Determination of 9 kinds of volatile halogenated alkane and chlorobenzene compounds in water by gas chromatography-mass spectrometry with purge and trap method

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Abstract—In this study, in the face of water environmental pollution, a more simple and efficient detection method was obtained for simultaneous determination of 9 kinds of volatile halogenated alkane and chlorobenzene compounds in water by PT/GCMS. By optimizing the purge and trap conditions, the optimal experimental conditions were obtained as follows: purge time was 15 min, purge temperature was 35 ℃, purge velocity was 40 mL/min, desorption time was 2 min, desorption temperature was 240 ℃. The linearity of the method was good, and the correlation coefficients were all greater than 0.999. The minimum detection limit(MDL) of the method was 0.1 μg/L. The average recovery rate ranged from 85.4 %~102.1 % in surface water and drinking water with relative standard deviation (RSD) ranged from 5.3 %-9.2 % in the spiked concentration levels of 5 μg/L and 10 μg/L. This method has the advantages of simple operation, good separation effect, rapid detection, high recovery and good precision, and can simultaneously meet the requirements of 9 kinds of volatile organic compounds detection in drinking water and surface water. This work provides a new method for the detection of volatile organic compounds in water and will have great significance for the detection of water quality.

1. Introduction

According to the definition of the World Health Organization, a class of organic compounds that exist in the air in the form of vapor at room temperature are volatile organic compounds [1]. There are many kinds of these substances, which are irritating and volatile, such as chlorobenzene, halogenated hydrocarbon, aromatic hydrocarbon. Although the content of volatile organic compounds in drinking water sources is very low, most of them have carcinogenic, teratogenic and mutagenic chemical toxicity [2]. At present, domestic and foreign methods for the determination of volatile organic pollutants in water include headspace gas chromatography [3], solid phase microextraction gas chromatography [4], purge and trap with gas chromatography [5], purge and trap with GC-MS [6]. As a pre-treatment technology for volatile organic pollutants in water, purge and trap has the advantages of small sample sampling, high enrichment efficiency and no solvent pollution, and has become the most advanced pre-treatment method for analyzing volatile organic compounds in the world [7]. Nowadays, in the face of environmental pollution, it is very meaningful to study how to apply purge and trap with GC-MS technology to the detection of water for safe water. In this study,
PT/GC-MS was applied to detect nine kinds of volatile halogenated alkane and chlorobenzene compounds in drinking water in the city, which is simple, rapid, strong extension and can simultaneously detect these substances.

2. Experiment

2.1. Instruments and reagents

GC-8890 gas chromatograph (Agilent Technologies Inc.). MSD-5977 mass spectrometer (Agilent Technologies Inc.) with EI source and a single four-stage mass analyser. Purge and trap (PT) system with AQUATek 100 automatic sampler (Teledyne Tekmar). 5 mL venting pipe (Teledyne Tekmar). 40 mL brown sample bottle (Agilent Technologies Inc.). 1/3 Tenax, 1/3 silica gel, 1/3 activated carbon mixed adsorbent trap tube. DB624 capillary column (6 % nitrile propyl phenyl /94 % dimethyl polysiloxane fixing solution).

2.2. Working conditions of PT/GCMS

Gas chromatography conditions: Carrier gas: high purity nitrogen; Column flow rate: 1.0 mL /min; Inlet temperature: 220 ℃; Injection mode: split injection; Shunt ratio: 30:1; Heating procedure: the initial temperature is 35 ℃, the temperature is kept for 5 min, then the temperature is raised to 160 ℃ at a rate of 6 ℃/min, the temperature is kept for 6 min, and then the temperature is raised to 210 ℃ at a rate of 20 ℃/min and the temperature is kept for 5 min.

Mass spectrum conditions: EI ionization, standard electron energy: 70 eV; Scanning range: 35 amu ~ 300 amu; Detection mode: Full scan mode; Interface temperature: 250 ℃; Ion source temperature: 230 ℃; Transmission line temperature: 220 ℃; Four-stage mass analyser temperature: 150 ℃; Injection volume: 1μL. The retention time and characteristic quantitative ions of the target compounds to be measured are shown in Table 1.

Purge and trap conditions: purge gas: high purity nitrogen; Purge temperature: 25 ℃; Purge time: 10 min; Purge sample size: 5.0 mL; Purge flow: 40 mL/min; Desorption temperature: 250 ℃; Desorption back blow gas flow rate: 15 mL/min; Desorption time: 2 min; Baking temperature: 260 ℃.

Sample collection and treatment: water samples were quickly taken at the scene and placed in a 40 mL brown bottle. No top space and bubbles were left when sampling, and a PTFE gasket cap was added for sealing and preservation. The samples were stored in a refrigerator at 4 ℃ without interference from other organic substances, and the analysis was completed within 24 h.

| Compounds                    | Retention time(min) | Qualitative ion (M /Z) | Quantitative ion (M/Z) |
|------------------------------|---------------------|------------------------|------------------------|
| Methylene chloride           | 4.772               | 86,49                  | 84                     |
| 1,1, 1-trichloroethane       | 8.557               | 99,61                  | 97                     |
| 1, 2-dichloroethane          | 9.425               | 98,49                  | 62                     |
| Dichloro-bromomethane        | 11.997              | 85,127                 | 83                     |
| Monochloro-dibromomethane    | 15.679              | 49,130                 | 128                    |
| Chlorobenzene                | 17.148              | 77,114                 | 112                    |
| Tribromomethane              | 19.167              | 175,252                | 173                    |
| 1,4-dichlorobenzene          | 23.045              | 111,148                | 146                    |
| 1,2-dichlorobenzene          | 23.984              | 111,148                | 146                    |

3. Test Results and Discussions

3.1. Results of chromatographic separation

After purging and trapping, it was separated and detected by gas chromatography-mass spectrometer. The chromatographic separation results were shown in Fig.1.
3.2. Effect of purge conditions on quantitative analysis

We fixed purge temperature, purge flow velocity, desorption time and desorption temperature, and investigated the effects of purge time from 5 min to 30 min on the signals of compounds (Fig. 2(a)). When the purge time ranged from 5 to 30 min, the response signal of each compound varies with purge time in two ways. For the less volatile compounds, such as 1,4-dichlorobenzene and 1,2-dichlorobenzene, the response signal increased with the increase of purge time. For the highly volatile compounds, such as 1, 2-dichloroethane, methylene chloride and chlorobenzene, the response signal firstly increased and then decreased with the increase of purge time. Prolonging the purge time will
not only lead to the removal of compounds by the purge gas and reduce the purge efficiency, but also generate the decrease of the column efficiency due to the increase of the purge water. 1, 2-dichloroethane and methylene chloride were most significantly affected by purge time. The purge time increased from 5 min to 15 min, and the peak area of 1, 2-dichloroethane and methylene chloride increased 2.46 and 2.05 times, respectively. Therefore, the optimal purge time was 15 min.

3.2.2. Effect of purge temperature on quantitative analysis

Purge temperature is an important factor affecting purge efficiency, and the high water-soluble components are more obviously affected. The purging efficiency of high boiling point substances is improved by increasing the temperature, but it is not conducive to the purging of low boiling point substances. At the same time, excessive purging temperature will increase the water entering the column, which will affect the detection results and shorten the service time of the column. Therefore, it is very important to choose the right purge temperature. Under the same conditions, the effect of purge temperature from 25 ℃ to 65 ℃ on the peak area of the compounds were investigated respectively, as shown in Fig.2 (b). The response of most compounds at 25~35 ℃ was not significantly affected by temperature, but when the temperature gradually increased from 35 ℃ to 65 ℃, the response of those compounds gradually decreased with the increase of temperature. The response of 1,2-dichlorobenzene at 65 ℃ is the highest, but at the same time, a large amount of methanol and water are purged out, which interferes with the response of 1,2-dichlorobenzene. All the results showed that the 35 ℃ was the optimum purge temperature.

3.2.3. Effect of purge velocity on quantitative analysis

Purge velocity not only affects the capture efficiency, but also affects the analysis time. Low purge velocity affects the purge efficiency firstly, which leads to the extension of the analysis time. However, high purge velocity will affect the trap efficiency of sample components, and even blow out a large amount of water. In addition to affecting the drying effect, it will also affect the baseline drift of mass spectrometry. Therefore, the purge velocity is very important to optimize the pretreatment conditions of this experiment. As can be seen from Fig.2 (c), when the purge velocity is less than 40 mL /min, the peak area increases rapidly with the increase of purge velocity, and the increasing trend gradually slows down with the increase of purge velocity. When the purge velocity was greater than 40 mL /min, the peak area almost no longer changed with the increase of the purge velocity, indicating that the volatile component in the water was almost completely blown out. In conclusion, the optimum purge velocity was 40 mL /min when the purge efficiency was guaranteed and the desiccant's dewatering effect and MSD sensitivity were not affected.

3.3. Effect of desorption on quantitative analysis

3.3.1. Effect of desorption time on quantitative analysis

As can be seen from Figure 3(a), when the desorption time is 1~2 min, methylene chloride, 1, 2-dichloroethane and dichloro-bromomethane are most significantly affected by the desorption time and the response signal of that was maximum at 5 min. The responses of other compounds were not significantly affected by desorption time. Therefore, the optimal desorption time was determined to be 2 min.

3.3.2. Effect of desorption temperature on quantitative analysis

Under the same conditions, the influence of desorption temperature at 180~250 ℃ on the peak area of the target was studied respectively, and the results were shown in Fig.3 (b). When the desorption temperature is too low, the target compounds desorption is incomplete; If the desorption temperature is too high, the compounds with low stability will decompose. Fig.3 (b) shows that the desorption temperature has no obvious effect on each target compounds. The peak area of methylene chloride and
1, 2-dichloroethane were slightly higher at 220–240 °C. The optimum desorption temperature was 240 °C.

![Effect of desorption time on the signal](image1)

![Effect of desorption temperature on the signal](image2)

Fig. 3 Effect of desorption on quantitative analysis

3.4. Standard curve and detection limit of the method

The standard solution of the target compounds was diluted with pure water to prepare a standard series of mixed solutions with concentrations of 5μg/L, 10μg/L, 20μg/L, 40μg/L, 50μg/L and 100μg/L. The standard curve was determined by PT/GC-MS. The standard curve was drawn with the peak area versus the mass concentration, which with good linearity and a correlation coefficient greater than 0.999 as shown in Table 2.

| Compounds                  | Linear equation | Correlation coefficient | MDL/(μg/L) |
|----------------------------|-----------------|-------------------------|------------|
| Methylene chloride         | y = 5239x - 5192| 0.9996                  | 0.3        |
| 1,1, 1-trichloroethane     | y = 1648x - 3374| 0.9998                  | 0.8        |
| 1, 2-dichloroethane        | y = 8659x - 7274| 0.9998                  | 0.6        |
| Dichloro-bromomethane      | y = 5377x - 19878| 0.9997                | 0.8        |
| Monochloro-dibromomethane  | y = 3694x - 20483| 0.9992                | 0.4        |
| Chlorobenzene              | y = 7230x - 46755| 0.9993                | 0.4        |
| Tribromomethane            | y = 2301x - 17972| 0.9995                | 0.1        |
| 1,4-dichlorobenzene        | y = 9113x - 20332| 0.9994                | 0.3        |
| 1,2-dichlorobenzene        | y = 6670x - 31283| 0.9993                | 0.3        |

3.5. Precision and accuracy of the method

In order to study the recovery rate and precision of each target compounds in pure water, tap water and surface water samples, each target compounds was added into pure water and actual water samples to prepare the spiked samples with different mass concentration levels. Samples with different mass concentration levels were independently determined for 6 times according to the analysis steps. The results are shown in Table 3. In pure water, the recoveries of the method are 89.7 %~103.3 %, and the relative standard deviations are 4.9 %~8.1 %. The accuracy and precision of the method can meet the experimental requirements. When the method is applied to the determination of tap water and surface water, the recoveries are 85.4 %~102.1 %, and the relative standard deviations are 5.3 %~9.2 %, indicating that the method is accurate and reliable.

| Compounds                  | Concentration (μg/L) | Pure water | Tap water | Surface water |
|----------------------------|----------------------|------------|-----------|---------------|
|                           |                      | Recovery rate (%) | RSD (%) | Recovery rate (%) | RSD (%) | Recovery rate (%) | RSD (%) |
| Methylene chloride         | 5                    | 96.3%       | 5.3       | 95.1%         | 6.0     | 91.7%          | 5.8     |
|                           | 10                   | 93.5%       | 5.6       | 92.3%         | 6.3     | 89.0%          | 6.1     |
1, 1-trichloroethane 5 98.1% 8.1 96.9% 9.2 93.4% 8.8 10 97.5% 7.8 96.3% 8.8 92.9% 8.5
1, 2-dichloroethane 5 95.3% 5.4 94.1% 6.1 90.8% 5.9 10 96.4% 4.9 95.2% 5.5 91.8% 5.3
Dichloro-bromomethane 5 95.7% 6.1 94.5% 6.9 91.1% 6.6 10 94.5% 5.7 93.3% 6.4 90.0% 6.2
Monochloro-dibromomethane 5 90.8% 6.4 89.6% 7.2 86.5% 7.0 10 92.8% 6.2 91.6% 7.0 88.4% 6.8
Chlorobenzene 5 98.7% 5.9 97.5% 6.7 94.0% 6.4 10 101.2% 5.3 100.0% 6.0 96.4% 5.8
Tribromomethane 5 101.6% 6.3 100.4% 7.1 96.8% 6.9 10 99.8% 5.9 98.6% 6.7 95.0% 6.4
1,4-dichlorobenzene 5 103.3% 6.4 102.1% 7.2 98.4% 7.0 10 96.4% 5.9 95.2% 6.7 91.8% 6.4
1,2-dichlorobenzene 5 93.6% 6.2 92.4% 7.0 89.1% 6.8 10 89.7% 5.7 88.5% 6.4 85.4% 6.2

4. Conclusion
A method for simultaneous determination of nine kinds of volatile organic compounds in water by PT/GCMS was established in this paper. After optimizing the method conditions, the linearity of the method was good, and the correlation coefficients were all greater than 0.999. The method has the advantages of simple operation, good separation effect, rapid detection, high recovery and good precision, and can simultaneously meet the requirements of volatile organic compounds detection in drinking water and surface water. It provides a new method for the detection of volatile organic compounds in water and will have great significance for the detection of water quality.

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