Comparison of Extraction Methods for Phenol-Containing Compounds in Water Followed by *EZ*GC Optimized GC-MS

Erica Pack, Chrisopher Rattray

Wastewater

Comparison of the removal of 2,4-dichlorophenol and phenol from polluted water, by peroxidases from tomato hairy roots, and protective effect of polyethylene glycol

Paola Solange González, Elizabeth Agostini *, Silvia Raquel Milrad

Departamento de Biología Molecular, FCEFQN, Universidad Nacional de Río Cuarto, 5800 Río Cuarto, Córdoba, Argentina

Received 16 April 2007; received in revised form 3 August 2007; accepted 7 August 2007
Available online 27 September 2007

Experimental and statistical validation of SPME-GC–MS analysis of phenol and chlorophenols in raw and treated water

Natércia Guerra Simões [a], Vitor Vale Cardoso [d], Elisabete Ferreira [d], Maria João Benoliel [d], Cristina M.M. Almeida [b,c,*]

[a] *Master in "Food Toxicology and Quality Control", Faculdade de Farmácia da Universidade de Lisboa (FFUL), Av. das Forças Armadas, 1649-019 Lisboa, Portugal*
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[d] *Laboratório Central da EPAL, Rua do Alviela, 12 – 1170-012 Lisboa, Portugal*

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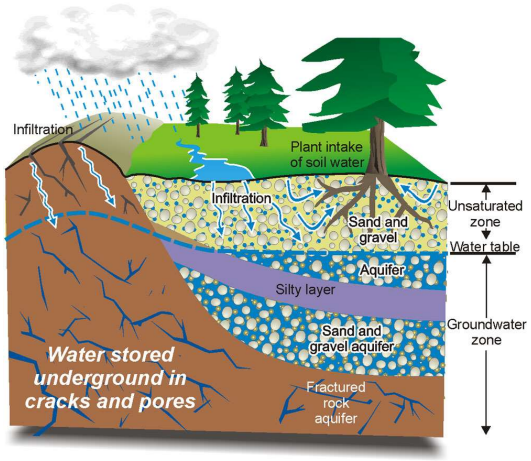
Available online 9 February 2007

Surface water



Levels and spatial distribution of chlorophenols – 2,4-Dichlorophenol, 2,4,6-trichlorophenol, and pentachlorophenol in surface water of China

Jijun Gao [a,b], Linghua Liu [b], Xiaoru Liu [b], Huaidong Zhou [b], Shengbiao Huang [a], Zijian Wang [a,*]

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[b] *Department of Water Environment, China Institute of Water Resources and Hydro-power Research, Yuyuantan Science and Technology Garden, Haidian District, Beijing 100038, China*

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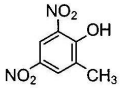
Sorption and Degradation of the Herbicide 2-Methyl-4,6-dinitrophenol under Aerobic Conditions in a Sandy Aquifer in Vejen, Denmark

METTE M. BROHOLM,* NINA TUXEN, KIRSTEN RUGGE,† AND POUL L. BJERG
Environment & Resources DTU, Groundwater Research Centre, Technical University of Denmark, DK-2800, Lyngby, Denmark

TABLE 1. Molecular Structure and Relevant Physical Chemical Parameters for DNOC

Chemical name	2-methyl-4,6-dinitro-phenol 4,6-dinitro-*o*-cresol
Molecular structure	
Molecular formula	$C_7H_8N_2O_5$
Solubility (mg/l)	130 (15 °C)
$LogK_{ow}$	2.12
pK_a	4.31

“Clean” water

CHLOROPHENOLS IN LAKE BOTTOM SEDIMENTS: A RETROSPECTIVE STUDY OF DRINKING WATER CONTAMINATION

Pentti Lampi[1], Kimmo Tolonen[2], Terttu Vartiainen[1], and Jouko Tuomisto[1]*

[1]National Public Health Institute, Division of Environmental Health, P.O.Box 95, SF-70701 Kuopio, Finland
[2]Department of Biology, University of Joensuu, P.O.Box 111, SF-80101 Joensuu, Finland

Aqueous Atmospheric Chemistry: Formation of 2,4-Dinitrophenol upon Nitration of 2-Nitrophenol and 4-Nitrophenol in Solution

DAVIDE VIONE,* VALTER MAURINO, CLAUDIO MINERO, AND EZIO PELIZZETTI
Dipartimento di Chimica Analitica, Università di Torino, Via Pietro Giuria 5, 10125 Torino, Italy

The Compounds

2-Chlorophenol
3-Chlorophenol
4-Chlorophenol
2,3,4,5-Tetrachlorophenol
2,3,4,6-Tetrachlorophenol
2,3,5,6-Tetrachlorophenol
2,4-Dichlorophenol
2,5-Dichlorophenol
2,6-Dichlorophenol
3,4-Dichlorophenol
3,5-Dichlorophenol
2,3,4-Trichlorophenol
2,3,5-Trichlorophenol
2,3,6-Trichlorophenol
2,4,5-Trichlorophenol
2,4,6-Trichlorophenol
3,4,5-Trichlorophenol
Pentachlorophenol

FE026429
ISSN 0335-3931

European standard

French standard

NF EN 12673
March 1999

Classification index: **T 90-126**

ICS: 13.060.50

Water quality

Gas chromatographic determination of some selected chlorophenols in water

F : Qualité de l'eau — Dosage par chromatographie en phase gazeuse de certains chlorophénols dans les eaux
D : Wasserbeschaffenheit — Gaschromatographische Bestimmung einiger ausgewählter Chlorphenole in Wasser

French standard approved

by decision of the Director General of AFNOR on February 20, 1999 taking effect on March 20, 1999.

The Compounds

Alkylphenols	Chlorophenols		Nitrophenols
Phenol	2-Chlorophenol	2,3,4-Trichlorophenol	2-Nitrophenol
2-Methylphenol	3-Chlorophenol	2,3,5-Trichlorophenol	3-Nitrophenol
3-Methylphenol	4-Chlorophenol	2,3,6-Trichlorophenol	4-Nitrophenol
4-Methylphenol	2-Chloro-5-methylphenol	2,4,5-Trichlorophenol	2,4-Dinitrophenol
4-Ethylphenol	4-Chloro-2-methylphenol	2,4,6-Trichlorophenol	2,5-Dinitrophenol
2,3-Dimethylphenol	4-Chloro-3-methylphenol	3,4,5-Trichlorophenol	2-Sec-butyl-4,6-dinitrophenol
2,4-Dimethylphenol	2,3-Dichlorophenol	2,3,4,5-Tetrachlorophenol	2-Methyl-4,6-dinitrophenol
2,5-Dimethylphenol	2,4-Dichlorophenol	2,3,4,6-Tetrachlorophenol	2-Cyclohexyl, 4,6-dinitrophenol
2,6-Dimethylphenol	2,5-Dichlorophenol	2,3,5,6-Tetrachlorophenol	
3,4-Dimethylphenol	2,6-Dichlorophenol	Pentachlorophenol	
3,5-Dimethylphenol	3,4-Dichlorophenol		
	3,5-Dichlorophenol		

Internal Standards: Naphthalene-d8; 1,4-Dichlorobenzene-d4; Acenaphthene-d10; Phenanthrene-d10; Chrysene-d12; Perylene-d12
Acid Surrogates: Phenol-d6; 2-Fluorophenol; 2,4,6-Tribromophenol

The Compounds

Alkylphenols	Chlorophenols		Nitrophenols
Phenol	2-Chlorophenol	2,3,4-Trichlorophenol	2-Nitrophenol
2-Methylphenol	3-Chlorophenol	2,3,5-Trichlorophenol	3-Nitrophenol
3-Methylphenol	4-Chlorophenol	2,3,6-Trichlorophenol	4-Nitrophenol
4-Methylphenol	2-Chloro-5-methylphenol	2,4,5-Trichlorophenol	2,4-Dinitrophenol
4-Ethylphenol	4-Chloro-2-methylphenol	2,4,6-Trichlorophenol	2,5-Dinitrophenol
2,3-Dimethylphenol	4-Chloro-3-methylphenol	3,4,5-Trichlorophenol	2-Sec-butyl-4,6-dinitrophenol
2,4-Dimethylphenol	2,3-Dichlorophenol	2,3,4,5-Tetrachlorophenol	2-Methyl-4,6-dinitrophenol
2,5-Dimethylphenol	2,4-Dichlorophenol	2,3,4,6-Tetrachlorophenol	2-Cyclohexyl, 4,6-dinitrophenol
2,6-Dimethylphenol	2,5-Dichlorophenol	2,3,5,6-Tetrachlorophenol	
3,4-Dimethylphenol	2,6-Dichlorophenol	Pentachlorophenol	
3,5-Dimethylphenol	3,4-Dichlorophenol		
	3,5-Dichlorophenol		

Internal Standards: Na… d12; Perylene-d12
Acid Surrogates: Phen…

Resource Conservation and Recovery Act (RCRA)

The Compounds

Alkylphenols	Chlorophenols		Nitrophenols
Phenol	2-Chlorophenol	2,3,4-Trichlorophenol	2-Nitrophenol
2-Methylphenol	3-Chlorophenol	2,3,5-Trichlorophenol	3-Nitrophenol
3-Methylphenol	4-Chlorophenol	2,3,6-Trichlorophenol	4-Nitrophenol
4-Methylphenol	2-Chloro-5-methylphenol	2,4,5-Trichlorophenol	2,4-Dinitrophenol
4-Ethylphenol	4-Chloro-2-methylphenol	2,4,6-Trichlorophenol	2,5-Dinitrophenol
2,3-Dimethylphenol	4-Chloro-3-methylphenol	3,4,5-Trichlorophenol	2-Sec-butyl-4,6-dinitrophenol
2,4-Dimethylphenol	2,3-Dichlorophenol	2,3,4,5-Tetrachlorophenol	2-Methyl-4,6-dinitrophenol
2,5-Dimethylphenol	2,4-Dichlorophenol	2,3,4,6-Tetrachlorophenol	2-Cyclohexyl, 4,6-dinitrophenol
2,6-Dimethylphenol	2,5-Dichlorophenol	2,3,5,6-Tetrachlorophenol	
3,4-Dimethylphenol	2,6-Dichlorophenol	Pentachlorophenol	
3,5-Dimethylphenol	3,4-Dichlorophenol		
	3,5-Dichlorophenol		

Internal Standards: Naphthalene-d8; 1,4-Dichlorobenzene-d4; Acenaphthene-d10; Phenanthrene-d10; Chrysene-d12; Perylene-d12
Acid Surrogates: Phenol-d6; 2-Fluorophenol; 2,4,6-Tribromophenol

The Compounds

Phenyl Acetates

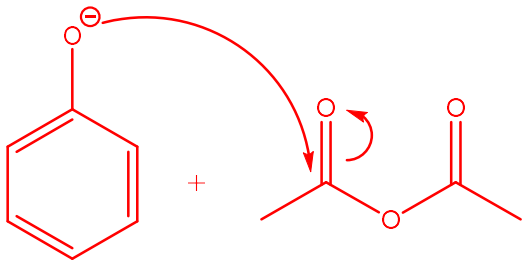
The Compounds

Phenyl Acetates

Derivatization Via
Base Catalyzed Nucleophilic Acyl Substitution

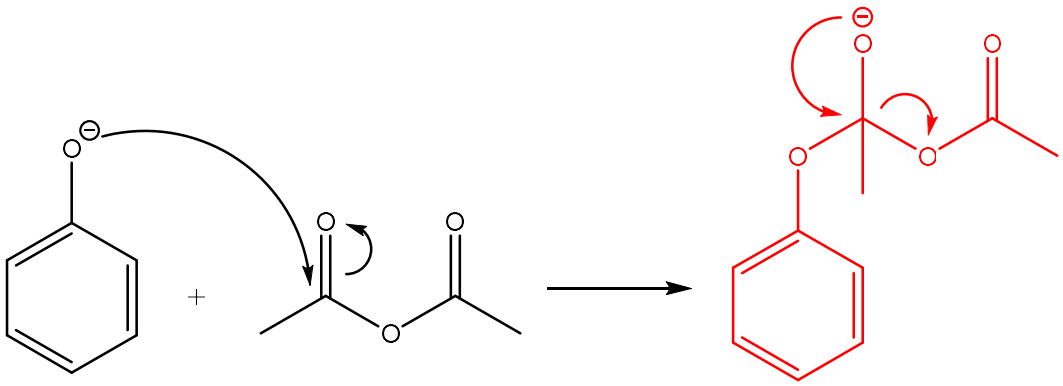
The Compounds

Phenyl Acetates



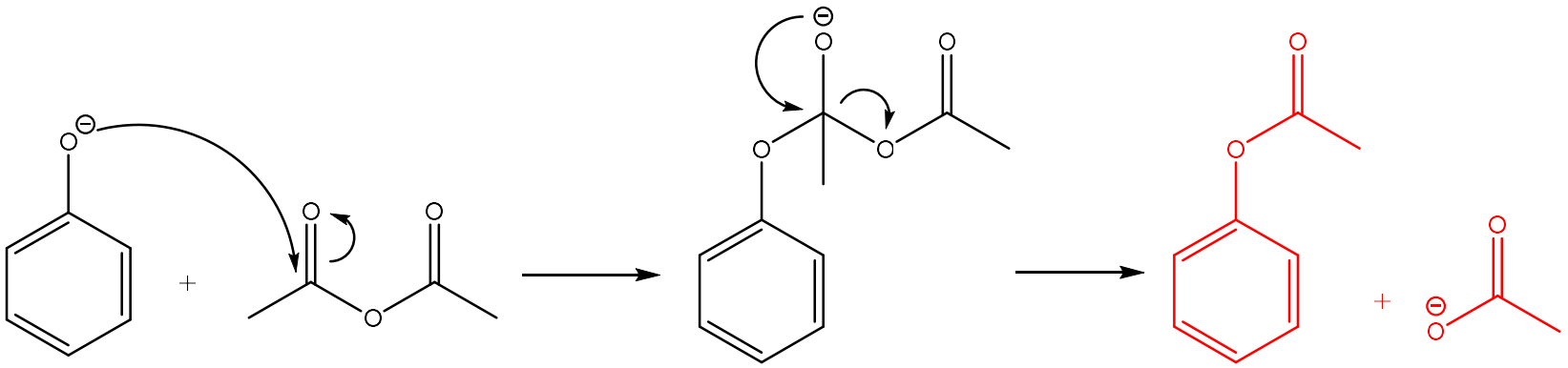
The Compounds

Phenyl Acetates



The Compounds

Phenyl Acetates

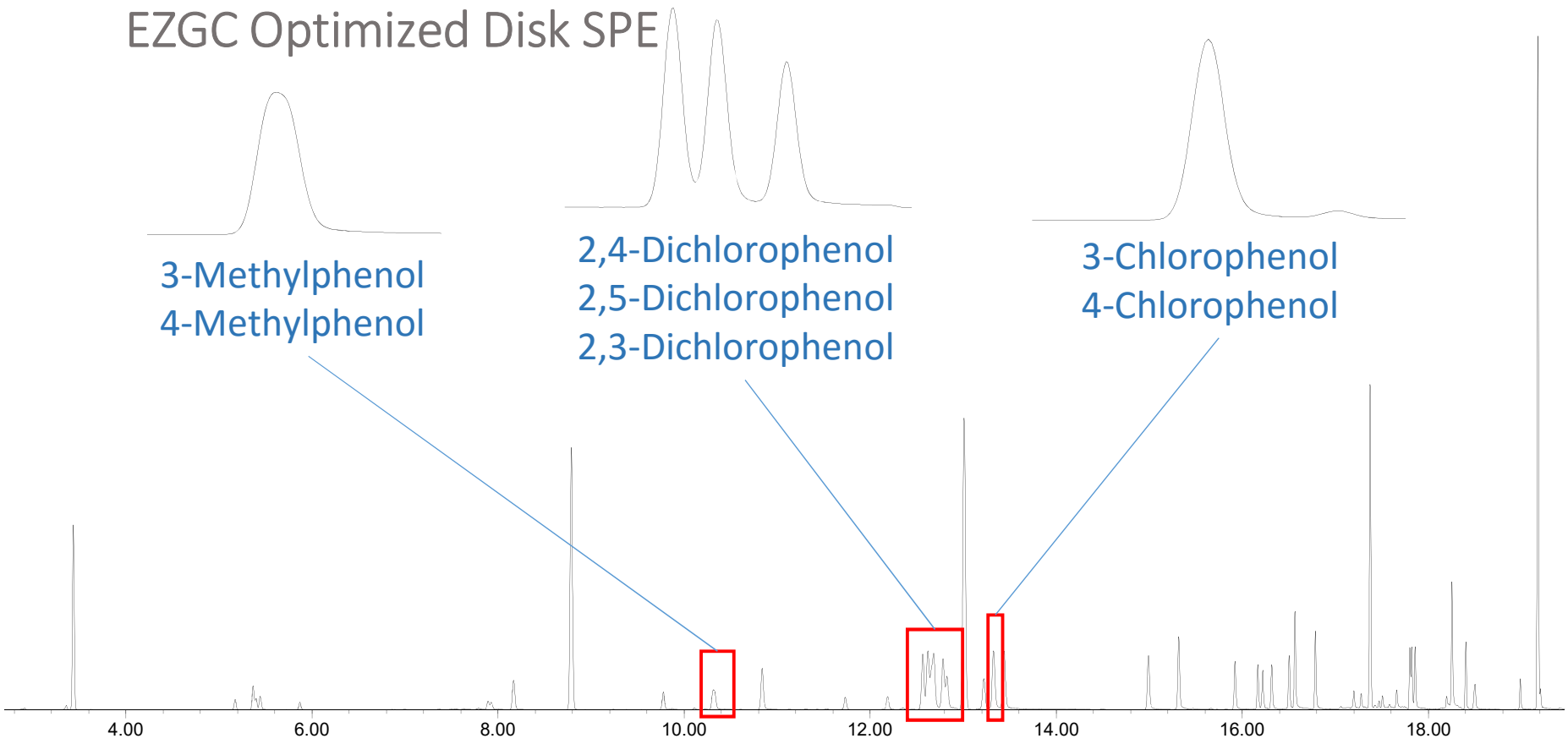


Phenyl Acetic Acid Ester (Acetate)

Method Comparisons

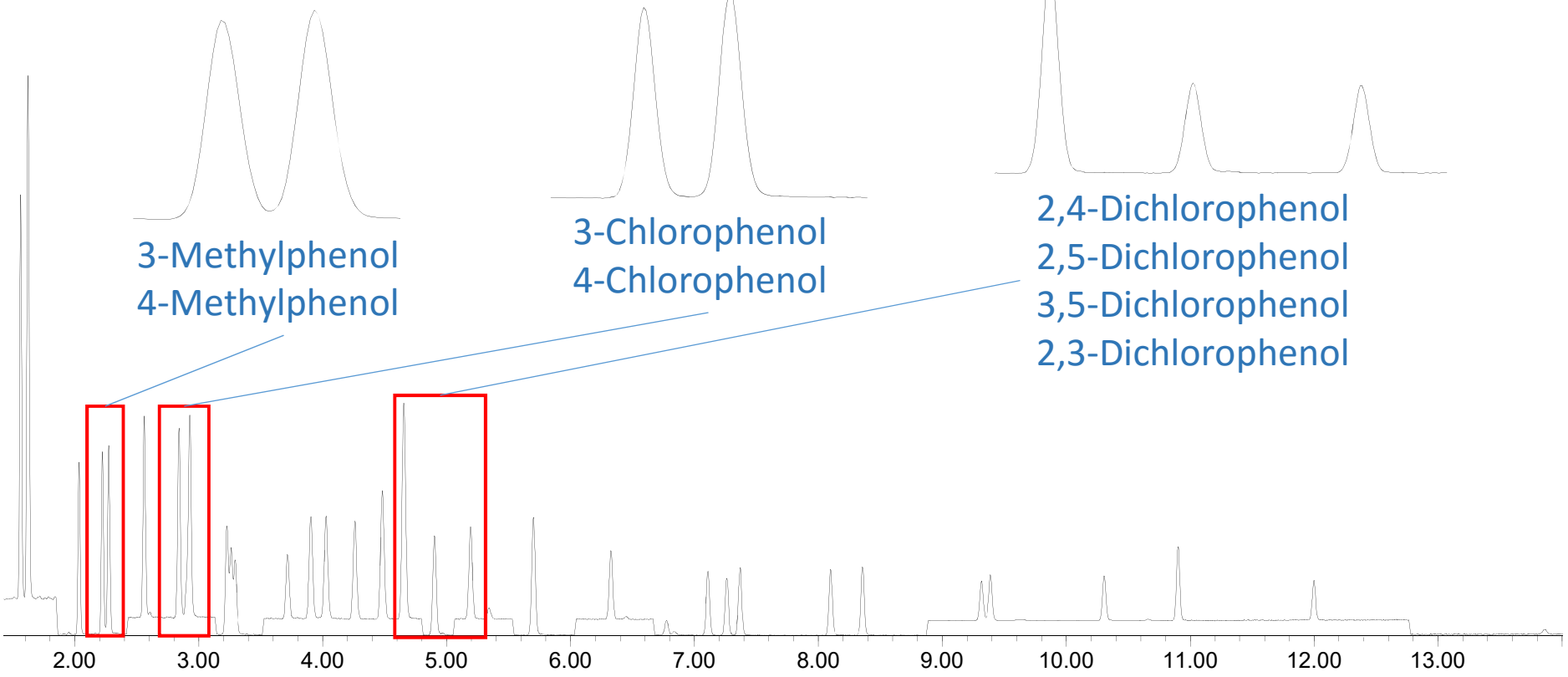
Disk SPE	Derivatization
*EZ*GC optimized 22 minute run time	*EZ*GC optimized 19 minute run time
Minimum 25 minutes	Minimum 25 minutes
500-1000 mL sample size	50 mL sample size
Identifies alkylphenols, chlorophenols, and nitrophenols	Identifies alkylphenyl acetates and chlorophenyl acetates

Method Comparisons



Method Comparisons

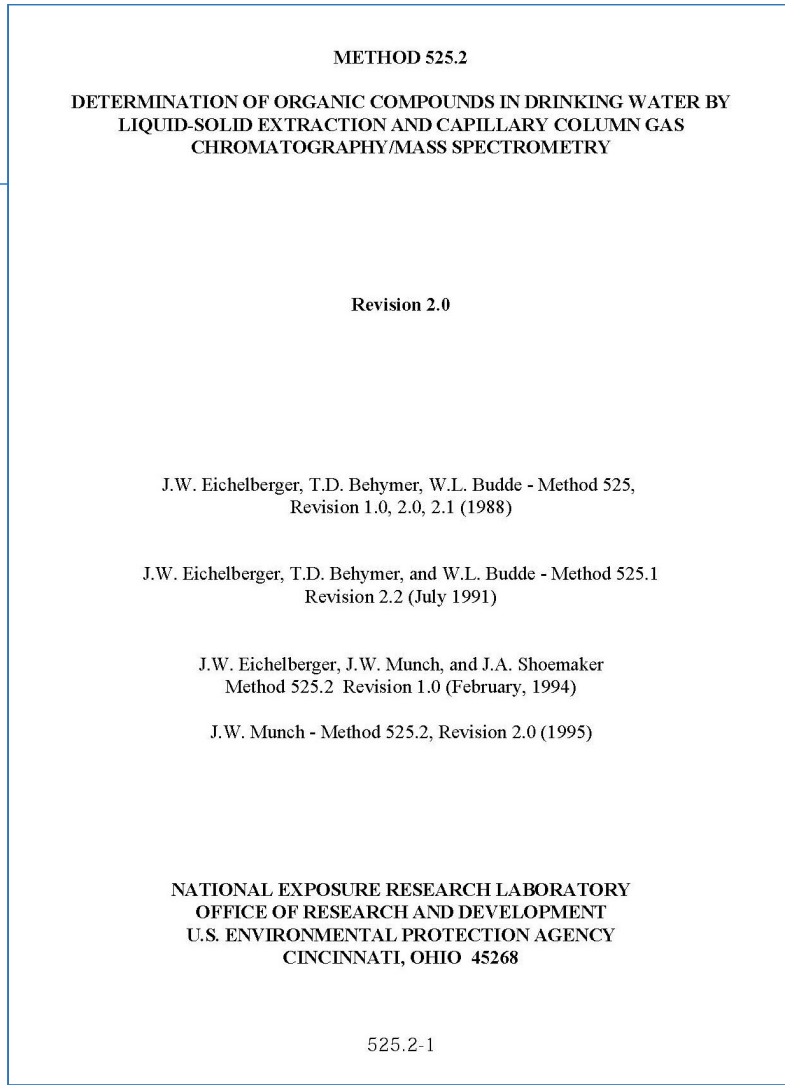
EZGC Optimized Derivatization



Method Comparisons

Disk SPE

1. Adjust pH to ~2
2. Disk prep with methanol and water
3. 1.0 L of aqueous sample passes through disk.
4. Dichloromethane and ethyl acetate used to elute phenols from disk once water has passed
5. Solvent dried and evaporated down to 1.0 mL



METHOD 525.2

DETERMINATION OF ORGANIC COMPOUNDS IN DRINKING WATER BY LIQUID-SOLID EXTRACTION AND CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

Revision 2.0

J.W. Eichelberger, T.D. Behymer, W.L. Budde - Method 525, Revision 1.0, 2.0, 2.1 (1988)

J.W. Eichelberger, T.D. Behymer, and W.L. Budde - Method 525.1 Revision 2.2 (July 1991)

J.W. Eichelberger, J.W. Munch, and J.A. Shoemaker Method 525.2 Revision 1.0 (February, 1994)

J.W. Munch - Method 525.2, Revision 2.0 (1995)

NATIONAL EXPOSURE RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

525.2-1

Method Comparisons

Disk SPE

- 1.0L of aqueous sample
- 5 solvents
- 2 collection tubes
- ~5.0g anhydrous sodium sulfate
- Large glass manifold with vacuum pump
- Condenser (not featured)

Method Comparisons

Disk SPE

common leak areas!

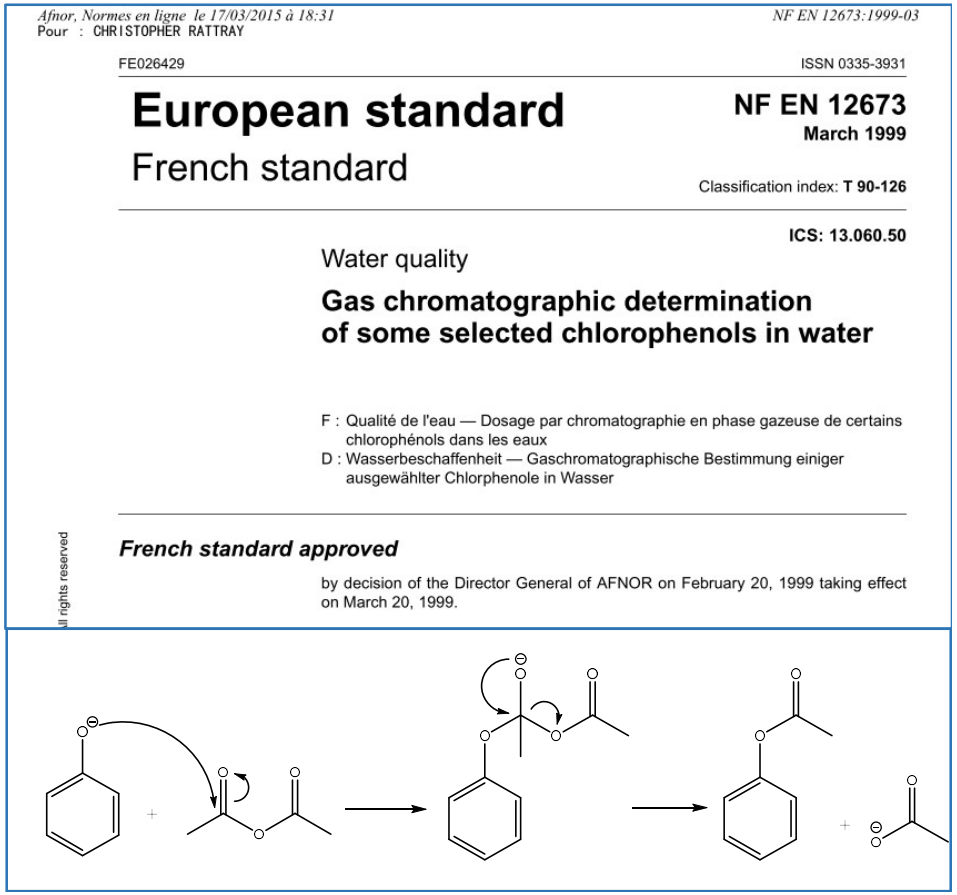
Method Comparisons

Disk SPE

Method Comparisons

Derivatization

1. Adjust pH to ~12
2. Acetic anhydride added to 50mL aqueous sample and stirred
3. Hexane layer added
4. Hexane layer extracted using separatory funnel
5. Hexanes layer dried



FE026429
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European standard

French standard

NF EN 12673
March 1999

Classification index: **T 90-126**

ICS: 13.060.50

Water quality

Gas chromatographic determination of some selected chlorophenols in water

F : Qualité de l'eau — Dosage par chromatographie en phase gazeuse de certains chlorophénols dans les eaux
D : Wasserbeschaffenheit — Gaschromatographische Bestimmung einiger ausgewählter Chlorphenole in Wasser

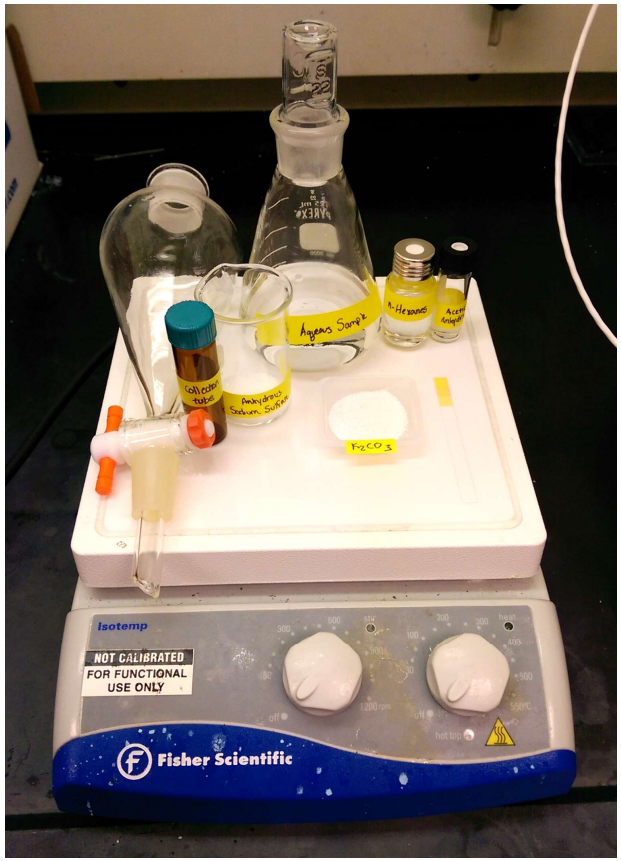
French standard approved

by decision of the Director General of AFNOR on February 20, 1999 taking effect on March 20, 1999.

Method Comparisons

Derivatization

- 50mL of aqueous sample
- 5.0mL hexanes
- 1.0mL acetic anhydride
- ~1.0 g anhydrous sodium sulfate
- 1 collection tube
- 125 mL flask and separatory funnel
- Stir plate



Method Comparisons

De

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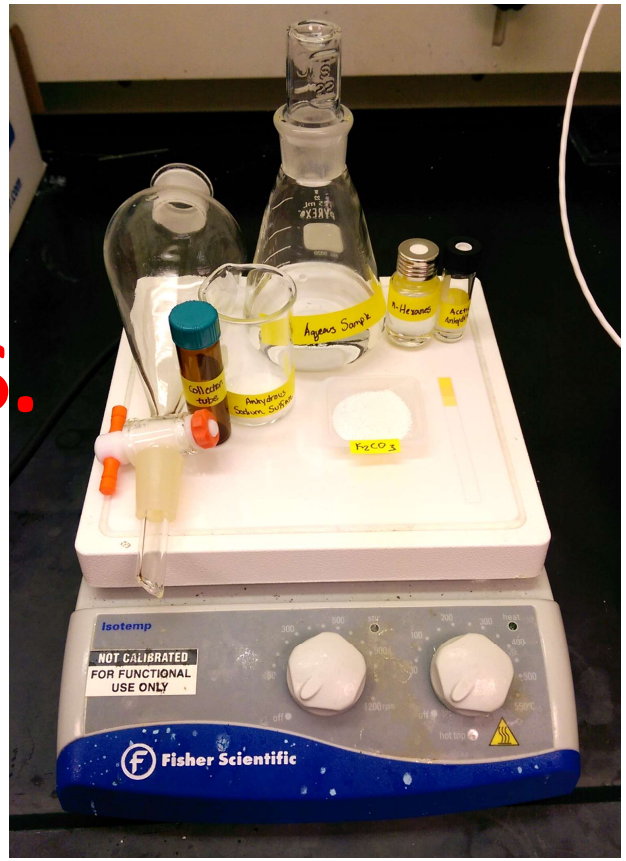
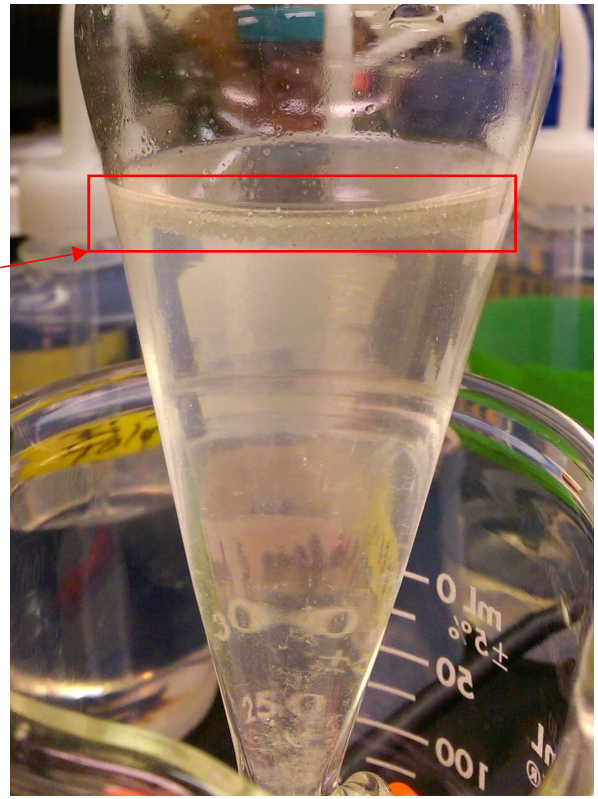
VS.

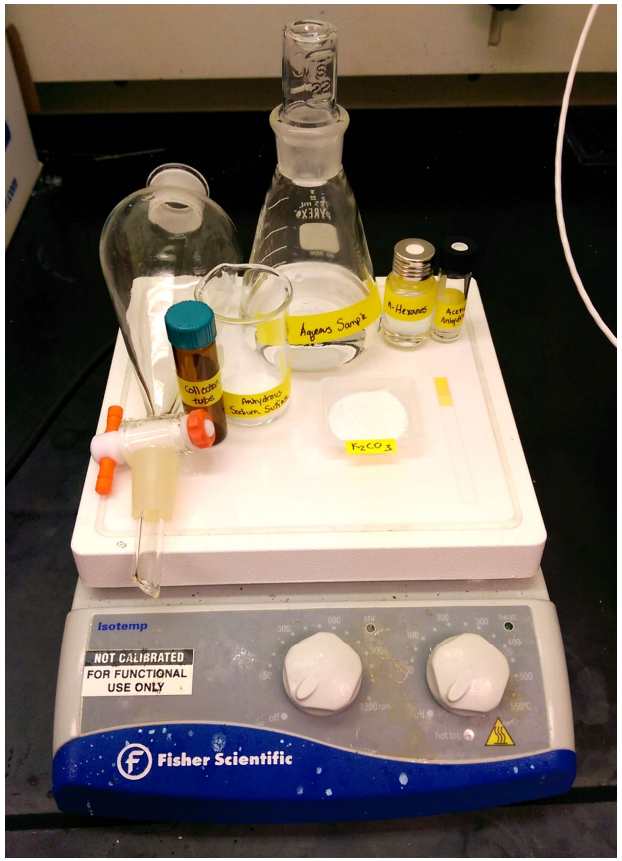


Method Comparisons

Derivatization

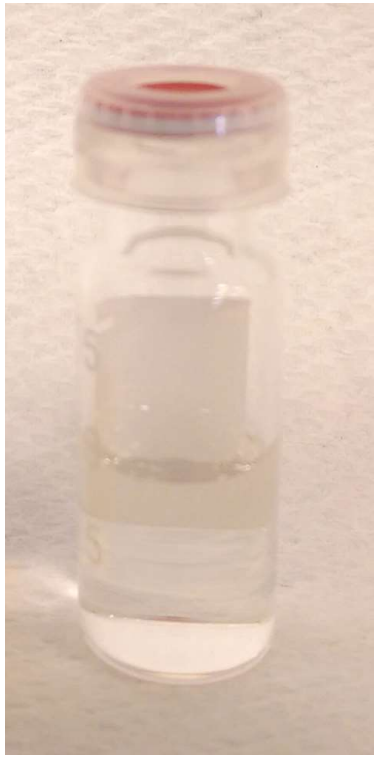
Emulsion in hexane layer

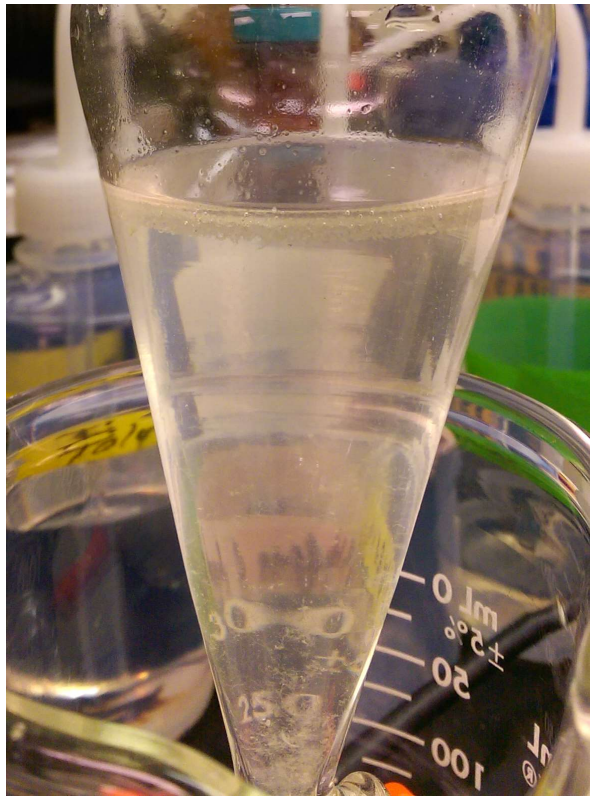


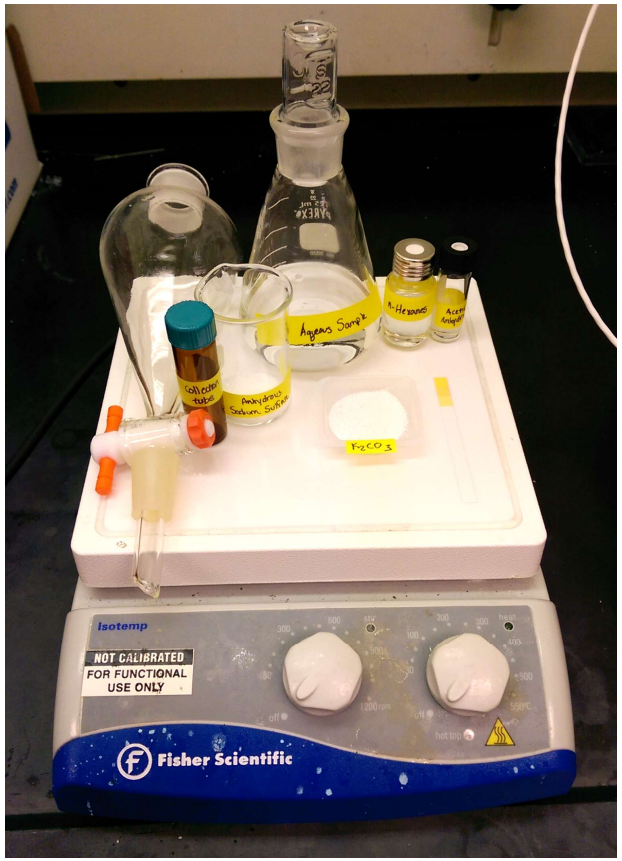


Method Comparisons

Derivatization

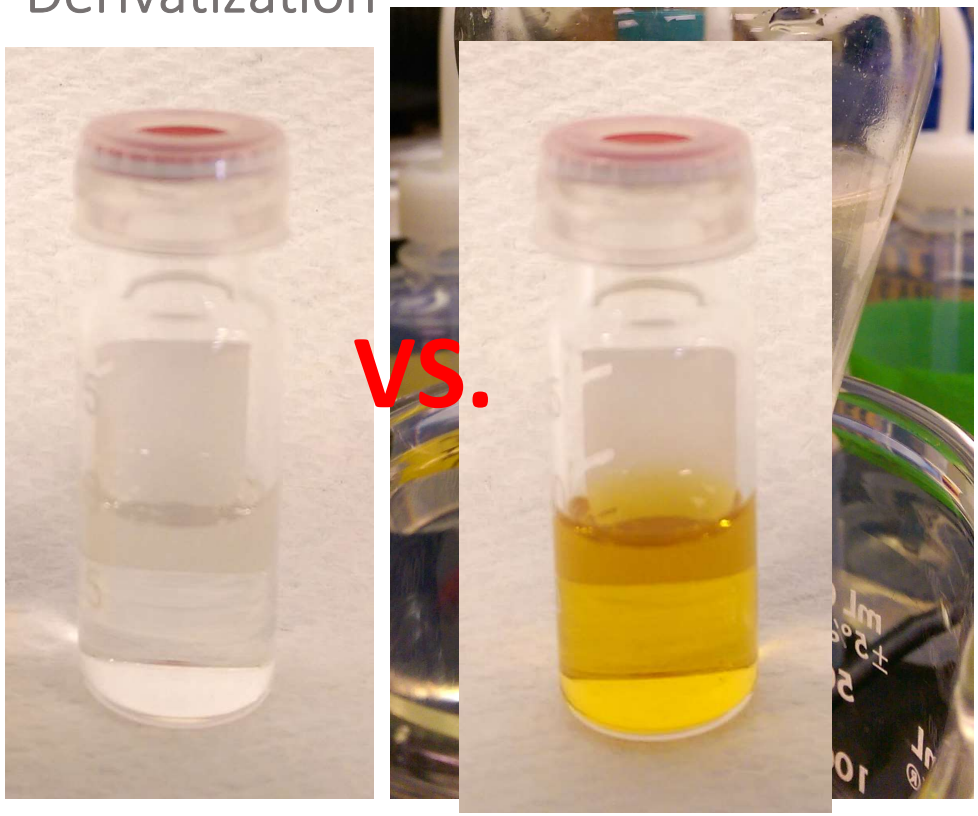


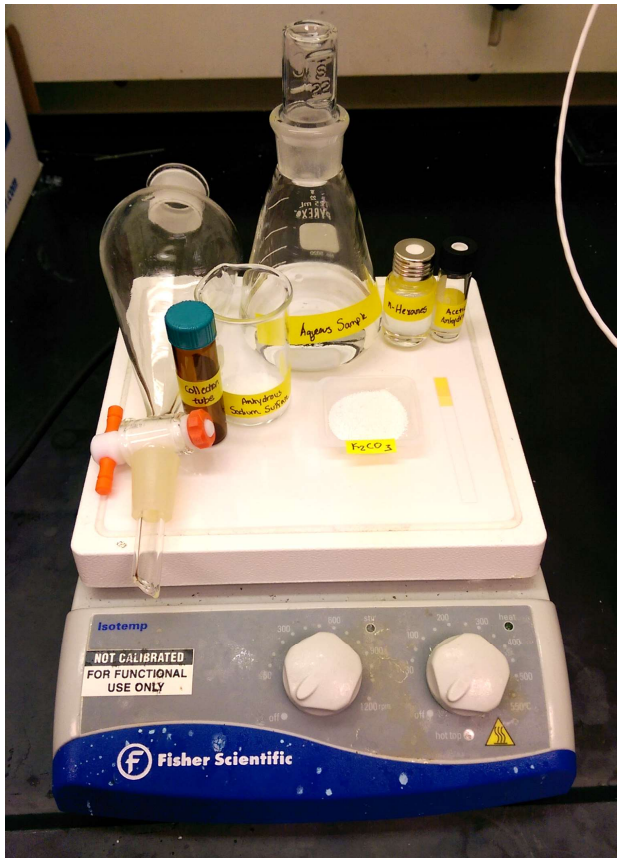




Method Comparisons

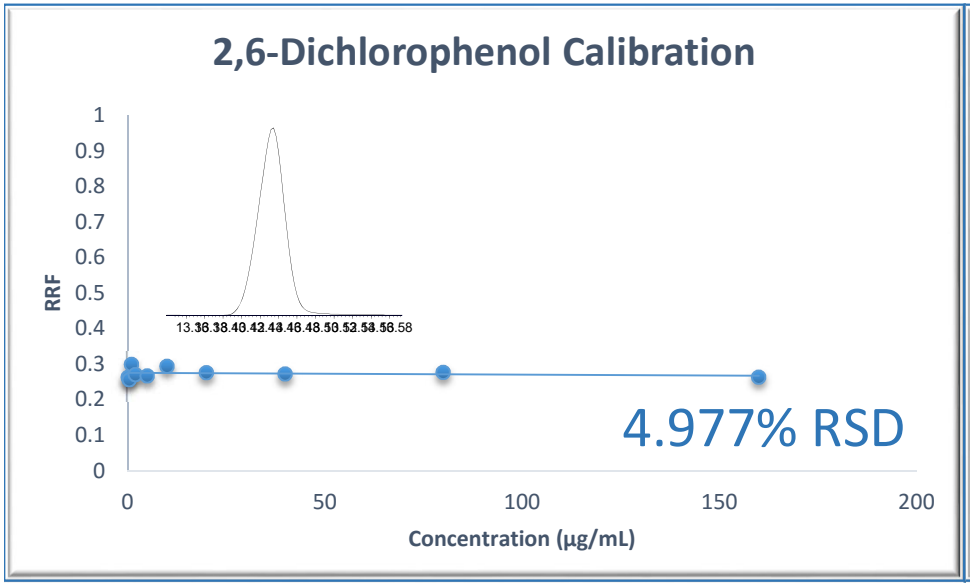
Derivatization

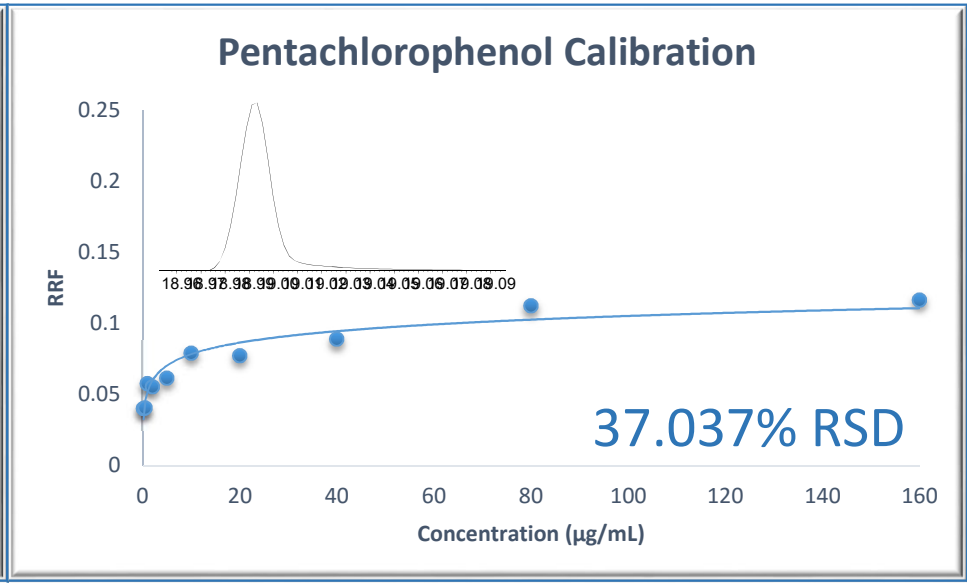




Method Comparisons

Disk SPE, Relative Response Factor (RRF)



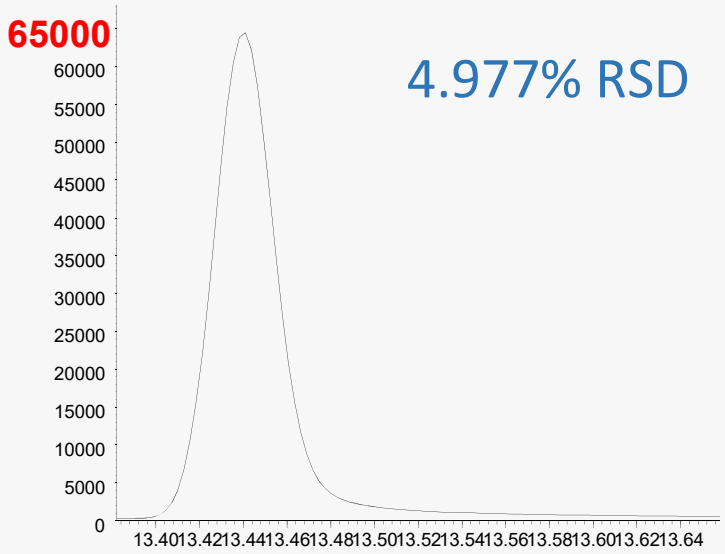


$$\text{RRF} = \frac{[\text{I.S.}] * \text{Target Response}}{[\text{Target}] * \text{I.S. Response}} \qquad \%\text{RSD} = \frac{\text{St.Dev.}}{\text{RRF}} * 100$$

Method Comparisons

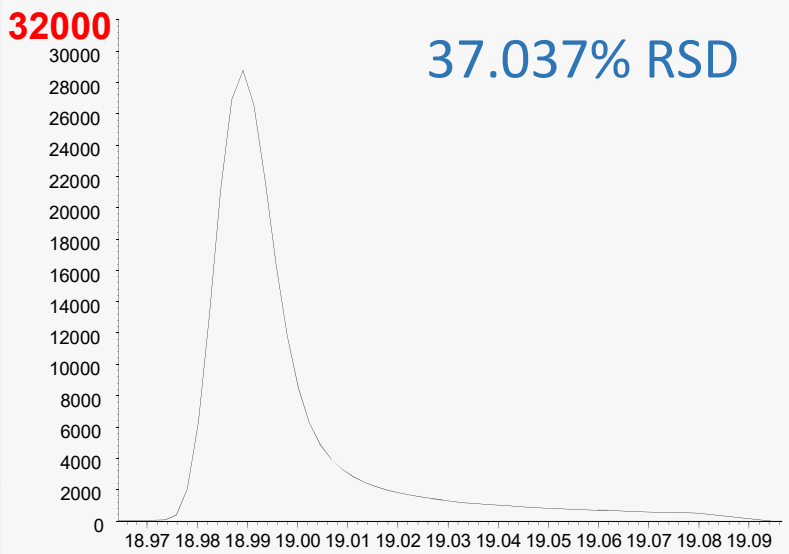
Disk SPE

2,6-Dichlorophenol



4.977% RSD

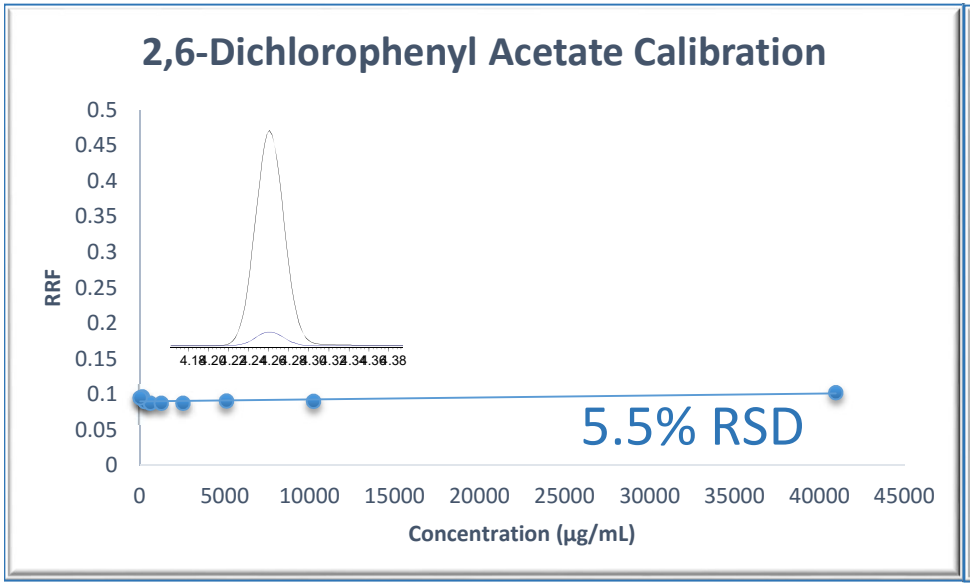
Pentachlorophenol

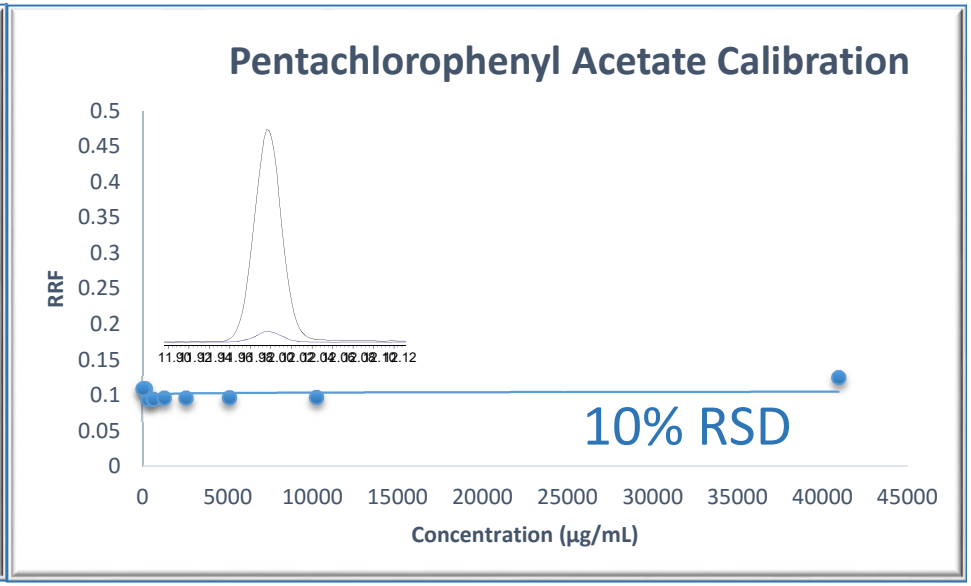


37.037% RSD

Method Comparisons

Derivatization, Relative Response Factor





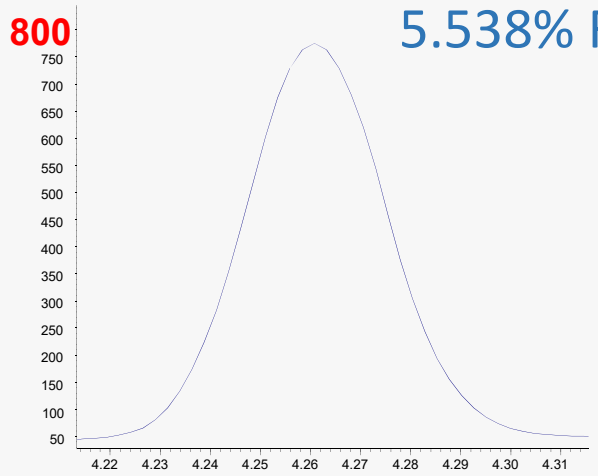
$$\text{RRF} = \frac{[\text{I.S.}] * \text{Target Response}}{[\text{Target}] * \text{I.S. Response}} \qquad \%\text{RSD} = \frac{\text{St.Dev.}}{\text{RRF}} * 100$$

Method Comparisons

Derivatization

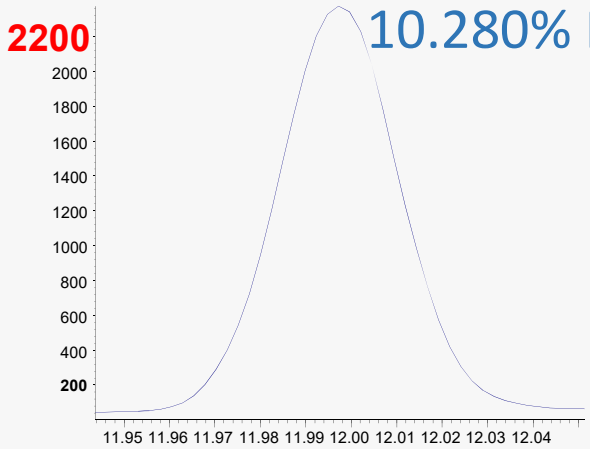
2,6-Dichlorophenyl Acetate

5.538% RSD



Pentachlorophenyl Acetate

10.280% RSD



Method Comparisons

Derivatization, Efficiency and Reproducibility

- Six representative phenyl acetate standards
  - Pentachlorophenyl acetate
  - 3-Methylphenyl acetate
  - 3,5-Dimethylphenyl acetate
  - 4-Nitrophenyl acetate
  - Phenyl acetate
  - 2-sec-butyl-4,6-dinitrophenyl acetate
- 3 Identical derivatizations of pre-derivatized standards (STD)
- 3 Identical derivatizations of non-derivatized standards (EXP)

Method Comparisons

Derivatization, Efficiency

Name	%Efficiency
Phenyl acetate	47%
3-Methylphenyl acetate	49%
3,5-Dimethylphenyl acetate	53%
4-Nitrophenyl acetate	48%
Pentachlorophenyl acetate	68%
2-Sec-butyl-4,6-dinitrophenyl acetate	65%

Method Comparisons

Derivatization, Reproducibility

Name	(STD) STDEV	(STD) AVG RF	(STD) %RSD	(EXP) STDEV	(EXP) AVG RF	(EXP) %RSD
Phenol acetate	0.028	0.85	3.3	0.022	0.81	2.7
3-Methylphenol acetate	0.039	1.2	3.3	0.034	1.2	2.8
3,5-Dimethylphenol acetate	0.019	1.2	1.7	0.042	1.2	3.4
4-Nitrophenol acetate	0.0022	0.030	7.5	0.0059	0.029	21
Pentachlorophenol acetate	0.027	0.29	9.0	0.025	0.41	6.2
2-sec-butyl-4,6-dinitrophenyl acetate	2.0E-5	0.0037	5.3	1.0E-4	0.0049	14

Method Comparisons

Derivatization, Method Detection Limit (MDL)

Average Concentration	MDL Range	Average MDL	Standard Dev.	% RSD
1.1 µg/L	**0.22-0.51** µg/L	**0.40** µg/L	**0.11** µg/L	**10%**

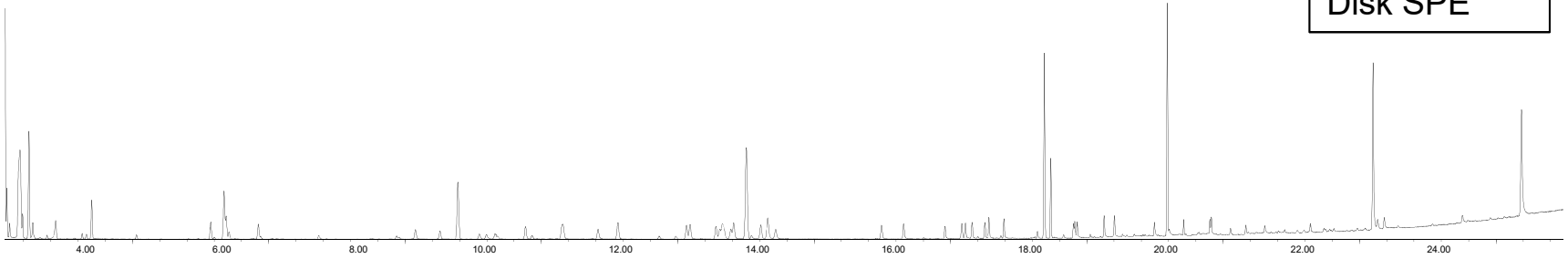
- 8 Samples derivatized
- 1.0 µg/L RCRA and non-RCRA phenols

Intent to also perform at 0.16 µg/L RCRA and non-RCRA phenols

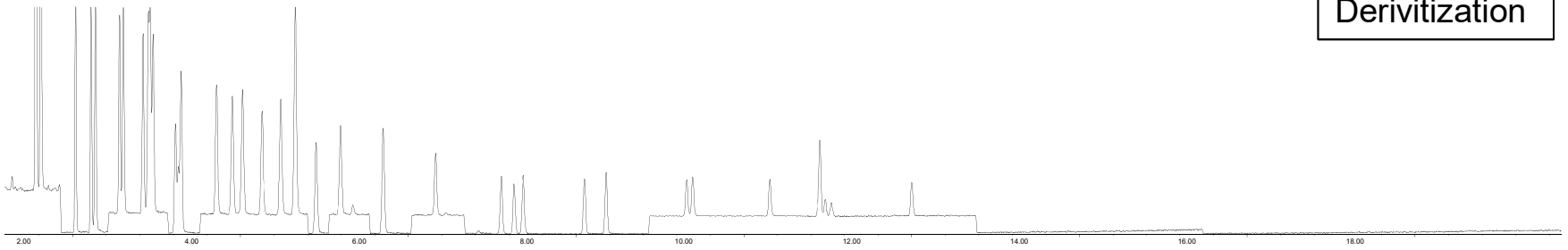
Sample Comparisons

Elk River, Surface Water, 5.0ppb spike

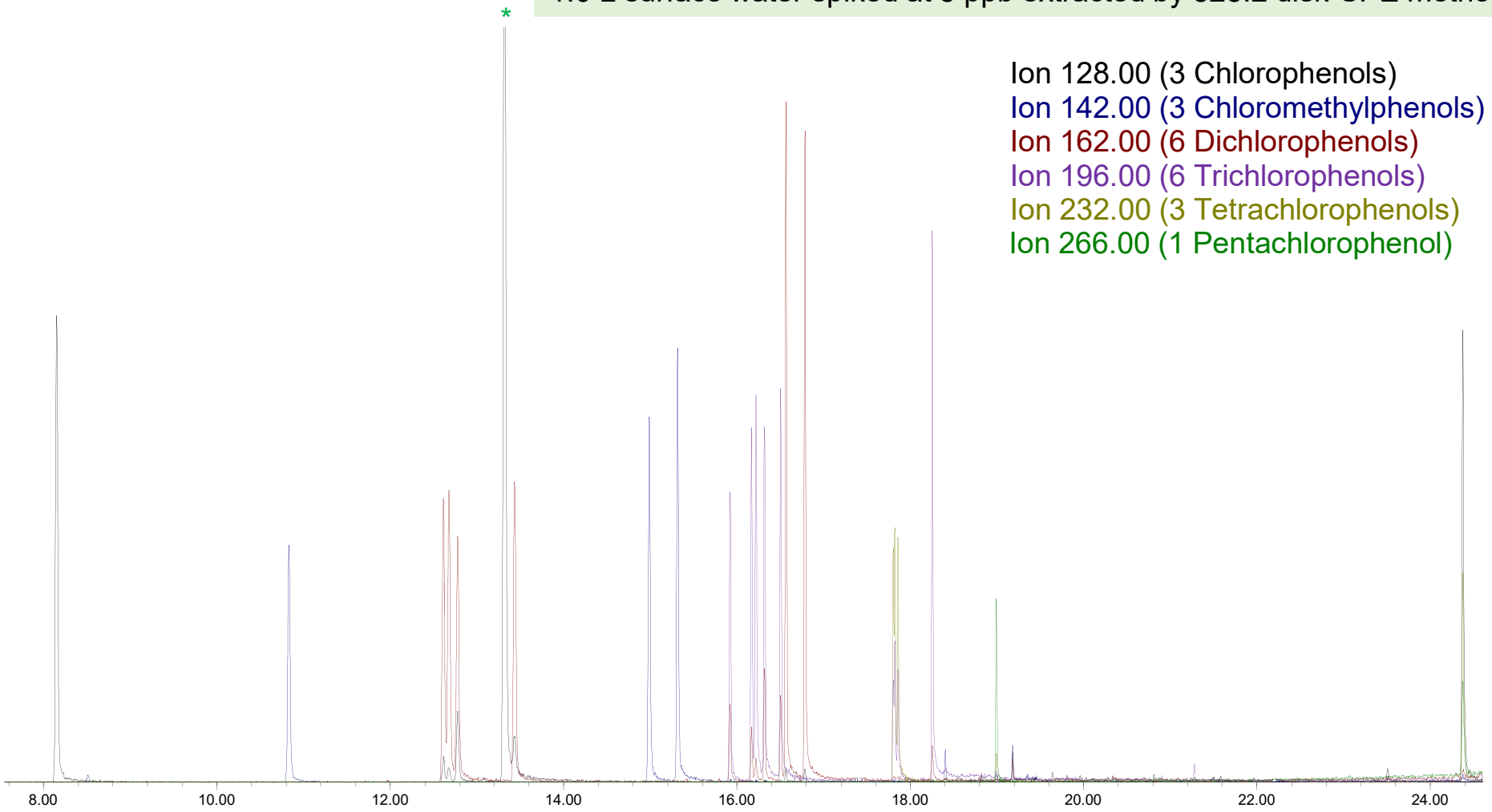
Disk SPE



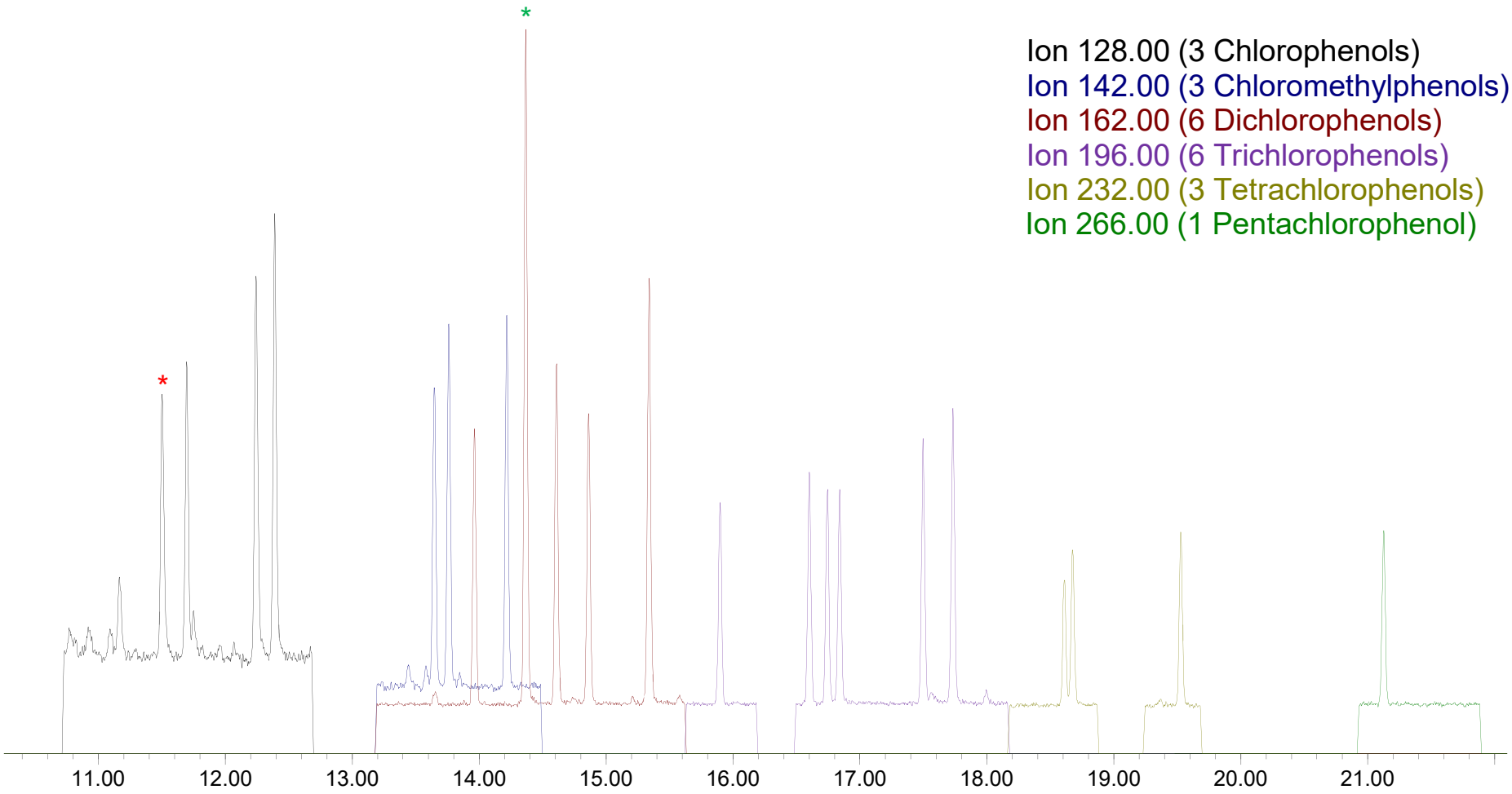
Derivitization



1.0 L surface water spiked at 5 ppb extracted by 525.2 disk-SPE method



50 mL surface water spiked at 5 ppb extracted by NF EN 12673



Sample Comparisons

Elk River, Surface Water, 5.0 µg/L Phenol Spike

Disk SPE	Conc. (µg/L)	Derivatization	Conc. (µg/L)
Phenol	**0.74**	Phenyl acetate	**5.8**
2-Methylphenol	**3.7**	2-Methylphenyl acetate	**5.4**
2-Chlorophenol	**3.4**	2-Chlorophenyl acetate	**5.5**
2-Chloro-5-methylphenol	**2.9**	2-Chloro-5-methylphenyl acetate	**5.4**
2,6-Dimethylphenol	**4.5**	2,6-Dimethylphenyl acetate	**5.8**
2,4-Dichlorophenol	**1.4**	2,4-Dichlorophenyl acetate	**4.9**
2,3,5-Trichlorophenol	**2.2**	2,3,5-Trichlorophenyl acetate	**4.7**
2,3,5,6-Tetrachlorophenol	**2.5**	2,3,5,6-Tetrachlorophenyl acetate	**5.1**
Pentachlorophenol	**2.3**	Pentachlorophenyl acetate	**2.7**

Sample Comparisons

Elk River, Surface Water, 5.0 µg/L Phenol Spike

Disk SPE	Conc. (µg/L)	Derivatization	Conc. (µg/L)
Phenol	**0.74**	Phenyl acetate	**5.8**
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2-Chlorophenol	**3.4**	2-Chlorophenyl acetate	**5.5**
2-Chloro-5-methylphenol	**2.9**	2-Chloro-5-methylphenyl acetate	**5.4**
2,6	**5**	2,6-	**5.8**
2,4-Dichlorophenol	**1.4**	2,4-Dichlorophenyl acetate	**4.9**
2,3,5-Trichlorophenol	**2.2**	2,3,5-Trichlorophenyl acetate	**4.7**
2,3,5,6-Tetrachlorophenol	**2.5**	2,3,5,6-Tetrachlorophenyl acetate	**5.1**
Pentachlorophenol	**2.3**	Pentachlorophenyl acetate	**2.7**

Average 2.4 µg/L

Average 4.3 µg/L

Sample Comparisons

PSU Effluent Wastewater, Derivatization, Reproducibility

- 5.0ppb spike of RCRA and non-RCRA phenols
- 3 identical derivatizations

Average Concentration	Average St Dev.	Average% RSD
4.4 µg/L	**0.36** µg/L	**10%**

Summary

	Benefits
Disk SPE	• Nitrophenol detection • Not dependent on reaction efficiency
Derivatization	• Lower sample volume • Fewer solvents and materials • Higher peak resolution and symmetry • Lower detection limit