

Purge-trap Gas Chromatography and Mass Spectrometric Method for Analysis of Isoprene in Natural Waters



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Abstract: Gas chromatography with mass spectrum detector (GC-MSD) coupled with purge-and-trap system was developed to analyze the concentration of isoprene in natural waters. The experimental conditions were optimized, including purge gas flow rate (50 mL min^{-1}), purge time (15 min), capillary column (Rt-Alumina BOND/KCl) and its appropriate temperature programming. The precision was less than 4% ($n = 6$), the detection limit was 0.5 pM, and the recovery was 91%–102%. The analytical results of preservative experiments showed that no obvious variation was observed in the concentrations of isoprene within 60 days under the preservation conditions. The concentrations of isoprene measured with the method ranged from 60.8 pM to 278.7 pM in the Jiaozhou Bay and its adjacent river estuaries, and from 44.7 pM to 77.2 pM in the Yellow River estuary, respectively, which were in good accord with those reported in literatures in other coastal waters. In conclusion, the analytical method meets completely the requirements of the analysis of concentration of isoprene in natural waters.

Key Words: Isoprene; Purge-and-trap system; Gas chromatography-mass spectrometry; Natural waters

1 Introduction

Non-methane hydrocarbons (NMHCs) emitted from biogenic and anthropogenic origins are important components in the atmosphere and play significant roles in generating tropospheric ozone and secondary organic aerosol particles^[1–4]. Isoprene (2-methyl-1,3-butadiene, C_5H_8), one of quantitatively the most important of all the NMHCs, not only participates in various atmospheric reactions to affect the balance of atmospheric oxidants, but also contributes to the global carbon cycle^[5,6]. It is well known that isoprene is emitted into the atmosphere mainly from terrestrial vegetation^[7]. However, the photosynthesis of phytoplankton and the degradation of organic matter are also important sources of isoprene, which is ubiquitous in natural waters^[8,9]. The emission rate of isoprene from the ocean to the atmosphere was estimated to be about 1 Tg yr^{-1} ^[10,11], which should not be ignored to impact on the global carbon cycle and climate change. Therefore, measuring

isoprene in natural waters has extreme biogeochemical significance for understanding the distribution and sea-air flux of isoprene as well as its environmental effect.

The concentrations of isoprene in natural waters are generally in the range of $10\text{--}10^2 \text{ pM}$ ^[12]. Because of the low concentrations, pre-enrichment of isoprene is needed for the analysis by gas chromatography (GC). At present, trace NMHCs were determined by GC coupled with different detectors, such as flame ionization detector (FID), electron capture detector (ECD) and mass spectrometry detector (MSD)^[6,10,13]. The domestic literatures about the determination and distribution of isoprene in natural waters have not been reported. Therefore, the purge-and-trap method coupled with gas chromatography with mass spectrometry detector (GC-MSD) was established to analyze the concentration of isoprene in natural waters in this study. Compared with existing methods, the method not only reduced the sample volume but also improved the experimental accuracy.

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Moreover, the introduction of inverse-blowing system would greatly reduce the interference of residual sample and guarantee the reproducibility of analytical results. The developed method had the advantages such as simple operation, high precision and low detection limit, and was successfully applied to analyze the natural water samples collected from the Jiaozhou Bay, its adjacent river estuaries and the Yellow River estuary.

2 Experimental

2.1 Instruments and reagents

Main instruments used in this study included Agilent 7890A GC equipped with MSD and pre-treatment device (purge-and-trap system established in lab) that consisted of extracting glass chamber with 4# aperture, stainless steel trap tube (length: 1.5 m; ID: 1/8 inches), inverse-blowing system, H₂O and CO₂ absorbers (Merck, Germany) and six-way switch valve (VICI, USA). Chemical reagents mainly included isoprene standard solution (> 99.5%, Sigma-Aldrich, USA), methyl alcohol (Merck, Germany), anhydrous Mg(ClO₄)₂ (Analytical Grade, Tianjin Guangcheng Chemical Reagent Limited Company), ultra-high-purity nitrogen and helium (> 99.9995%, Qingdao Tianyuan Gas Limited Company).

2.2 Experimental apparatus

As a volatile trace gas in natural waters, the extraction and enrichment of isoprene is one of the most fundamental and key processes for accurate measurement. Based on the current extraction methods in literatures, a purge-and-trap system was established in our laboratory, where isoprene was blown out and enriched at liquid nitrogen temperature (−196 °C), and then was desorbed in boiling water before transferring into GC-MSD for detection (Fig.1). The main analysis processes were as follows. Water samples of 50–100 mL were first injected into the extracting chamber with a tightly closed syringe; isoprene and other volatile organic compounds (VOCs) were blown out from the samples through ultra-high-purity N₂ bubbling, and then passed through two tubes filled with Mg(ClO₄)₂ and NaOH to remove H₂O and CO₂, respectively. The gas stream was cryotrapped in a stainless steel tube immersed in liquid nitrogen. After 15 min, the purge gas of ultra-high-purity N₂ was closed and the stainless steel tube was quickly put into boiling water (100 °C). The trapped gases were desorbed and introduced into the GC system with ultra-high-purity He gas. After separated from other VOCs by the capillary column, trace isoprene was finally determined by MSD.

2.3 GC-MSD analysis conditions

The analysis conditions of isoprene in natural waters were

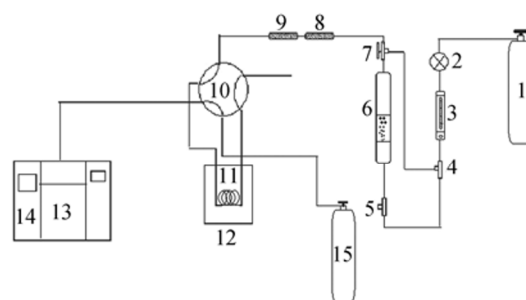


Fig.1 Analytical device of isoprene in natural waters

1. Purge gas (N₂); 2. Main valve; 3. Flow adjustment valve; 4. Three-way switch valve; 5. Injection port/drainage port; 6. Extracting chamber; 7. Three-way switch valve; 8. Drying tube; 9. CO₂ absorber; 10. Six-way switch valve; 11. 1/16 Stainless steel trap-tube; 12. Liquid nitrogen trap/Boiling water bath; 13. GC; 14. MSD; 15. Carrier gas (He)

optimized using the above experimental apparatus. The specific GC-MSD working parameters were obtained as follows: (1) Injector temperature: 150 °C; (2) Temperature programming: started at 60 °C for 3 min; raised at the rate of 10 °C min^{−1} to 120 °C and held for 1 min; increased to 160 °C at 30 °C min^{−1} and held for 3 min; (3) Carrier gas (He) flow rate: 1.5 mL min^{−1}; split ratio: 10:1; (4) MSD conditions: quadrupole temperature of 150 °C, ion source temperature of 230 °C and electron ionization (EI) operating voltage of 70 eV.

3 Results and discussion

3.1 Selection of chromatographic column

The parameters of capillary column such as type, diameter and length are most important factors affecting the separation effect between isoprene and other VOCs. By comparing four types of capillary columns, including DB-1 (30 m × 0.32 mm, 0.25 μm), DB-624 (60 m × 0.25 mm, 1.4 μm), RTX-624 (60 m × 0.32 mm, 1.8 μm) and Rt-Alumina BOND/KCl (30 m × 0.32 mm, 5 μm), it was found that Rt-Alumina BOND/KCl was the optimum capillary column with the lower interference of other VOCs, better peak shape and shorter analysis time.

3.2 Optimizing purge and trap conditions

Purge flow rate could effectively affect the trap efficiency and analysis time of the experiment. Lower flow rate had an obvious effect on the scavenging efficiency per unit time and prolonged the analysis time. Higher flow rate was unfavorable for the capture of isoprene in the stainless steel trap-tube. In addition, higher flow rate blew out over much water that could influence the effect of drying and the sensitivity of MSD. With a certain purging time, a known concentration of isoprene standard solution of 364 pM was measured repeatedly at different flow rates. Meanwhile, parallel experiments were conducted (*n* = 5) to ensure the accuracy of the experimental results. The corresponding relationship

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