Contents lists available at ScienceDirect

Atmospheric Pollution Research

journal homepage: www.elsevier.com/locate/apr

A new method for the determination of imidazole-like brown carbons using gas chromatography-mass spectrometry

Pingping Chen [a,b], Qinhao Lin [a,b,*], Taicheng An [a,b,c]

[a] Guangdong-Hong Kong-Macao Joint Laboratory for Contaminants Exposure and Health, Guangdong Key Laboratory of Environmental Catalysis and Health Risk Control, Institute of Environmental Health and Pollution Control, Guangdong University of Technology, Guangzhou 510006, China
[b] Key Laboratory for City Cluster Environmental Safety and Green Development of the Ministry of Education, School of Environmental Science and Engineering, Guangdong University of Technology, Guangzhou 510006, China
[c] Chemistry and Chemical Engineering Guangdong Laboratory, Shantou 515031, China

ARTICLE INFO

ABSTRACT

Imidazole-like compounds were important components of brown carbon, which played a significant role in radiative forcing in the atmosphere. In this study, a new detection method of imidazole-like compounds in the atmosphere was developed using gas chromatography-mass spectrometry (GC-MS) due to its high resolution and sensitivity. Seven imidazole-like compounds, including imidazole (IM), 4 (5)-methylimidazole (4MEI), 2-ethylimidazole (2EI), 2,4-dimethylimidazole (2,4-DMI), 2-methylimidazole-4-carbaldehyde (2MI4C), 2,2-biimidazole (BI) and 2-phenylimidazole (2PI) were performed using the GC-MS method. Acetonitrile, pyridine, anhydrous ethanol and isobutyl chloroformate were used to conduct the derivatization of imidazole-like compounds before GC-MS analysis. Optimal amounts of 90 μL acetonitrile, 60 μL pyridine, 200 μL anhydrous ethanol and 70 μL isobutyl chloroformate ensured the derivatization of the 7 imidazole-like compounds. The pH value influenced imidazole-like compounds extraction from the aqueous phase. The result showed that the pH value for the extraction of 7 imidazole-like compounds was adjusted to be 8.0. Limits of detection and quantification for the 7 imidazole-like compounds were 0.0553–0.8914 and 0.2370–1.9373 μg/mL, respectively, using this method. The spiked recoveries for the 7 imidazole-like compounds ranged from 58.84% to 160.99%. The method was further applied to measure imidazole-like compounds from aqueous reactions in the experiment study and atmospheric aerosols in the field study. IM, BI, 4MEI and 2,4-DMI were observed in the aqueous reaction of carbonyls with reduced nitrogen. Furthermore, for the first time in the atmospheric particles quantitative IM and 4MEI, China's northern coast. The developed method would help us better understand the source and evolution of imidazole-like brown carbon aerosols in the atmosphere.

1. Introduction

Brown carbon (BrC) is one of the important light-absorbing organic aerosols in the atmosphere. BrC can absorb solar radiation over a spectral range from visible to ultraviolet wavelengths (Formenti et al., 2003; Kirchstetter et al., 2004).

The BrC in the atmosphere can originate from primary and secondary formation pathways. The secondary formation pathways of BrC involve the oxidation of volatile organic compounds in gas as well as particle phases and the aqueous reaction of carbonyls with ammonia or amines (De Haan et al., 2018a; Liu et al., 2015a; Yan et al., 2018).

Nitrogen-containing compounds, such as imidazole-like compounds, were the significant secondary BrC substances (Galloway et al., 2014; Liu et al., 2015b; Schwier et al., 2010).

Imidazole-like compounds were five-membered heterocyclic compounds with two interstitial nitrogen atoms in their molecular structures. These compounds were determined to be the key factors in brown carbon absorption characteristics (De Haan et al., 2011; Feng et al., 2013; Laskin et al., 2015; Moise et al., 2015; Yu et al., 2011). Moreover, imidazole (IM), imidazed-2-carboxaldehyde (IC), and 2,2-biimidazole (BI) can be used as photosensitizers in the atmosphere (Aregahegn et al., 2013). These photosensitizers could cause the growth of

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secondary organic aerosols and modify the aerosol aging process (Li et al., 2016; Tsui et al., 2017).

Many laboratory studies confirmed that the aqueous reaction of carbonyl compounds with reduced nitrogen (e.g., ammonia, amines or amino acids) can produce abundant imidazole-like compounds. Kampf et al. (2012) detected the imidazole-like compounds including IM and BI in the aqueous reaction of glyoxal and ammonium sulfate using liquid chromatography tandem secondary mass spectrometry (HPLC-E-SI-MS/MS). Yu et al. (2011) employed the nuclear magnetic resonance (NMR) technique to identify IM in the aqueous reaction of glyoxal and ammonium sulfate. Rodriguez et al. (2017) reported that 4 (5)-methyl-imidazole (4MEI) and 2,4-dimethylimidazole (2,4-DMI) were found in the aqueous reaction of methylglyoxal with ammonium sulfate using NMR hydrogen spectroscopy. Lee et al. (2013) also found that glyoxal can rapidly react with ammonium salts to form IM. De Haan et al. (2011) simulated the reaction of methylglyoxal with ammonium sulfate, methylamine and amino acids in the laboratory and formed imidazole-like compounds such as methylimidazole and 2-methylimida-zole. Other laboratory studies observed that 1,3-dimethylimidazole existed in the aqueous reaction of glyoxal and amino acids (De Haan et al., 2009).

Aside from laboratory research, observations of imidazole-like compounds in atmospheric aerosols have been reported. A minor number of aerosols were discovered in the surroundings of imidazole in existing research using electrospray ionization mass spectrometry (ESI-MS) (Dou et al., 2015; Laskin et al., 2009). Lian et al. (2020) provided field evidence of molecule-based compounds and regenerative nitrogen substances forming molecules at the individual particle level in the cloud for the first time using a single particle mass spectrum (SPMS), confirming a secondary source of imidazole-like compounds in the atmosphere. However, the majority of research was limited to qualitative studies, with very few quantitative studies. Teich et al. (2016) used capillary electrophoresis electrospray ionization time-of-flight mass spectrometry to first measure imidazoles in atmospheric aerosol, but some polar imidazoles could not be evaluated in the study. Gao et al. (2021) enabled the quantification of imidazoles using ultra-performance liquid chromatography and quadrupole time-of-flight mass spectrometry. He et al. (2022) used high-performance liquid chromatography and tandem mass spectrometry for the quantification of imidazoles. However, the liquid chromatography method of matrix effects would lead to quantitative errors in imidazoles (Gao et al., 2021).

A gas chromatography-mass spectrometry (GC-MS) method has been widely used for the detection of imidazole-like compounds in food and pharmaceuticals due to its high resolution and sensitivity (Casal et al., 2002; Cunha et al., 2011; Fernandes and Ferreira, 1997; Lim and Shin, 2012). Purification was required to extract imidazole-like compounds from the aqueous phase in order to successfully perform GC-MS analysis due to the complexity in the aqueous phase. These methods included solvent extraction, solid-phase extraction (Lim and Shin, 2012) or ion-pair extraction (Gyllenhaal et al., 1980; Hoogewijs and Massart, 1979; Modin and Schill, 1975). However, the determination of imidazole-like compounds from aqueous reactions or atmospheric aerosols was rarely reported using the GC-MS method.

In this work, we used isobutyl chloroformate (IBCF) as a derivati-zation reagent to improve the volatility of imidazole-like compounds. Their qualitative and quantitative information were further character-ized using GC-MS. Moreover, the method was finally used to measure imidazole-like compounds from aqueous reactions and atmospheric aerosols.

2. Materials and methods

2.1. Reagents and solutions

Bis (2-ethylhexyl) phosphate (BEHPA; purity $\geq$98%), isobutyl chloroformate (IBCF; purity $\geq$98%), potassium hydroxide (KOH; 8 M),

hydrochloric acid (AR), pyridine (purity $\geq$99%), anhydrous ethanol (purity $\geq$99.5%), sodium bicarbonate (AR), potassium dihydrogen phosphate (purity $\geq$99%), dipotassium hydrogen phosphate (purity $\geq$99%), N-methylformylaniline (IS; purity $\geq$99%), 2-methylimidazole-D6 (purity $\geq$98%), glyoxal (40% solution), methylglyoxal (40% solution), glycine (AR), ammonium sulfate (99%), methylamine (40% solution) were purchased from Guangzhou Chemical Reagent Factory. Acetonitrile, dichloromethane and methanol were purchased from Merck, Germany. Structures and molecular weights of the 7 standard imidazole-like compounds are shown in Table S1. They were IM, 4MEI, 2EI, BI, 2,4-DMI, 2-methylimidazole-4-carbaldehyde (2MI4C) and 2-phenylimidazole (2PI). These standard imidazole-like compounds were purchased from Beijing Inokai Technology Co.

2.2. Methods for standard imidazole-like compounds

The 7 standard imidazole-like compounds were diluted to 1–250 μg/mL using 0.1 M HCl and were stored at 4 °C until using. The pre-treatment process is shown in Fig. S1. The prepared standard solution with a volume of 2 mL was transferred into a centrifuge tube and added 30 μL 400 μg/mL 2-methylimidazole-D6 to calculate the recovery rate. The mixture was vortexed for 30 s at room temperature and added 2 mL 0.2 mol/L phosphate buffer and adjusted to the appropriate pH by adding KOH dropwise. A volume of 3 mL of solution was further transferred into the second centrifuge tube and added 3 mL 0.1 M BEHPA prepared with dichloromethane as the solvent. The mixture was also vortexed for 30 s at room temperature and finally centrifuged at 3500 r/min for 2 min. After stratification, 2.5 mL lower phase was transferred into the third centrifuge tube, added 1.5 mL 0.1 mol/L hy-drochloric acid, vortex for 30 s at room temperature and then centri-fuged at 3500 r/min for 2 min. The upper phase of the third centrifuge tube was transferred into the fourth centrifuge tube, added acetonitrile, pyridine, anhydrous ethanol and vortexed for 4–5 s at room tempera-ture. Next, IBCF solution, 1 mL 1 mol/L NaHCO3 solution and 250 μL dichloromethane were also added. After vortex mixing for 4–5 s, 200 μL upper phase was transferred to the autosampling vial, and 100 μL 2.5 μg/mL N-methylformylaniline was added before GS-MS analysis.

The derivatization of 7 standard imidazole-like compounds was further analyzed by the GC-MS (Agilent 7890 B–5977 B) analysis. The chromatographic column used a 30 m HP-5MS quartz capillary column (0.25 mm inner diameter, 0.25 μm film thickness, 19011s-433 ui, Agi-lent, USA). The GC temperature program was shown as follows: The temperature started at 70 °C and was maintained for 1 min, then increased to 100 °C with a heating rate of 20 °C/min, 5 °C/min to 140 °C, 20 °C/min to 280 °C and finally maintained at 280 °C for 3 min. The temperature of the injector and the transfer line was kept at 280 °C. High purity helium was used as the carrier gas and the flow rate was set to 1 mL/min. A splitless injection model was used for 1 μL samples. The electron energy was set to 70 eV and the mass of the scan range mass-to-charge ratio (m/z) 50–550 was monitored.

2.3. Methods for imidazole-like compounds in the laboratory study

Aqueous reactions of 100 mL 10 mM carbonyls (i.e., glyoxal or methylglyoxal) with 100 mL 10 mM reduced nitrogens (i.e., ammonium sulfate, methylamine and glycine) were simulated in the laboratory study. The qualitative and quantitative information on imidazole-like compounds from the aqueous reactions was characterized using the above analysis method.

2.4. Methods for imidazole-like compounds in the field study

The quartz filters were placed in a high flow sampler (Tianhong In-struments, flow rate of 1.05 m^3/min) to collect atmospheric aerosols. The quartz filters were first baked in a muffle furnace at 500 °C for 4 h. After being allowed to cool at room temperature, they were placed in a

container equilibrated at a temperature of 20 °C and a relative humidity of 30% for 24 h, and then weighed and stored in a −20 °C refrigerator until analysis. Sample period was performed for 3 days in January 2021 in the coastline of Qingdao city, North China. Each sample collected lasted for 8 h. The atmospheric samples were first extracted utilizing ultrasonication with 0.1 M HCl for 15 min and then repeated three times. The three extractions were further transferred to a flat bottom flask, dried in a fume hood and re-dissolved using 0.1 M HCl. The above analysis method was used to perform the qualitative and quantitative information of imidazole-like compounds.

3. Results and discussion

Fig. 1 shows the total ion chromatograms and retention times of the 7 standard imidazole-like compounds. The retention times in the GC increased from 7.34 min for IM to 16.80 min for 2BI. The qualitative and quantitative ions for the 7 standard imidazole-like compounds are summarized in Table 1. The qualitative ions for IM included m/z 168, 95, 68, 57 and 41, the quantitative ion was m/z 168. The qualitative ions for 4MEI were m/z 182, 109, 82, 68, 57 and 41, the quantitative ion was m/z 182. Note that there were two distinct peaks with 4MEI due to the presence of isomers (Fernandes and Ferreira, 1997). The qualitative ions for 2EI comprised of m/z 196, 95, 57, 41 and its quantitative ion was m/z 95. The qualitative ions for 2,4-DMI consisted of m/z 196, 96, 57 and 41, and its quantitative ion was m/z 96. The qualitative ions for 2MI4C contained m/z 210, 110, 57 and 41, the quantitative ion was m/z 210. The qualitative ions for 2PI were m/z 244, 144, 57 and 41, the quantitative ion was m/z 244. The qualitative ions for BI consisted of m/z 334, 134, 57 and 41, the quantitative ion was m/z 134.

3.1. Optimal amount of solvents for derivation efficiency

In order to optimize the derivatization efficiencies of the 7 standard imidazole-like compounds, the amounts of acetonitrile, pyridine, anhydrous ethanol and IBCF would be evaluated. An orthogonal experiment designed by the software SPSS was used to optimize the amounts of acetonitrile, pyridine, anhydrous ethanol and IBCF, and the statistical procedure is shown in Fig. S2. Amounts of 90–180 μL acetonitrile, 60–120 μL pyridine, 200–350 μL anhydrous ethanol and 60–75 μL IBCF used for the derivatization of the 7 standard imidazole-like compounds were considered in this study. A total of 16 amount combinations of acetonitrile, pyridine, anhydrous ethanol and IBCF were finally obtained (Table S2).
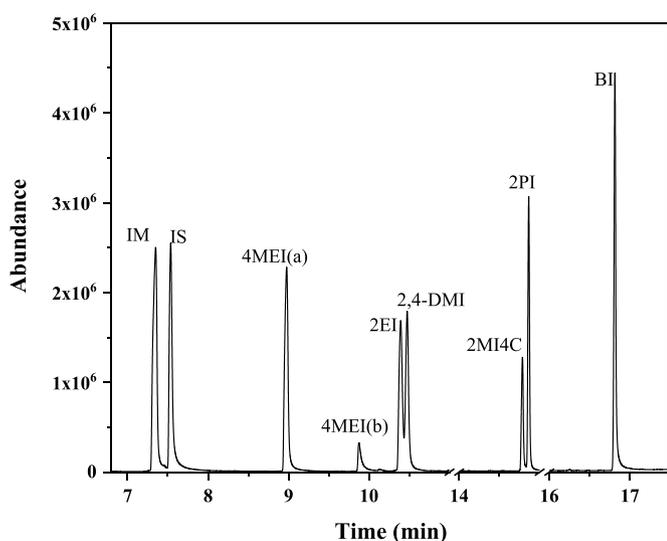

Fig. 1. Ion chromatography of 7 standard imidazole-like compounds derivatized with isobutyl chloroformate.

Table 1

Qualitative ions and quantitative ions of 7 standard imidazole-like compounds.

RT (min)	Compounds	Qualitative ion and quantitative (m/z)
7.34	Imidazole	**168** , 95 , 68 , 57 , 41
8.97	4 (5)-Methylimidazole	**182** , 109 , 82 , 68 , 57 , 41
9.88		**182** , 109 , 82 , 57 , 41
10.39	2-Ethylimidazole	196 , **95** , 57 , 41
10.49	2,4-Dimethylimidazole	196 , **96** , 57 , 41
13.08	2-Methyl-1H-Imidazole-4-carbaldehyde	**210** , 110 , 57 , 41
14.88	2-Phenylimidazole	**244** , 144 , 57 , 41
16.80	2,2′-Biimidazole	334 , **134** , 57 , 41

Bold markers represent the quantitative ions.

ANOVA analysis was used to assess the interaction effect of acetonitrile, pyridine, anhydrous ethanol and IBCF on the derivatization efficiencies of the 7 standard imidazole-like compounds. The P values for 2EI, 2, 4-DMI, 2M4NI, 2PI and BI above 0.05 (Table S3) suggest that the interaction effect of acetonitrile, pyridine, anhydrous ethanol and IBCF was a minor contributor to the derivatization efficiencies of these imidazole-like compounds. Therefore, individual uses of acetonitrile, pyridine, anhydrous ethanol and IBCF would influence the derivatization efficiencies of 2EI, 2, 4-DMI, 2M4NI, 2PI and BI. It had been found that the maximum peak areas of 2EI, 2, 4-DMI, 2M4NI, 2PI and BI formed in individuals using either 90 μL acetonitrile or 60 μL pyridine for the derivatization, as shown in Fig. 2. In addition to acetonitrile and pyridine, 200 μL anhydrous ethanol was the optimal amount for the derivatization efficiencies of 2M4NI, 2PI and BI (Fig. 2). The increase in amount of anhydrous ethanol were found for 2, 4-DMI (250 μL) and 2EI (350 μL). The optimal amount of IBCF for the derivatization efficiencies of 2EI, 2,4-DMI, 2M4NI and BI was 70 μL, but not found for 2PI (75 μL).

Oppositely, the P values for IM and 4MEI below 0.05 (Table S3) using the ANOVA analysis indicate that the interaction effects of acetonitrile, pyridine, anhydrous ethanol and IBCF would alter the derivatization efficiencies of IM and 4MEI. A range analysis method was used to distinguish which of those solvents contribution to the derivatization efficiencies of IM and 4MEI. The R and K values were indicators of contributor and corresponding amount to the derivatization efficiencies of IM and 4MEI in the range analysis method. The R values of acetonitrile, pyridine, anhydrous ethanol and IBCF were 428,181, 206,745, 63,854 and 82,911, respectively (Table S4), for the derivatization efficiencies of IM. A similar feature of R values for the acetonitrile, pyridine, anhydrous ethanol and IBCF was observed for 4MEI. These results suggest that acetonitrile was the most important solvent for the derivatization efficiency of IM and 4MEI, followed by pyridine and IBCF, and the minimum effect was anhydrous ethanol. Furthermore, the maximum K values corresponding to amounts of acetonitrile, pyridine, IBCF and anhydrous ethanol were 90, 80, 250 and 65 μL, respectively, for the derivatization efficiency of IM (Fig. 2). The optimal amounts of acetonitrile, pyridine, IBCF and anhydrous ethanol were 90, 60, 250 and 65 μL, respectively, for the derivatization efficiency of 4MEI (Fig. 2). In order to simultaneously improve the derivatization efficiencies of the above 7 imidazole-like compounds in this study, the amounts of 90 μL acetonitrile, 60 μL pyridine, 200 μL anhydrous ethanol and 70 μL IBCF were finally used to conduct the derivatization of these imidazole-like compounds.

3.2. Optimal pH in imidazole-like compounds extraction

At different pHs, the extracted imidazole-like compounds partition differently in the organic and aqueous phases. In order to achieve complete recovery of the extracted imidazole brown carbon involving ion-pair formation, the optimum pH range generally occurs between the imidazole brown carbon and the BEHPA value (Hoogewijs and Massart, 1979). In this study, the 7 imidazole-like compounds extraction from the
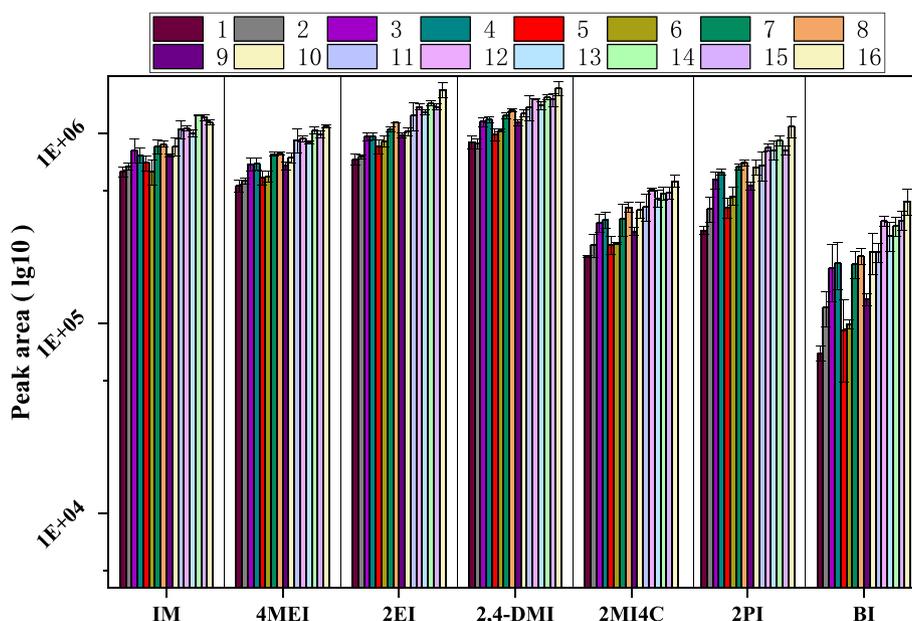
Fig. 2. Derivatization efficiencies (expressed by peak area (lg10)) of 7 standard imidazole-like compounds under 16 solvent combinations of acetonitrile, pyridine, anhydrous ethanol and IBCF.

aqueous phase was investigated at pH ranges of 6.0–8.5. Fig. 3 exhibits peak areas for the 7 imidazole-like compounds' extraction from the aqueous phase at different pH values. The variation in peak areas of IM, 2MI4C, 2EI and 4MEI with pH value showed a similar feature: peak areas increased from pH 6.0 to pH 7.0 and gradually decreased with increasing pH value. This suggests that pH 7.0 was the optimal value for imidazole-like compounds' extraction from the aqueous phase. The peak areas of 2,4-DMI, 2PI and BI were found to generally increase with increasing pH value. The maximum peak area of 2,4-DMI appeared at pH 8.0, while the maximum peak areas of 2PI and BI occurred at pH 8.5. Therefore, the extraction of target imidazole-like compounds would be performed at the appropriate pH values.

In order to simultaneously extract the 7 imidazole-like compounds from the aqueous phase, the ANOVA method was used to assess an appropriate pH value. The P values of IM, 2MI4C and 2EI were above 0.05 under pH 7.0 and 7.5 (Table S5), indicating that IM, 2MI4C and 2EI

extraction did not show statistically significant differences under either pH 7.0 or 7.5. There was not a statistically significant difference for 4MEI extraction under either pH 7.5 or 8.0. The P values of 2,4-DMI and 2PI above 0.05 existed in pH 8.0 and 8.5. Therefore, using pH 8.0 was performed to extract the 7 imidazole-like compounds, although IM and 2MI4C had relatively low extraction efficiencies. It was worth mentioning that IC was highly dependent on pH (Ackendorf et al., 2017). Gao et al. (2021) and Teich et al. (2016) only detected hydrated imidazole carboxaldehyde (HIC) in the atmospheric aerosol particles. In this study, the pH was adjusted to be 6.0–8.5 to reduce matrix interference as well as optimize derivatization efficiency, which may lead to difficulties in the characterization of IC.

3.3. Method validation

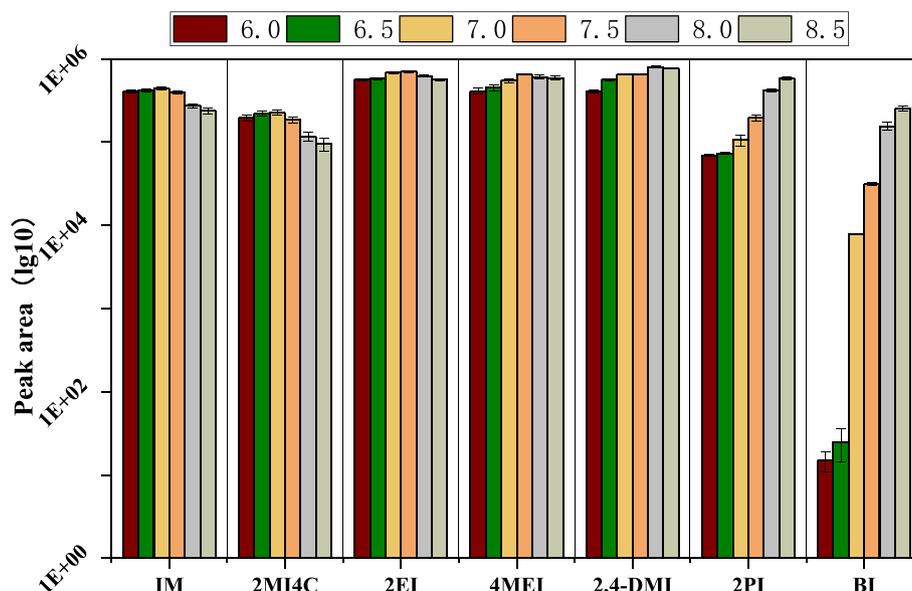Table 2 summarizes the parameters of the calibration curves for the 7

Fig. 3. Derivatization efficiencies (expressed as peak area (lg10)) of the 7 standard imidazole-like compounds at different pH.

Table 2
Limit of detection (LOD), limit of quantification (LOQ) and calibration curve parameters of 7 standard imidazole-like compounds.

Compounds	Linear Range (μg/mL)	Correlation coefficient (R²)	LOD (μg/mL)	LOQ (μg/mL)
IM	1–250	0.9992	0.1210	0.5121
4MEI	1–250	0.9987	0.0625	0.2370
2EI	1–250	0.9989	0.0682	0.2597
2,4-DMI	1–250	0.9990	0.0553	0.2458
2MI4C	1–250	0.9988	0.0886	0.3274
2PI	1–250	0.9971	0.0830	0.3428
BI	1–250	0.9958	0.8914	1.8573

imidazole-like compounds, including the linear range, correlation coefficient (R^2), limit of detection (LOD) and limit of quantification (LOQ). The LOD and LOQ values of the 7 imidazole-like compounds were calculated based on a signal-to-noise (S/N) = 3 and S/N = 10 in the GC-MS analysis. The R^2 values of the 7 imidazole-like compounds ranged from 0.9903 to 0.9992. The LOD and LOQ values varied from 0.0553 to 0.8914 and 0.2370–1.9373 μg/mL, respectively. The blank matrix plus standard samples were used to calculate the recoveries and relative standard deviation (RSD) of the 7 imidazole-like compounds with their concentrations of 5.0, 50.0, and 100.0 μg/mL. The recoveries and RSD of the 7 imidazole-like compounds are listed in Table 3. The recoveries ranged from 58.84% for IM to 160.99% for BI. The RSD varied from 0.71% for 4MEI to 14.83% for 2,4-DMI. The recoveries and RSD of imidazole-like compounds were 10.4–78.9% and 29.9–46.4%, respectively, using liquid chromatography (Teich et al., 2016), suggesting that a highly precise and reliable method was used in this study.

3.4. Application for laboratory and field studies

Fig. 4 shows the concentrations of imidazole-like compounds from the aqueous reaction of carbonyl compounds with reducing nitrogen as a function of time. The products of IM and BI were detected in the aqueous reaction of glyoxal with ammonium sulfate. The level of IM increased from 1686.07 μg/mL in the initial reaction to 4301.78 μg/mL after 720 h. Similarly, the concentration of BI from 31.67 μg/mL in the initial reaction to 59.94 μg/mL after 720 h. The detection of IM and BI in the aqueous reaction of glyoxal with ammonium sulfate had also been reported in previous studies using NMR and HPLC-ESI-MS/MS(Kampf et al., 2012; Yu et al., 2011). The products of 4MEI and 2,4-DMI had

Table 3
Recoveries, relative standard deviation (RSD) (n = 3) of 7 standard imidazole-like compounds.

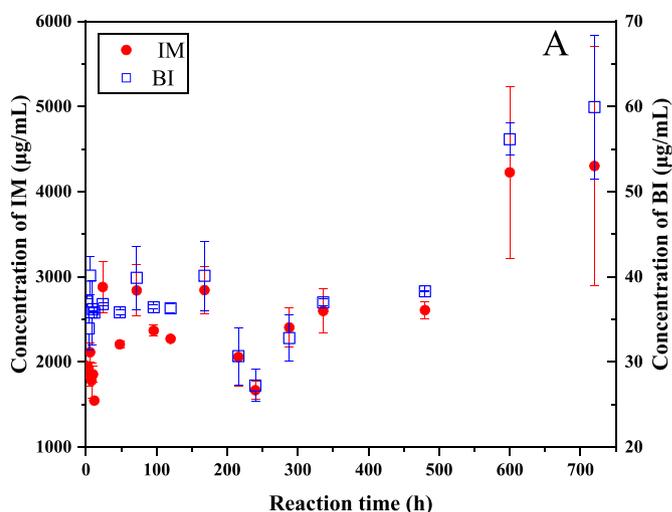| Compounds	Spiked (μg/mL)	Recovery (%)	RSD (%)
IM	5.0	86.57	4.69
	50.0	58.84	3.91
	100.0	61.98	5.64
4MEI	5.0	133.75	6.82
	50.0	131.36	0.71
	100.0	77.35	3.73
2EI	5.0	71.67	10.07
	50.0	76.42	1.87
	100.0	65.41	2.57
2,4-DMI	5.0	91.86	14.83
	50.0	103.77	3.47
	100.0	77.08	6.54
2MI4C	5.0	70.73	3.23
	50.0	69.31	7.51
	100.0	76.11	2.71
2PI	5.0	108.75	13.68
	50.0	76.47	1.37
	100.0	94.41	8.85
BI	5.0	135.44	11.30
	50.0	160.99	9.67
	100.0	83.52	4.66

Fig. 4. Concentrations of IM and BI from glyoxal and AS reaction products as a function of reaction time.

been found in the aqueous reaction of methylglyoxal with ammonium sulfate, glycine or methylamine (Fig. S4). This was in agreement with the previous observation using NMR hydrogen spectroscopy (Rodriguez et al., 2017).

De Haan et al. (2011) proposed that the product of imidazole dimers (m/z 124, $C_6H_8ON_2$) existed in the aqueous reaction of methylglyoxal and ammonium sulfate using NMR and ESI-MS. In this study, a peak appeared in the retention time of 12.07 min in the GC-MS method under the aqueous reaction of methylglyoxal and ammonium sulfate (Fig. S4). Its qualitative ions included m/z 41, 57, 82, 96, 109, 124 and 224, which corresponded to imidazole dimers (De Haan et al., 2011). Dimethyl-imidazole (m/z 97, $C_5H_9N_2$) and 2,4,5-trimethylimidazole (m/z 110, $C_6H_{10}N_2$) had also been proposed from the aqueous reaction of methylglyoxal with ammonium sulfate (De Haan et al., 2011, 2018b; Powelson et al., 2014). Two peaks presented in the retention times of 11.57 and 11.62 min in the products from aqueous reaction of methylglyoxal with ammonium sulfate in this study (Fig. S4). The qualitative ions of the former consisted of m/z 41, 57, 96 and 196, while the latter contained m/z 41, 57, 109, 110 and 210. Therefore, these two peaks likely contributed to the presence of dimethylimidazole and 2,4,5-trimethylimidazole (De Haan et al., 2011, 2018b; Powelson et al., 2014). Thus, it was expected that more imidazole-like compounds would be measured using the GC-MS method, although there were no commercially available standards for imidazole dimers, dimethylimidazole and 2,4,5-trimethylimidazole in this study.

IM and 4MEI were detected in the atmospheric aerosols (Table 4). The concentration of IM ranged from 18.78 to 23.93 ng/m³. The level of 4MEI varied from 21.27 to 39.09 ng/m³. Imidazole-like compounds, including 2EI and 4MEI (0.06–13.98 ng/m³), have also been found in other regions, such as China and Europe (Gao et al., 2021; Hu et al., 2022; Teich et al., 2016, 2020). The sample period experienced air pollution events, which might lead to higher concentrations of IM and 4MEI in this study relative to other studies. Recently, Hu et al. (2022) measured IM and 4MEI in atmospheric aerosol particles, likely due to the aqueous reaction of carbonyl compounds with reducing nitrogen. The presence of IM in this study might be attributed to the aqueous reaction in the atmosphere.

4. Conclusion

In this work, a new method for the determination of imidazole-like compounds was developed using the GC-MS. Amounts of acetonitrile, pyridine, anhydrous ethanol and IBCF in the derivatization of the 7 imidazole-like compounds were optimized. Furthermore, the pH for the

Table 4

Concentrations of IM and 4MEI in the atmospheric aerosols in the present and the previous studies (ng/m^3).

Compounds	Qingdao, China[a]	Beijing, China[b]	Leipzig, Germany[c]	Wuqing, China[d]	Leipzig, Germany[d]	Guangdong, China[e]
IM	18.78–23.93	ND	ND	ND	ND	ND
4MEI	21.27–39.09	ND-2.11	0.06–4.86	1.95–13.98	1.79–6.48	ND-20.99

a in the present study; b (Gao et al., 2021); c (Teich et al., 2016); d (Teich et al., 2020); e(He et al., 2022).

imidazole-like compounds' extraction from the aqueous phase was also assessed. The LOD, LOQ, recoveries and RSD of the 7 imidazole-like compounds verified the performance of this method. The method was also further applied to measure imidazole-like compounds from the aqueous reaction of carbonyl compounds with reducing nitrogen. In addition, the presence of imidazole-like compounds in the atmospheric aerosols was also detected using the method.

Credit author statement

Pingping Chen: Methodology, Formal analysis, Writing – original draft. **Qinhao Lin**: Conceptualization, Supervision. **Taicheng An**: Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apr.2023.101701.

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