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SHORT COMMUNICATION

Simple Determination of Acrolein in Surface and Drinking Water by Headspace SPME GC–MS

Hyun-Hee Lim · Ho-Sang Shin

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Abstract An automatic method to detect acrolein in surface and drinking water is described. This method is based on derivatization with 2,2,2-trifluoroethylhydrazine (2,2,2-TFEH) and consecutive headspace solid-phase micro extraction and gas chromatography-mass spectrometry (HS-SPME GC–MS). The HS-SPME parameters (selection of fiber, extraction/derivatization temperature, heating time and pH) were optimized and selected. Under the established condition, the detection and the quantification limits were 0.06 and 0.2 μg L^{-1} using 4 mL of surface water or drinking water, respectively, and the intra- and inter-day relative standard deviation was less than 10 % at concentrations of 0.5 and 2.5 μg L^{-1}. The calibration curve showed good linearity with $r^2 = 0.9977$. The method is suitable for use in the routine analysis of acrolein in surface water or drinking water.

Keywords Gas chromatography-mass spectrometry · Headspace solid-phase micro extraction · Surface water and drinking water · Acrolein

Introduction

Acrolein is a carbonyl compound that is also known as acrylic aldehyde or 2-propenal, and at room temperature acrolein is a colorless to yellowish flammable liquid. It is released to the environment through manufacturing processes and has been used as an intermediate for the synthesis of glycerine, methionine, glutaraldehyde and other organic chemicals [1, 2]. It is also released into the environment through auto exhaust gas and tobacco combustion processes [1, 2], and formed from glycerol during the heating of fatty food [2–4]. Furthermore, it is also a natural ingredient in several foodstuffs such as fruits, vegetables and beverages [5–10].

Acrolein is very toxic via all routes of administration and may cause respiratory and ocular irritation. The Deutsche Forschungsgemeinschaft (DFG) classified acrolein as a group 3B carcinogen based on a carcinogenic potential revealed by in vitro and animal experiments [11]. Otherwise, both the International Agency for Research on Cancer (IARC) [12] and the US Environmental Protection Agency (US EPA) [13] concluded that acrolein is not classifiable as a human carcinogen.

Many methods for the detection of acrolein in water or foods have been reported, such as capillary electrophoresis [14], high-performance liquid chromatography (HPLC) [15–19], liquid chromatography tandem mass spectrometry (LC–MS/MS) [20], gas chromatography [21, 22] and gas chromatography-mass spectrometry [23–27]. Among these methods, many assays are based on reactions with derivatization reagents that usually involve 5,5-dimethyl-1,3-cyclohexanedione, *N*-methylbenzothiazolon-(2)-hydrazone, pentafluorophenylhydrazine (PFPH), and 2,4-dinitrophenylhydrazine (2,4-DNPH) [15, 16, 20]. The problem associated with these methods is the interference of many carbonyl compounds, including acetone, acetaldehyde and other low-molecular compounds existing in sample.

Several researchers have developed a headspace (HS) GC–MS method for detecting acrolein in a food or biological sample [23, 24]. The analyte is vaporized and

H.-H. Lim
Department of Environmental Science, Kongju National University, Kongju 314-701, Republic of Korea

H.-S. Shin (✉)
Department of Environmental Education, Kongju National University, Kongju 314-701, Republic of Korea
e-mail: hshin@kongju.ac.kr

injected without derivatization [23], or after derivatization with PFPH, in which the detection limits are inadequate in most complex matrices.

A solid-phase micro extraction (SPME) GC–MS method for detecting acrolein in a food was developed. In this method, acrolein was derivatized with 2,4-DNPH to acrolein-DNPhydrazone, which adsorbed onto the fiber and desorbed in the injector of GC [25]. This method has the drawbacks of a short fiber life time and a severe interference.

HS-SPME GC–MS is a popular technique in the analytical area routinely used to analyze volatile compounds. Several researchers have developed a method for detecting acrolein in a beverage or urine sample which relies on HS-SPME GC–MS [26, 27]. In these methods, acrolein is adsorbed directly from a gaseous phase onto the fiber [26] or onto the fiber coating with a derivatizing agent [27], and later thermally desorbed in the injector of GC. The methods have many advantages, such as convenience, and rapid and automatic extraction, but it also has the drawbacks of low recovery due to the high water solubility of acrolein; polymerization of acrolein due to the high temperature; and especially for the later, the long loading time of the SPME fiber with derivatization reagent; and a short fiber life time.

Recently, we developed and validated an analytical method of detecting aldehydes and acetone in water by HS-SPME GC–MS after derivatization with 2,2,2-trifluoroethylhydrazine (2,2,2-TFEH) [28, 29]. The derivatization with 2,2,2-TFEH has many advantages. The derivatization requires mild reaction conditions at low temperature and no daily purification of the reagent. For all cases, the hydrazone product is volatile enough to use HS-SPME and an automatic extraction system.

The present study aimed to develop a HS-SPME GC–MS method to detect acrolein in water, and to apply the new method to real sample analysis. Derivatization was performed by the reaction of acrolein and 2,2,2-TFEH, a very volatile hydrazine, in sample contained in a headspace vial. The formed volatile acrolein-hydrazone was vaporized, and simultaneously adsorbed in fiber, and then desorbed in GC–MS.

Materials and Method

Materials

All organic solvents used were HPLC grade. Sodium chloride, hydrazine (98 %), methyl hydrazine (98 %), 2,2,2-trifluoroethylhydrazine (70 wt % solution in water), acrolein (99.0 %) and propionaldehyde (PPA) (97 %) as internal standard were obtained from Sigma-Aldrich (St. Louis, MO, USA). Commercially available SPME fibers [100 μm polydimethylsiloxane (PDMS), 65 μm polydimethylsiloxane-divinylbenzene (PDMS-DVB), 85 μm polyacrylate (PA), and 85 μm carboxen-polydimethylsiloxane (CAR-PDMS) fused-silica fibers) were purchased from Supelco (Bellefonte, PA, USA). The fiber was initially conditioned according to the instructions of the manufacturer in order to remove contaminants and to stabilize the solid phase. Conditioning was carried out in an extra split/splitless port with helium carrier gas prior to each adsorption.

Extraction/Derivatization Procedure

Sample preparation (extraction and derivatization) was carried out in 10-mL headspace vials with carried-lined screw caps. To a solution containing 4 mL of water sample, 1.6 g of NaCl, 200 μL of TFEH solution (20,000 mg L^{-1}) were added. pH was controlled with 0.1 M HCl or 0.1 M KOH. A derivatization/adsorption was carried out simultaneously in a headspace vial with continuous shaking, and the derivatives were desorbed in the injection port for successive analysis and passed onto the column for analysis. Derivatization was performed for different SPME adsorption times (15, 30, 40, 50 and 60 min) at different temperatures (40, 50, 60, 70 and 80 °C) at different amounts of TFEH (0.5, 1.0, 2.0, 4.0 and 6.0 mg) and at different pH (4.0, 5.0, 6.0, 7.0, 8.0, 9.0. 10.0, 11.0 and 12.0). The optimum conditions for derivatization of acrolein were determined by the amounts of the formed TFEH-hydrazone.

Apparatus

All mass spectra were obtained with an Agilent 7890/5975B instrument. The ion source was operated in the electron ionization mode (EI; 70 eV). Full-scan mass spectra (*m/z* 35–400) were recorded for analyte identification. An HP-InnoWax capillary column (60 m × 0.25 mm ID × 0.25 μm film thickness) was used. Samples were injected in the splitless mode. The flow rate of helium as carrier gas was 1.0 mL min^{-1}. The injector temperature was set at 220 °C. The oven temperature programs were set as follows. The initial temperature of 40 °C was held for 5 min and then increased to the final temperature of 205 °C at 15 °C min^{-1}. The ions selected by SIM were *m/z* 55, 83, and 152 for acrolein-TFEH and *m/z* 69, 85 and 154 for PPA-TFEH (internal standard).

Calibration and Quantification

The calibration curve for acrolein was established by derivatization after adding 0.4, 1.0, 2.0, 4.0, 10.0 and 20.0 ng of acrolein standard solution in 4 mL of milli-Q water. The corresponding concentrations of the standards

were 0.1, 0.25, 0.5, 1.0, 2.5 and 5.0 μg L^{-1}. The ions selected for quantification were *m/z* 152 for acrolein-TFEH and *m/z* 154 for PPA. The ratio of the peak area of the standard to that of the internal standard was used to quantify the compound.

The limit of detection (LOD) and limit of quantification (LOQ) were defined as the concentration resulting in a signal-to-noise ratio of 3:1 and 10:1, respectively, from samples spiked in pure water.

Results and Discussion

Optimization of SPME Fibers and Derivatization Conditions

Until now, high mass hydrazine compounds such as PFPH and 2,4-DNPH have been used for the derivatization of acrolein, but it is hard to analyze their derivatives with the HS extraction method due to low vapor pressure. Hydrazine, methyl hydrazine and TFEH as volatile hydrazines were reviewed in this study. The boiling points of hydrazine, methyl hydrazine and TFEH are 113, 88–90 and 83.1 °C, respectively; hydrazine and methyl hydrazine are toxic and carcinogenic based on their IARC or EPA classification. TFEH is the most volatile hydrazine and less toxic among the three hydrazines, moreover, our previous works [28, 29] showed that carbonyl compounds reacted with TFEH to form volatile hydrazone, which could be used for the determination of carbonyl compounds in water or foods by HS-SPME GC–MS. Therefore, TFEH was selected as an optimum derivatization reagent of acrolein in water matrix.

Four SPME fibers were evaluated to select a suitable fiber for detecting acrolein. The adsorption efficiencies on the SPME fibers were evaluated by comparing the peak areas of the acrolein derivative. The highest efficiency among the four fibers was obtained using 85 μm carboxen-polydimethylsiloxane (CAR-PDMS), as shown in Fig. 1, therefore, CAR-PDMS was selected as a fiber suitable for detecting acrolein.

In the study on the reaction yield of acrolein in relation to the amount of TFEH, a maximum area was achieved by 4.0 mg of TFEH (Fig. 2). To insure the complete reaction of acrolein, an excess amount of TFEH is required. In the following study, a sufficient amount (20.0 mg) of TFEH should be used in the reaction for considering its consumption on the other substances in the real sample. The derivatization was tested at various pH values of 4–12. The reaction of acrolein with hydrazine showed good yield at the pH value of 10. Recovery declined above or below a pH of 10.0 as shown in Fig. 2; therefore, the pH of a sample must be controlled exactly at 10.0. Generally, the production of hydrazones should occur rapidly in acid solution (pH 1.5–2.2), otherwise hydrazones have bad volatility in HS because they form ions; therefore the reaction yield of acrolein with hydrazine in this study is more favorable in the alkaline condition.

The reaction rate of acrolein with hydrazine in relation with the reaction temperature and time was studied. The

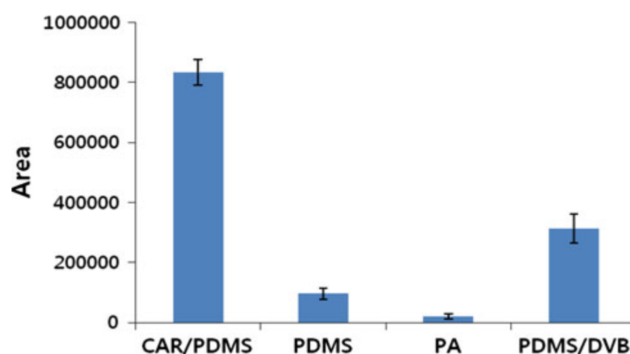

Fig. 1 Extraction efficiencies of acrolein in relation to various solid-phase micro extraction fibers (this experiment was performed at a reaction time of 50 min and reaction temperature of 60 °C)

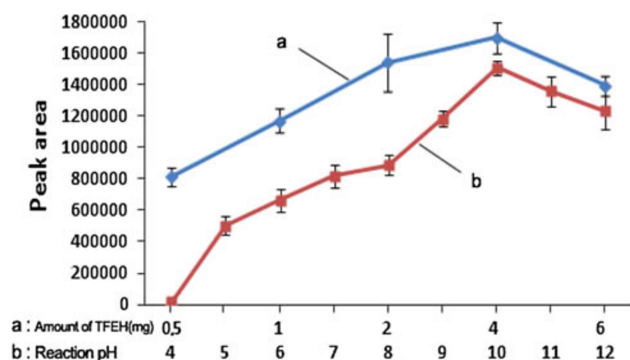

Fig. 2 Reaction yield of acrolein in relation to the amount of TFEH (**a**) and reaction pH (**b**) (this experiment was performed at a reaction time of 50 min and at a reaction temperature of 60 °C)

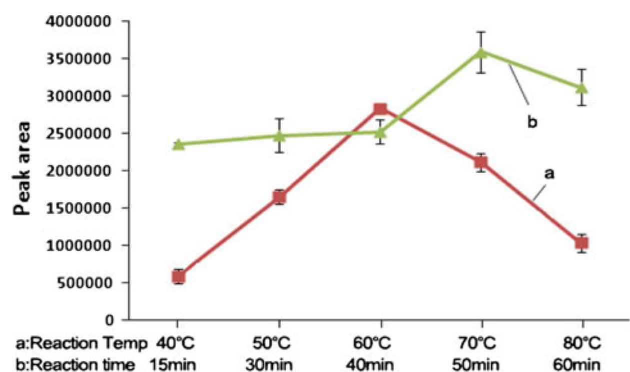

Fig. 3 Effect of reaction temperature (**a**) and reaction/adsorption time (**b**) on the reactivity of acrolein with TFEH (this experiment was performed at a reaction time of 50 min and at a reaction temperature of 60 °C)

optimal reaction temperature and time were 50 min at 60 °C (Fig. 3). The recovery declined slowly beyond the reaction time of 50 min.

When sodium chloride was used as a salting-out agent, the signal of acrolein increased to about 1.6 times. Therefore, all water samples were saturated with sodium chloride before capping vial containing water sample.

Chromatography and Mass Spectrometry

The optimum derivatization conditions (TFEH amount of 20.0 mg, the reaction solution pH of 10.0, reaction temperature and time of 60 °C and 50 min) were applied to the analysis of acrolein in surface water and drinking water. Figure 4 shows a GC–MS chromatogram after the derivatization of acrolein. For the GC separation of the derivative, the use of a polar stationary phase (InnoWax) was found to be efficient. The derivative of acrolein showed a sharp peak and the compound was quantified as the integration of the peak area.

The mass spectrum of acrolein-TFEH by electron ionization at 70 eV was obtained. The molecular ion at *m/z* 152 and diagnostic ions at *m/z* 42, 55, 69, 83, 110 and 131 indicate that acrolein was derivatized to the corresponding

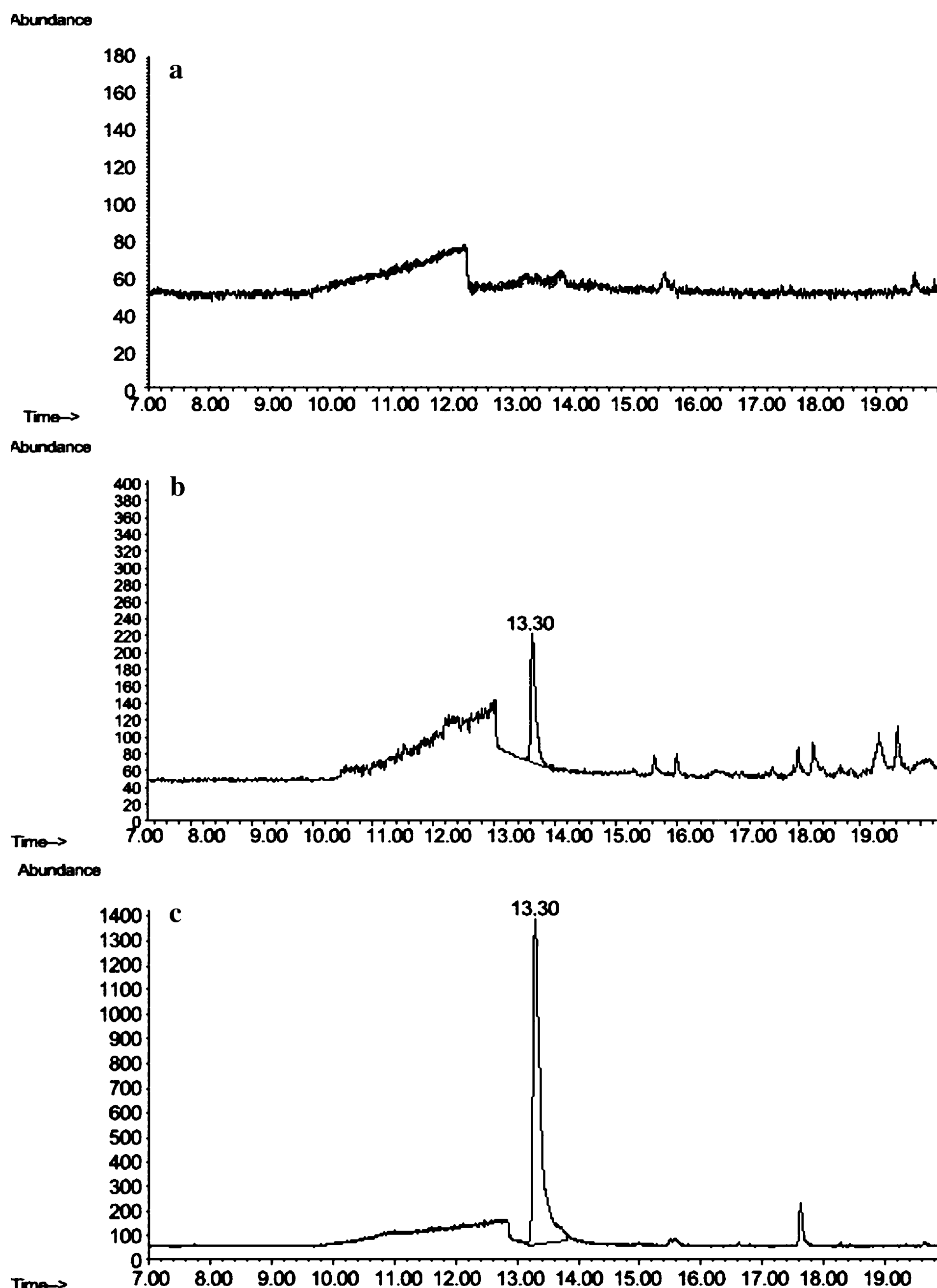

Fig. 4 Gas chromatography-mass spectrometry chromatogram from blank (**a**), spiked sample to a concentration of 0.5 μg L^{-1} (**b**) and 5 μg L^{-1} (**c**)

Table 1 Intra and inter-day laboratory accuracy and precision results for the analysis of acrolein in surface water and drinking water ($n = 5$)

Matrix	Matrix blank ($\mu g\ L^{-1}$)	Spiked conc. ($\mu g\ L^{-1}$)	Intra-day measured value			Inter-day measured value		
			Mean ± SD ($\mu g\ L^{-1}$)	Accuracy (%)	Precision (%)	Mean ± SD ($\mu g\ L^{-1}$)	Accuracy (%)	Precision (%)
Surface water	nd	0.5	0.51 ± 0.018	101.1	3.52	0.52 ± 0.03	101.2	5.80
		2.5	2.39 ± 0.167	95.4	7.01	2.59 ± 0.14	103.8	5.43
Drinking water	nd	0.5	0.45 ± 0.04	91.9	9.47	0.50 ± 0.03	100.2	6.44
		2.5	2.27 ± 0.17	91.1	7.81	2.50 ± 0.15	100.0	5.94

acrolein-TFEH. The fragments of *m/z* 131 and *m/z* 110 were accounted for by the loss of a fluorine atom and a [C_3H_6] from the molecular ion, respectively. The fragments of *m/z* 69 and *m/z* 83 were, respectively, accounted for itself of a [CF_3^+] and the loss of a [CF_3] from the molecular ion.

Validation of the Assay

The combination of a high derivatization yield and the high sensitivity of the derivative by EI-MS (SIM) permits the detection of acrolein at concentrations well below to those reported previously. LOD and LOQ in this study were calculated as 0.06 and 0.2 $\mu g\ L^{-1}$, respectively.

Examination of the typical standard curve by computing a regression line of the peak area ratios of acrolein-TFEH to PPA-TFEH on the concentration using a least-squares fit demonstrated a linear relationship with a correlation coefficient of 0.998. The line of best fit for acrolein is $y = 0.012x - 0.0001$ over a range of 0.1–5.0 $\mu g\ L^{-1}$ where x is the analyte concentration ($\mu g\ L^{-1}$) and y is the peak area ratio of the analyte to the internal standard. The precision and accuracy of the assay were very good, as shown in Table 1. Intra-day accuracy was evaluated by five spiked samples at concentrations of 0.5 and 2.5 $\mu g\ L^{-1}$ and inter-day accuracy was determined by their recovery on 5 different days. The accuracy was in range of 91–104 % and precision of the assay was less than 10 %.

Conclusion

In this paper, we present a simple and automatic method to detect acrolein in surface water and drinking water. Derivatization was performed by the reaction of acrolein and TFEH, a very volatile hydrazine, in water contained in a headspace vial. The formed volatile acrolein-TFEH was vaporized, and simultaneously adsorbed in SPME fiber, and then desorbed in GC–MS. All reagents are spiked in the preparation step and the analysis is performed automatically after capping. This method has many advantages: acrolein in nature is unstable and undergoes polymerization under heating conditions. In this method, it changes to a stable acrolein-TFEH and then the derivative is vaporized, and simultaneously adsorbed in SPME fiber. Also, TFEH does not require daily purification. For all cases, the hydrazone product is volatile enough to use the HS-SPME. This method may also be applicable to food, beverage and biological sample with a minor modification.

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