphere by DNPH derivatization and LC–ESI-MS/MS detection

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Abstract

A method of determination of 32 carbonyl compounds by high performance liquid chromatography (HPLC) and electrospray ionization (ESI) tandem mass spectrometry (MS/MS) after derivatization with 2,4-dinitrophenylhydrazine (DNPH) was developed and successfully applied to the atmosphere sample of a residential area of Liwan District (S1) and a research institute of Tianhe District (S2) in Guangzhou, China. Some operation conditions of ESI-MS/MS in the negative ion mode including selection of parent and daughter ions, declustering potential (DP), entrance potential (EP), collision energy (CE), collision cell exit potential (CXP) and effect of buffer in ESI-MS/MS process were optimized. The regression coefficient of the calibration curves (R^2), recovery, reproducibility (R.S.D., $n = 5$) and limit of detection (LOD) were in the range of 0.9938–0.9999, 90–104%, 1.7–11% and 0.4–9.4 ng/m³, respectively. Among most of the samples, acetone was the most abundant carbonyl in two sampling sites and formaldehyde, acetaldehyde and butyraldehyde/2-butanone were also abundant carbonyls. In contrast to LC–UV method, the LOD, the separation of some co-eluting compounds and the precision (mainly to higher molecular weight carbonyls) are all improved by LC–ESI-MS/MS.

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1. Introduction

Carbonyl compounds in air are important photochemical oxidation products of virtually all hydrocarbons and precursors of free radicals, ozone, and peroxyacyl nitrates [1–3]. Moreover, several carbonyls also have received regulatory attention as toxic air contaminants, mutagens, eye irritants and carcinogens, such as formaldehyde, acetaldehyde, and acrolein [4,5]. Therefore, it is essential to develop a method for the determination of carbonyl compounds.

The quantitative method most frequently used for measuring carbonyls in air samples is based on derivatization with 2,4-dinitrophenylhydrazine (DNPH) in acid medium

during sampling. The formed 2,4-dinitrophenylhydrazones are separated by reversed-phase liquid chromatography and detected by UV [6–10]. This method was widely used as an international standard and mainly applied to the determination of C1–C5 aldehydes and ketones in the United States and Europe [5,11]. The reasons were the low content of higher molecular weight (HMW) carbonyls in air and the interference of the sample matrices. In order to solve the problem, LC–MS and LC–MS/MS were applied for quantitative analysis and identification of carbonyl-DNPHs (in our knowledge, few studies focused on quantitative analysis of carbonyls by LC–MS/MS) [12–21]. In these studies, the best detection method was atmospheric pressure chemical ionization in the negative ion mode (APCI–), and the detection for carbonyls could achieve low-picomogram quantities. However, there are also other ion sources and ion modes were used for the detection. Karst and coworkers found APCI and ESI in the positive mode were suitable to

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determine aldehydes and ketones derivatized by the Hantzsch reaction [22–24]. Van den Bergh et al. [25] considered that both ESI and APCI in the negative ion mode were suitable for the detection of the DNPH derivatives of carbonyls and found ESI (–) in combination with single ion monitoring (SIM) detection showed the lowest detection limits. Moreover, Richardson et al. [26] determined polar disinfection by-products in water by LC–ESI-MS. Zwiener et al. [27] optimized some conditions of determination carbonyls and identified several carbonyls from swimming pool water by LC–ESI-MS/MS in the negative ion mode, and the detection limits were achieved $\mu\text{g/L}$ degree by SIM measurements without sample preconcentration. Recently, Karst et al. [12] also applied APPI-MS in the negative ion mode method for the determination of aldehydes and ketones after DNPH derivatization and LC separation. Compared to APCI-MS, the lower detection limits were obtained under the same conditions. At present, the studies of carbonyls were mainly focused on air [6–19,22–25,28,29], water [26,27] and plants [30,31]. Due to the special action of carbonyls in air (important photochemical oxidation products of virtually all hydrocarbons and precursors of free radicals, ozone, and peroxyacyl nitrates), people were much more attention to the detection of carbonyls in air.

In our work, we extend the method of Zwiener et al. [27] and develop a method of quantitative analysis of 32 carbonyl compounds by DNPH derivatization and LC–ESI-MS/MS detection. This method is successfully applied to the air samples of a residential area and a research institute of Guangzhou, China. In contrast to other methods, some new target compounds are quantitative determine and much lower LOD are achieved by LC–ESI-MS/MS. Study shows that the negative ion mode is suitable for determining carbonyl-DNPHs. The influence of several operation conditions in quantitative process is explored, and a description of the process of their values optimized is provided. We detail the development of sensitive, selective, and dependable methods to quantify carbonyl compounds in air by LC–ESI-MS/MS.

2. Experimental

2.1. Reagents and materials

All solvents employed were HPLC grade. Water was double distilled and filtered by Milli-Q. The acetonitrile (ACN) and the 2,4-dinitrophenylhydrazine (DNPH) were purchased from Merck (Germany) and Fluka (USA). Ammonium acetate (Analytical grade) was purchased from Tianjin Chemical Reagent No. 1 Plant (Tianjin, China). Standard solutions containing 21 kinds of carbonyl-DNPHs (DNPH derivatives of formaldehyde, acetaldehyde, acetone, acrolein, benzaldehyde, butyraldehyde, crotonaldehyde, valeraldehyde, isovaleraldehyde, propionaldehyde, *o*-tolualdehyde, *m*-tolualdehyde, *p*-tolualdehyde, 2-butanone, cyclohexanone, heptaldehyde, octylaldehyde, nonanaldehyde, decylaldehyde, 2,5-dimethylbenzaldehyde, hexaldehyde) were purchased from ChemService (West Chester, USA). Other standard solutions including 12 DNPH derivatives of the following

carbonyls were synthesized in our lab: 2-hexanone, 2-nonanone, methacrolein, cyclopentanone, acetophenone, 4-methyl-2-pentanone, 2-pentanone, undecanal, dodecanal, tridecanal, and 2-OH-benzaldehyde.

2.2. DNPH derivatization of some carbonyls

The derivatives of carbonyls were prepared according to the method described in other literatures [32–34]. Proceed as follows. Firstly, 0.4 g DNPH (recrystallization in HPLC grade ACN twice) was dissolved in 2 mL H_2SO_4 , and then 3 mL water and 10 mL ethanol were slowly added to this solution, respectively. Secondly, 50% molar excess of the respective carbonyls was dissolved in 20 mL ethanol and then the solution of carbonyl was slowly added to the solutions of DNPH. Finally, the precipitate formed was filtered off, recrystallized from 30 mL hot ethanol or ACN, washed with ethanol and dried in a desiccator. Purities of the products were identified by LC–MS, and no impurity peaks were found.

2.3. Sample preparation and sampling sites selection

The sampling method for carbonyls was described in our previous reports [8,9]. The sampling medium was a Sep-Pak Silica Gel cartridge (waters, Millipore Corp.). DNPH was recrystallized from ACN (HPLC grade) three times. Each cartridge was rinsed by 10 mL of ACN, and then coated with 7 mL of the freshly made coated solution, which contained 60 mL DNPH-ACN-saturated solution and 4 mL concentrated *ortho*-phosphoric acid in 500 mL ACN. When there was no more solution flowing out, they were dried with a gentle flow of high-purity nitrogen. Each cartridge was wrapped in a piece of filter paper, which impregnated with the DNPH-ACN solution to prevent contamination before use, wrapped in an aluminum foil, and sealed in a Teflon bag. All the processes were carried out in the high-purity nitrogen-filled glovebox. Finally, cartridges were stored in refrigerator at 4 °C [35,36] until use.

Samples were collected by drawing the air with a sampling pump (Thomas, USA) through the cartridge. A potassium iodide (KI) denuder was connected to the upstream of the cartridge to prevent the interference of ozone [37]. Before sampling, two cartridges in series were tested for breakthrough under the same sampling conditions and no compounds were detected in the back cartridge. After sampling, each cartridge was wrapped in an aluminum foil, resealed in a new Teflon bag, taken back to the laboratory and stored in the refrigerator.

The sampled cartridges were eluted with 2 mL of ACN into a 2 mL volumetric flask. This eluted solution was directly injected into the LC–MS system.

2.4. Instrument analysis

The LC–MS/MS system included an Agilent 1100 HPLC system equipped with quaternary Pump, on-line vacuum degassing system, autosampler and Variable Wavelength Detector (VWD, at 360 nm) and an API 4000 triple quadrupole mass spectrometer

(Applied Biosystems, Foster City, CA, USA) equipped with electrospray ionization (ESI).

LC separation of carbonyls was conducted by using a mixture of acetonitrile (ACN), water and 1 mmol/L ammonium acetate solution as mobile phase. The gradient program was as follows: constant 65% ACN and 35% water during 0–27 min, then changes of 65–80% ACN, 35–0% water and 0–20% ammonium acetate solution were taken in 27–30 min. The content of ACN increased to 95% in 30–35 min and kept constant until 50 min, and then restored to 80% at 55 min, in these times (30–55 min) constant 0% water was kept. During 55–60 min, changes of 80–65% ACN, 0–15% water and constant 20% ammonium acetate solution were taken. Changes of 15–35% water, 20–0% ammonium acetate solution and constant 65% ACN were taken in 60–61 min, and then followed by a 5 min equilibration time. An Agilent Zorbax Eclipse XDB-C18 column (250 mm × 4.6 mm, particle size 5 μm) was used as the analytical column. Flow rate was 0.6 mL/min and injection volumes were 5 μL. The mass spectra (MS) scanning from $m/z=0$ to 500 was applied for the determination of m/z values. Electrospray mass data were acquired in the negative mode with a spray voltage of -4.5 kV. The source temperature was 450 °C. Nitrogen was used as the curtain gas (setting 10), nebulizer gas (setting 15) and turbo gas (setting 40). MS/MS was performed using nitrogen as collision gas (CAD gas setting 6). Other operating conditions of MS/MS were shown in Table 1. The data were acquired with the Sciex Analyst software, version 1.3.1 (Applied Biosystems, Foster City, CA, USA).

3. Results and discussion

3.1. Operating conditions of ESI-MS/MS

The optimized numerical values of some parameters (spray voltage, source temperature, curtain gas, nebulizer gas and turbo gas) of ESI-MS/MS have been described already in Section 2. These parameters were of the same numerical values for all carbonyl compounds in the experiment. In addition, declustering potential (DP), entrance potential (EP), collision energy (CE) and collision cell exit potential (CXP) were also important parameters of ESI-MS/MS. For these parameters, different carbonyl compounds need different numerical values and the results are shown in Table 1. Because the stability to collision-induced dissociation (CID) of ion source increased with the aldehyde carbon-chain length [27], the DP of the higher aldehydes was larger than those of the lower aldehydes. Aromatic aldehydes and ketones had the most stable molecular structure among all carbonyls and provided the largest DP values (setting 50). Moreover, the intensity of the CE also acquired the same behavior. CE was important parameter of the product ion spectra and the intensities of CE affected the formation of daughter ions and the degree of parents ions reduced. In general, the more stable the compounds were, the larger intensities of CE needed. The same conclusion also had been acquired in other literature [27]. For EP and CXP, there had not found any obvious influences in the experiment.

The selection of fragment ions is also an important condition in the quantitative process of carbonyls. The processes of frag-

Table 1
Operating conditions for MS/MS analysis of different carbonyl-DNPHs

Carbonyl compounds	DNPH derivative [M – H] (m/z)	Fragment ion for quantification (m/z)	Decluse-ring potential DP (V)	Entrance potential EP(V)	Collision energy CE (rel. units)	Collision cell exit potential CXP (V)
Formaldehyde	209.1	162.9	–25	–6	–16	–6
Acetaldehyde	223.1	163.1	–27	–6	–18	–6
Propionaldehyde	236.8	162.9	–30	–6	–18	–6
Butyraldehyde/2-butanone	251.1	152.1	–30	–10	–21	–6
Valeraldehyde	265	162.9	–30	–6	–20	–5
Hexaldehyde/2-hexanone	279	151.8	–35	–10	–20	–6
Heptaldehyde	293.0	162.6	–35	–12	–21	–6
Octylaldehyde	306.9	162.9	–35	–13	–22	–6
Nonanaldehyde/2-nonanone	321	151.8	–30	–12	–23	–6
Decylaldehyde	335.0	162.9	–40	–10	–23	–6
Undecanal	349.1	162.8	–40	–14	–24	–12
Dodecanal	362.9	163.4	–40	–14	–25	–12
Tridecanal	376.8	162.8	–50	–13	–26	–10
2-OH-benzaldehyde	301.1	181.6	–30	–10	–24	–6
Acetone	237.1	206.6	–27	–6	–21	–8
Acrolein	235.1	162.9	–27	–8	–20	–10
Methacrolein	249.1	162.4	–28	–11	–21	–8
Crotonaldehyde	248.9	172.1	–30	–11	–20	–6
Cyclopentanone	263.0	232.6	–30	–13	–20	–6.0
Cyclohexanone	276.9	230.8	–30	–13	–23	–6
Acetophenone	299	254.1	–50	–13	–25	–8
4-Methy-2-pentanone	279	151.6	–35	–10	–21	–6
Benzaldehyde	285	162.8	–50	–13	–23	–10
o/m/p-Tolualdehyde	299	162.6	–50	–14	–25	–10
2,5-Dimethylbenzaldehyde	313	162.6	–50	–12	–25	–10
Isovaleraldehyde/2-pentanone	265.0	151.6	–30	–6	–23	–10

ment ions selected were based on product ion spectra of each DNPH derivative of carbonyls. m/z 163 is a typical fragment ion for all aldehyde-DNPHs. Aldehyde and ketone-DNPHs show a typical fragment ion at m/z 152. The formations of ion m/z 163 and m/z 152 have already been explained by Kölliker [13]. Moreover, under the conditions listed in Table 1, acetone, crotonaldehyde, cyclopentanone, cyclohexanone, 2-OH-benzaldehyde and acetophenone also show a high signal intensity fragment ion at m/z 207, 172, 233, 231, 182 and 254, respectively (see Table 1). These fragment ions have much higher signal intensities than typical fragment (m/z 163 and 152). Therefore, these ions were selected as the quantitative daughter ions in the next experiment.

3.2. Selection of mobile phases

Since some conditions of the mobile phase such as pH and ionic strength, influence ion formation in the electrospray process [27], the ammonium acetate as a buffer solution was introduced in this experiment. Zwiener et al. [27] compared ammonium acetate in both mobile phase with no buffer addition and buffer addition, and found both mobile phase addition got maximum signal intensity. However, little differences were found in our experiment.

The experiments demonstrated that ammonium acetate in both mobile phases was abandoned, because it was found difficult to completely dissolve ammonium acetate into 100% ACN. The peak areas of 10–20 $\mu\text{g/L}$ aldehydes using 1 mmol/L ammonium acetate solution/ACN as mobile phases were compared with the peak areas of H₂O/ACN as mobile phases. The results are shown in Fig. 1. From the figure we could see that the buffered mobile phases provided larger peak area for higher aldehydes. However, for <C6 aldehydes, the peak areas

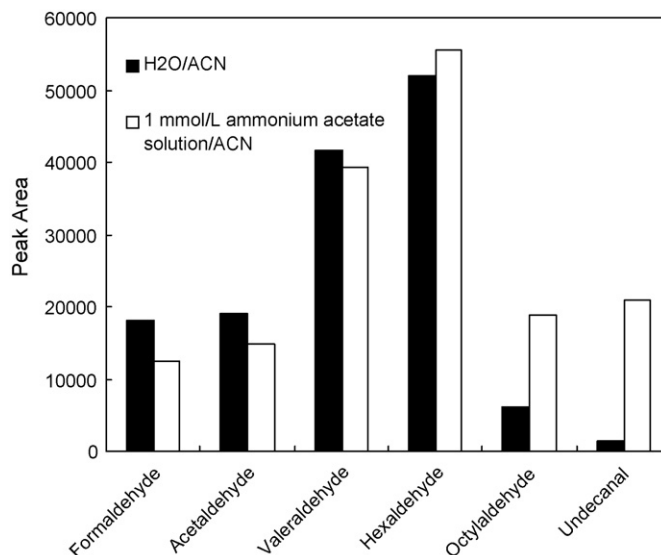


Fig. 1. Effect of buffer solution on the peak area of several aldehydes.

of the buffered were similar or little lower than those of non-buffered. Therefore, ammonium acetate solution as the third mobile phase was introduced into detection system at 27 min in the next experiment. Under the conditions of LC separation, 18 kinds of them were baseline separated among 32 kinds of carbonyl-DNPHs. The result is shown in Fig. 2. Fig. 2 demonstrated the total ion current chromatogram of a standard mixture of 32 carbonyl-DNPHs. The concentrations of standard solution were 200 $\mu\text{g/L}$ for formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, hexaldehyde and crotonaldehyde, and 100 $\mu\text{g/L}$ for other carbonyls. Due to the different parents and daughter ions between co-eluting compounds, the separation of some co-eluting compounds, such as valeraldehyde,

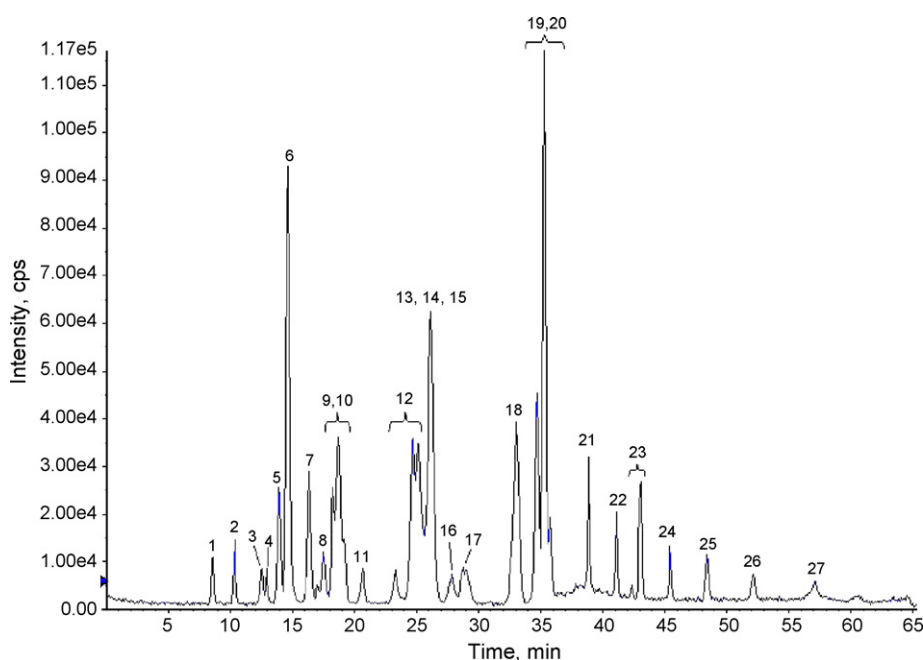


Fig. 2. Total ion current chromatogram of a standard mixture of 32 carbonyl-DNPHs. The peak numbers were consistent with the compound numbers of Table 3.

Table 2

Some analytical performance dates of the proposed method and 32 carbonyl compounds contents in two sample site

Compounds	Limit of detection (ng/m ³)	Reproducibility (R.S.D.%, <i>n</i> = 5)	Recovery (%, mean ± S.D., <i>n</i> = 3)	Concentrations (μg/m ³)	
				S1	S2
Formaldehyde	1.9	3	100 ± 3	4.10	5.25
Acetaldehyde	5.2	2	92 ± 4	4.80	7.11
Acrolein	2.5	2.8	96 ± 2	0.11	0.07
Acetone	4.3	1.7	103 ± 3	6.99	8.92
Propionaldehyde	5.3	1.8	102 ± 4	1.24	0.85
2-OH-benzaldehyde	0.4	3.3	100 ± 3	0.05	0.02
Crotonaldehyde	3.4	2.2	95 ± 1	0.17	0.05
Methacrolein	3.5	9.3	97 ± 7	0.78	0.27
Butyraldehyde/2-butanone	3.3	4.3	94 ± 8	4.02	3.52
Cyclopentanone	4.0	2.2	98 ± 1	0.04	0.03
Benzaldehyde	2.1	11	104 ± 4	0.50	0.31
Isovaleraldehyde/2-pentanone	2.2	5.2	99 ± 3	3.99	0.69
Valeraldehyde	2.7	2.2	96 ± 6	6.00	0.36
Cyclohexanone	2.0	7.3	90 ± 2	0.74	0.28
Acetophenone	7.6	5.7	92 ± 4	0.11	0.46
<i>p</i> -Tolualdehyde	4.8	8.7	96 ± 5	0.02	0.01
<i>o/m</i> -Tolualdehyde	4.9	9.3	97 ± 1	0.13	0.07
4-Methy-2-pentanone	2.0	3.0	90 ± 1	0.11	0.08
Hexaldehyde/2-hexanone	3.3	4.6	97 ± 7	1.39	0.64
2,5-Dimethyl-benzaldehyde	6.0	5.7	90 ± 6	0.04	0.02
Heptaldehyde	2.5	4.6	103 ± 8	0.18	0.31
Octylaldehyde	1.7	5.7	93 ± 6	0.16	0.48
Nonanaldehyde/2-nonanone	5.2	4.7	92 ± 3	0.95	1.08
Decylaldehyde	9.0	5.2	97 ± 1	0.16	0.38
Undecanal	5.4	5.2	96 ± 1	0.05	0.56
Dodecanal	8.3	5.5	94 ± 3	0.07	0.09
Tridecanal	9.4	6.5	95 ± 6	0.04	0.13

cyclohexanone and acetophenone, were also achieved by ESI-MS/MS. Some carbonyls have the same molecular weight were still not separated by ESI-MS/MS, including butyraldehyde/2-butanone, *o/m*-tolualdehyde, isovaleraldehyde/2-pentanone, hexaldehyde/2-hexanone, and nonanaldehyde/2-nonanone.

3.3. Method evaluation

In order to evaluate the proposed method, some parameters were determined under the above optimized conditions and results are shown in Table 2.

Linearity was investigated over a concentration range of 10–450 μg/L. Good linearities with correlation coefficients (R^2) ranging from 0.9938 to 0.9999 were obtained. The recoveries were determined as follows. Firstly, the standard solutions were directly added to the blank sampled cartridges. Secondly, the cartridges were eluted with 2 mL ACN. Finally, the eluted solutions were determined by LC-ESI-MS/MS. The added quantities of carbonyl-DNPHs were 8 μg for formaldehyde and acetaldehyde, 4 μg for acetone, 0.3 μg for butyraldehyde/2-butanone and hexaldehyde/2-hexanone, 0.2 μg for propionaldehyde, isovaleraldehyde/2-pentanone, crotonaldehyde and nonanaldehyde/2-nonanone, and 0.1 μg for other carbonyls. Recoveries were in the range of 90–104%. Reproducibilities (R.S.D., *n* = 5) were in the range of 1.7–11% which were measured by repeated determination of standard solutions containing 30 μg/L

butyraldehyde/2-butanone and hexaldehyde/2-hexanone, 20 μg/L propionaldehyde, isovaleraldehyde/2-pentanone, crotonaldehyde and nonanaldehyde/2-nonanone, and 10 μg/L other carbonyl-DNPHs. Limit of detection (LOD) was determined by using seven replicate analyses of the working standards at the lowest concentration (signal-to-noise ratio, $S/N = 3$), for which an approach was described in detail in 40 CFR Part 136B (Code of Federal Regulation, 2001). The LOD of the proposed method were in the range of 0.4–9.4 ng/m³ for various carbonyls assuming a sampling volume of 180 L air and these values were about 1–2 order of magnitude better than LC-UV detection. Brombacher et al. [14] reported a LOD range of 1–15 ng/m³ on a quadrupole ion-trap system (LCQ classic, ThermoFinnigan, San Jose, CA, USA) in APCI (–). In the study of Grosjean [15], the LOD of formaldehyde was 20 pg. In the present study, a 6 pg LOD of formaldehyde could be achieved.

3.4. Application to air samples

The samples collected in two sampling sites (a residential area of Liwan District (S1) and a research institute of Tianhe District (S2) in Guangzhou, China), were determined by the proposed method. Thirty-two target carbonyl compounds were all identified and quantified, in which butyraldehyde/butanone, isovaleraldehyde/2-pentanone hexaldehyde/2-hexanone, nonanaldehyde/2-nonanone and *o/m*-tolualdehyde could not be separated by LC-ESI-MS/MS

Table 3
Comparison of ESI-MS/MS and UV detection

Compounds	S_a concentration ($\mu\text{g}/\text{m}^3$) mean \pm S.D., $n = 6$	S_b concentration ($\mu\text{g}/\text{m}^3$) mean \pm S.D., $n = 6$	S_c concentration ($\mu\text{g}/\text{m}^3$) mean \pm S.D., $n = 6$
Formaldehyde			
UV	6.37 \pm 0.10	6.95 \pm 0.06	7.13 \pm 0.04
ESI-MS/MS	6.13 \pm 0.10	6.32 \pm 0.06	6.45 \pm 0.38
Acetaldehyde			
UV	9.50 \pm 0.20	8.50 \pm 0.07	9.32 \pm 0.05
ESI-MS/MS	8.97 \pm 0.14	8.04 \pm 0.16	8.89 \pm 0.21
Acetone			
UV	8.14 \pm 0.11	7.17 \pm 0.05	7.73 \pm 0.05
ESI-MS/MS	8.11 \pm 0.13	7.92 \pm 0.08	6.97 \pm 0.18
Propionaldehyde			
UV	0.89 \pm 0.05	0.94 \pm 0.04	0.83 \pm 0.01
ESI-MS/MS	0.97 \pm 0.02	0.88 \pm 0.01	0.89 \pm 0.02
Heptaldehyde			
UV	0.32 \pm 0.02	0.34 \pm 0.03	0.31 \pm 0.03
ESI-MS/MS	0.36 \pm 0.01	0.41 \pm 0.01	0.35 \pm 0.03
Octylaldehyde			
UV	0.62 \pm 0.03	0.78 \pm 0.01	0.57 \pm 0.02
ESI-MS/MS	0.58 \pm 0.02	0.62 \pm 0.03	0.55 \pm 0.05
Decylaldehyde			
UV	0.62 \pm 0.02	0.88 \pm 0.06	0.46 \pm 0.07
ESI-MS/MS	0.43 \pm 0.01	0.73 \pm 0.03	0.43 \pm 0.04

S.D.: standard deviation.

method. Therefore, their sum concentrations were determined in this study. The concentrations of carbonyl compounds are listed in Table 2.

3.5. Compare to LC–UV method

The LC–ESI-MS/MS method was compared with the LC–UV detection at 360 nm method described in our previous work [8,9]. Three samples (S_a , S_b and S_c) in S2 were detected six times by the both methods, respectively. The results of seven carbonyls: formaldehyde, acetaldehyde, acetone, propionaldehyde, heptaldehyde, octylaldehyde and decylaldehyde, are listed in Table 3.

Table 3 shows that for low molecular weight (LMW) carbonyls, such as formaldehyde, acetaldehyde, acetone and propionaldehyde, good agreement existed between the two detection methods and the deviations between the two methods were 3.9–10%, 4.8–5.9%, 0.4–11% and 7–9%, respectively. But for HMW carbonyls (such as heptaldehyde, octylaldehyde and decylaldehyde), since most of their concentrations were below $0.6 \mu\text{g}/\text{m}^3$, small difference maybe resulted in a large deviation. The deviations of heptaldehyde, octylaldehyde and decylaldehyde were in the range of 11–20%, 7–42%, and 7–44%, respectively. The R.S.D. of the studied seven carbonyls detected by LC–UV method were all <9.7% and <9.3% by ESI-MS/MS, and results were both acceptable.

The LOD of LC–ESI-MS/MS method was already described in method evaluation. The 32 carbonyls LOD of LC–ESI-MS/MS were in the range of 0.4 – $9.4 \text{ ng}/\text{m}^3$ and were much lower than those of UV detection [8], which were in the range

of 50 – $150 \text{ ng}/\text{m}^3$ for 21 carbonyls. Because of the lower LOD, the determination of low concentration carbonyls in air samples (mainly HMW carbonyls) was much more precise by LC–ESI-MS/MS than that by UV.

Compared with UV detection, more carbonyls were identified and quantified by LC–ESI-MS/MS method and study shows that if more carbonyls standards were applied, much more carbonyls also could be determined by the method. Moreover, other disadvantages of LC–UV detection, such as the HMW carbonyls (because of the low concentrations in air sample and the interference of the sample matrix) [5,11] and the co-eluting compounds (with different molecular weight, but same property), were also overcome by LC–ESI-MS/MS. This was mainly due to the lower LOD and the higher selectivity of LC–ESI-MS/MS.

4. Conclusions

This study demonstrated that DNPH derivatization and LC–ESI-MS/MS detection is an better analytical method for determination of HMW carbonyl compounds in air sample. Good Linearity, reproducibility and recovery are all obtained. Compared with LC–UV detection, the proposed method obtained much lower LOD and could detect more carbonyl compounds. The application of the method to air samples also achieved excellent result. Thirty-two carbonyl compounds were all identified and quantified in the samples of two sampling sites of Guangzhou. Among most of the samples, acetone was the most abundant carbonyls, followed by formaldehyde, acetaldehyde and butyraldehyde/2-butanone. Study shows that if more carbonyls standards were applied, much more carbonyls

also could be analyzed by the proposed method. Moreover, the identification of the unknown carbonyls in air samples will be an interesting direction.

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