

Research Article



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액-액 추출과 아세틸화 후 GC-MS를 이용한 물 중 phenol의 분석

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Quantitative Determination of Phenol in Water Using GC-MS after Liquid-Liquid Extraction and Acetylation

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Abstract

BACKGROUND: The phenol concentrations in water samples were determined using gas chromatography after derivatization of the analyte to phenyl acetate followed by extraction using a large volume of solvent. However, this procedure requires an additional purification step and is not analytically efficient.

METHODS AND RESULTS: In this study, phenol was first extracted from an acidified water sample using ethyl acetate and then acetylated using acetic anhydride in the presence of a small amount of water and K₂CO₃. The derivative was extracted using 1 mL of *n*-butyl acetate. One microliter of the extract was analyzed by GC-MS without further purification. The calibration curve showed good linearity with the *r*² value of 0.9968. The method detection limit and the limit of quantitation were estimated to be 0.18 µg/L and 0.56 µg/L, respectively. Repeatability (RSD, n=3) and recovery (n=3) were 9.1%-4.3% and 90.6%-110.5%, respectively. The concentrations of phenol in a few samples of stream water were distributed in the range of 2.51-7.51 µg/L.

CONCLUSION: This method is simpler and faster to implement than those currently utilized and shows high analytical reliability. It can be applied to the quantitative determination of phenol concentrations in surface water and groundwater samples.

Key words: Acetylation, GC-MS, Liquid-liquid extraction, Phenol, Water

서 론

Phenol() , , , , , , phenol (ATSDR, 2008; IRIS, 2002; Saha *et al.*, 1999). phenol 가 (CCME, 1999). (US EPA) phenol (priority pollutant) (EPA, 2014), phenol 5 µg/L (, 2016). phenol gas chromatography-mass spectrometry(GC-MS) , (Farhadi *et*

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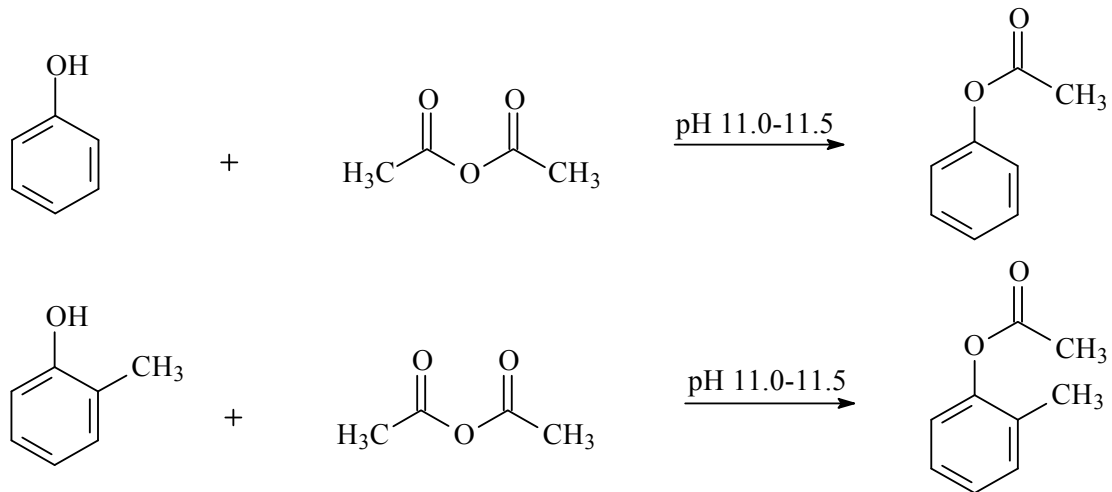


Fig. 1. Acetylation reactions of phenol and o-cresol (surrogate standard) with acetic anhydride at pH 11.0-11.5.

al., 2014),
 (Bagheri *et al.*, 2004).
 가 phenyl acetate (Fig. 1),
 phenol phenyl acetate acetyl
 (Rodríguez *et al.*, 2000).
 phenol
 phenyl acetate
n-hexane (Faraji, 2005;
 Llompart *et al.*, 2002).
 phenol phenyl acetate
 GC-MS

재료 및 방법

시약 및 재료

Phenol, phenyl acetate, o-cresol, potassium carbonate
 acetic anhydride Sigma-Aldrich (Missouri, USA)
 HPLC methanol, ethyl acetate
 dichloromethane(DCM) Tedia(Ohio, USA), sodium
 chloride Junsei Chemical Co. Ltd(Tokyo, Japan),
n-butyl acetate, sodium sulfate hydrochloric acid(35%)
 Daejung(Busan, Korea)
 sodium thiosulfate Fluka(Bunch, Switzerland)

표준용액의 제조

Phenol 5000 mg/L phenol
 methanol 1000, 100 10 mg/L
 (-24°C)

(surrogate standard, SS) o-cresol methanol
 207 mg/L
 추출
 50 mL o-cresol(SS) 2 µL
 35% HCl 가 pH 2
 50 mL ethyl acetate 가
 shaker(SR-2DS, Taitec, Koshigaya, Japan) 15
 acetate Ethyl acetate (100 mL) 1
 g sodium sulfate 가
 (Model HS 2000, Hahn-Shin Science Co., Bucheon,
 Korea) 가
 1 mL , 0.5 mL
 5% K₂CO₃ 0.1 mL acetic anhydride 가 ,
 vortex mixer 20 10
 0.1 mg NaCl 가 1 mL *n*-butyl acetate
 vortex mixer 1 . *n*-Butyl
 acetate vial 1 µL GC- MS

기기 분석

GC-MS 7890A GC 5975C
 inert MSD(Agilent Technology Inc., Santa Clara, USA)
 Table 1 DB-
 WAX , 240°C,
 EI
 , phenyl acetate
 (m/z) 66, 94 136

유효성 검증

1-10 µg/L
 4 µg/L 10 µg/L 3

Table 1. Operating conditions of GC-MS for quantitative determination of phenol in water as phenyl acetate form

GC	Carrier gas, flow rate	99.999% He gas, 1 mL/min
	Column	Agilent DB-WAX (30 m×0.25 mm×0.25 μm)
	Oven temperature program	40°C (3 min)→150°C at a rate of 10°C/min→230°C at a rate of 25°C/min→230°C (20 min)
	Inlet port temperature	240°C
	Injection mode, volume	Splitless mode, 1 μL
MS	Transfer line temperature	240°C
	Mode	Electron impact (EI), 70 eV
	Ion source temp.	230°C
	Quadrupole temp.	150°C
	Selected ions (m/z)	Phenyl acetate: 66, 94, 136 o-Cresyl acetate: 107, 108, 150

가 (method detection limit, MDL) (limit of quantitation, LOQ) S/N 3 2 7 3.14 10

하천수 중 phenol 분석

2015 8 11
1 L
40-50 mg sodium thiosulfate 가 , 6 N HCl 가
pH 2
4°C , 0.2 μm (Whatman, Little Chalfont, UK) (US EPA, 2000).

결과 및 고찰

전처리 조건 확립

phenol (phenyl acetate) ester
가
n-butyl acetate, ethyl acetate DCM
가 (Fig. 2). *n*-butyl acetate가
1.5 , *n*-butyl acetate phenyl acetate
phenol 50 mL
phenyl acetate *n*-hexane 20 mL (NCASI, 2007).

n-hexane *n*-butyl acetate
가

(Copestake and Malcolm, 2005)

n-butyl acetate phenol

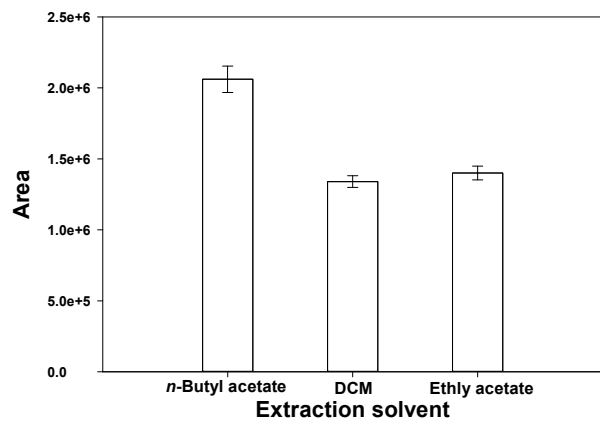


Fig. 2. Comparison of solvent extraction of phenyl acetate from the acetylation reaction mixture. *n*-Butyl acetate showed the highest extraction efficiency.

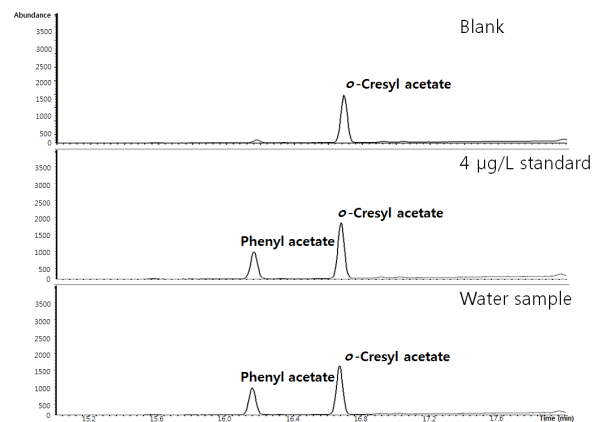


Fig. 3. Chromatograms of a blank, a standard, and a water sample.

ethyl acetate
1 mL
acetate , *n*-butyl acetate GC-MS

선택성 및 직선성

Fig. 3 phenol SS α -cresol ester
가
(r^2)가 0.9968
SS

반복성과 회수율

4 μ g/L 10 μ g/L 3
(relative standard deviation, RSD)
9.1% 4.3% , 90.6% 110.5%
acetate
m-hexane
RSD(4.1-12.4%) (102-105%)
(NCASI, 2007).

방법검출한계 및 정량한계

μ g/L 0.56 μ g/L MDL LOQ 0.18
5 μ g/L 10 1 LOQ
phenol
MDL MDL(0.16-0.32 μ
g/L) (NCASI, 2007).

하천수 시료 분석

4.84 μ g/L 2.51-7.51 μ g/L
(Table 2).
(0.1-1.5 μ g/L)
(ATSDR, 2008) (60%)
(5 μ g/L)

요 약

phenyl acetate
phenol
가
phenol
phenyl acetate
GC-MS
phenol

Table 2. Concentrations of phenol in stream water samples

Site	Concentration (μ g/L)
1	5.07
2	6.03
3	3.07
4	2.51
5	7.51
Mean	4.84
Standard deviation	2.07
Range	2.51-7.51

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