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Simple and Sensitive Determination of 2,4-Xylenol in Surface Water Samples from River and Sea by Gas Chromatography–Mass Spectrometry

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Abstract A simple and selective method was developed for determination of the concentration of 2,4-xylenol in river and sea water samples using gas chromatography/mass spectrometry (GC/MS). Trace amounts of 2,4-xylenol were collected in a Oasis HLB Plus cartridge, eluted with acetonitrile. The method detection limit of 2,4-xylenol was 1.4 ng/L. The trace peaks of 2,4-xylenol were found in water samples from the river and the sea, and the concentrations were all less than 1.4 ng/L. The nine peaks of the 2,3-, 2,4-, 2,5-, 2,6-, 3,4-, 3,5-xylenol, and *o*-, *m*-, *p*-ethyl phenol that gave the same *m*/*z* ratio were separated efficiently.

Keywords 2,4-Xylenol · Gas chromatography/mass spectrometry (GC/MS) · River water · Sea water

The 2,4-xylenol (Fig. 1; CAS No.; 105-67-9, mw: 122.17) is used as insecticide, medicinal intermediate, and synthetic materials (Trapido et al. 1998; Takeda et al. 1995). The 2,4-xylenol was designated a Class II chemical substance (NOAEL; 30 mg/kg/day) by the Pollutant Release and Transfer Register (PRTR). The PRTR system has been adopted in various countries. In Japan, it was institutionalized in 1999. The PRTR requires businesses to submit notifications of chemical substances they release into the environment. Judging from their physical and chemical properties, "Class II Chemical Substances" are anticipated to persist in the environment for extended periods over considerable areas if the amounts manufactured, imported, or used are increased, and thus will pose a risk to the environment. Japanese Ministry of the Environment has been concerned about this persistence in the environment.

Gas chromatography with mass spectrometry (GC/MS) methods and liquid chromatography with mass spectrometry (LC/MS) methods for analyzing insecticides and pesticides in water have been reported (Bossi et al. 2002; Fernandez et al. 2001; Heberer and Stan 1997; Lacassie et al. 1999; Santana et al. 2002; Schreiber et al. 2000; Wu et al. 2004). GC/MS method for analyzing 2,4-xylenol has been reported (Environmental Health Department, Ministry of the Environment in Japan 1998). However, the two peaks of 2,4-xylenol and 2,5-xylenol were not separated by their method, and this analytical method was time-consuming and complicated for using derivatization reagents. In this paper, we describe a simple and selective method for the quantification of 2,4-xylenol in surface water samples from river and sea using GC/MS. Furthermore, the nine peaks of the 2,3-, 2,4-, 2,5-, 2,6-, 3,4-, 3,5-xylenol, and *o*-, *m*-, *p*-ethyl phenol that gave the same *m*/*z* ratio were separated efficiently.

Materials and Methods

The 2,3-, 2,4-, 2,5-, 2,6-, 3,4-, and 3,5-xylenols, and *o*-, *m*-, *p*-ethyl phenols standards were purchased from Wako Pure Chemical Industries (Osaka, Japan). The 2,4-xylenol-d_3 (98%), internal standard and surrogate, was purchased from Cambridge Isotope Laboratories, Inc. (MA, USA). Acetonitrile and

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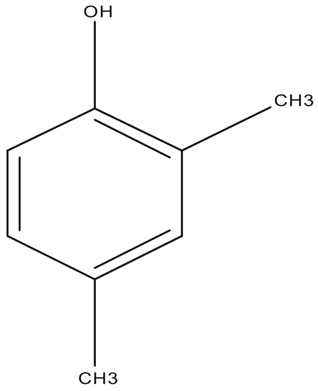


Fig. 1 Structure of 2,4-xylenol

sodium sulfate anhydride of pesticide and PCB grade were from Kanto Chemical Co., Inc. (Tokyo, Japan). The ultra pure water of LC/MS grade was from Wako.

Surface water samples from river and sea in northern Kyushu and the Japan Sea were collected. Water sampling was carried out in October 2006. Each 1 L water sample was passed through a solid phase extraction cartridge (preconditioned Oasis HLB Plus with 20 mL acetonitorile and 20 mL ultrapure water; Waters, Milford, MA) at a flow rate of 10 mL/min. The 2,4-xylenol was eluted with 5 mL acetonitorile from the Oasis HLB Plus cartridge connected with Sep-Pak Dry cartridge (preconditioned with 10 mL acetonitorile, Waters, Milford, MA). After addition of about 1 g of sodium sulfate anhydrous to this acetonitorile solution, this solution was transferred to another tube. This solution was dried to 1 mL using nitrogen stream, and analyzed by GC/MS.

The 2,4-xylenol, five isomers of 2,4-xylenol, and *o*-, *m*-, *p*-ethyl phenol were determined by using the GC/MS QP2010 Plus instrument (Shimadzu, Japan). GC/MS was operated under the following condition: injector temperature, 250°C; oven temperature program, 2 min isothermal at 40°C, raised at 40°C/min to 85°C, held for 35 min, and then raised at 40°C/min to 250°C, held for 10 min; column, 60 m × 0.25 mm i.d., 0.25 µm film thickness, SGE BPX-5 (5% phenyl and 95% methyl polysiloxane); interface temperature, 250°C; ionization voltage, 70 eV. The carrier gas was helium and the flow rate was 1.8 mL/min. The mass spectrometer was operated either in a selected ion-monitoring mode (SIM) or in a scanning mode. When working in the SIM mode, the major fragment ion of the standard and IS was monitored at *m*/*z* 107 (122) and 125 (110), respectively. Quantification of the standard was carried out by comparing the peak area to the IS area.

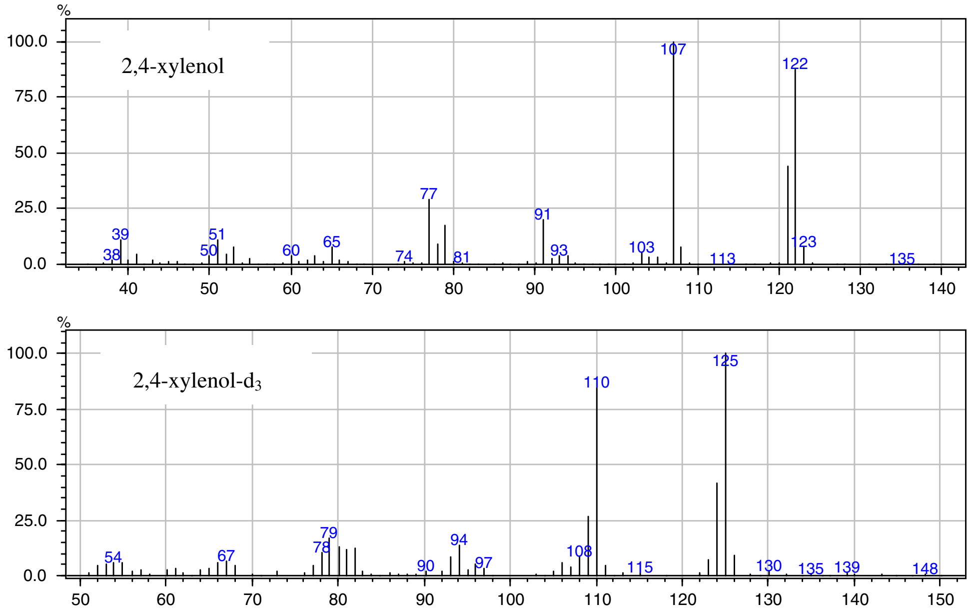
Results and Discussion

Figure 2 illustrates the mass spectra acquired for 1 mg/L 2,4-xylenol and 2,4-xylenol-d_3. Ions of 2,4-xylenol were intense at *m*/*z* 107 and 122, and ions of 2,4-xylenol-d_3 were intense at *m*/*z* 125 and 110. Therefore, *m*/*z* 107 and 125 were monitored for SIM, and also *m*/*z* 122 and 110 was monitored as a confirmation of the detection. Figure 3 shows the SIM chromatogram of 50 µg/L of 2,4-xylenol and 20 µg/L of 2,4-xylenol-d_3.

The calibration curve of 2,4-xylenol and the correlation coefficients calculated from the concentration and the peak areas ratio of 2,4-xylenol to 2,4-xylenol-d_3 are shown in Fig. 4. The curve showed good linearity in the range 5–100 µg/L.

To select the best solid phase cartridge for effective and selective investigation of 2,4-xylenol, extractions of standard solutions were performed using five cartridges ((1) Sep-Pak

Fig. 2 Mass spectra of 2,4-xylenol and 2,4-xylenol-d_3



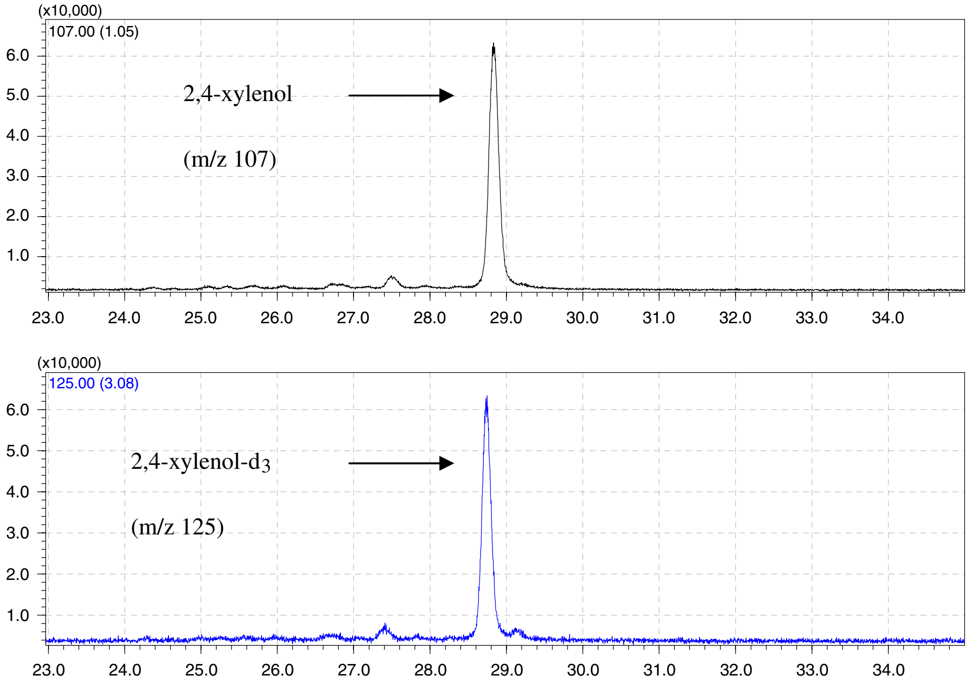


Fig. 3 GC/MS-SIM chromatogram of 2,4-xylenol (50 μg/L) and 2,4-xylenol-d_3 (20 μg/L)

plus tC18; surface functionality: –$SiC_{18}H_{37}$, (2) Sep-Pak plus C18; surface functionality: –$Si(CH_3)_2C_{18}H_{37}$, (3) Oasis HLB Plus; *N*-vinylpyrrolidone and divinylbenzene copolymer, (4) Sep-Pak plus PS-2; surface functionality: styrene and divinylbenzene copolymer, ((1)–(4); Waters, Milford, MA) (5) GL-Pak Aqusis PLS-3 Jr.; surface functionality: nitrogen-containing methacrylate and divinylbenzene copolymer (GL Sciences Inc., Tokyo, Japan)). Five millilitre of 100 μg/L 2,4-xylenol solution was passed through solid phase cartridges preconditioned with 10 mL acetonitorile and 10 mL ultrapure water, and 2,4-xylenol was eluted with 5 mL acetonitorile from the cartridge. This procedure was carried out three times on each cartridge. The recoveries were detected of each cartridge (Fig. 5). The Oasis HLB Plus cartridge was selected for extraction of 2,4-xylenol because the recovery was 89%, and the best of five cartridges.

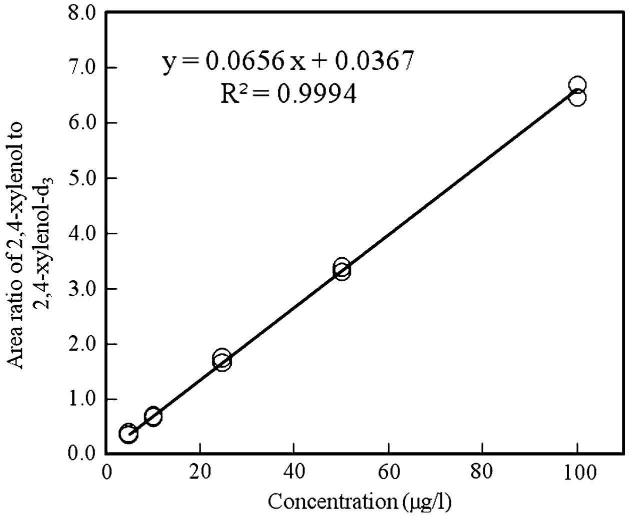


Fig. 4 Representative calibration curve of 2,4-xylenol

The method detection limit (MDL) was determined using ultrapure water spiked with 2,4-xylenol. Samples of water (10 L) were spiked with 200 ng of 2,4-xylenol to give a concentration of 20 ng/L. The MDL was calculated as two times the t-ratio (1.9432; 6 degrees of freedom, 5% level of significance) multiplied by the standard deviation for seven replicate determinations. The MDL of this method was 1.4 ng/L. The MDL that Japanese Ministry of the Environment had demanded for safety to the environment was 2.5 ng/L, therefore our method was satisfied for sensitive and selective detection of 2,4-xylenol in the environment, in addition, the sample collection and extraction of our method was very simple.

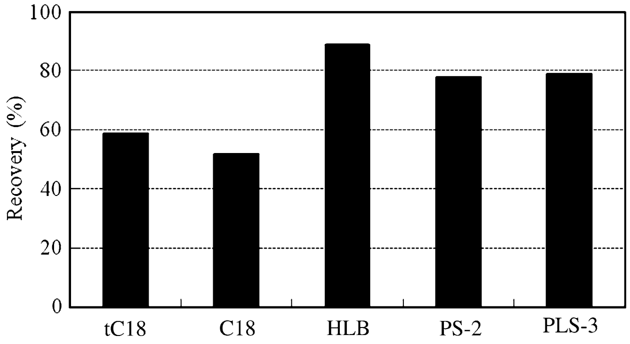


Fig. 5 Recoveries of 2,4-xylenol by five SPE cartridges with acetonitrile

Table 1 Recoveries of 2,4-xylenol in ultrapure water, river water and sea water (n = 5)

Water samples	Spiking level (ng/L)	Detected concentration (ng/L)	Recovery (%)	Precision (RSD) (%)
Ultrapure water	0	n.d.	–	–
	50	51.5	103.0	4.2
River water	0	<1.4	–	–
	50	49.2	98.3	1.3
Sea water	0	<1.4	–	–
	50	50.0	99.9	2.9

n.d.–not detected

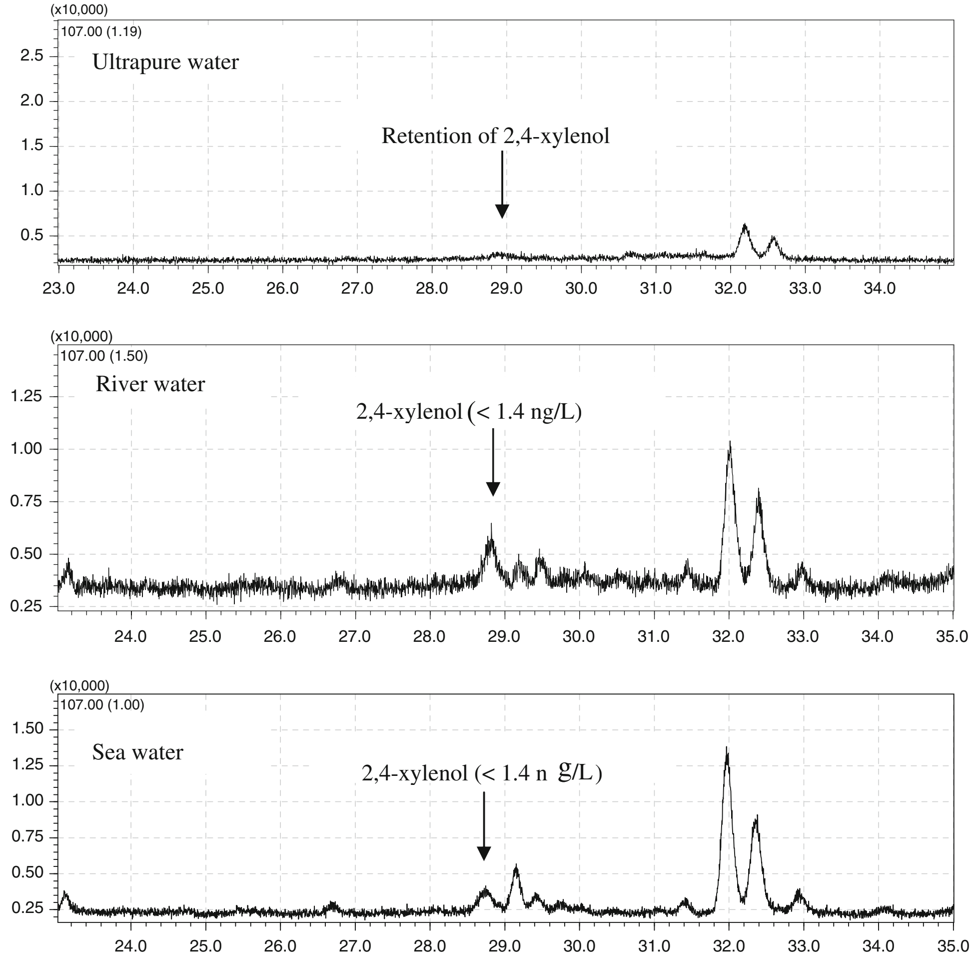


Fig. 6 GC/MS-SIM chromatogram of ultrapure, river, and sea water

Recoveries for 2,4-xylenol, expressed as the overall mean from a series of five analyses, are shown in Table 1. The recovery for a standard aqueous solution containing 50 ng/L was 103%, and the relative standard deviation was 4.2%. The recoveries of 2,4-xylenol in surface water from the river and sea were 98.3% and 99.9%, respectively. The relative standard deviations were 1.3% and 2.9%, respectively.

Surface waters from three different sites of the same river and three different sites of the bay in Fukuoka Prefecture were sampled in October 2006. Representative SIM chromatograms of river and sea waters are shown in Fig. 6. Trace amounts of 2,4-xylenol were found in all water samples from the river and the sea, and the concentrations were all less than 1.4 ng/L (MDL).

Representative SIM chromatograms of the 2,3-, 2,4-, 2,5-, 2,6-, 3,4-, 3,5-xylenol, and *o-, m-, p*-ethyl phenol that give the same *m/z* ratio are shown in Fig. 7. This shows that nine peaks are separated efficiently, and identification and quantification of 2,4-xylenol is possible.

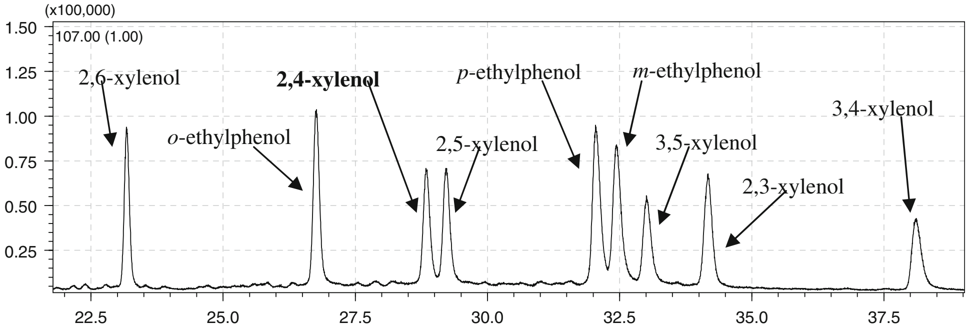


Fig. 7 GC/MS chromatogram of 2,3-, 2,4-, 2,5-, 2,6-, 3,4-, 3,5-xylenol, and *o*-, *m*-, *p*-ethylphenol (100 µg/L each)

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