DETERMINATION OF ALIPHATIC AMINES AND HETEROCYCLIC AMINES IN INDOOR AIR BY A MODIFIED GC AND GC/MS METHODS

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ABSTRACT
A modified GC and GC/MS methods to determine the levels of aliphatic amines and heterocyclic amines in residential air is described. This method was successfully applied to the determination of a few kinds of amines in indoor air from 40 selected homes at random in Beijing region. A total of 15 compounds were identified and quantified, and varied in concentration from 0.08 µg/m³ to 100 µg/m³. These amines that have been detected included methyamine, di-methylamine, tri-methylamine, and ethylamine, di-ethylate amine, 2-methyl-1-propyl amine, N-butyl-N-nitro-1-butylamine, 2-methyl aniline, N-propyl-1-propyl amine, cyclohexane, 4-amidocyanogen pyridine, amphetamine, 2-methyl pyridine, 2,6-dimethyl aniline, 2,4,6-trimethyl pyridine. Most of these compounds exhibited offensive odors, in despite of those compounds were present at low concentration. These compounds maybe are the main pollutants of the olfaction of the indoor air quality.

INDEX TERMS
aliphatic amines, heterocyclic amines, GC and GC/MS, odor,

INTRODUCTION
As the problems of environmental pollution are very close to daily life of people everywhere in the world, the occurrence and toxicity of hazardous chemicals in indoor air have received great deal of attention in recent years. The environment contains a variety naturally occurring and man-made mutagens and carcinogens to which humans are exposed. Among these compounds, a series of amines has been found in indoor air. These amines are organic bases of low molecular weight, which can be formed and degraded during the cellular metabolism in plants, animals and microorganisms, then released to the air. Most of these compounds exhibited offensive odors, in despite of those compounds were present at low concentration. These compounds maybe are the main pollutants of the olfaction of the indoor air quality.

Gas chromatography has been widely used for amine analysis because of its inherent advantages of simplicity, high resolving power, high sensitivity and low cost. Most aliphatic amines and heterocyclic amines are polar and volatile, and tend to elute as broad and tailing peaks due to the strong adsorption to the column and injector during GC analysis. Therefore, they cannot be detected in low concentration without derivatization. Derivatization of amines may be employed not only to reduce the polarity but also to improve the volatility, selectivity, sensitivity and separation of these amines.

Gas chromatography-mass spectrometry ideally combines the advantages of the high resolution of capillary GC with the high sensitivity and selectivity of MS, being coupled to different pre-concentration techniques, this instrument can be applied to determination many organic pollutants.

Up to the present, there is a lack of published analytical methods to measure amines in residential air at environmental concentration levels. In this paper we report a modified GC and GC/MS method that is suitable for measuring residential air, and the application of this method to measure the concentration of aliphatic amines and heterocyclic amines in 40 selected residential homes from Beijing region.

EXPERIMENTAL
Chemicals

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Seven target chemicals were selected for this study, all chemicals and solvents were purchased from commercial sources. Methylamine, di-methylamine, tri-methylamine are 33% purity in water, tri-ethylate amine, N,N-di-methyl formamide, anilin and cyclohexane are equal to or greater than 98% in purity.

Sampling and sample preparation
Sampling aliphatic amines such as methylamine, di-methylamine, tri-methylamine by Using dual channels gas sampling instrument, the pump were regulated at a rate of 0.3L/min and would sample 10L of air in about 0.5 h. An appropriate amount of pure water was added to the absorbed bottle as adsorbent. When the sampling work was done then ready for injection 2uL water sample into the GC system.

The other amines were sampled using thermal desorption tubes (7mm outside-diameter and 150mm long) packed with 90 mg Tenax TA adsorbent (mesh size of 60/80, Supelco, Bellefonte, PA, USA) and appropriate amount of silicon cotton within the heated zone of the tube. After being packed, the tubes were initially conditioned under nitrogen gas (99.999%) at 250℃ for 15 min, 300℃ for 15 min, 330℃ for 15 min, and 350℃ for 15 min. In addition to indoor air samples collected in each home, at least one outdoor air, one duplicate indoor air, and one field blank were collected among homes each sampling day. The sampling tubes for indoor samples were located in the middle of the room, while for outdoor samples were located in the front porch or the backyard deck, both at a height of about 1.5m from the ground. 9 L of air were sampled at a rate of 0.3L/min for 30 minutes using a gas sampler. The flow rate was pre-calibrated in the laboratory. Following sample collection and immediately prior to GC/MS, the tube was sealed with two caps before analysis.

Instrument and analysis method
(1) GC analysis
The series 4000 DongXi instrument gas chromatography was equipped with a split/splitless injector, a flame ionization detector. The carrier gas was nitrogen (99.999%), The column (30m×0.53mm×1.0um) was special for analyzing amines in aqueous. The respective injector and detector temperatures were 200℃ and 250℃. Analytical programs were used as follows: carrier gas pressure: 60kPa; injected liquid volume: 2uL; split ratio: 5; oven temperature program: 50℃ for 3 min, followed by an increase to 120℃ at 5℃/min and a final 3 min hold at 120℃.

(2) GC/MS analysis
A trace GC and trace DSQ (Thermal Finnigan, USA) was used for the analysis. Samples were introduced the GC/MS through SGE pyrolysis unit (SGE inc., Australia), which was directly connected to GC injector through a heated transfer line. Pure helium gas (99.999%) was used for both thermal desorption and GC/MS analysis. Thermal desorption conditions for air sample as follows: dry purge: 1min at room temperature; 2 min at 300℃ with desorption flow rate of 30 ml/min without split, liquid nitrogen trap collect sample; then removed the trap, start the analysis program. Thermal desorbed analytes were separated on a DM-1MS column (60m×0.25mm×0.25um, Dikma inc, USA) with the following oven temperature program: initial temperature was set at 50℃ for 3 min, then increased to 200℃ at 10℃/min and kept at 200℃ for 10 min. MS conditions: EI full scan mode with an electron energy of 70eV; ion source temperature 200℃, Aux line temperature 250℃.

RESULTS AND DISCUSSION
Determination aliphatic amines by GC
Five kinds of aliphatic amines standard mixed solution was injected into GC, these compounds were separated well using the above mentioned method (fig.1).
Figure 1. 5 kinds of aqueous aliphatic amines separated on gas chromatography
1. methylamine; 2. di-methylamine; 3. tri-methylamine; 4. N,N-diethyl formamide; 5. triethanolamine

Determination of amines by GC/MS
Sampling the indoor air in selected homes, then introduced the sample into the GC/MS for analysis. In one of our selected sample, we have detected 5 kinds of amines (fig.2), they are ethylamine, 2-methyl-1-propyl amine, N-propyl-1-propyl amine, 2-methyl aniline, cyclohexane. The other peaks were volatile organic compounds not amines.

Figure 2. TIC of a air sample in new building determinated by GC/MS
1. ethylamine; 2. 2-methyl-1-propyl amine; 3. N-propyl-1-propyl amine; 4. 2-methyl aniline; 5. cyclohexane

The frequency of the amine pollutants in selected 40 homes
Sample which collected in different site contains different kind of amines, we calculated the detection frequency of the amines that have detected in selected 40 homes at random in Xuanwu district, fig.3 shows that these amines appeared at low frequency and occasionally, which may due to the different house has used the different building materials and paints and other house products.
The detection frequency of the target pollutants in selected homes in Beijing


The concentration level of the target pollutants

Cyclohexane of 5 concentration levels were used for make standard curve, the detected amines’ concentration level was calculated according to the Cyclohexane’s levels, see table1.

<table>
<thead>
<tr>
<th>Pollutant name</th>
<th>Detection frequency</th>
<th>( C_{\text{min}} ) (ug/m(^3))</th>
<th>( C_{\text{max}} ) (ug/m(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>methylamine</td>
<td>3</td>
<td>0.10</td>
<td>0.18</td>
</tr>
<tr>
<td>di-methylamine</td>
<td>4</td>
<td>0.08</td>
<td>0.20</td>
</tr>
<tr>
<td>tri-methylamine</td>
<td>2</td>
<td>0.08</td>
<td>0.15</td>
</tr>
<tr>
<td>ethylamine</td>
<td>6</td>
<td>0.21</td>
<td>0.35</td>
</tr>
<tr>
<td>di-ethylate amine</td>
<td>4</td>
<td>15</td>
<td>100</td>
</tr>
<tr>
<td>2-methyl-1-propyl amine</td>
<td>4</td>
<td>32</td>
<td>50</td>
</tr>
<tr>
<td>N-butyl-N-nitro-1-butylamine</td>
<td>6</td>
<td>16</td>
<td>30</td>
</tr>
<tr>
<td>2-methyl aniline</td>
<td>5</td>
<td>0.50</td>
<td>2.1</td>
</tr>
<tr>
<td>N-propyl-1-propyl amine</td>
<td>3</td>
<td>1.2</td>
<td>1.8</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>5</td>
<td>60</td>
<td>85</td>
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<tr>
<td>4-amidocyanogen pyridine</td>
<td>3</td>
<td>0.70</td>
<td>1.5</td>
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<tr>
<td>amphetamine</td>
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<td>0.04</td>
<td>0.08</td>
</tr>
<tr>
<td>2-methyl pyridine</td>
<td>2</td>
<td>0.06</td>
<td>0.12</td>
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<tr>
<td>2,6-dimethyl aniline</td>
<td>4</td>
<td>0.10</td>
<td>0.23</td>
</tr>
<tr>
<td>2,4,6-trimethyl pyridine</td>
<td>3</td>
<td>0.05</td>
<td>0.12</td>
</tr>
</tbody>
</table>

CONCLUSION

The results described in this paper show that the amines contamination are exist in indoor air at a low frequency, the source of these amines are likely due to the widespread presence of this amines in paints, cleaning fluids and house products. Though these amines are present at low concentration (ranged from 0.08ug/m\(^3\) to 100ug/m\(^3\)), these compounds maybe are the main pollutants of the olfaction of the indoor air quality for their odor smell.

REFERENCES