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Determination of very volatile organic compounds in water samples by purge and trap analysis with a needle-type extraction device

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ABSTRACT

Very volatile organic compounds (VVOCs), such as methanol, acetaldehyde, ethanol, acetone, acetonitrile, and dichloromethane, were extracted from water samples using a needle-type extraction device based on purge and trap analysis. The extracted analytes could then be determined by gas chromatography–mass spectrometry. By introducing carbon molecular sieves as the extraction medium, aqueous VVOCs could be successfully extracted using the extraction needle. The limit of quantification for methanol, acetaldehyde, ethanol, acetone, acetonitrile, and dichloromethane were 75, 75, 7.5, 0.5, 10 and 0.5 μg/L, respectively. This newly developed method was also successfully applied to the determination of VVOCs in commercial samples, such as fruit juice.

1. Introduction

Quantification of volatile organic compounds (VOCs) in environmental samples is essential due to their adverse effects on human health. The World Health Organization (WHO) classifies VOCs with boiling points from 0 °C to 50–100 °C as very volatile organic compounds (VVOCs) [1]. The guidelines and typical measurement methods for VOCs in water have been defined by the relevant agencies, such as the US Environmental Protection Agency [2] and WHO [3].

Gas chromatography–mass spectrometry (GC–MS) is one of the most promising techniques for VOC analysis because of its high sensitivity and selectivity. However, an adequate extraction process is typically required before GC–MS analysis for the determination of trace amounts of VOCs in aqueous samples. Purge and trap (PT) extraction is the most common technique for preparation of aqueous samples [4]. Currently, the PT process is fully automated, and PT-GC–MS has been achieved for sensitive determination of several VOCs in aqueous samples; however, relatively expensive instrumentation is required for sample preparation and the process is still difficult due to the high volatility of VVOCs. Determination of water soluble VVOCs, such as methanol (MeOH) and acetaldehyde (AA), is especially challenging owing to their high volatility, lower purge efficiencies, and detector responses. Hence direct injection of aqueous samples [5] or headspace (HS) gas [6] into the GC instrument have been employed for the determination of VVOCs in aqueous samples. A sensitive determination of VVOCs with direct injection was reported by introducing lithium chloride-packed precolumn [7]. However, analysis of aqueous sample including non-volatile compounds with direct injection method is quite difficult. A sensitive determination of MeOH, AA, and acetone is also reported with proton transfer reaction mass spectrometer (PTR-MS) [8]. The PTR-MS method is suitable for real-time measurement of gaseous sample, such as environmental air, although the method could not suitable for the measurement of volatile compounds included in a small volume of aqueous sample. Sensitive determination of water soluble VVOCs involving an extraction process by conventional quadrupole GC–MS could be both valuable and novel.

Needle-type sample preparation devices have been introduced for simple and rapid determination of VOCs using GC analysis [9–12]. This device contains porous particles in a stainless steel needle as the extraction medium, which can be easily optimized for the target analytes. Multibed-type devices have also been introduced for the extraction of a wide range of VOCs [13,14]. Extraction of VVOCs from gaseous [15] and breath samples [16] has also been performed with the in-needle extraction device, where

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the VVOCs were extracted using carbon molecular sieves (CMS) having stronger extraction power for typical organic compounds. The needle-type extraction device contains small amounts of extraction media compared to typical extraction devices designed for thermal desorption or solvent extraction. In addition, the stainless steel needle used has high thermal conductivity. Therefore, the in-needle extraction device can easily desorb the extracted analytes with a flow of desorption gas and heating of the GC injection port to remove target analytes that were strongly adsorbed onto the extraction medium. These devices have also been applied for the determination of VOCs in aqueous samples based on HS extraction [17] or the PT method [18–20], where a wide range of VOCs were successfully extracted and determined without cryogenic focusing [19].

In this study, we investigated the extraction of water soluble VVOCs (MeOH, AA, ethanol (EtOH), acetone (AC), acetonitrile (ACN), and dichloromethane (DCM)) in aqueous samples based on the PT method with a needle-type extraction device. CMSs were introduced as the extraction medium to extract the VVOCs. Several extraction parameters, such as sampling volume of HS gas, concentration of sodium chloride (NaCl), and purge temperature, were systematically optimized. The applicability of the proposed method was confirmed by the determination of VVOCs in complex matrix samples of non-alcoholic beer and fruit juice.

2. Experimental

2.1. Chemicals

MeOH (99.8%), EtOH (99.5%), AC (99.5%), ACN (99.8%), and NaCl were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). AA (90.0%) was obtained from Nacalai Tesque (Kyoto, Japan). DCM (99.0%), 2-propanol (99.5%), and ethyl acetate (EtOAc) (99.5%) were obtained from Wako Pure Chemical Industries, Ltd. (Osaka, Japan).

2.2. Needle-type extraction device

CMSs particles (60–80 mesh) (Shinwa Chemical Industries, Kyoto, Japan) were employed as the extraction medium due to their high extraction performance for gaseous VVOCs [16]. The extraction needle was prepared by packing CMSs into an empty tip hole-type stainless steel needle (85 mm length, 0.5 mm ID, and 0.7 mm OD) to a length of 35 mm. A bundle of heat-resistant polymeric fibers of Zylon filaments (Toyobo, Shiga, Japan) (11.5 μm diameter, 5 mm length, 166 filaments) [21] were packed at each end of the packed section to fix the CMS sorbent.

2.3. GC measurements

GC–MS analysis was conducted using a JEOL JMS-Q1000GCMk-II instrument (JEOL, Tokyo, Japan) and an AQUATIC fused-silica capillary column (25% diphenyl–75% dimethylpolysiloxane), 60 m × 0.25 mm with a 1.0 μm film thickness (GL Sciences, Tokyo, Japan). All injections were performed using a split mode with a ratio of 5:1 using a split liner with 3.5 mm ID. The injector temperature was optimized from 150 °C to 320 °C. Helium was used as the carrier gas at a head pressure of 150 kPa. The GC–MS interface temperature and the ionization voltage were set to 250 °C and 70 eV, and electron impact ionization was employed. The column temperature was initially maintained at 40 °C for 4 min, after which it was programmed to increase to 180 °C at a rate of 20 °C/min. The mass spectrometer was operated in selected-ion-monitoring (SIM) mode (*m*/*z*: 31, 41, 43, 44, 45, 49, 58, and 84).

2.4. PT method with needle-type extraction device

An aqueous sample (20 mL) and NaCl were placed in a 50 mL glass vial. The plastic cap of the vial had two silicon plug-type septa to insert both the extraction needle and a stainless steel blank needle supplying pure N_2 as the purge gas. The solution was ultrasonicated for 1 min to dissolve the NaCl. The vial was then immersed in a water bath kept at a constant temperature for 5 min while the solution was stirred with a polytetrafluoroethylene-coated magnetic stir bar at 350 rpm. The PT temperature was optimized from 20 to 40 °C. Sampling volume of the HS gas was also investigated from 10 to 200 mL. The extraction was performed using a vacuum-sampling device (Komyo Rikagaku Kogyo, Tokyo, Japan). The blank needle was immersed into the aqueous sample that the needle tip just reached the bottom of the glass vial. N_2 gas was continuously supplied from a gas sampling bag (Smart bag PA, GL Sciences) via the blank needle. After extraction, 100 mL of dried N_2 gas was collected through the extraction needle using the vacuum-sampling device to remove excess water trapped on the CMS sorbent.

After the extraction and dry purge process, the extraction needle was attached to a gas tight syringe (1.0 mL volume) and pure N_2 gas was collected via the needle. The extraction needle was then inserted into the heated GC injection port. The desorption temperature and volume of the desorption gas were optimized in this study, as discussed below.

3. Results and discussion

3.1. Optimization of the method

First, the possibility of the dry purging process was investigated for repeatable analysis. By collecting 100 mL of N_2 gas as the dry purging gas, the repeatability was significantly improved as the analytes were excluded from the GC instrument through evaporation of excess water in the injection port. To ensure successful extraction of water soluble VVOCs, several PT conditions were optimized. Optimization of sample solution volume was investigated from 10 to 40 mL. Only DCM showed an increase in peak area with increasing sample volume, whereas all other compounds showed a slight decrease in peak area. This is because the HS volume in the glass vial decreases with increasing sample volume. Based on the above results, sample solution volume was fixed at 20 mL. Variations in analyte peak area due to sampling volume of HS gas are depicted in Fig. 1, where the dry purging process was conducted after each sampling. For EtOH, AC, and ACN, a linear increase in peak area was found with increasing sampling volume of HS gas. MeOH showed increased peak area when increasing the sampling volume from 10 to 100 mL, reaching a plateau at volumes greater than 100 mL. This could be due to breakthrough of MeOH from the extraction needle. DCM also showed a plateau for the peak area with a sampling volume of 100–200 mL. This is because DCM is relatively hydrophobic and was successfully purged from the aqueous sample up to 100 mL. Based on these results, sampling volume of HS gas was fixed at 100 mL.

Fig. 2A shows variations in the desorption rate of the analytes when using different desorption temperatures (injection port temperature). The desorption rate was calculated by a ratio of the peak area obtained in the first desorption to the total peak areas obtained in the first and second desorptions. The second desorption was performed at 300 °C. The desorption rates were clearly improved with increasing desorption temperature for all investigated analytes. To ensure successful desorption, the desorption temperature was set at 300 °C. The variation in desorption rates of VVOCs due to different volumes of N_2 gas used for desorption is shown in Fig. 2B. The