Short Communication

Purge-and-Trap Extraction with a Miniaturized Extraction Capillary for the Determination of Aqueous Formic Acids in Ion Chromatography

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Abstract
Aqueous formic acid (FA) was determined by purge-and-trap extraction with a miniaturized extraction capillary using ion chromatography (IC). The extraction capillary was prepared by packing particulate activated carbon in a stainless-steel capillary (0.8 mm i.d., 1.6 mm o.d.). FA was purged from the sample solution and extracted on the extraction medium in its molecular form. Following extraction, the extraction capillary was connected directly to a six-port valve of the IC. The extracted analyte was eluted with sodium hydroxide solution as the formate ion and introduced to a conventional IC. The extraction capillary can be reused after conditioned by passing hydrochloric acid solution. The limit of detection of FA in a standard aqueous sample is 0.5 mg/L. The method was successfully applied to determine FA in fruit juices without significant interference.

Keywords: Formic acid; Purge-and-trap; Sample preparation; Ion chromatography

1. Introduction
Formic acid (FA) is a low-molecular-weight carboxylic acid that is water soluble. The boiling point of FA is 101°C, and therefore, it shows relatively high volatility. FA is widely present in plants and animals and is also used to contribute flavor to foods and drinks [1].

To determine volatile organic compounds (VOCs) in a sample, gas chromatography (GC) is typically used. A flame ionization detector (FID) and mass spectrometry (MS) are widely used for GC analysis of VOCs [2]. An FID is a conventional and inexpensive detector; however, its sensitivity regarding low carbon content molecules such as FA is relatively low. An MS also does not offer satisfactory sensitivity for the detection of FA. Therefore, sometimes, a derivatization reaction is used for sensitive detection of FA when a GC is used for analysis [3]. The GC analysis of FA had also been accomplished using a barrier discharge ionization detector with satisfactory sensitivity without derivatization [4,5]. Ion chromatography (IC) is the most popular method for determining the concentration of FA [6,7] in aqueous samples. When using the IC method, an ionized analyte is sensitively detected by an electro conductivity detector [8].

Several sample preconcentration methods have been used for the determination of VOCs. Among them, the purge-and-trap (PT) method is the most commonly used sample preparation and preconcentration method for VOCs in aqueous samples [9,10]. In the PT method, VOCs are purged from the aqueous sample into the headspace above the sample by the continuously introduced purge gas. Then, the purged VOCs are collected by the extraction device which is typically packed with a particulate extraction medium. The extracted VOCs are thermally desorbed from the extraction medium and are transferred to the GC-MS. The PT method has become an automated process and it is sufficiently sensitive for most target VOCs [11]. However, the above automated method requires expensive PT instruments.

We have previously developed a miniaturized needle-type extraction device for sample preparation of VOCs in GC analysis [12-14]. The extraction needle was prepared by packing the adsorbent into a stainless steel
After the extraction of VOCs by collecting the air sample, the extracted analytes were thermally desorbed in the GC injection port by direct insertion of the extraction needle [15,16]. Therefore, the analytical method with the needle-type extraction device offers rapid and sensitive determination for several types of VOCs [17,18]. The extraction needle has also been applied to PT analysis of VOCs in aqueous samples [19-23]. The method does not require expensive instruments, and VOC analytes can be rapidly and sensitively determined.

Based on experience with the needle-type extraction device, a miniaturized extraction capillary was developed for the analysis of volatile aldehydes in high-performance liquid chromatography (HPLC) [24]. The extraction capillary consists of a particulate adsorbent (silica gel) in a stainless steel capillary (0.8 mm i.d., 1.6 mm o.d.). After derivatization and concentration of the analytes in the extraction capillary, the capillary was connected directly to a six-port valve using a PEEK nut. Desorption and injection of the analytes were simultaneously accomplished by passing a desorption solvent. The extraction capillary was further applied to the PT-HPLC analysis of aqueous formaldehyde [25].

In this study, we introduce a method of PT extraction of aqueous FA with a miniaturized extraction capillary followed by IC analysis. After optimizing several extraction parameters, including the amount of desorption solvent and conditioning solvent, FA was quantitatively determined by collecting it with the adsorbent in its molecular form and desorbing it as ions. To the best of our knowledge, this study is the first to report the determination of FA in aqueous samples using PT and IC.

2. Experimental

2.1. Chemicals

FA (99.5%), sulfuric acid (H₂SO₄), hydrochloric acid (HCl), and sodium hydroxide (NaOH) were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan), and sodium chloride (NaCl) was obtained from Kanto Chemical Co., Inc. (Tokyo, Japan).

2.2. Miniaturized extraction capillary

The miniaturized extraction capillary was prepared by packing the particulate extraction medium into a stainless steel capillary (0.8 mm i.d. and 1.6 mm o.d.). The lengths of the capillary and packing of the adsorbent were 50 mm and 25 mm, respectively. The amount of the extraction medium was approximately 5 mg and it was fixed by synthetic Zylon fiber (Toyobo, Osaka, Japan). The Zylon fiber was not affected to the adsorption of the analyte. For the extraction medium, Carboxen 1000 (60/80 mesh, Sigma-Aldrich Japan, Tokyo, Japan) and a styrene- divinylbenzene copolymer of Sunpak-H (60/80 mesh, Shinwa Chemical Industries Ltd., Kyoto, Japan) were investigated. Figure 1 presents a schematic illustration of the miniaturized extraction capillary. Before PT extraction, the extraction capillary was conditioned with 1 mL of HCl solution (0.2 mol/L), which was purged by 100 mL of pure N₂ gas.

2.3. Sampling and desorption methods

A 10 mL aqueous sample was placed in a glass vial where the two septa were attached to the plastic cap of the vial. A magnetic stir bar, 3.7 g of NaCl, and 0.1 mL of 1.0 mol/L of H₂SO₄ were added. In our previous study, the addition of NaCl caused an increase in the FA purge efficiency. Because the pKₐ value of FA is 3.8, the pH of the sample solution was adjusted to below 2 to form the molecule and increase purge efficiency. Then, the vial was immersed in a 40ºC water bath and was magnetically stirred for 3 min. Thereafter, a stainless steel needle (23 gauge, 0.6 mm o.d., 0.4 i.d.) was connected to the extraction capillary, and a vacuum sampling device was inserted into the vial via the septa. Another needle was connected to a gas sampling bag, which was filled with pure N₂ gas, and was also inserted into the vial via another septa, as shown in Fig. 1. During gas collection, the purge gas (N₂) was continuously supplied to the sample solution. The sampling time was approximately 10 min for the collection of 100 mL of head space gas.

After the PT extraction, the extraction capillary was connected to the six-port valve of the IC using the PEEK connector. Then, the extracted analyte was desorbed using the desorption solvent (0.2 mol/L NaOH solution) and introduced into the IC. The following experiment optimized the desorption process. The extraction capillary can be reused after washing the adsorbent using NaOH solution.

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*Fig. 1. Illustration of PT extraction of FA with extraction capillary using IC analysis.*
2.4. IC measurement
A Dionex ICS-1100 ion chromatography system (Thermo Scientific, MA, USA) equipped with an electrical conductivity detector and a Dionex IonPac AS22 column (4 mm × 250 mm) was used to separate and determine the analytes. Separation was conducted by isocratic elution with 4.5 mM Na₂CO₃ and 1.4 mM NaHCO₃ aqueous eluent (1.2 mL/min) at 30ºC.

2.5. Real samples
Fruit juices (grape and orange juice, not from concentrate) were purchased at a local market in Kofu. To avoid bubble formation during PT extraction, the juice samples were diluted five times with pure water.

3. Results and discussion
3.1. Optimization for extraction and desorption of FA
The desorption solvent was optimized initially, and Carboxen 1000 was used as the extraction medium. Water, methanol, acetonitrile, and NaOH solution (0.1 mol/L) were evaluated for their effectiveness as the desorption solvent. The extracted FA was not desorbed by water. A large solvent peak interfered with the determination of FA when using methanol as the desorption solvent. Acetonitrile showed a lower desorption ratio, and an extracted FA desorption ratio of approximately 13%. NaOH solution provided a better desorption ratio and no interference peak was observed. Therefore, NaOH solution was selected as the desorption solvent for further investigation of the proposed method.

Based on our previous research, FA was successfully purged from the sample solution by adding NaCl and adjusting the pH of the sample to 2 with H₂SO₄ [5]. The extraction efficiency of the purged FA molecules using two extraction capillaries packed with Sunpak-H and Carboxen 1000 was evaluated using different preconditioning solvents for the adsorbent, which included pure water, HCl solution (0.1 mol/L), and NaOH solution (0.1 mol/L). When the adsorbent was preconditioned with NaOH solution, FA was not extracted by Sunpak-H or Carboxen 1000. However, Carboxen 1000 showed higher extraction efficiency than Sunpak-H when preconditioned with pure water and HCl solution, and a significantly higher extraction efficiency was obtained when the HCl solution was used. Therefore, Carboxen 1000 was selected as the adsorbent and the system was preconditioned with HCl solution before PT extraction was employed.

The HCl preconditioning solution was investigated, and the results indicated that better extraction efficiency was obtained when a higher concentration of HCl solution was used for preconditioning. However, when the higher concentration of HCl solution was used, a higher concentration and/or large amount of NaOH solution was needed for desorption of the extracted FA. In addition, there was more interference in the determination of FA when using a higher concentration of NaOH solution as the desorption solvent (> 1.0 mol/L). Therefore, the optimal concentration of preconditioning solution (HCl solution) and desorption solution (NaOH solution) were determined to be 0.2 mol/L.

The void volume in the extraction capillary was 30 μL and the sample loop was 25 μL. Therefore, the volume of the desorption solvent was fixed at 55 μL. The desorption method was optimized based on the desorption ratio of the analyte, and the desorption ratio was calculated based on a comparison of the peak areas obtained in two sequential desorption. Table 1 presents the desorption ratios of the extracted FA under different desorption conditions. The desorption conditions included the volume of the desorption solvent (μL), the waiting time (min), and the volume of the remaining desorption solvent (μL). Based on the obtained desorption ratio and required desorption time, the optimal desorption condition was determined to be 30 μL loading first and 5 min waiting, and then 25 μL loading.

The proposed method could also be used to extract and determine acetic acid (AA). However, extracted AA was not successfully desorbed in the above optimized desorption conditions, and a significant amount of NaOH solution was needed. Therefore, in this stage, further investigation is needed for sensitive and simultaneous determination of aqueous FA and AA using the proposed method.

| Desorption method (μL-(min)-μm) | Desorption ratio (%) |
|---------------------------------|----------------------|
| 55-(0)-0                       | 35                   |
| 30-(1)-25                      | 35                   |
| 30-(5)-25                      | 77                   |
| 30-(10)-25                     | 75                   |

3.2. Evaluation and application of the method
The limit of detection (LOD) of the method was determined using the standard deviation (SD) of the peak area from the measurement of a blank sample and slope (S) of the calibration curve as 3.3SD/S, and the limit of quantification (LOQ) was calculated as 10SD/S. The LOD and LOQ of the proposed method for aqueous FA were 0.5 and 1.5 mg/L, respectively. The relative SD of the peak area for measuring 10 mg/L of standard solution was 8.5% (n = 5).

The recovery of FA from river water and diluted orange juice samples were investigated. FA was not detected from the two river water samples (Fuji river and Nigori river, Kofu, Yamanashi). Then, the recovery was calculated by
comparing the peak area obtained by standard solution (50 mg/L) and spiked river water samples (50 mg/L). The recovery of FA from the spiked river water samples was 98±8%. FA was found in orange juice sample, and, therefore, the recovery of FA was calculated by comparing quantitative the results obtained using the absolute calibration and standard addition (spiked with 50 mg/L) method. The result showed a 96±10% recovery for FA from the diluted orange juice sample.

Table 2. Quantitative results for FA in real samples.

| Sample          | Concentration of FA (mg/L) |
|-----------------|-----------------------------|
| Tap water       | N.D.                        |
| River water     | N.D.                        |
| Orange juice    | 175                         |
| Grape juice     | 55                          |

N.D.; Not detected, n = 3.

Table 2 gives the quantitative results of FA from real samples. FA was not detected in tap water or river water samples. On the other hand, relatively higher concentrations of FA were found in the orange and grape juice samples. These quantitative results were relatively consistent with the results in our previous study [5]. Figure 2 shows a typical chromatogram for the determination of FA in the orange juice sample. FA was clearly detected without significant interference, included in the juice sample. The peak eluted in front of the analyte was derived from NaOH, and the obtained chromatogram was almost the same as that of a standard solution.

![Typical chromatogram for the determination of FA in diluted orange juice sample.](image)

**Fig. 2.** Typical chromatogram for the determination of FA in diluted orange juice sample.

4. Conclusion

A novel analytical method for the detection of aqueous FA based on PT extraction and IC analysis was developed using a miniaturized extraction device. Because the proposed method employed PT extraction, volatile FA was selectively purged and determined using an IC without significant interference in complex matrices. Further application of this method may be possible for the determination of AA or ammonia in aqueous samples using an IC.

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