Electronic Supplementary Material (ESI) for Analytical Methods.

ELECTRONIC SUPPLEMENTARY INFORMATION FOR THE PAPER

Combined headspace single-drop microextraction and solid-phase microextraction for the determination of phenols as their methyl ethers by gas chromatography-mass spectrometry

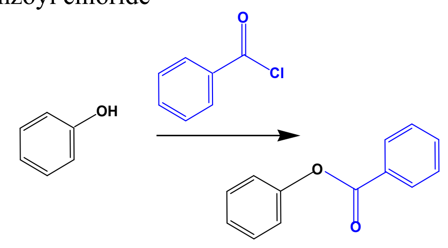
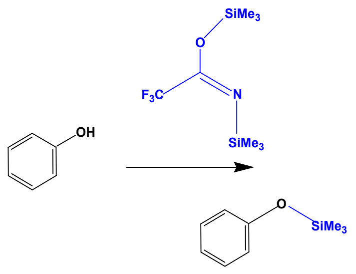
Archana Jain, Soumitra Soni, Kishan Reddy-Noone, Aradhana K.K.V. Pillai and Krishna K. Verma*

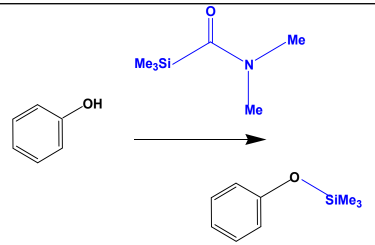
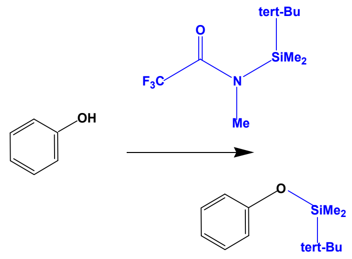
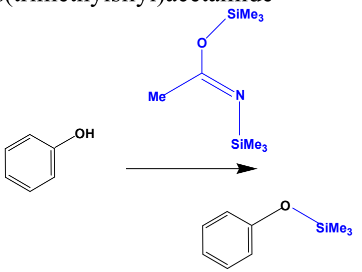
Department of Chemistry, Rani Durgavati University, Jabalpur 482001, Madhya Pradesh, India

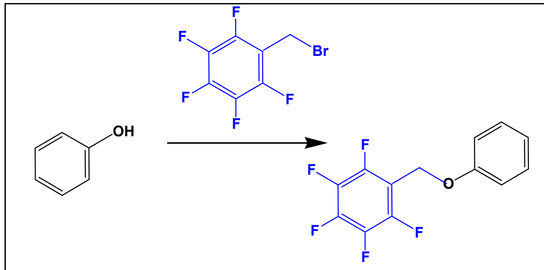
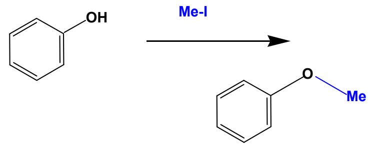
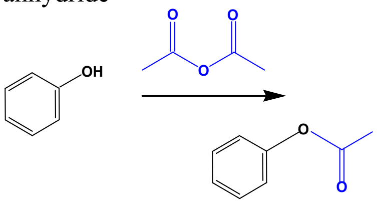
* Corresponding author
Tel.: +91 761 2605103.
E-mail: **arichna@sancharnet.in** (Krishna K. Verma)

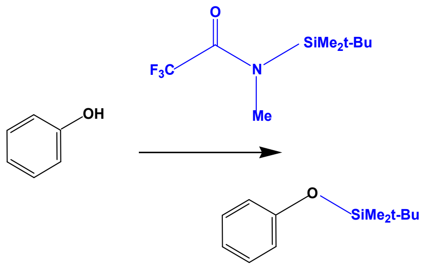
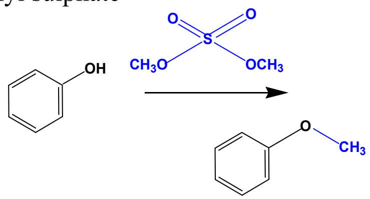
ORCID
Krishna K. Verma: 0000-0003-2223-3027

Table S1 The analytical features of merit of methods based on different strategies of derivatization and extraction in the determination of phenols by GC

Derivatizing reagent/reaction scheme	Detection technique	Matrix (phenolics)	Extraction/derivatization method	Linear range/ (LOD; S/N = 3)	Ref.
None	GC-FID	Water (phenol, and chlorophenols)	SPME (polyaniline film electrodeposited on the platinum wire inserted into the needle of homemade syringe); 15 mL sample.	0.05-5 mg L^{-1} (0.69-3.7 μg L^{-1})	1
None	GC-MS	Human urine (chlorophenols)	In-syringe dispersive μ-SPE using carbon fibres; 10 mL sample.	1-1000 μg L^{-1} (0.1-0.9 μg L^{-1})	2
None	GC-MS	Bio-mass combustion smoke (alkyl- and methoxy-phenols)	HS-SPME (CW-DVB, 65 μm); 5 mL of total 100 mL impinger extract used for SPME.	2-30 μg L^{-1} (1.1-4.2 μg L^{-1})	3
Benzoyl chloride 	GC-MS	Water (phenol, nitro- and chlorophenols)	Multi-valve SPE of benzoates (PS-DVB, 8 μm); 1 μL of 200 μL extract injected. Sample 80 mL.	0.1-100 μg L^{-1} (8-90 ng L^{-1})	4
N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) 	GC-MS/MS	Human urine (chlorophenols)	SPE (PS-DVB, 100 mg); 2 mL aqueous sample; 1 μL of 50 μL extract injected.	0.1-32 μg L^{-1} (0.01-0.03 μg L^{-1})	5
Trimethylsilyl-*N,N*-dimethylcarbamate	GC-MS	Water (phenol, alkyl- and chlorophenols)	SPE (hypercrossed linked PS-DVB); 100 mL sample; 2.5 mL of extract concentrated to 1 mL, 10 μL injected.	0.001-25 mg L^{-1} (0.05-100 ng L^{-1})	6

					
tert-Butyldimethylsilyl-*N*-methyltrifluoroacetamide 	GC-MS	Sewage influent and effluent (alkylphenols, parabens, phenylphenol, bisphenol)	SPE (Oasis MAX); 1 L sample; 1 µL of final 1 mL extract injected.	0.01-10 µg L^{-1} (0.01-0.1 µg L^{-1})	7
N,O-Bis(trimethylsilyl)acetamide 	GC-MS	Water (chlorophenols)	SDME (2.5 µL of hexyl acetate); in-syringe silylation by drawing the 0.5 µL of reagent into the same syringe, sealing by placing GC septum at needle tip, and heating; 3 mL sample; the whole mixture injected.	0.05-50 µg L^{-1} (4-61 ng L^{-1})	8
2,3,4,5,6-Pentafluorobenzyl bromide (PFBBr)	GC-ECD	Wastewater irrigated soil (pentachloro-phenol)	LLE (10 g soil extracted with 100 mL hexane and acetone, 1:1 v/v); extract concentrated to 1 mL, and 1 µL injected.	5-1000 µg L^{-1} (0.4 µg L^{-1})	9

					
Methyl iodide 	GC-FID	Water (phenol, methyl-, chloro- and nitrophenols)	LLE (tetraalkylammonium bromide as phase transfer catalyst, and 1 mL of dichloromethane); 45 min reaction at 65^{o}C; extract concentrated to 200 µL, and 2 µL injected.	250-760 µg L^{-1} (0.5-12 µg L^{-1})	10
Acetic anhydride 	GC-ECD	Water (chlorophenols)	CSDFME; 10 mL aqueous sample; 0.5 µL of 11 µL extract injected.	0.01-300 µg L^{-1} (0.005-0.5 µg L^{-1})	11
Acetic anhydride	GC-ECD	Water (Chlorophenols)	Dispersive LLME; 5 mL aqueous sample; 0.5 µL of 10 µL extract injected.	0.02-400 µg L^{-1} (0.01-2 µg L^{-1})	12
Acetic anhydride	GC-ECD	Wine (chloro- and bromophenols)	Dispersive LLME (150 µL of carbon tetrachloride in 1.3 mL of acetone, and reagent); 5 mL sample; 0.5 µL of extract injected.	10-500 ng L^{-1} (2.2-5.3 ng L^{-1})	13
Acetic anhydride	GC-ECD	Water (chlorophenols)	Coupled HF-LLLME and SPME; 5 mL aqueous sample.	0.001-500 µg L^{-1} (0.4-120 ng L^{-1})	14
Acetic anhydride	GC-MS	Water (phenol, methyl- and chlorophenols)	HS-SPME (PDMS, 100 µm and CAR-PDMS, 74 µm); 5 mL sample.	0.08-13.3 µg L^{-1} (0.3-18 ng L^{-1})	15
Acetic anhydride	GC-MS	Water (bromo- and chlorophenols)	HS-SPME (CAR-PDMS, 75 µm); 10 mL sample.	0.1-10 µg L^{-1} (1.3-46 ng L^{-1})	16
Acetic anhydride	GC-ECD	Water (chlorophenols)	Coupled SPE (PS-DVB, 100 mg) and dispersive	0.001-20 µg L^{-1}	17

			LLME; 100 mL aqueous sample; 0.5 μL of 13 μL extract injected.	(0.5-100 ng L^{-1})	
N-(*tert*-Butyldimethylsilyl)-*N*-methyl-trifluoroacetamide 	GC-MS	Water (chlorophenols)	Electromembrane extraction followed by ultrasound assisted emulsification extraction; 100 mL aqueous sample; 1 μL of 30 μL extract injected.	0.05-10 μg L^{-1} (5-20 ng L^{-1})	18
Dimethyl sulphate 	GC-MS	Water (chlorophenols)	Coupled HS-SDME (1-butanol, 10 μL) and HS-SPME (DVB/CAR/PDMS); up to 2 mL of aqueous sample.	0.001-5 mg L^{-1} (8-45 ng L^{-1})	This work

LOD, limit of detection; SPME, solid-phase microextraction; HS-SPME, headspace solid-phase microextraction; CW-DVB, carbowax-divinylbenzene; SPE, solid-phase extraction; PS-DVB, polystyrene-divinylbenzene; SDME, single drop microextraction; LLE, liquid-liquid extraction; CSDFME, continuous sample drop flow microextraction; dispersive LLME, dispersive liquid-liquid microextraction; HF-LLLME, hollow fiber liquid-liquid-liquid microextraction; PDMS, polydimethylsiloxane; CAR-PDMS, carboxene-polydimethylsiloxane; DVB/CAR/PDMS, divinylbenzene/carboxene/polydimethylsiloxane.

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Table S2. Structures of phenols and their methyl derivatives, and their recorded/library EI mass spectra

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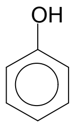
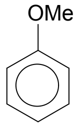
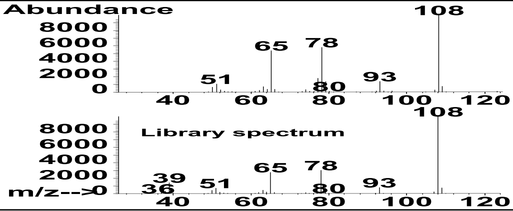
</td><td>Anisole
</td><td></td></tr>
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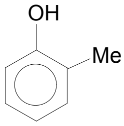
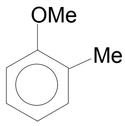
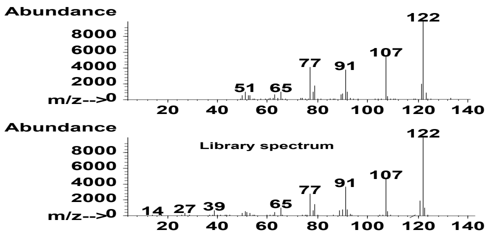
</td><td>2-Methylanisole
</td><td></td></tr>
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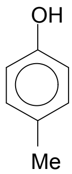
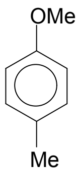
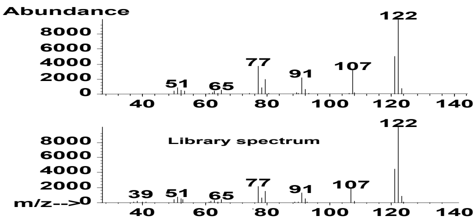
</td><td>4-Methylanisole
</td><td></td></tr>
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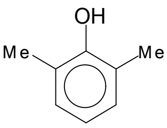
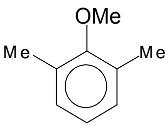
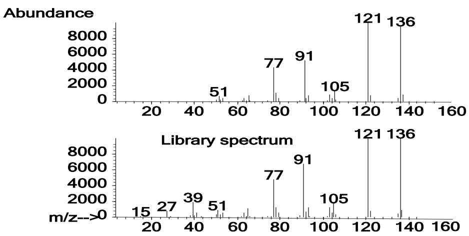
</td><td>2,6-Dimethylanisole
</td><td></td></tr>
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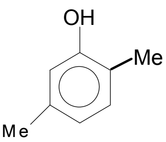
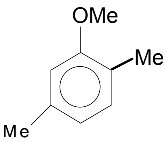
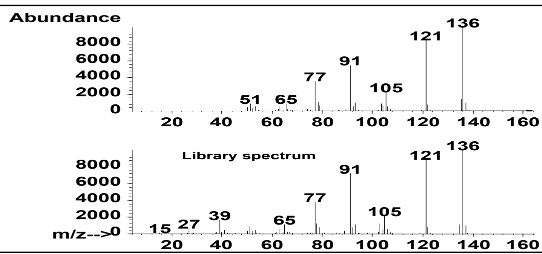
</td><td>2,5-Dimethylanisole
</td><td></td></tr>
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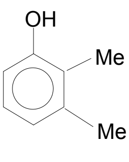
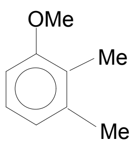
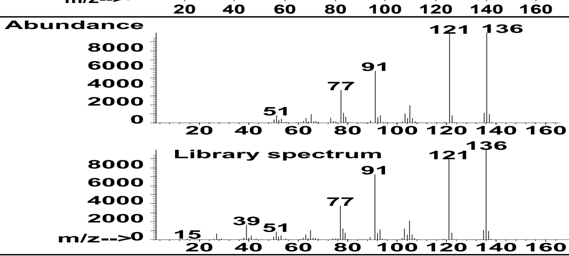
</td><td>2,3-Dimethylanisole
</td><td></td></tr>
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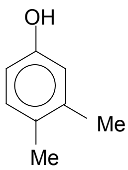
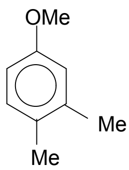
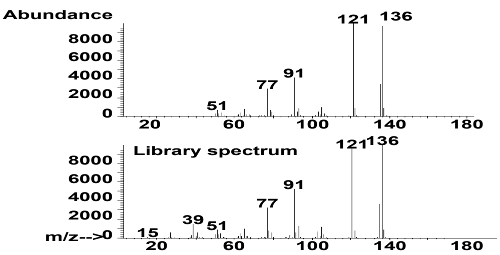
</td><td>3,4-Dimethylanisole
</td><td></td></tr>
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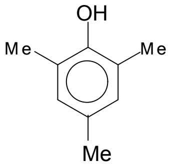
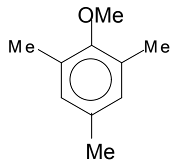
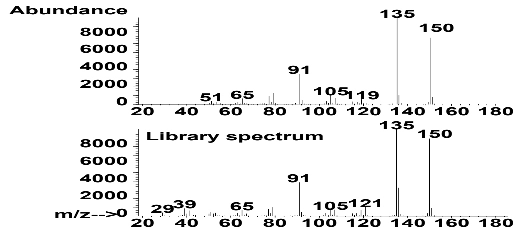
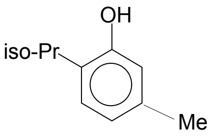
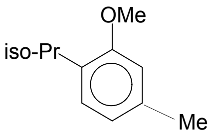
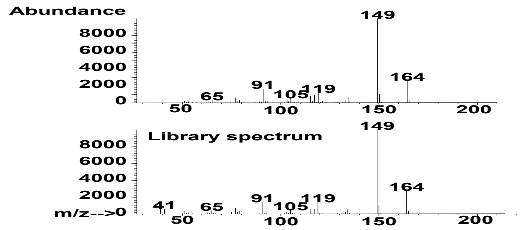
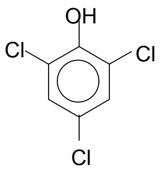
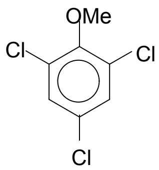
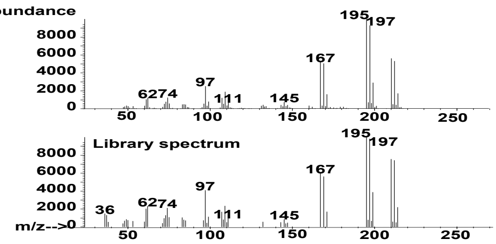
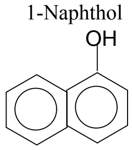
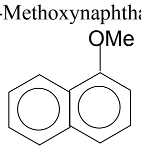
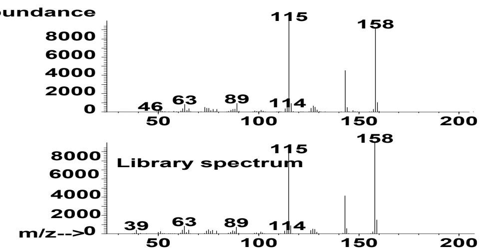
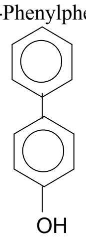
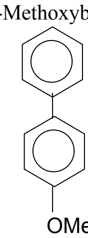
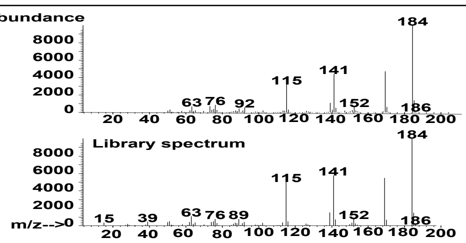
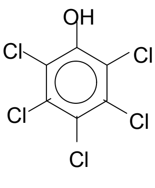
8	2,4,6-Trimethylphenol 	2,4,6-Trimethylanisole 	
9	2-Isopropyl-5-methylphenol 	2-Isobutyl-5-methylanisole 	
10	2,4,6-Trichlorophenol 	2,4,6-Trichloroanisole 	
11	1-Naphthol 	1-Methoxynaphthalene 	
12	4-Phenylphenol 	4-Methoxybiphenyl 	
13	Pentachlorophenol 	Pentachloroanisole