

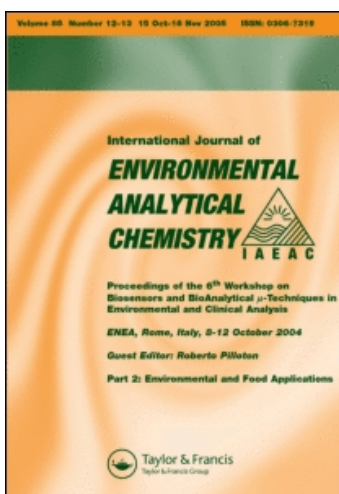
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## Determination of trace volatile fatty acids in ambient air by capillary gas chromatography–mass spectrometry in SIM mode

Ting Wu<sup>ab</sup>, Xinming Wang<sup>a\*</sup>, Dejun Li<sup>a</sup>, Guoying Sheng<sup>a</sup> and Jiamo Fu<sup>a</sup>

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A simple, rapid and sensitive method was developed and validated for the analysis of C<sub>2</sub>–C<sub>5</sub> volatile fatty acids (VFAs) in ambient air. This method involves preconcentration of VFAs with a sodium carbonate-impregnated silica gel tube, ultrasonic extraction with pure water, partition of VFAs to diethyl ether and determination using gas chromatography with a mass selective detector in the selected ion monitoring mode. A water-resistant free fatty acid phase capillary column was used to directly separate C<sub>2</sub>–C<sub>5</sub> VFAs without the time-consuming derivatisation process. The limits of detection ranged from 0.001 to 0.003 µg m<sup>-3</sup> and the limits of quantification ranged from 0.003 to 0.010 µg m<sup>-3</sup>. The validated method was successfully applied to the analysis trace-level VFAs in ambient air and in air samples from a landfill with perceived odour pollution.

**Keywords:** volatile fatty acids (VFAs); GC–MS; selected ion monitoring mode (SIM); FFAP column

### 1. Introduction

Organic acids in the atmosphere are either primarily emitted from anthropogenic or biogenic sources, or secondarily formed during photochemical oxidation of organic precursors [1–4]. Apart from their important roles in atmospheric chemistry and precipitation acidity [4,5], volatile fatty acids (VFAs), especially those with 2–5 molecular carbon atoms (C<sub>2</sub>–C<sub>5</sub>), are primary irritants and ubiquitous odour pollutants with very low sensory thresholds [6] and potential adverse health effects [7,8].

Volatile fatty acids in ambient air are at trace levels with mixing ratios from parts per billion down to parts per trillion [9,10], therefore they need preconcentration before instrumental determination in the laboratory. Among various approaches collecting organic acids in ambient air [11], the most common is based on adsorption [12,13] or absorption by alkaline matters [9,14–21], although solid-phase microextraction (SPME) technique has been recently tested [22,23]. As polar organics, VFAs prepared in solutions can be directly measured by high-performance liquid chromatography (HPLC) [13,20,24], ion chromatography (IC) [19,25,26] or capillary electrophoresis (CE) [17,18,27,28]. Gas chromatography (GC) is also frequently used to determine VFAs [21,29,30], owing to its effective separation, high selectivity and excellent sensitivity. Moreover, the combination

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of GC with mass spectrometry (MS) has been proved to be an extremely versatile source of qualitative and quantitative information about VFAs on a variety of environmental samples [22,23,28]. However, derivatisation is usually a necessary pretreatment for VFAs before injected into GC [12,19,28,29,31], otherwise poor separation or bad peak shapes would be observed. Apart from the time-consuming and labourious derivatisation process, the derivatisation reagents are usually toxic and harmful to the environment and human health.

For biological samples such as urine and faeces, a column with a free fatty acid phase (FFAP), which is quite water resistant, has been successfully used to separate VFAs prepared in water solution without the derivatisation process [32,33]. In the present study, to develop a simple, rapid and environmentally friendly method for the determination of C<sub>2</sub>–C<sub>5</sub> VFAs in ambient air, sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>)-coated silica gel was used for trapping C<sub>2</sub>–C<sub>5</sub> VFAs, and FFAP capillary column was used for separation of VFAs to avoid the derivatisation process during analysis by GC–MS. Moreover, selected ion monitoring (SIM) mode of MS is adopted to increase sensitivity and specificity.

## 2. Experimental

### 2.1 Reagents and materials

Acetic acid (C<sub>2</sub>), propionic acid (C<sub>3</sub>), *i*-butyric acid (*i*-C<sub>4</sub>), *n*-butyric acid (*n*-C<sub>4</sub>), *i*-valeric acid (*i*-C<sub>5</sub>) and *n*-valeric acid (*n*-C<sub>5</sub>) were obtained from Aldrich (Milwaukee, WI, USA). Their physical and chemical properties are shown in Table 1. All these chemicals were analytical reagent (AR) grade and used as standards. Deuterium-substituted valeric acid (CD<sub>3</sub>(CD<sub>2</sub>)<sub>3</sub>COOH, d<sub>9</sub>-*n*C<sub>5</sub>), used as an internal standard (IS), was obtained from Cambridge Isotope Laboratories, Inc (Andover, MA, USA). Diethyl ether (DEE) used as solvents were AR grade and purchased from Merck (Darmstadt, Germany). Sodium chloride (NaCl, AR grade) was supplied by Beijing Chemical Plant (Beijing, China). All water used was prepared by a Milli-Q reagent water system (Jiapeng, Shanghai, China).

Detailed procedures for preparing Na<sub>2</sub>CO<sub>3</sub>-impregnated silica gel absorbent tubes were described elsewhere [34]. Briefly, silica gel (20–40 mesh) was Soxhlet extracted with dichloromethane for 36 h, and activated at 180°C for 12 h. To prepare the adsorbent tube, the treated silica gel was soaked with 0.1 M Na<sub>2</sub>CO<sub>3</sub> for 30 min, and then dried at room temperature under a gentle flow of pure nitrogen. After dried, about 450 mg

Table 1. Parameters of molecular weight (MW), density (d), melting point (m.p.), boiling point (b.p.), vapour pressure and solubility in water are given to characterise physical and chemical properties of VFAs (database: chemical abstracts).

VFAs	CAS No.	MW (g mol <sup>-1</sup> )	d (g mL <sup>-1</sup> )	m.p. (°C)	b.p. (°C)	Vapour pressure, <i>p</i> <sub>o</sub> (hPa)*	Solubility in water* (g L <sup>-1</sup> )
C <sub>2</sub>	64-19-7	60.05	1.05	16.7	118.1	15.4	Highly soluble
C <sub>3</sub>	79-09-4	74.08	0.99	-22.0	140.7	2.9	Highly soluble
<i>i</i> -C <sub>4</sub>	79-31-2	88.11	0.95	-47.0	154.5	12.0	210
<i>n</i> -C <sub>4</sub>	107-92-6	88.11	0.96	-7.9	163.5	0.9	Soluble
<i>i</i> -C <sub>5</sub>	503-74-2	102.13	0.93	-29.3	176.7	0.6	25
<i>n</i> -C <sub>5</sub>	109-52-4	102.13	0.94	-33.8	186.1	0.3	40

Note: \*Vapour pressure and water solubility at 20°C.

Na<sub>2</sub>CO<sub>3</sub>-impregnated silica gel was packed into each clean glass tube (8 cm × 5 mm i.d.) with both ends filled with heat-treated (300°C, 4 h) silanised glass wool and stopped with Teflon caps immediately after packing. Prior to field use and after sampling, tubes were zipped in Teflon bags and stored in a refrigerator at −20°C.

## 2.2 Instruments and conditions

A HP 6890 gas chromatograph combined with a HP 5973 mass selective detector (MSD) was used in this study. A HP-FFAP capillary column (30 m × 0.32 mm i.d., 0.25 μm film) was used to for GC separation of the target compounds. The GC oven temperature was programmed as follows: initial temperature 60°C for 2.0 min, 6°C min<sup>−1</sup> to 145°C, and then 20°C min<sup>−1</sup> to 240°C and holding for 3.0 min. Helium was used as carrier gas at a flow rate of 1.2 mL min<sup>−1</sup>. The inlet was operated in split mode with a split ratio of 10 : 1. Injector temperature was 250°C. For MSD, ionisation mode was electron impacting (EI, 2000 V; 175°C); Acquisition was performed in SIM mode using the retention windows indicated in Table 2. Table 2 also reports the elution time of these analytes and their selected ions for qualification and quantification. Deuterium-labelled valeric acid was adopted as an IS for the quantification of VFAs.

## 2.3 Preparation of stock solutions and calibration standards

The mixed stock standard solution of VFAs were prepared in DEE at concentrations of 1000 mg L<sup>−1</sup> and stored at −20°C in dark conditions until used. The mixed stock solution was diluted in DEE to obtain a series of working standard solutions, with concentrations ranging from 0.005 to 50 mg L<sup>−1</sup>. When the air sampling volume was 60 L, the concentrations of VFAs in air varied from 0.01 to 83.33 μg m<sup>−3</sup>. This authentic standard suite covered the desired range of VFAs in the air [9,10].

## 2.4 Field sampling

To collect VFAs in ambient air, a Thomas pump (Sheboygan, WI, USA) was used to draw air through two Na<sub>2</sub>CO<sub>3</sub>-impregnated silica gel tubes connected in series at a rate of 2 L min<sup>−1</sup> for 30 min. The flow rate was monitored by a rota-meter (Yinhuan Ltd., Zhejiang, China), which was calibrated with a soap-membrane flowmeter. During sampling, each tube

Table 2. Details of the GC–MS program (SIM) applied to the experiments.

VFAs	<i>t<sub>R</sub></i> (min) <sup>a</sup>	Retention window (min)	Selected ions ( <i>m/z</i> ) <sup>b</sup>
C <sub>2</sub>	8.96 ± 0.01	8.00–10.00	43, <u>45</u> , 60
C <sub>3</sub>	10.82 ± 0.02	10.00–11.20	29, <u>45</u> , <u>74</u>
<i>i</i> -C <sub>4</sub>	11.42 ± 0.01	11.20–12.00	41, 43, <u>73</u>
<i>n</i> -C <sub>4</sub>	12.68 ± 0.01	12.00–13.20	<u>60</u> , <u>73</u>
<i>i</i> -C <sub>5</sub>	13.50 ± 0.00	13.20–14.00	29, 57, <u>74</u>
<i>n</i> -C <sub>5</sub>	14.85 ± 0.03	14.00–15.20	<u>60</u> , <u>73</u>
C <sub>5</sub> (d <sub>9</sub> - <i>n</i> C <sub>5</sub> )	14.63 ± 0.02	14.00–15.20	<u>45</u> , 63

Notes: <sup>a</sup>Each value = mean value ± SD (*n* = 5).

<sup>b</sup>Ions with underlines are target ions used for quantitation.

was wrapped with aluminium foil to avoid sunlight, which may induce photochemical reaction of the VFAs trapped on the alkaline silica gel. In this study, air samples were collected on the roof of a high building (30 m above the ground level) and at a landfill, respectively. The rooftop sample is representative of ambient air with relatively low levels of VFAs and the landfill sample might have relatively higher levels of these irritants. After sampling, samples were placed in a refrigerator at  $-20^{\circ}\text{C}$  until analysis.

### 2.5 Sample preparation

In the laboratory, after the field trapping of ambient VFAs the alkaline silica gel in the tubes was put into glass vials and extracted under ultrasonication with 2 mL Milli-Q water twice, each for 30 min. Saturated with NaCl and centrifuged for 10 min at  $4000\text{ r min}^{-1}$ , the upper aqueous extracts (AE) were put together and transferred into volumetric flasks using pipettes, and then acidified to  $\text{pH} < 4$  with 1 M sulphuric acid ( $\text{H}_2\text{SO}_4$ ) [35]. The acidified extracts were then partitioned with 2 mL DEE twice, and the ether phase were put together and 5  $\mu\text{L}$  IS ( $100\text{ }\mu\text{g mL}^{-1}$   $d_9$ -*n*C5 in DEE) were added before concentrating under a gentle stream of nitrogen to about 100  $\mu\text{L}$ . After concentrating, 1  $\mu\text{L}$  volume of ether phase was injected directly into GC-MS without any derivatisation.

## 3. Results and discussion

### 3.1 GC separation of VFAs

Figure 1(a) is a typical chromatogram of standard mixtures containing the six VFAs. The HP-FFAP column satisfactorily separated the VFAs within 15 min. They were identified by their GC retention times and their MS characteristic ions in comparison with known standard compounds. The six VFAs eluted in the following order: (1) acetic acid; (2) propionic acid; (3) *i*-butyric acid; (4) *n*-butyric acid; (5) *i*-valeric acid; (6) *n*-valeric acid. Figure 1(b) and (c) is the chromatograms of VFAs in ambient air from a rooftop and a landfill, respectively. As indicated by Figure 1(a) of a standard mixture and by Figure 1(b) and (c) of the field samples, stable baselines and good separation were obtained with sharp and symmetric peaks of VFAs. This would allow easy identification and accurate quantification of VFAs by GC-MS using a FFAP column. Compared to the standard method GBZ/T 160.59, more VFAs, especially higher ones, can be detected in this method.

### 3.2 Extraction efficiency

The volumetric ratio between the AE and DEE was proven to be crucial for obtaining quantitative recoveries of VFAs, especially short-chain acids such as acetic acid and propionic acid [35]. An amount of 40  $\mu\text{L}$  volume of the stock solution of VFAs was injected into a volumetric flask containing 4 mL pure water, extracted with five different volumes of DEE and analysed as above, respectively. The tests were conducted with five duplicates. Table 3 showed the recoveries of  $\text{C}_2$  and  $\text{C}_3$  increased significantly with the increasing ratios of DEE to AE until a ratio of 1:1, while those of  $\text{C}_4$ - $\text{C}_5$  acids were less affected by the volumetric ratios. Thus, the recovery of each target VFA was adequate for obtaining quantitative yields when the volumetric ratio of DEE to AE reached 1:1.

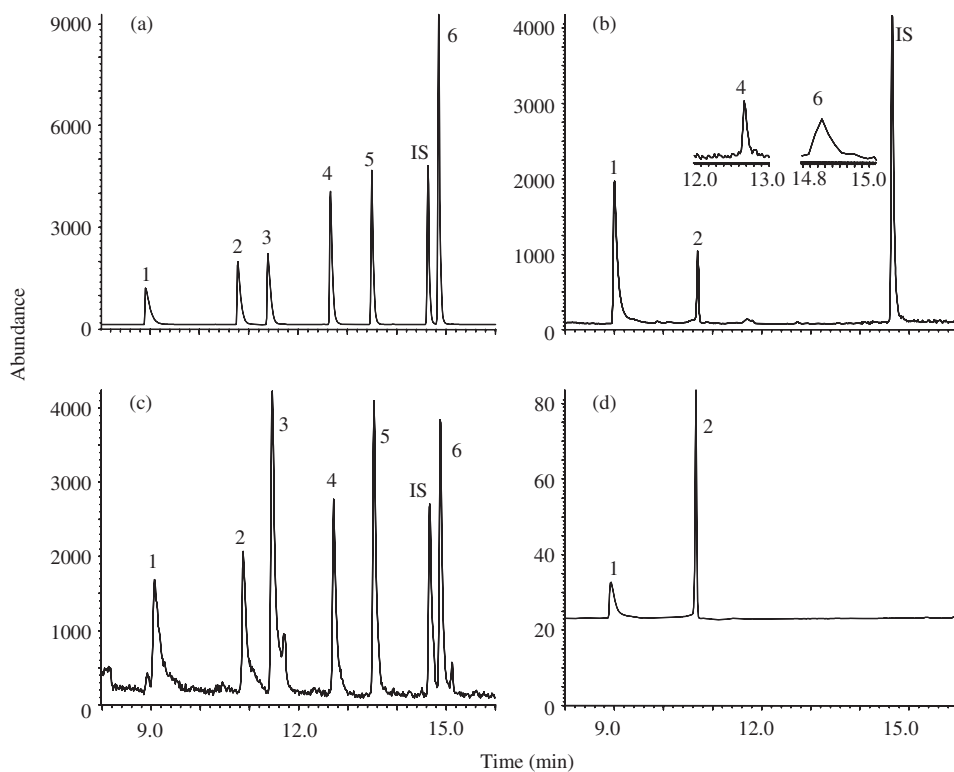


Figure 1. Chromatograms of VFAs of (a) a standard solution with IS, (b) an air sample with IS, (c) an odour sample with IS and (d) field blank. The numbered peaks represent the VFAs: (1) acetic acid,  $m/z$  45; (2) propionic acid,  $m/z$  74; (3) *i*-butyric acid,  $m/z$  43; (4) *n*-butyric acid,  $m/z$  60; (5) *i*-valeric acid,  $m/z$  74; (6) *n*-valeric acid,  $m/z$  60. IS is valeric acid ( $d_9$ -*n*C5).

Table 3. Changing of extraction efficiencies for the VFAs with the volumetric ratio of AE ( $\sim 10 \text{ mg L}^{-1}$  for each VFAs) to DEE.

VFAs	Recoveries (%) at different volumetric ratios of AE to DEE ( $n = 5$ )				
	4 : 1.6 mL	4 : 2 mL	4 : 4 mL	4 : 8 mL	4 : 10 mL
$C_2$	$14.0 \pm 1.4^a$	$56.0 \pm 2.0$	$91.3 \pm 1.2$	$91.0 \pm 1.5$	$90.8 \pm 1.5$
$C_3$	$46.0 \pm 2.0$	$68.0 \pm 1.9$	$94.0 \pm 2.0$	$93.6 \pm 2.0$	$94.0 \pm 2.1$
<i>i</i> - $C_4$	$82.0 \pm 1.3$	$91.7 \pm 1.2$	$100.0 \pm 2.8$	$100.0 \pm 1.5$	$99.8 \pm 1.2$
<i>n</i> - $C_4$	$98.6 \pm 2.4$	$102.5 \pm 1.8$	$105.3 \pm 1.8$	$106.7 \pm 2.1$	$102.5 \pm 1.6$
<i>i</i> - $C_5$	$99.2 \pm 1.5$	$100.0 \pm 2.7$	$102.0 \pm 2.0$	$100.0 \pm 2.3$	$101.5 \pm 2.4$
<i>n</i> - $C_5$	$99.5 \pm 2.1$	$105.0 \pm 3.0$	$103.5 \pm 1.5$	$106.7 \pm 1.5$	$100.0 \pm 2.0$

Note: <sup>a</sup>Mean  $\pm$  SD ( $n = 5$ ).

### 3.3 Method validation

#### 3.3.1 Efficiency of absorbent tubes to trap VFAs

In order to examine the efficiency of the absorbent tubes to trap atmospheric VFAs, air samples were collected with two tubes that were connected in series with Teflon tube and

Table 4. Concentrations of VFAs in ambient air on the roof of a building (sample A) and at a landfill (sample B), trapped in two absorbent tubes in series ( $\mu\text{g m}^{-3}$ ).

Samples	C <sub>2</sub>	C <sub>3</sub>	<i>i</i> -C <sub>4</sub>	<i>n</i> -C <sub>4</sub>	<i>i</i> -C <sub>5</sub>	<i>n</i> -C <sub>5</sub>	Total
<b>Sample A</b>							
Total	2.282	0.248	ND	0.110	ND	0.068	2.708
1st tube	2.214	0.237	ND	0.110	ND	0.068	2.629
2nd tube	0.069	0.011	ND	ND	ND	ND	0.079
2nd/1st (%)	3.10	4.46	–	0.00	–	0.00	3.01
<b>Sample B</b>							
Total	2.732	0.264	3.123	0.248	4.062	0.410	10.839
1st tube	2.609	0.253	3.080	0.236	4.016	0.392	10.585
2nd tube	0.123	0.012	0.043	0.012	0.046	0.018	0.253
2nd/1st (%)	4.71	4.58	1.40	5.00	1.13	4.65	2.39

Note: <sup>a</sup>ND, not detected.

analysed individually as described above. Table 4 gave the concentrations of the ambient VFAs trapped by the two absorbent tubes. The percentages of C<sub>2</sub>–C<sub>5</sub> VFAs trapped by the back tubes to those by the front tubes were all <5% even for the landfill sample with relatively higher VFAs, indicating that a single absorbent tube can trap C<sub>2</sub>–C<sub>5</sub> VFA effectively and there was no breakthrough of the absorbent tubes when collecting 60 L air samples.

### 3.3.2 Field blank

Field blanks were run together with the samples. Acetic acid and propionic acid have appeared as major contaminants as shown in Figure 1(d). Their amounts, however, were usually <3% of the ambient samples. Other volatile organic acids were not detected in the blanks. VFAs concentrations presented in this study were corrected for the field blanks.

### 3.3.3 Calibration curves

The calibration curves were obtained by analysing a series of standard solutions, which covers a wide range enough to bracket the possible amounts or concentrations in ambient air or in odour pollution samples. As shown in Table 4, the dose-response linearity for the VFAs is excellent, with square correlation coefficients ( $r^2$ ) better than 0.99.

### 3.3.4 Limit of detection and limit of quantification

The limits of detection (LODs) and limits of quantification (LOQs) of the VFAs, based on signal-to-noise ratios (S/N) of 3:1 and 10:1, respectively, were determined. The LODs and LOQs of the VFAs are under the order of micrograms per cubic metre (data shown in Table 5). This sensitivity was adequate for the analysis of VFAs in ambient air or in odour pollution. Due to the avoiding of derivatisation process by using a polar FFAP column and the MS analysis in SIM mode, the present method obtained lower limits and increased sensitivity than those previously obtained by other authors. Sollinger *et al.* [12] determined VFAs in ambient air and obtained LODs of 2.3, 2.6, 2.2  $\mu\text{g m}^{-3}$  for C<sub>2</sub>, C<sub>3</sub> and *n*-C<sub>4</sub>, respectively, using an ion-exchange resin sampling, methylation by methyl formate and

Table 5. Calibration equations, LODs and LOQs of the VFAs.

VFAs	Inearity range <sup>a</sup> (mg L <sup>-1</sup> )	Linear equation $Y = aX + b^b$	Correlation coefficient ( $r^2$ )	LOD ( $\mu\text{g m}^{-3}$ ) <sup>c</sup>	LOQ ( $\mu\text{g m}^{-3}$ ) <sup>d</sup>
C <sub>2</sub>	0.005–50	$Y = 63098X + 2764.3$	0.9975	0.002	0.008
C <sub>3</sub>	0.005–50	$Y = 19953X + 823.72$	0.9957	0.002	0.006
<i>i</i> -C <sub>4</sub>	0.005–50	$Y = 39139X + 2353.1$	0.9991	0.003	0.010
<i>n</i> -C <sub>4</sub>	0.005–50	$Y = 40849X + 271.24$	0.9993	0.001	0.003
<i>i</i> -C <sub>5</sub>	0.005–50	$Y = 54882X - 7625$	0.9925	0.002	0.006
<i>n</i> -C <sub>5</sub>	0.005–50	$Y = 51518X - 109.73$	0.9996	0.001	0.004

Note: <sup>a</sup>When the air sampling volume is 60 L, the concentrations of VFAs in standard solutions are equal to those from 0.01 to 83.33  $\mu\text{g m}^{-3}$  in air.

<sup>b</sup> $Y$  is the peak area relative to IS and  $X$  is the concentration of specific VFAs in the working standard solution.

<sup>c</sup>Based on a S/N of 3:1 referred to an air volume of 60 L for VFAs.

<sup>d</sup>Based on a S/N of 10:1 referred to an air volume of 60 L for VFAs.

separation with a RTx-Volatile capillary column. Suzuki [25] obtained LODs of 0.29 ppb (0.77  $\mu\text{g m}^{-3}$ ) and 0.32 ppb (1.07  $\mu\text{g m}^{-3}$ ) for C<sub>2</sub> and C<sub>3</sub>, respectively, by a microporous tube diffusion scrubber system coupled to IC. Desauziers *et al.* [17] obtained LODs ranging from 4 to 60  $\mu\text{g m}^{-3}$  for VFAs, determined by CE. Willig *et al.* [21] observed LODs of 0.5, 0.6, 4.2, 4.8, 4.4 and 4.3  $\mu\text{g m}^{-3}$  for C<sub>2</sub>, C<sub>3</sub>, *i*-C<sub>4</sub>, *n*-C<sub>4</sub>, *i*-C<sub>5</sub> and *n*-C<sub>5</sub>, respectively, using GC-FID. Godoi *et al.* [22] obtained LODs of 5.7  $\mu\text{g m}^{-3}$  for C<sub>2</sub>, determined by ion-trap GC-MS and separated with a CPWAX 52 capillary column. In the Chinese standard method GBZ/T 160.59 using Na<sub>2</sub>CO<sub>3</sub>-coated silica gel tubes for sampling and GC-FID for the determination, LODs for C<sub>2</sub> and C<sub>3</sub> were as high as 8000 and 4000  $\mu\text{g m}^{-3}$ , respectively.

### 3.3.5 Recovery and reproducibility

The recovery and reproducibility tests were conducted by using standard gaseous mixtures with the concentration of 1  $\mu\text{g m}^{-3}$  for each VFA, which were generated by the method described in the previous study [22]. The standard gases were sampled and analysed as described above. The test had five duplicates. The recoveries (in percentage) and their relative SD (RSD) were 90.2 ± 3.5 for C<sub>2</sub>, 92.8 ± 2.1 for C<sub>3</sub>, 99.8 ± 1.2 for *i*-C<sub>4</sub>, 100.0 ± 1.8 for *n*-C<sub>4</sub>, 101.0 ± 0.9 for *i*-C<sub>5</sub> and 99.7 ± 2.0% for C<sub>5</sub>. These recovery values are fairly good and acceptable, and no significant differences were encountered. Thus, this method is reliable for accurate quantitative determination of VFAs in ambient air.

## 3.4 Application in the field

The validated method has been successfully used to determine the VFAs in ambient air. Chromatograms of VFAs in air samples collected on the roof of a building and at a landfill are shown in Figure 1(b) and (c). VFA concentrations in air were quantified by the IS calibration procedure. Table 4 gives the concentrations of VFAs. In the rooftop ambient air sample, acetic acid (2.282  $\mu\text{g m}^{-3}$ ) was the predominant species followed by propionic acid (0.248  $\mu\text{g m}^{-3}$ ), *n*-butyric acid (0.110  $\mu\text{g m}^{-3}$ ) and *n*-valeric acid (0.068  $\mu\text{g m}^{-3}$ ). No *i*-butyric and *i*-valeric acids were detected. This observation is consistent with results



reported by Nolte [9]. In the landfill air sample, all VFAs were detected with higher concentrations compared to those in the rooftop air sample. The concentrations were 2.732, 0.264, 3.123, 0.248, 4.062 and 0.410  $\mu\text{g m}^{-3}$  for  $\text{C}_2$ ,  $\text{C}_3$ ,  $i\text{-C}_4$ ,  $n\text{-C}_4$ ,  $i\text{-C}_5$  and  $i\text{-C}_5$ , respectively. In addition to  $\text{C}_2$ ,  $i\text{-C}_4$  and  $i\text{-C}_5$  were found to be the predominant VFAs in the landfill sample. A similar observation was made in air samples collected in landfill stations [3]. Accordingly, the method described in the present study can be successfully applied to the analysis of VFAs in ambient air samples as well as in odour pollution.

#### 4. Conclusions

The proposed method allows the simple and rapid determination of VFAs in ambient air or VFAs-related odour pollution.  $\text{Na}_2\text{CO}_3$ -impregnated alkaline silica gel absorbent tubes can efficiently trap analytes in air samples. There is no need to derivatise VFAs owing to the use of polar FFAP–GC column. Under the optimised extraction and analysis conditions, the linearity and repeatability are good, and the recovery is adequate. SIM mode is well suited for the detection of trace VFAs in ambient air below micrograms per cubic metre in ambient air with much lower detection limits and increased sensitivity. Therefore, GC–MS technique using FFAP capillary column is a reliable method applicable to the determination of trace VFAs in ambient air.

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