Efficient Sample Workflow from Extraction to Analysis for Pesticides using EPA 608/8081

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Pesticides

HOME / HEALTH NEWS

Common pesticides linked to wheezing in farmers

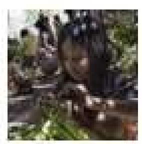
Many of the chemicals with the strongest link to wheezing conditions are increasingly being used in residential settings, researchers warn.

By Stephen Feller | Aug. 3, 2016 at 12:40 PM Follow @upi

Zika virus: Wynwood gets pesticides sprayed by Miami-Dade County plane

Miami Herald - 1 day ago

News · Sports · Business · Real Estate ... Plane sprays Zika **pesticides** over Wynwood.



Indonesian Children Face Hazards on Tobacco Farms, Report Says MAY 25, 2016

The New York Times | 纽约时报中文网 中国

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Introduction

- Solid-phase extraction has been developing for more than three decades and is well characterized and used in both disk and cartridge formats
- Used extensively in environmental to capture analytes
- Used in food sample preparation to capture analytes or for cleanup, capturing unwanted materials

Regulatory Methods

- Many drinking water methods include SPE as an alternative or the preferred extraction method
- Included in US EPA SW-846 sample prep method 3535A
- Can be coupled with methods 8270, 8081, 8082, 8061, 8141, 8330, 8095 and 8321 for the determinative step
- Method 1664 is a popular method incorporating SPE for Oil & Grease extraction
- Method 625 in the MUR will include SPE as an alternative with certain requirements
- Currently, US EPA method 608 a wastewater method incorporating solid phase extraction (ATP for disk technology), included in MUR

Method 608.3 Overview

- Includes pesticides and a full table (2)of PCBs
- SPE can be set up to follow the method identically

- However the solvent exchange from methylene chloride (DCM) to hexane for detection with ECD is time consuming and runs the risk of losing analytes

- This paper will discuss the analysis of wastewater using method 608.3 as written with DCM as the eluent
- It will then extend method 608.3 to capture of the analytes via SPE and elution using hexane directly

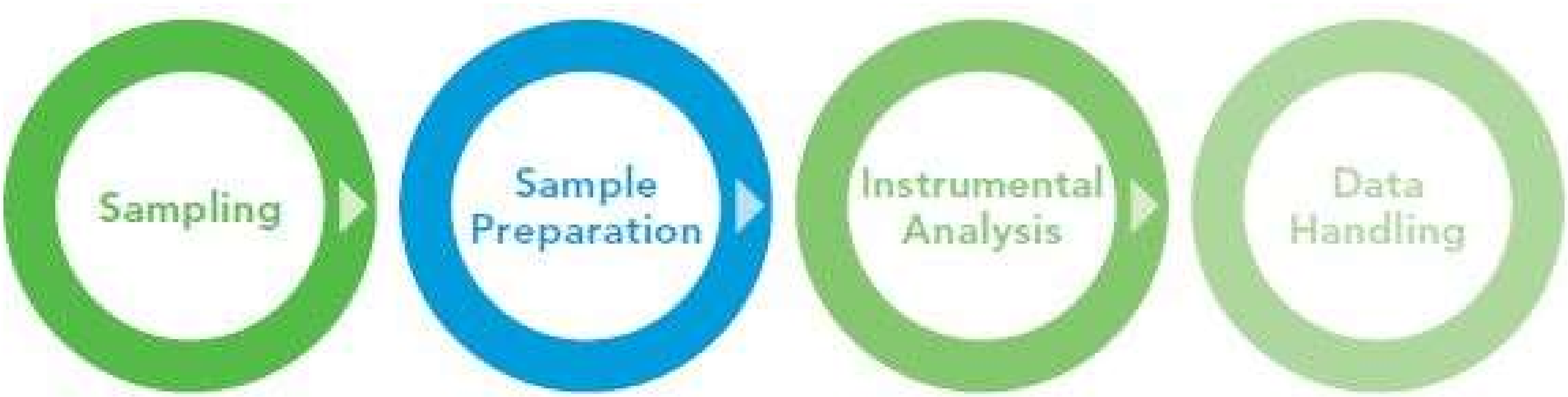
Reason for DCM L-L Extraction

- Octanol/water partition coefficients

- Methylene Chloride (DCM) 3.25
- Hexane 4.0

- Good general extraction solvent
- Less flammable than hexane
- More toxic than non-chlorinated compounds

Modern Workflow



Extraction
Extract Drying
Evaporation

Hardware for Automated SPE, Drying, and Concentration

SPE-DEX® 4790
Extractor

DryVap®
Drying and Concentrator System

Extraction Procedure

608 Extraction Method:			
Step	**Solvent**	**Soak Time**	**Dry Time**
Prewet 1	Methylene Chloride	1 min	1 min
Prewet 2	Methanol	1 min	10 s
Prewet 3	Reagent Water	1 min	10 s
Sample Process			
Air Dry 3:00 min			
Rinse 1	Acetone	3:00 min	3:00 min
Rinse 2	Methylene Chloride	3:00 min	3:00 min
Rinse 3	Methylene Chloride	2:00 min	2:00 sec
Rinse 4	Methylene Chloride	2:00 min	2:00 sec
Rinse 5	Methylene Chloride	2:00 min	3:00 min

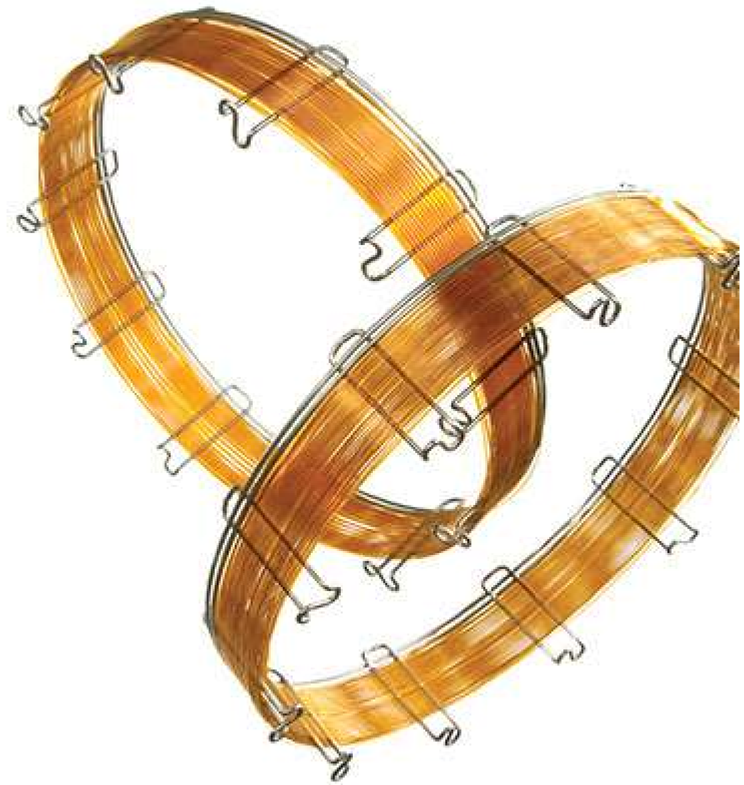
Then solvent exchange to hexane

Extract Drying

- Membrane drying rather than sodium sulfate for nonpolar solvents
  - No material preparation required
  - No chance of fines carrying through
  - No adsorption of analytes

GC Analysis

- Analysis and confirmation with dual ECD columns
- Worked with several clients so different columns were used in different facilities



Comparison of SPE and LLE- LCS

	SPE	LLE
beta-BHC	111.0	106.0
delta-BHC	87.7	106.0
Heptachlor Epoxide A	91.3	90.9
trans-Chlordane	93.7	90.3
cis-Chlordane	93.0	91.6
Endosulfan I	95.2	95.8
Endosulfan II	91.8	94.0
Endosulfan Sulfate	86.8	109.0
Endrin Aldehyde	65.5	61.4
Endrin Ketone	101.0	99.0
trans-Nonachlor	93.1	92.2
Mirex	90.3	80.4
alpha-BHC	88.5	95.3
Lindane (gamma-BHC)	99.3	93.8
Heptachlor	89.6	79.5
Aldrin	73.7	63.4
Dieldrin	90.9	91.5
Endrin	100.0	96.3
Methoxychlor	84.0	76.1
o,p'-DDE	91.3	86.0
p,p'-DDE	98.8	95.4
o,p'-DDD	97.5	98.4
p,p'-DDD	102.0	104.0
o,p'-DDT	94.3	93.7
p,p'-DDT	93.5	93.2
DCB, surrogate	95.5	94.8
TCMX, surrogate	81.3	64.0

Matrix Spike-Final Effluent

	SPE		LLE
beta-BHC	107.0		109.0
delta-BHC	79.1		95.7
Heptachlor Epoxide A	81.0		87.0
trans-Chlordane	84.7		82.2
cis-Chlordane	83.5		85.5
Endosulfan I	85.7		93.7
Endosulfan II	89.1		96.4
Endosulfan Sulfate	66.1		123.0
Endrin Aldehyde	54.3		56.3
Endrin Ketone	89.6		102.0
trans-Nonachlor	86.0		84.3
Mirex	82.1		69.3
alpha-BHC	85.0		100.0
Lindane (gamma-BHC)	123.0		117.0
Heptachlor	84.5		82.9
Aldrin	59.0		58.6
Dieldrin	95.0		95.4
Endrin	98.6		105.0
Methoxychlor	91.5		91.5
o,p'-DDE	92.1		77.3
p,p'-DDE	90.2		77.2
o,p'-DDD	91.4		92.4
p,p'-DDD	98.6		100.0
o,p'-DDT	91.1		79.9
p,p'-DDT	86.5		78.4
DCB, surrogate	81.1		50.3
TCMX, surrogate	61.8		83.9

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Matrix Spike and Duplicate- Final Effluent

	SPE-1	SPE-2	RPD
beta-BHC	107.0	107.0	0
delta-BHC	79.1	81.5	3.0
Heptachlor Epoxide A	81.0	83.0	2.4
trans-Chlordane	84.7	87.8	3.6
cis-Chlordane	83.5	86.5	3.5
Endosulfan I	85.7	87.9	2.5
Endosulfan II	89.1	90.4	1.4
Endosulfan Sulfate	66.1	97.5	38.4
Endrin Aldehyde	54.3	50.2	-7.8
Endrin Ketone	89.6	92.7	3.4
trans-Nonachlor	86.0	88.8	3.2
Mirex	82.1	86.0	4.6
alpha-BHC	85.0	86.0	1.2
Lindane (gamma-BHC)	123.0	126.0	2.4
Heptachlor	84.5	87.4	3.4
Aldrin	59.0	61.3	3.8
Dieldrin	95.0	97.1	2.2
Endrin	98.6	100.0	1.4
Methoxychlor	91.5	89.3	-2.4
o,p'-DDE	92.1	96.0	4.1
p,p'-DDE	90.2	94.3	4.4
o,p'-DDD	91.4	96.4	5.3
p,p'-DDD	98.6	103.0	4.4
o,p'-DDT	91.1	96.0	5.2
p,p'-DDT	86.5	90.7	4.7
DCB, surrogate	81.1	86.4	6.3
TCMX, surrogate	61.8	85.3	32.0

Smaller Sample Size-Final Effluent

	1000 mL	500 mL
beta-BHC	107.0	106.0
delta-BHC	81.5	83.7
Heptachlor Epoxide A	83.0	84.0
trans-Chlordane	87.8	91.6
cis-Chlordane	86.5	89.5
Endosulfan I	87.9	91.7
Endosulfan II	90.4	87.1
Endosulfan Sulfate	97.5	85.5
Endrin Aldehyde	50.2	49.1
Endrin Ketone	92.7	92.8
trans-Nonachlor	88.8	90.0
Mirex	86.0	84.4
alpha-BHC	86.0	89.0
Lindane (gamma-BHC)	126.0	111.0
Heptachlor	87.4	91.5
Aldrin	61.3	67.2
Dieldrin	97.1	91.9
Endrin	100.0	100.0
Methoxychlor	89.3	91.0
o,p'-DDE	96.0	90.0
p,p'-DDE	94.3	95.0
o,p'-DDD	96.4	99.0
p,p'-DDD	103.0	105.0
o,p'-DDT	96.0	94.0
p,p'-DDT	90.7	90.6
DCB, surrogate	86.4	79.7
TCMX, surrogate	85.3	87.6

Results

- SPE performs well for extraction of pesticides compared to LLE
- SPE performs well in wastewater final effluent, routinely tested at a treatment facility
- SPE performs well on a smaller sample (500 mL) as well as the 1 L samples generally tested

- Now, how does direct hexane elution from the disk compare?

Extraction Procedure

608 Extraction Method:			
Step	Solvent	Soak Time	Dry Time
Prewet 1	Acetone	1:00 min	1:30 min
Prewet 2	Hexane	1:00 min	2:00 min
Prewet 3	Methanol	30 sec	2 sec
Prewet 4	Reagent Water	10 sec	0 sec
Sample Process			
Air Dry 3:00 min			
Rinse 1	Acetone	3:00 min	2:00 min
Rinse 2	Hexane	3:00 min	2:00 min
Rinse 3	Hexane	1:00 min	1:00 min
Rinse 4	Hexane	1:00 min	1:00 min
Rinse 5	Hexane	1:00 min	1:00 min

Results – Hexane Elution

Pesticide Compounds	Concentration (ug/L)	Primary Column	Secondary Column
		Recovery%	Recovery%
Alpha-BHC	0.5	98.0	86.0
Gamma-BHC (Lindane)	0.5	100.0	88.0
Beta-BHC	0.5	94.0	85.0
Delta-BHC	0.5	100.0	87.0
Heptachlor	0.5	91.0	82.0
Aldrin	0.5	87.0	80.0
Heptachlor Epoxide	0.5	92.0	82.0
Gamma-Chlordane	0.5	87.0	82.0
Alpha-Chlordane	0.5	91.0	84.0
4,4'DDE	1.25	97.0	85.0
Endosulfane I	0.5	88.0	81.0
Dieldrin	1.25	95.0	78.0
Endrin	1.25	92.0	81.0
4,4'DDD	1.25	98.0	86.0
Endosulfane II	1.25	89.0	76.0
DDT	1.25	90.0	86.0
Endrin Aldehyde	1.25	90.0	76.0
Methoxychlor	5	89.0	81.0
Endosulfan Sulfate	1.25	94.0	87.0
Endrin Ketone	1.25	98.0	86.0
Tcmx	1	81.0	76.0
DCB	1	88.0	76.0

Extension of this Approach

- In Europe there is concern about the toxicity of chlorinated solvents
- Although DCM is an excellent solvent and easy to work with and evaporate, there are concerns about its carcenogenicity
- Demonstrate some work done to develop methodology to elute PAHs with hexane rather than DCM

Extraction Procedure

PAH Extraction:			
Step	Solvent	Soak Time	Dry Time
Prewet 1	Methanol	2:00	5 sec
Prewet 2	Reagent Water	1:00	5 sec
Prewet 3	Reagent Water	30 sec	2 sec
Sample Process			
Air Dry 1:00 min			
Rinse 1	Acetone	2:00	2:00 min
Rinse 2	Hexane	2:00	2:00 min
Rinse 3	Hexane	1:00	1:00 min
Rinse 4	Hexane	1:00	1:00 min

Results- PAH with Hexane Eluent

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Final Volume	1.0 mL Final Volume				
Compound	% Rec	% Rec	% Rec	Ave % Rec	% RSD
Naphthalene	81.2	82.2	81.1	81.5	0.78
Acenaphthylene	91.3	86.9	87.2	88.4	2.77
Acenaphthene	90.8	86.8	89.8	89.1	2.32
Fluorene	96.4	92.2	92.4	93.7	2.52
Phenanthrene	98.3	94.0	94.0	95.5	2.58
Anthracene	100.7	94.2	94.3	96.4	3.87
Fluoranthene	100.5	96.0	91.8	96.1	4.53
Pyrene	101.9	98.5	92.5	97.6	4.87
Benz(a)anthracene	101.9	96.4	98.0	98.7	2.87
Chrysene	103.7	96.0	96.1	98.6	4.44
Benzo(b)fluoranthene	103.9	92.7	96.4	97.6	5.83
Benzo(k)fluoranthene	101.7	94.4	99.9	98.7	3.85
Benzo(a)pyrene	102.7	94.0	96.4	97.7	4.61
Indeno(1,2,3-cd)pyrene	97.7	92.7	94.0	94.8	2.74
Dibenz(ah)anthracene	98.8	91.5	93.0	94.4	4.10
Benzo(ghi)perylene	99.5	94.4	95.0	96.3	2.87

Conclusions

- SPE is a useful tool for pesticide extraction for method 608
- Even though the method was accepted through an ATP in 1995 we show additional data for comparison of SPE vs. LLE for an LCS and treated wastewater samples
- Smaller samples (in this case 500 mL) also give excellent spike recoveries
- Data from samples eluted with hexane rather than DCM show excellent recoveries
- Elution with hexane can save time and effort required in solvent exchange required for an ECD detector, improving the workflow in a busy laboratory
- This type of approach can be expanded for toxicity reasons in addition to detector performance and this has been shown for PAHs