Water Analyses

Bisphenol A Analysis in Water by GC/MS Using an ENVIRO-CLEAN® 200 mg C18 Extraction Cartridge

UCTUCT Part Numbers:
EEC1812Z (Endcapped C18 - 200 mg/10 mL)

February 2009

1. **Prepare Sample**
   a) Using 100 mL of sample water, adjust the pH to 7 or less using 100mM acetic acid
   b) Add internal standard to water sample

Bisphenol A has a pKa value of approximately 9.5

2. **Condition Cartridge**
   a) Place a cartridge(s) on a multistation vacuum manifold or automated extraction system
   b) Condition the cartridge by adding 3 mL of methanol
   c) Partially draw the methanol through until the surface of the liquid reaches the top of the cartridge frit
   d) Wait 1 minute then add 3 mL of DI water to the cartridge.
   e) Add 1 mL of 100 mM acetic acid
   f) Draw liquid through until it touches the top of the frit
   g) Cartridge is now ready for sample extraction

Note: Do not allow the sorbent to completely dry out after the addition of methanol, otherwise repeat procedure

3. **Apply Sample**
   a) Add sample to cartridge at a rate of approximately 5 mL/minute by adjusting vacuum

4. **Wash Cartridge**
   a) Wash by drawing through 5 mL of deionized water
   b) Dry sorbent (5 minutes at > 10 inches Hg)

5. Elute

a) Insert a collection vial in the vacuum manifold
b) Rinse sample bottle with 3 mL of methanol
c) Add the methanol to the cartridge
d) Elute at 5 mL per minute
e) Add 3 mL of methanol to the cartridge
f) Elute at 5 mL per minute

6. Evaporate

a) Evaporate methanol eluate using gentle N_2 (< 40°C) to dryness
b) Add 50 µL of ethyl acetate to dissolve
c) Add 50 µL of reagent MTBSTFA* or BSTFA** to derivatize. Vortex
d) Heat mixture for 20-30 minutes @ 70°C
e) Cool. Sample is now ready for GC injection

*MTBSTFA-- N-(t-butyldimethylsilyl)-N-methyltrifluoroacetamide
**BSTFA-- *N,O* -Bis(trimethylsilyl)trifluoroacetamide

7. Instrument Conditions

- **Column:** Rtx-5MS, 30m, 0.25 mm ID, 0.50 µm df (5% diphenyl/95% dimethyl polysiloxane)
- **Injector Temperature:** 250°C
- **Detector Temperature:** 250° C
- **Oven Program:** Initial 70°C, ramp @ 20°C/minute to 320°C, hold 3.0 min
- **Purge Flow:** Initially Off. On at 0.75 minutes
- **Split Flow:** 30 mL/minute
- **Inject:** 2 µL

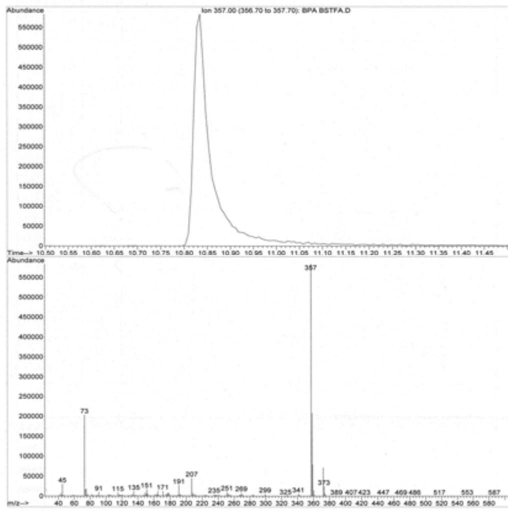
8. Quantitate

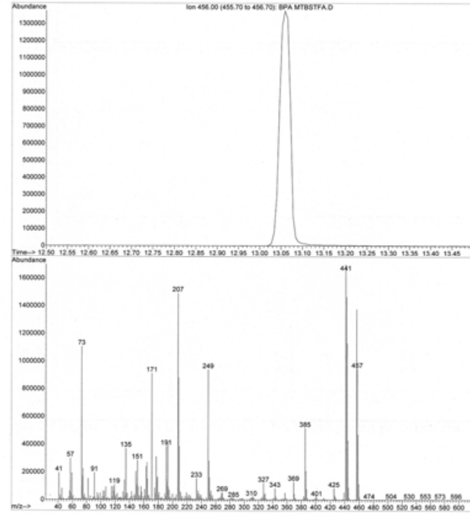
MS in EI (+) mode:

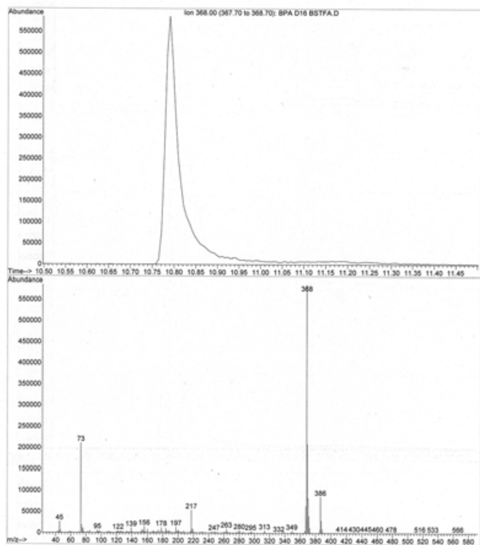
BSTFA	Primary ion	Secondary ion	Tertiary ion
BPA	357	373	207
BPA-D16	368	386	217

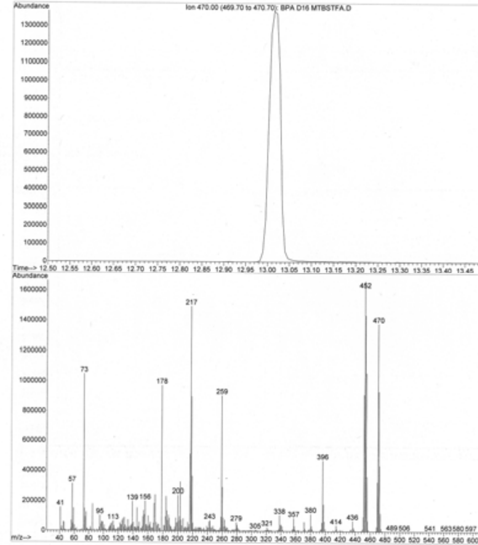
MTBSTFA	Primary ion	Secondary ion	Tertiary ion
BPA	441	457	207
BPA-D16	452	470	217

Chromatogram Showing Retention Time for Bisphenol A in Water









Spike Concentration: 0.15 µg/L Calc Concentration: 0.157 µg/L Recovery: 105%

Bisphenol A Analysis in Water by LC/MS/MS Using an ENVIRO-CLEAN® 200 mg C18 Extraction Cartridge

UCT Part number:
EEC1812Z (Endcapped C18 - 200 mg/10 mL)

February 2009

Procedure

1. Prepare Sample

a) Using 100 mL of sample water, adjust the pH to 7 or less using 100mM acetic acid

b) Add internal standard to water sample

Note: Bisphenol A has a pKa value of approximately 9.5

2. Condition Cartridge

a) Place a cartridge(s) on a multistation vacuum manifold or automated extraction system

b) Condition the cartridge by adding 3 mL of methanol

c) Partially draw the methanol through until the surface of the liquid reaches the top of the cartridge frit

d) Wait 1 minute then add 3 mL of DI water to the cartridge

e) Add 1 mL of 100 mM acetic acid

f) Draw liquid through until it touches the top of the frit

g) Cartridge is now ready for sample extraction

Note: Do not allow the sorbent to completely dry out after the addition of methanol, otherwise repeat procedure.

3. Apply Sample

a) Add sample to cartridge at a rate of approximately 5 mL/minute by adjusting vacuum

4. Wash Cartridge

a) Wash by drawing through 5 mL of deionized water

b) Dry sorbent (5 minutes at > 10 inches Hg)

5. Elute

a) Insert a collection vial in the vacuum manifold

b) Rinse sample bottle with 3 mL of methanol

c) Add the methanol to the cartridge

d) Elute at 5 mL per minute

e) Add 3 mL of methanol to the cartridge

f) Elute at 5 mL per minute

6. Evaporate

a) Evaporate methanol eluate using gentle N_2 (< 40°C) to less than 500 µL

b) Bring sample volume to 500 µL

c) Sample is ready for injection

7. Quantitate

a) LC-MS/MS MRM transition **(**negative ion mode)

Instrumental & Conditions:

Column: 100 x 2.1 (3 µm) Selectra® Phenyl, UCT, INC
Instrument: Applied Biosytems Triplequad LC/MS/MS (other systems may be used)

- Detector: API3200 QTrap
- bisphenol A Precursor ion mass 226.9, product ion mass 109.1
- *bisphenol A standard deuterated A-D16. Precursor ion mass 241.1, Product ion mass 223.1

Inject: 5-10 µL

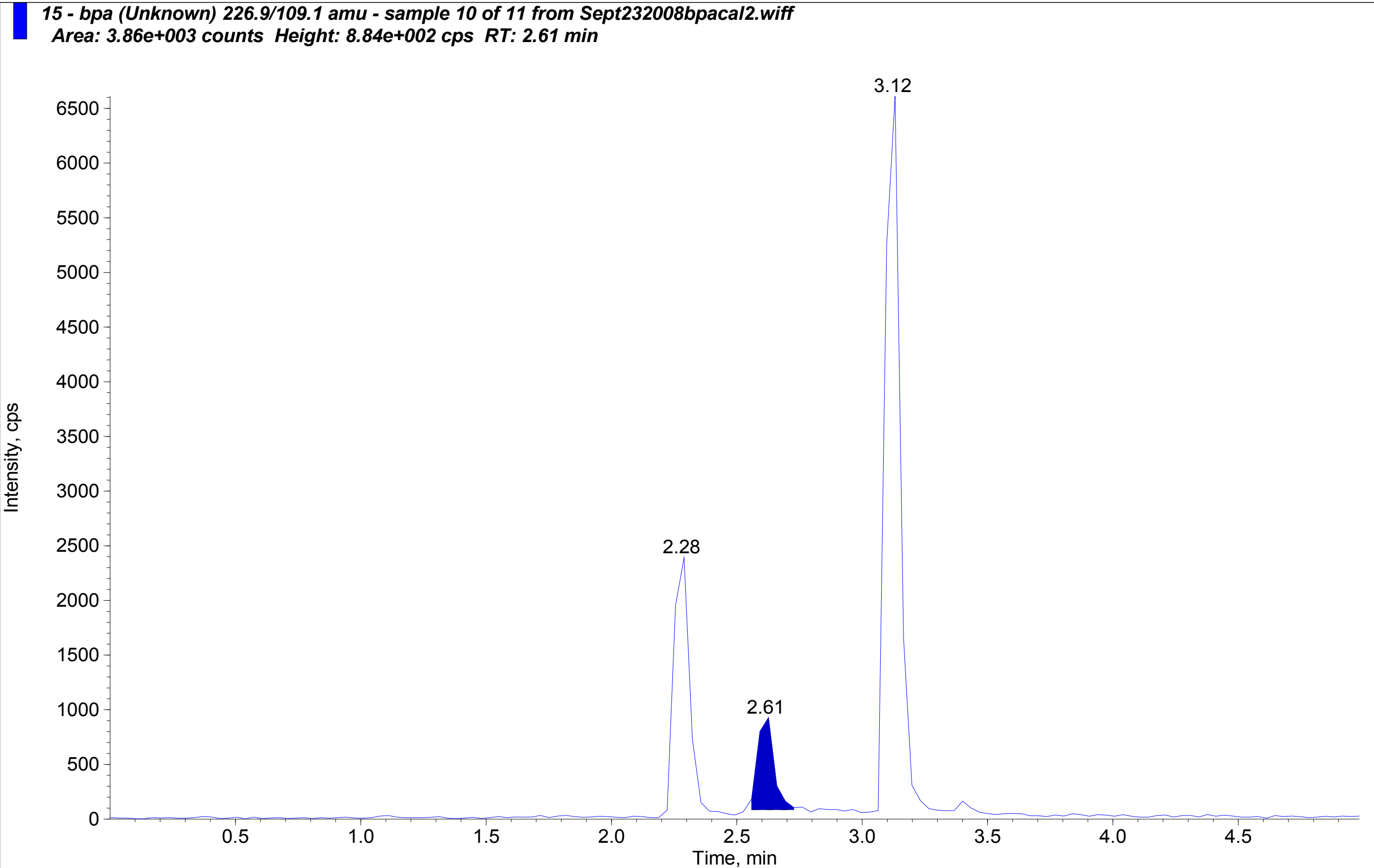
Mobile Phase: acetonitrile/0.1% formic acid
Flowrate: 0.5 mL/ minute

Flow Program

Time in minutes	**% Acetonitrile**	**% 0.1% Formic Acid**
0	30	70
3.0	90	10
3.5	30	70
5.0	30	70

Chromatogram Showing Retention Time for Bisphenol A in Water

Spike concentration: 15 µg/L, **Calc Recovery:** 15.70 µg/**L, Recovery:** 105%



DCN-905020-131

Determination of Hormones in Water by Solid-Phase Extraction (SPE) and Liquid Chromatography – Tandem Mass Spectrometry (LC-MS/MS)*

UCT Part Numbers:
EUC18156 (500 mg unendcapped C18, 6 mL)

November 2012

Analytes Determined Using This Method

Analyte	CASRN
Estriol 16α-Hydroxyestradiol	50-27-1
17β-Estradiol	50-28-2
17α-Ethynylestradiol	57-63-6
Testosterone	58-22-0
Estrone 3-hydroxy-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrocyclopenta[a]phenanthren-17-one	53-16-7
4-Androstene-3,17-dione	63-05-8
Equilin 3-hydroxyestra-1,3,5,7-tetraen-17-one	474-86-2

Method Summary

Water samples are dechlorinated with sodium thiosulfate and protected from microbial degradation with 2-mercaptopyridine-1-oxide sodium salt during collection. Samples are fortified with surrogates and extracted using C18 cartridges before elution with methanol. The extract is concentrated to dryness with N_2 before adjusting to a 1 mL volume with 50:50 methanol:water. An aliquot is injected into an LC equipped with a C18 column interfaced to a MS/MS. Detection limits of 0.02-0.37 ng/L can be obtained using this application from samples fortified at 0.25-0.875 ng/mL.

Safety

- The toxicity and carcinogenicity of each reagent has not been defined
- Each chemical should be treated as a potential health hazard and exposure minimized by the use of PPE (personal protective equipment) such as gloves, respirators and other personal safety equipment
- Pure standard materials and stock standard solutions of the method compounds should be handled with suitable protection
- Ammonium hydroxide, used during method development as a pH modifier for the HPLC mobile phase, should be fresh* and handled in a fume hood

*NH_4OH loses its strength after opening due to evaporation. A fresh bottle should be used

Sample Collection, Preservation, and Storage

- Use one-liter amber glass bottles with PTFE-lined screw caps
- If smaller sample sizes are used, adjust the amount of preservatives and surrogate/analyte fortification levels according to the sample size
- Fill sample bottles taking care not to flush out the preservatives. Analytes are not volatile so bottles need not be headspace-free
- When sampling from a cold water tap, remove the aerator and allow the system to flush until the water temperature has stabilized. Invert the bottles several times to mix the sample with the preservation reagents
- Samples should be chilled during shipment and should not exceed 10° C during the first 48 hours after collection
- In the laboratory, store samples at or below 6° C and protect from light until analysis. **Do not freeze unprocessed samples**
- All compounds listed in the method have adequate stability for 28 days when collected, preserved, shipped and stored as described
- Samples should be extracted as soon as possible for best results
- After sample preparation, extracted samples should be stored at 0° C or less and analyzed within 28 days after extraction

Sample Preservatives

Compound	Amount	Purpose
Sodium thiosulfate	80 mg/L	Removes free chlorine
2-mercaptopyridine-1-oxide sodium salt	65 mg/L	Microbial inhibitor

Note: Preservation reagents listed above should be added to each sample bottle prior to shipment to the field or prior to sample collection

Interferences

- Matrix interferences may be caused by contaminants that are co-extracted from the sample and will vary from source to source
- Humic and/or fulvic material in environmental samples may be co-extracted during SPE and can cause enhancement and/or suppression in the electrospray ionization source. Total organic carbon (TOC) is an indicator of the humic content of a sample
- Use only high purity analogs. Depending on the source and purity, labeled analogs used as internal standards may contain a small percentage of the corresponding native analyte which may be significant when attempting to determine LCMRLs and DLs
- Nitrile gloves should be worn at all times. Handling clean glassware may be a potential source of interference

- It may be appropriate to include a Field Blank with the sampling bottles depending on the sampling site. The Field Blank is analyzed along with the samples to ensure that no human hormones were introduced into the samples during the collection and handling process

Internal Standards

Internal Standard	CASRN	Neat Material Cat #	Solution Standard Cat #
16α-Hydroxyestradiol-*d*2 (Estriol-*d*2)	53866-32-3	C/D/N Isotopes Cat. No. D-5279	N/A
$^{13}C6$-Estradiol	None	None	Cambridge Isotope Labs 100 µg/mL in Methanol Cat. No. CLM-7936-1.2
$^{13}C2$-Ethynylestradiol	None	None	Cambridge Isotope Labs 100 µg/mL in Acetonitrile Cat. No. CLM-3375-1.2
Testosterone-*d*3	77546-39-5	None	Sigma Drug Std., 100 µg/mL in dimethoxyethane Cat. No. T5536

Internal Standard Stock Standards

ISSSS 500 µg/mL - Weigh 5 mg of α-hydroxyestradiol-*d*2 (estriol-*d*2) into a tared 10 mL volumetric flask and dilute to volume with methanol. The remaining internal standards can be purchased as100 µg/mL solutions

Internal Standard Primary Dilution Standard (IS-PDS)

IS PDS 1.0 – 4.0 μg/mL: The table below can be used as a guide for preparing the IS PDS. The IS PDS is prepared in acetonitrile and is stable for about six months if stored at a temperature < 6° C. Use 5 μL of the 1.0 – 4.0 μg/mL IS PDS to fortify the final 1 mL extracts. This will yield a final concentration of 5.0 – 20 ng/mL of each IS.

Internal Standard Concentrations

Internal Standard	Conc IS Stock μg/mL	Volume of IS Stock, μL	Final Volume of IS PDS,	Final Conc. of IS PDS (μg/mL)
16α-Hydroxyestradiol-*d*2 (Estriol-*d*2)	500	40	10	2.0
^{13}C6-Estradiol	100	400	10	4.0
^{13}C2-Ethynylestradiol	100	400	10	4.0
Testosterone-*d*3	100	100	10	1.0

Internal Standard Fortification Standard

5 μL of the IS PDS is difficult to accurately and reproducibly transfer into HPLC vials. Therefore, a 1-in-10 dilution of the IS PDS is prepared by transferring 1 mL of the 1.0 – 4.0 μg/mL IS PDS into a 10 mL volumetric flasks and diluting to volume with methanol. This results in a 0.1-0.4 μg/mL IS solution

50 μL of the prepared ISPDS is added to the samples prior to analysis

Surrogate Analytes

Two isotopically labeled surrogates are listed below. Select the surrogate that performs best under the LC-MS/MS conditions employed for the analysis

For this application, Bisphenol A-d$_{16}$ was chosen as surrogate analyte

Surrogate Analytes

Surrogate Analyte	CASRN	Neat Materials Catalog No.
Ethynylestradiol-d_4	350820-06-3	C/D/N Isotopes, Cat. No. D-4319
Bisphenol A-d_{16}	96210-87-6	Sigma, Cat. No. 451835

Surrogate Stock Standards

1000 µg/mL - Prepare individual solutions of the surrogate standards by weighing 10 mg of the solid material into tared 10 mL volumetric flasks and diluting to volume with methanol

Surrogate Analyte Primary Dilution Standard

SUR PDS 2.5 – 7.0 µg/mL
Use the table below as a guide for preparation of the **SUR PDS** in methanol.

Use 10 µL of **SUR PDS** to fortify 1-L samples yielding a final concentration of 70 ng/mL ethynylestradiol-d_4 or 25 ng/mL bisphenol A-d_{16} in the 1 mL extracts

Surrogate Analyte Solutions

Surrogate Analyte	Conc of SUR Stock (µg/mL)	Volume of SUR Stock (µg/mL)	Final Volume of SUR PDS (mL)	Final Conc. Of SUR PDS (µ g/mL)
Ethynylestradiol-d_4	1000	70	10	7.0
Bisphenol A-d_{16}	1000	25	10	2.5

Surrogate Fortification Standard (SUR PDS)

10 µL of the **SUR PDS** is difficult to accurately and reproducibly transfer into samples. Therefore, a 1-in-10 dilution of the **SUR PDS** is prepared by transferring 1 mL of the 2.5 µg/mL IS PDS into a 10 mL volumetric flask and diluting to volume with methanol, resulting in a 0.25 µg/mL IS solution. Use 100 µL of this fortification standard to fortify 1-L samples yielding a final concentration of 25 ng/mL bisphenol A-d_{16} in the 1 mL extracts

Analyte Stock Standard Solution

Each concentration equals 1000 µg/mL - Obtain the analytes listed in Table 1 above as standard solutions or as neat materials. Prepare stock standards individually by weighing 10 mg of the solid standards into tared 10 mL volumetric flasks and diluting to volume with methanol

Analyte Primary Dilution Standard

Prepare concentrations of the stock standard solutions between 1.0 – 3.5 µg/mL – Dilute the Analyte Stock Standard solutions into 50% methanol in reagent water. The concentrations vary based on the instrumental sensitivity. The Analyte PDS is used to prepare calibration standards, and to fortify LFBs, LFSMs, and LFSMDs with the method analyte

Analyte Stock	Stock Concentration µg/mL	Stock Volume µL	Final Volume (ml, 50% MeOH)	Analyte PDS Concentration µg/L
Estriol, 16α- Hydroxyestradiol	1000	20	10	2.0
Estrone	1000	20		2.0
17β-Estradiol	1000	25		2.5
17α-Ethynylestradiol	1000	35		3.5
Equilin	1000	20		2.0
Androstenedione	1000	10		1.0
Testosterone	1000	10		1.0

Analyte Fortification Standard

10 µL of the Analyte PDS is difficult to accurately and reproducibly pipette into samples. Therefore, a 1-in-10 dilution of the Analyte PDS is prepared by transferring 1 mL of the 1.0 – 3.5 µg/mL Analyte PDS into a 10 mL volumetric flask and diluting to volume with 50% methanol, resulting in a 0.1 – 0.35 µg/mL solution. Use 100 µL of this fortification standard to fortify 1-L samples yielding a final concentration of 10 – 35 ng/mL in the 1 mL extracts.

An additional 1-in-10 dilution of the 0.1 – 0.35 µg/mL fortification solution is prepared in a 10 mL volumetric flask using 50% methanol. This yields a 0.01 – 0.035 µg/mL solution that is used to fortify 1-L samples yielding a final concentration of 1 – 3.5 ng/mL in the 1 mL extracts.

Procedure

1. **Sample Preparation**

   a) Add a 100-µL aliquot of SUR Fortification Standard to each 1-L sample for a final concentration of 25 ng/L bisphenol A-d_{16}

   b) Fortify LFBs, LFSMs, or LFSMDs with an appropriate volume of Analyte

Fortification Standard

c) Cap and invert each sample several times to mix

2. **Cartridge Preparation**

a) Assemble a vacuum manifold. Automated extraction equipment may also be used

b) Place **EUC18156** cartridge(s) on the manifold

c) Add a 10 mL aliquot of methanol to the cartridge and draw through the cartridge until dry

d) Add another 5 mL aliquot of methanol and draw through the cartridge until dry

Note: Do Not Let the Cartridge Go Dry after Starting the Following Steps

e) Add approximately 10 mL of methanol to each cartridge

f) Draw about 1 mL of solvent through the cartridge and turn off the vacuum temporarily

g) Let the cartridge soak for about one minute then draw most of the remaining solvent through the cartridge leaving a thin layer of methanol on the surface of the cartridge

h) Add 10 mL of reagent water to each cartridge and draw through leaving a thin layer of liquid on the surface of the cartridge

i) Add another 10 mL aliquot of reagent water

j) Draw the water through the cartridge keeping the water level above the cartridge surface

k) Turn off the vacuum

3. **Sample Extraction**

a) Add the sample to the extraction reservoir containing the conditioned cartridge and turn on the vacuum (approximately 10 to 15 in. Hg). Flow of sample through the cartridge should be a fast drip. Adjust vacuum if necessary

b) Do not let the cartridge go dry before the entire sample volume is extracted

c) After the entire sample has been drawn through the cartridge, add a 10 mL aliquot of 15% methanol to the sample container and wash the cartridge with the rinsate from the container

d) Using full vacuum, draw air through the cartridge by maintaining full vacuum for 10–15 minutes

e) After drying, turn off and release the vacuum

4. **Sorbent Elution**

   a) Insert collection tubes into the manifold to collect the cartridge extracts. The collection tube should fit around the drip tip of the base to ensure collection of all the eluent
   b) Add 5 mL of methanol to the cartridge and draw the methanol into the cartridge to soak the sorbent
   c) Allow the cartridge to soak for about one minute
   d) Using vacuum, draw the remaining methanol slowly through the cartridge into the collection tube
   e) Elute with an additional 2 x 5 mL aliquots of methanol

> **Note:** The methanol can be eluted directly into a 15 mL tube (or larger). Otherwise 5 mL MeOH can be eluted into a 5 mL culture tube and evaporated to near dryness prior to adding the second 5 mL eluate. This process is repeated until all 15 mL MeOH has been added to the 5 mL culture tube.

5. **Extract Concentration**

   a) Concentrate the extract to dryness under a gentle stream of N_2 in a warm water bath (~45° C)
   b) Rinse the collection tube with 950 µL of 50% methanol, vortex for 2 min and transfer the rinse into a HPLC vial
   c) Add 50 µL IS Fortification Standard (ISFS) and vortex for an additional 1 min

6. **Sample Filtration**

   a) It is highly recommended that extracts be filtered with at least a 0.45 micron syringe filter prior to analysis to remove the particulates in a sample.
   b) If filtering is incorporated as part of the sample preparation, the first lot of syringe filters should be included in the procedure to document the potential interferences that are introduced or analytes are retained on the filter.
   c) Subsequent lots of syringe filters can be verified by examining CAL standards.

Sample Analysis

HPLC Conditions

HPLC instrument: Thermo Scientific Dionex UltiMate 3000 System**		
Column: Thermo Scientific Accucore C18, 100 x 2.1 mm, 2.6 µm with 10 mm guard column		
Column Temperature: 35° C		
Column Flow Rate: 0.200 mL/min		
Injection Volume: 20 µL		
Gradient		
Time (min)	**Moblie phase A** **H_2O + 0.02% NH4OH**	**Moblie phase B** **MeOH +0.02% NH4OH**
0	70	30
1	35	65
9	35	65
9.1	15	85
11	15	85
11.1	70	30
15	70	30

ESI-MS/MS Method Conditions

MS Parameters	
MS instrument	Thermo Scientific TSQ Vantage**
Polarity	$HESI^+$ & $HESI^-$
Spray Voltage V	+4500 / -3500 V
Vaporizer Temperature	350°C
Ion Transfer Capillary	300 °C
Sheath Gas Pressure	45 arbitrary units
Auxiliary Gas Pressure	40 arbitrary units
Q1 and Q3 Peak Width (FWHM)	0.4 and 0.7 Da
Collision Gas and Pressure	Ar at 1.5 mTorr
Scan Type	SRM
Cycle Time	0.75 Sec

**Alternative LC-MS/MS systems may be used

LC-ESI-MS/MS Analyte Retention Times, Precursor and Product Ions, S-lens, and Collision Energy

Analyte	Ret. Time (min.)	ESI Mode	Precursor Ion	Product Ion	S-lens V	Collision Energy eV	Internal Standard
Estriol	4.99	ESI-	286.75	144.96	100	39	Estriol-d_2
Bisphenol A-d_{16}	6.20	ESI-	240.91	223.02	60	18	$^{13}C_6$-Estradiol
Equilin	7.03	ESI-	266.80	142.97	67	37	$^{13}C_6$-Estradiol
17β-Estradiol	7.14	ESI-	270.93	144.98	67	40	$^{13}C_6$-Estradiol
Androstenedione	7.18	ESI+	286.87	96.88	76	20	Testosterone-d_3
17α-Ethynylestradiol	7.19	ESI-	294.79	244.97	80	39	$^{13}C_2$-Ethynylestradiol
Estrone	7.24	ESI-	268.78	144.97	109	39	$^{13}C_2$-Ethynylestradiol
Testosterone	7.76	ESI+	288.96	96.88	76	20	Testosterone-d_3

LC-ESI-MS/MS Internal Standard Retention Times, Precursor and Product Ions, S-lens, and Collision Energy

Internal Standard	Ret. Time (m	Precursor Ion	Product Ion	S-Lens V	Collision Energy eV
Estriol-*d*2	5.00	288.75	146.96	100	39
$^{13}C_6$-Estradiol	7.13	276.93	146.98	67	40
$^{13}C_2$-Ethynylestradiol	7.16	296.80	144.97	80	39
Testosterone-*d*3	7.73	291.96	96.88	70	20

Analyte Recovery

n = 5	Estriol	Equilin	Estradiol	Androstenedione	Testosterone	Ethynylestradiol	Estrone
Fortified Conc (ng/mL)	20	20	25	10	20	10	35
Mean	97.61	82.81	96.98	92.88	90.76	96.49	93.95
SD	6.45	5.90	5.17	2.55	3.47	1.31	2.02
RSD	6.60	7.13	5.33	2.75	3.82	1.36	2.15

n = 5	Estriol	Equilin	Estradiol	Androstenedione	Testosterone	Ethynylestradiol	Estrone
Fortified Conc (ng/mL)	2	2	2.5	1	1	3.5	2
Mean	83.05	96.34	93.68	98.31	104.63	109.45	106.10
SD	4.02	8.92	7.02	3.90	4.95	6.96	6.19
RSD	4.84	9.26	7.49	3.96	4.73	6.36	5.84

*Based on EPA Method 539, Version 1.0, November 2010, Glynda A. Smith (U.S. EPA, Office of Ground Water and Drinking Water) Alan D. Zaffiro, (Shaw Environmental, Inc.) M. L. Zimmerman (Shaw Environmental, Inc.) D. J. Munch (U.S. EPA, Office Of Ground Water And Drinking Water), Technical Support Center , Standards And Risk Management Division, Office Of Ground Water And Drinking Water, U. S. Environmental Protection Agency, Cincinnati, Ohio 45268

Determination of Diesel Range Non-halogenated Organics Using GC/FID by Method 8015D*

UCT Product Number:
ECUNIPAH (2000 mg unendcapped C18, 83 mL cartridge)

February 2011

Method Summary

Method 8015D may be used to determine the concentrations of several nonhalogenated volatile organic compounds and semivolatile organic compounds using GC with flame ionization detection.

- Diesel Range Organics (**DRO**) corresponds to the range of alkanes from C_{10} to C_{28} and covering a boiling point range of approximately 170° C - 430° C

Sample Collection, Preservation, and Storage

- See sample collection options EPA Method 5035A

Interferences

- Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis
- All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks
- Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary
- Contamination by carryover occurs whenever high-concentration and low-concentration samples are analyzed in sequence. To reduce the potential for carryover, the sample syringe or purging device must be rinsed out between samples with an appropriate solvent
- All glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used followed by detergent washing with hot water, and rinses with tap water and organic-free reagent water
- Drain the glassware and dry it in an oven (except volumetric glassware) at 130° C for several hours or rinse it with methanol
- FID is a non-selective detector. There is a potential for many non-target compounds present in samples to interfere with this analysis and potential for analytes to be resolved poorly, especially in samples that contain many analytes.

Reagents and Standards

- Reagent grade chemicals must be used in all tests
- Organic-free reagent water
- Methanol, CH_3OH - Pesticide quality or equivalent
- Methylene Chloride – unpreserved, pesticide residue quality or equivalent
- Fuels, e.g., diesel - Purchase from a commercial source
- Alkane standard - Standard contains a homologous series of *n*-alkanes for establishing retention times (e.g., C_{10}-C_{28} for diesel)

Stock Standards

- Prepared from pure standard materials or purchased as certified solution
- Standards must be replaced after 6 months

Secondary Dilution Standards

- Using stock standard solutions, prepare secondary dilution standards, as needed either singly or mixed together
- Secondary dilution standards should be stored with minimal headspace for volatiles
- Check frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards

Recommended GC Columns

The choice of GC column will depend on the analytes of interest, expected concentrations, and intended use of the results. The capillary columns are necessary for petroleum hydrocarbon analyses and are recommended for all other analyses. Other columns and may be employed if the analyst can demonstrate acceptable performance.

- Establish the GC operating conditions appropriate for the GC column being utilized and the target analytes specified in the project plan
- Optimize the instrumental conditions for resolution of the target analytes and sensitivity
- Suggested operating conditions and GC programs are given below for the recommend columns:

(DRO) 30-m x 0.53-mm ID fused-silica capillary column chemically bonded with 5% methyl silicone (DB-5, SPB-5, RTx, or equivalent), 1.5-µm film thickness

- Carrier gas (He) flow rate: 5-7 mL/min
- Makeup gas (He) flow rate: 30 mL/min
- Injector temperature: 200° C
- Detector temperature: 340° C
- Temperature program: Initial temperature: 45° C, hold for 3 minutes
- Program: 45° C to 275° C, at 12° C/min
- Final temperature: 275° C, hold for 12 minutes

Procedure**

1. **Condition Cartridge**
   a) Place a **ECUNIPAH** cartridge(s) on the vacuum manifold*
   b) With vacuum off add 10 mL of methylene chloride to the cartridge
   c) Let it soak for 1 minute
   d) Turn on vacuum and draw through to waste
   e) Draw vacuum through the cartridge to remove all methylene chloride
   f) Add 10 mL of methanol to the cartridge
   g) Let it soak for 1 minute
   h) Draw the methanol to the level of the frit
   i) Add 10 mL of deionized water to the cartridge
   j) Let it soak for 1 minute
   k) Draw most of the water to waste but do not allow the sorbent to dry

Note: Do not let the cartridge go completely dry after addition of methanol otherwise repeat starting at step 1.f)

2. **Sample Addition**
   a) Add required surrogates to the sample
   b) Shake
   c) Adjust the pH of the sample to 2 or less using 5 mL of 1:1 HCl
   d) Shake
   e) Add the sample to the cartridge under vacuum. Draw the sample through the cartridge no faster than 20 – 30 minutes per liter
   f) Allow the cartridge to dry under full vacuum for 5 minutes***

3. **Extract Elution**
   a) Place a collection tube or vial containing approximately 1 cm of pre-baked sodium sulfate anhydrous in the vacuum manifold
   b) Rinse sample bottle with 10 mL of methylene chloride to remove any analyte from the glass
   c) Add the methylene chloride rinse to the cartridge

d) Allow to soak for 2 minutes then draw through

e) Repeat this procedure three more times using 10 mL aliquots of methylene chloride

f) Dry the extract by passing it through 5 grams of **ECSS25K** anhydrous sodium sulfate

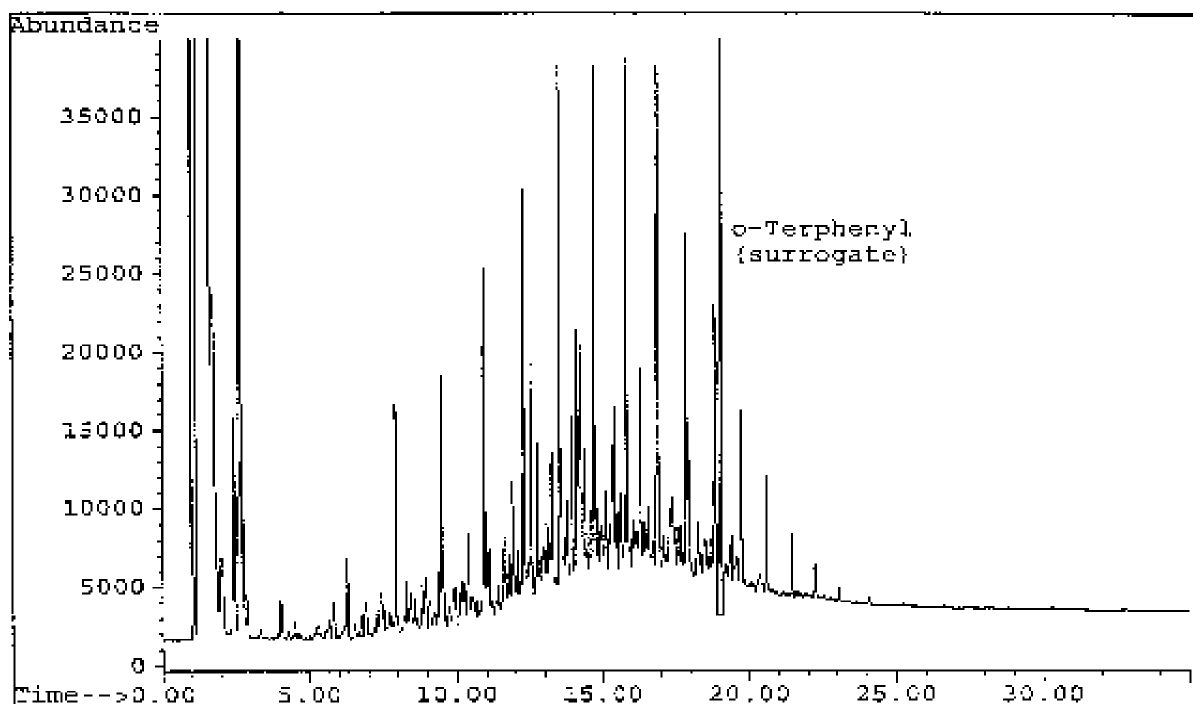
g) Thoroughly rinse the collection device with methylene chloride and add this solvent to the sodium sulfate

4. Concentration

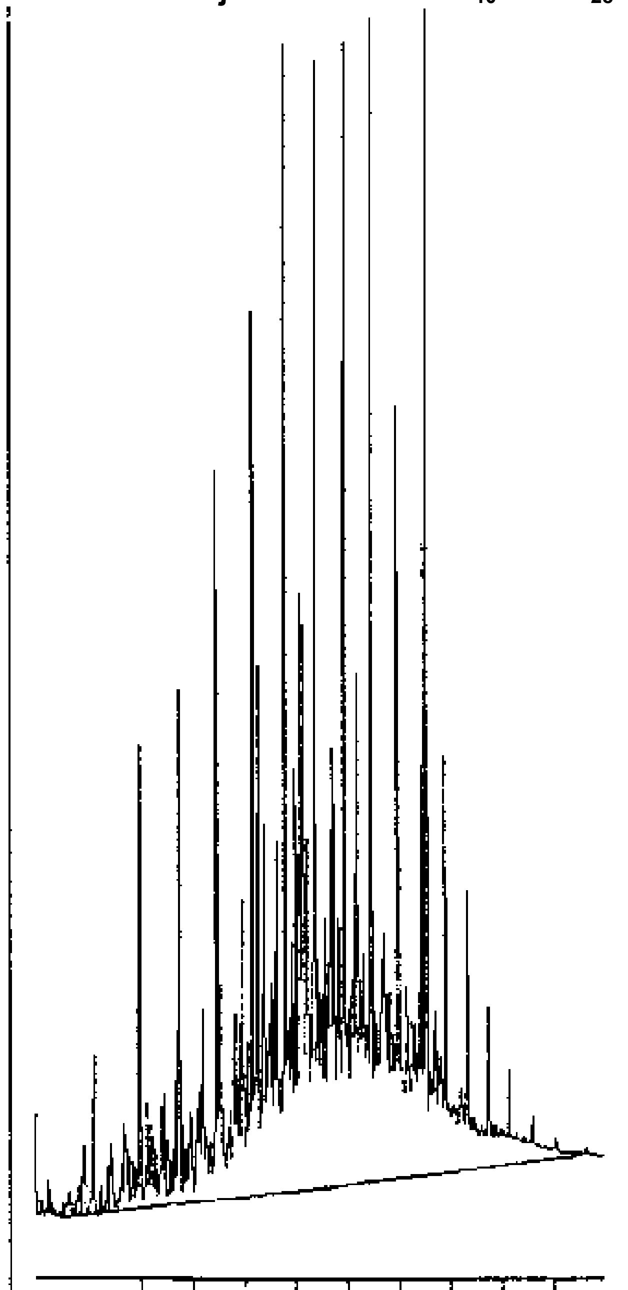
a) Concentration of final extract using a micro Kaderna-Danish flask equipped with a 3-ball Snyder column is recommended to avoid loss of low boiling alkanes. A micro-Snyder column can be used to evaporate the extract to a 1 mL final volume

b) Extracts should not be stored with headspace for extended periods of time as low recoveries will result

Example Chromatogram of a 30 PPM Diesel Standard



Example Chromatogram of a 30 Ppm Diesel Standard With The Baseline Projected Between C_{10} and C_{28}



*Summarized from Method 8015D Nonhalogenated Organics Using GC/FID, Revision 4, June 2003, and associated appropriate methods

**(steps 1- 4 added to this method summary for use with UCT PAH/DRO cartridges)

***Faster drying results can be obtained by removing the cartridge during drying and shaking or tapping the excess moisture from the bottom of the cartridge. Drying times are approximate. Do not over dry as low recoveries may result

Polycyclic Aromatic Hydrocarbons (PAH) from a Water Matrix

UCT Product Number:
ECUNIPAH (2000 mg, unendcapped C18, 83 mL cartridge)
ECSS25K (anhydrous sodium sulfate)

January 2011

Polynuclear Aromatic Compounds Recovered in this Method

PAH	CASRN	PAH	CASRN
Acenaphthene	83-32-9	Chrysene	218-01-9
Acenaphthylene	208-96-8	Dibenzo(a,h)anthracene	53-70-3
Anthracene	120-12-7	Fluoranthene	206-44-0
Benzo(a)anthracene	56-55-3	Fluorene	86-73-7
Benzo(a)pyrene	50-32-8	Indeno(1,2,3-cd)pyrene	193-39-5
Benzo(b)fluoranthene	205-99-2	Naphthalene	91-20-3
Benzo(g,h,i)perylene	191-24-2	Phenanthrene	85-01-8
Benzo(k)fluoranthene	207-08-9	Pyrene	129-00-0

1. Condition Cartridge

a) Place **ECUNIPAH** cartridge(s) on the vacuum manifold*
b) With vacuum turn off add 10 mL of methylene chloride to the cartridge
c) Let it soak for 1 minute
d) Turn on vacuum and draw through to waste
e) Add 10 mL of methanol to the cartridge
f) Let it soak for 1 minute
g) Draw the methanol to the level of the frit
h) Add 10 mL of deionized water to the cartridge
i) Let it soak for 1 minute
j) Draw most of the water to waste but do not allow the sorbent to dry

Note: Do not let the cartridge go dry after addition of methanol otherwise repeat starting at step 1. e)

2. Sample Addition

a) Add surrogates to the sample

b) Shake

c) Add the sample to the cartridge under vacuum. Draw the sample through the cartridge in 20 – 30 minutes (10 – 50 ml/min)

d) Allow the cartridge to dry under full vacuum for 10 minutes**

Optional: Before proceeding to the drying step use UCT Zero-Blank™ Filter (**ECBLANK**) to reduce potential background contamination

3. Extract Elution

a) Place a collection tube or vial in the vacuum manifold

b) Rinse sample bottle with 10 mL of methylene chloride

c) Add the methylene chloride rinse to the cartridge

d) Allow to soak for 1 minute then draw through

e) Repeat this procedure 3 more times using 10 mL aliquots of methylene chloride

f) Dry the extract by passing it through 5 grams of **ECSS25K** anhydrous sodium sulfate

g) Thoroughly rinse the collection device with methylene chloride

h) Add the methylene chloride rinse to the sodium sulfate

4. Concentration and Analysis

a) Using a standard analytical evaporator with gentle N_2 flow and low temperature (40° C) carefully concentrate the extract to a final volume for GC/MS analysis.

b) Solvent exchange into acetonitrile and bring to a 1 ml final volume for HPLC analysis

c) Sample is now ready for analysis

Note: Most analysis errors are caused by poor concentration technique. Do not concentrate below 0.5 mL as low recoveries may result

*The ENVIRO-CLEAN® Universal PAH cartridge can be used on standard vacuum manifolds (# VMFF016GL) and standard disk manifolds (#ECUCTVAC6) (with adapter part # ECUCTADP). The cartridge is designed to fit all automated extraction systems

**Faster drying results can be obtained by removing the cartridge during drying and shaking or tapping the excess moisture from the bottom of the cartridge. Drying times are approximate. Do not over dry as low recoveries may result

Organochlorine Pesticides and Polychlorinated Biphenyls by Solid-Phase Extraction

UCT Product Number:
EEC181M6 (1000 mg C18, 6 mL Cartridge) or
ECUNIC18 (1100mg C18, Universal Cartridge)

July 2011

Compounds Recovered Using This Method

Analyte	CASRN
1,2-Dibromo-3-chloropropane (DBCP)	96-12-8
4,4'-DDD	72-54-8
4,4'-DDE	72-55-9
4,4'-DDT	50-29-3
Alachlor	15972-60-8
Aldrin	309-00-2
Captafol	2425-06-1
Carbophenthion	786-19-6
Chlordane - not otherwise specified (n.o.s.)	57-74-9
Chlorobenzilate	510-15-6
Chloroneb	2675-77-6
Chloropropylate	5836-10-2
Chlorothalonil	1897-45-6
Dacthal (DCPA)	1861-32-1
Diallate	2303-16-4
Dichlone	117-80-6
Dichloran	99-30-9
Dicofol	115-32-2
Dieldrin	60-57-1
Endosulfan I	959-98-8
Endosulfan II	33213-65-9
Endosulfan sulfate	1031-07-8
Endrin	72-20-8
Endrin Aldehyde	7421-93-4
Endrin Ketone	53494-70-5
Etridiazole	2593-15-9
Halowax-1000	58718-66-4
Halowax-1001	58718-67-5
Halowax-1013	12616-35-2
Halowax-1014	12616-36-3
Halowax-1051	2234-13-1
Halowax-1099	39450-05-0
Heptachlor	76-44-8
Heptachlor epoxide	1024-57-3
Hexachlorobenzene	118-74-1
Hexachlorocyclopentadiene	77-47-4
Isodrin	465-73-6
Methoxychlor	72-43-5
Mirex	2385-85-5

Nitrofen	1836-75-5
Pentachloronitrobenzene (PCNB)	82-68-8
Permethrin (*cis* + *trans*)	52645-53-1
Perthane	72.56-0
Propachlor	1918-16-7
Strobane	8001-50-1
Toxaphene	8001-35-2
Trans-Nonachlor	39765-80-5
Trifluralin	1582-09-8
α-BHC	319-84-6
α-chlordane	5103-71-9
β-BHC	319-85-7
γ-BHC (Lindane)	58-89-9
γ-chlordane	5103-74-2
δ-BHC	319-86-8

PCB's Recovered Using This Method

Compound	CASRN	IUPAC #
Aroclor 1016	12674-11-2	-
Aroclor 1221	11104-28-2	-
Aroclor 1232	11141-16-5	-
Aroclor 1242	53469-21-9	-
Aroclor 1248	12672-29-6	-
Aroclor 1254	11097-69-1	-
Aroclor 1260	11096-82-5	-
2-Chlorobiphenyl	2051-60-7	1
2,3-Dichlorobiphenyl	16605-91-7	5
2,2',5-Trichlorobiphenyl	37680-65-2	18
2,4',5-Trichlorobiphenyl	16606-02-3	31
2,2',3,5'-Tetrachlorobiphenyl	41464-39-5	44
2,2',5,5'-Tetrachlorobiphenyl	35693-99-3	52
2,3',4,4'-Tetrachlorobiphenyl	32598-10-0	66
2,2',3,4,5'-Pentachlorobiphenyl	38380-02-8	87
2,2',4,5,5'-Pentachlorobiphenyl	37680-73-2	101
2,3,3',4',6-Pentachlorobiphenyl	38380-03-9	110
2,2',3,4,4',5'-Hexachlorobiphenyl	35065-28-2	138
2,2',3,4,5,5'-Hexachlorobiphenyl	52712-04-6	141
2,2',3,5,5',6-Hexachlorobiphenyl	52663-63-5	151
2,2',4,4',5,5'-Hexachlorobiphenyl	35065-27-1	153
2,2',3,3',4,4',5-Heptachlorobiphenyl	35065-30-6	170
2,2',3,4,4',5,5'-Heptachlorobiphenyl	35065-29-3	180
2,2',3,4,4',5',6-Heptachlorobiphenyl	52663-69-1	183
2,2',3,4',5,5',6-Heptachlorobiphenyl	52663-68-0	187
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	40186-72-9	206

Procedure

1. Condition Cartridge

a) Assemble a suitable vacuum manifold system

b) Place cartridge(s) in the bulkhead fittings or cartridge adapters of the vacuum manifold. If nylon fittings are used, UCT CLEAN-THRU® Tips (CLTTP050) are recommended to prevent damage to the fittings by sulfuric acid

c) Attach adapters and reservoirs to the cartridge(s) if necessary

d) Rinse cartridge with 10 mL of methylene chloride ($MeCl_2$)

e) Let the $MeCl_2$ soak for 1.5 min.

f) Using vacuum draw the $MeCl_2$ to waste

g) Add 10 mL of acetone. Let the acetone soak for 1.5 minutes

h) Draw the acetone to waste

i) Dry the cartridge using full vacuum for a few seconds

j) Add10 ml of methanol and allow the methanol to soak for 1.5 min.

Note: Do not allow the cartridge to go dry otherwise repeat starting with step 1) j)

k) Draw some of the methanol through leaving a layer just covering the frit

l) Add 20 mL of deionized water. Draw most of the water through to waste but do not allow the sorbent to completely dry

2. Sample Addition

a) Adjust sample pH to ≤ 2 using 1:1 sulfuric acid

Note: Use a pH meter to accurately determine sample pH in deionized water. Do not use pH paper

b) Mix thoroughly

c) Start vacuum and add the sample. Draw sample through the cartridge at a rate ≤ 50 mL/minute (1 L should pass through in 20 minutes or longer)

d) Allow the cartridge to dry under full vacuum for 10 minutes**

3. **Extract Elution**

a) Place a collection tube or vial under the cartridge
b) Add 5 mL of acetone to the sample bottle and swirl to remove any residue
c) Add the acetone to the cartridge. Allow the solvent to soak for 1 minute then draw into collection vial
d) Repeat this procedure 3 more times using a 10 mL portions of $MeCl_2$
e) Prepare a 5 gram bed of anhydrous sodium sulfate anhydrous in a funnel using glass wool
f) Dry the extract by passing it through the funnel of sodium sulfate anhydrous
g) Carefully rinse the collection vial with $MeCl_2$, then add to the sodium sulfate, rinsing the sodium sulfate and collect

4. **Concentration and Analysis**

a) Carefully concentrate the extract. Solvent exchange if necessary

Note: Most extraction errors are caused by poor concentration technique

K-D Concentration Technique

Sample extracts may be concentrated to the final volume necessary by using the K-D technique or nitrogen evaporation.

a) Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to an evaporation flask
b) Collect the dried extract in the K-D concentrator
c) Rinse the collection tube and drying funnel then quantitatively transfer into the K-D flask with an additional 20 mL portion of solvent
d) Add boiling chips to the flask then attach a three-ball Snyder column
e) Attach the solvent vapor recovery glassware (condenser and collection device to the Snyder column of the K-D apparatus)
f) Pre-wet the Snyder column by adding about 1 mL of methylene chloride or acetone
g) Place the K-D apparatus on a hot water bath (15 - 20°C) above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water

h) Adjust the vertical position of the apparatus and the water temperature as necessary to complete the concentration in 10 - 20 min. At the proper rate of distillation the boiling chips of the column will actively chatter, but the chambers should not flood
i) When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min.
j) If a solvent exchange is needed quickly remove the Snyder column, add 50 mL of the exchange solvent and a new boiling chip
k) Reattach the Snyder column. Concentrate the extract increasing the temperature of the water bath to maintain a proper distillation rate
l) Remove the Snyder column. Rinse the K-D flask and the lower joints of the Snyder column into the concentrator tube with 1 - 2 mL of solvent
m) Adjusted to a final volume of 5.0 - 10.0 mL using an appropriate solvent

Note: If further concentration is necessary, use either the micro-Snyder column technique or a N_2 evaporation technique described below

Micro-Snyder Column Technique

- Add a fresh clean boiling chip to the concentrator tube and attach a two-ball micro-Snyder column directly to the concentrator tube
- Attach the solvent vapor recovery glassware (condenser and collection device) to the micro-Snyder column of the K-D apparatus, following the manufacturer's instructions
- Pre-wet the Snyder column by adding 0.5 mL of methylene chloride or the exchange solvent
- Place the micro-concentration apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water
- Adjust the vertical position of the apparatus and water temperature, as necessary, to complete the concentration in 5 - 10 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood
- When the apparent volume of liquid reaches 0.5 mL, remove the apparatus from the water bath and allow it to drain and cool for at least 10 min.
- Remove the Snyder column and rinse its lower joints into the concentrator tube with 0.2 mL of solvent
- Adjust the final extract volume to 1.0 - 2.0 mL

Nitrogen Evaporation Technique

- Place the concentrator tube in a warm bath (30° C) and evaporate the solvent to 0.5 mL using a gentle stream of clean, dry N_2 (filtered through a column of activated carbon)

Note: New plastic tubing must not be used between the carbon trap and the sample as phthalate interferences may be introduced

- Rinse down the internal wall of the concentrator tube several times with solvent during the concentration
- Position the concentrator tube to avoid condensing water into the extract
- Do not allow extract to become dry. If the volume of solvent is reduced below 1 mL, some analytes may be lost
- The extract may now be cleaned up or analyzed for analytes using the appropriate technique(s)
- If the sample is not analyzed immediately, cover the concentrator tube and store in a refrigerator. If the extract will be stored longer than 2 days, transfer to a vial with a PTFE-lined screw-cap and store in a refrigerator

**Faster drying results can be obtained by removing the cartridge during drying and shaking or tapping the excess moisture from the bottom of the cartridge. Drying times are approximate. Do not over dry. Low recoveries could result

*For complete details on Method 8081B "Organochlorine pesticides by Gas Chromatography/Mass Spectrometry," December 1996,and 8082A, Polychlorinated Biphenyls by Gas Chromatography," the analyst is referred to Environmental Monitoring Systems Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, OH 45268

Solid-Phase Extraction of Pesticides in Water using Graphitized Carbon Black (GCB)

UCT Part Numbers:
EUCARB1M6 (1000 mg GCB (non-porous, 120/400 mesh), 6 mL)
AD0000AS (cartridge adaptor)
RFV0075P (reservoirs, 75 mL)

May 2013

Graphitized carbon black (GCB) is a reverse phase and anion exchange sorbent. GCB retains non-polar compounds, such as organochlorine pesticides, and some very polar compounds, such as surfactants, which are difficult to retain by other reverse phase sorbents. This simple SPE method uses UCT's proprietary, treated GCB for the determination of pesticides in water providing excellent recovery.

Procedure

1. **Cartridge Preparation**
   a) Transfer 100 mL of aqueous sample to a glass container
   b) Adjust pH to less than 2 using 6N HCl
   c) Spike as necessary
   d) Connect **RFV0075P** reservoirs to the top of the **EUCARB1M6** cartridges using **AD0000AS** adaptor
   e) Wash cartridges with 10 mL dichloromethane (DCM)
   f) Draw full vacuum to remove all DCM
   g) Add 10 mL methanol and draw down to top of frit
   h) Add 10 mL reagent water and draw down to top of frit
   i) Do not let cartridges go dry after step g)
2. **Extraction**
   a) Add samples to the reservoirs adjusting vacuum to give a dropwise flow, about 10 mL/min
   b) Rinse sample containers using 10 mL reagent water and add rinsate to cartridges
   c) Dry cartridges using full vacuum for 10 min
3. **Elution**
   a) Insert test tubes in the manifold then elute cartridges using 5 mL ethyl acetate dropwise followed by 5 mL of DCM dropwise

b) Dry extracts by passing through anhydrous Na_2SO_4

c) Rinse test tubes with DCM and add to Na_2SO_4

d) Concentrate extracts to 1 mL using a gentle stream of N_2 at 35 °C

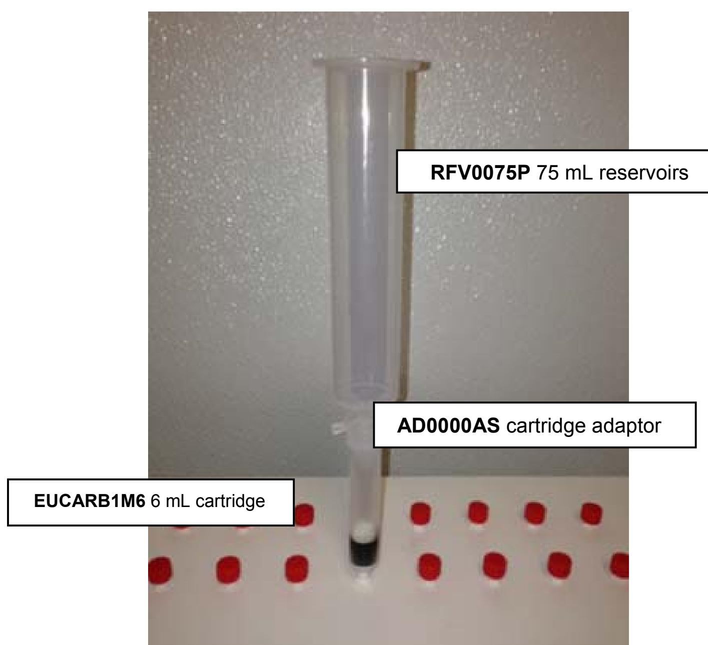
e) Add IS prior to GC/MS analysis

4. Analysis

Parameters

GCMS: Agilent 6890N GC coupled with 5975C MSD
MSD Injector: 1 µL splitless injection at 250 ºC
Injection Vol: 1 µL
Liner: 4 mm splitless gooseneck liner with deactivated glass wool (UCT: GCLGN4MM)
Column: Restek Rxi®-5sil MS 30m x 0.25mm x 0.25µm
Guard Column: 10 m
Column Flow Rate: 1.2 mL/min
Carrier Gas: He
Full Scan: 45-500 amu
Temperature Program: Initial T 55 ºC hold for 1 min; ramp at 10 ºC/min to 200 ºC; ramp at 7 ºC/min to 300 ºC; hold for 0.21 min.

Detail of Reservoir, Adaptor, and Cartridge Setup



Accuracy and Precision Data

Compound	Intra-day (n=4)		Inter-day (n=17)	
	Rec%	RSD	Rec%	RSD
alpha Lindane	93	2.1	89	9.3
beta Lindane	96	1.9	91	8.8
gamma Lindane	93	1.7	92	8.3
delta Lindane	95	3.3	89	11.7
Heptachlor	97	3.2	91	11.1
Aldrin	95	1.5	84	12.9
Heptachlor epoxide	102	2.4	97	12.0
trans-Chlordane	93	3.8	90	8.8
Endosulfan I	94	5.0	91	8.4
cis-Chlordane	96	3.3	91	9.7
p,p'-DDE	91	3.5	89	8.8
Dieldrin	98	1.9	93	9.4
Endrin	100	2.1	95	11.8
Endosulfan II	105	1.4	97	10.3
p,p'-DDD	98	2.2	92	9.8
Endrin aldehyde	95	5.4	92	9.3
Endosulfan sulfate	102	3.8	97	10.2
p,p'-DDT	99	3.0	94	9.6
Endrin ketone	106	2.1	99	10.9

Methoxychlor	105	2.7	99	10.5
Dichlofluanid	107	2.8	98	10.8
Dicofol	95	0.7	86	11.6
Tolyfluanide	106	3.1	98	11.6
Captan	119	4.2	105	13.4
Folpet	107	3.9	95	10.0
Overall average	**99**	**2.8**	**93**	**10.4**

Determination of Carbonyl Compounds In Water by Dinitrophenylhydrazine Derivatization and HPLC/UV*

EPA Method 8315A

UCT Part Number:

EUC1812M15 (Unendcapped C18 - 2000 mg/15 mL cartridge)

March 2013

Method Summary

This method provides procedures for the determination of free carbonyl compounds and aldehydes in water. A measured volume of sample is buffered to pH 3 and the analytes derivatized at 40°C for one hour using 2,4-dinitrophenylhydrazine (DNPH) then extracted through SPE cartridges containing 2000 mg of C18. The cartridge(s) are eluted with 10 mL of ethanol and the derivatives are determined by absorbance at 360 nm after separation by HPLC.

The following compounds can be determined using this method:

Analyte	CASRN
2,5-Dimethylbenzaldehyde	5779-94-2
Acetaldehyde	75-07-0
Acetone	67-64-1
Acrolein	107-02-8
Benzaldehyde	100-52-7
Butanal	123-72-8
Crotonaldehyde	123-73-9
Cyclohexanone	108-94-1
Decanal	112-31-2
Formaldehyde	50-00-0
Heptanal	111-71-7
Hexanal (hexaldehyde)	66-25-1
Hexanal	66-25-1
Isovaleraldehyde	590-86-3
m-Tolualdehyde	620-23-5
Nonanal	124-19-6
Octanal	124-13-0
o-Tolualdehyde	529-20-4
Pentanal (propionaldehyde)	110-62-3
Propanal	123-38-6
p-Tolualdehyde	104-87-0

Note: Do not rinse glassware with acetone or methanol. These solvents react with DNPH to form interferences

Stock Standard Solutions

Stock standard formaldehyde solution approximately 1 mg/mL--

- Prepare by diluting 265 µL of formalin to 100 mL with reagent water

Standardization of formaldehyde stock solution –

- Transfer 25 mL of a 0.1M Na_2SO_3 solution to a beaker
- Record the pH
- Add a 25.0 mL aliquot of the formaldehyde stock solution and record the pH
- Titrate this mixture back to the original pH using 0.1 N HCl
- Calculate the formaldehyde concentration using the following equation:

  Concentration (mg/mL) = 30.03 x (N HCl) x (mL HCl) / 25.0 where:

  N HCl = Normality of HCl solution used

mL HCl = mL of standardized HCl solution used

30.03 = MW of formaldehyde

Note: The pH value of the 0.1 Na_2SO_3 should be 10.5 ±0.2 when the stock formaldehyde solution and the 0.1 M Na_2SO_3 solution are mixed together. The pH should be 11.5 ±0.2. It is recommended that new solutions be prepared if the pH deviates from this value

Stock aldehyde(s) and ketone(s) –

- Prepare by adding an appropriate amount of the analyte to 90 mL of methanol
- Dilute to 100 mL to give a final concentration of 1.0 mg/mL. Replace after six weeks, or sooner, if comparison with check standards indicates a problem

Reaction Solutions

2,4-Dinitrophenylhydrazine (DNPH [2,4-$(O_2N)_2$ C_6 H_3]$NHNH_2$ **) (3.00 g/L) –**

- Dissolve 428.7 mg of 70% (w/w) reagent in 100 mL absolute ethanol. Sonication may be needed

Note: If the DHPH does not completely dissolve, filter the solution

Citrate buffer pH 3 (1 M) –

- Prepare by adding 80 mL of 1 M citric acid solution to 20 mL 1 M sodium citrate solution. Mix thoroughly. Adjust pH with 6N NaOH or 6N HCl

Sodium Chloride Solution (saturated) –

- Prepare by mixing an excess of the reagent grade solid with reagent water

Reducing agent, ammonium chloride (100 mg/L) –

- Add to all samples containing residual chlorine. The ammonium chloride may be added as a solid with stirring until dissolved, to each volume of water
- Sodium thiosulfate is not recommended because it may produce a residue of elemental sulfur that can interfere with some analytes

Procedure

1. Derivatization Procedure

a) Quantitatively transfer 100 mL of sample into a 250 mL Florence or Erlenmeyer flask

Note: Other volumes may be used depending on the expected concentration of the analytes. If less than 100 mL is used adjust volume to 100 mL using reagent water

b) Add 4 mL acetate buffer and adjust pH to 5.0 ± 0.1 with 6M HCl or 6M NaOH (if only formaldehyde is being analyzed)

c) Add 4 mL of citrate buffer and adjust the pH to 3.0 ± 0.1 with 6M HCL or 6M NaOH (if other aldehydes are being analyzed)

d) Add 6 mL of DNPH reagent, seal the flask and place in a heated orbital shaker at 40° C for 1 hour

e) Adjust the agitation to produce a gentle swirling of the reaction solution

2. Cartridge Conditioning

a) Assemble a vacuum manifold

b) Place **EUC1812M15** cartridge(s) on manifold

c) Condition the cartridge by adding 15 mL of acetonitrile (ACN)

d) Draw through then rinse using a 15 mL portion of reagent water

e) While cartridge is still wet add 10 mL of dilute citrate buffer (10 mL of 1M citrate buffer dissolved in 250 mL of water)

f) Remove the reaction vessel from the shaker after 1 hour and add 10 mL of

saturated NaCl solution to the flask

g) Quantitatively transfer the reaction solution to the SPE cartridge and apply a vacuum to draw the solution through at 3-5 mL/min
h) Continue to apply vacuum for about 1 minute after the liquid sample has passed through the cartridges

3. **Cartridge Elution**

a) Turn off vacuum and place 10 mL volumetric flasks under cartridges
b) Turn on vacuum and elute the cartridges with approximately 9 mL of acetonitrile directly into flasks
c) Bring the eluate to 10 mL volume with ACN, mix thoroughly, then transfer aliquot to analysis vial and seal

Note: Because this method uses an excess of DNPH, the cartridges will retain a yellow color after this step. The color does not indicate incomplete recovery of the analyte derivatives

HPLC Analysis (suggested)

- **HPLC Column:** C18, 250 mm x 4.6 mm i.d., 5 µm particle size
- **Mobile Phase:** 70/30 methanol/water (v/v)
- **Injection Vol:** 20µL
- **Flow Rate:** 1.2 mL/min
- **UV Detector:** 360 nm
- **Flow Program:**
  - 70/30 methanol/water (v/v) for 20 min,
  - to 100% acetonitrile in 15 minutes
  - hold at 100% acetonitrile for 10 minutes

Representative Retention Times in Reagent Water Using Specified Analysis Conditions

Analyte	Retention Time *(min)*
Formaldehyde	5.3
Acetaldehyde	7.4
Propanal	11.7
Crotonaldehyde	16.1
Butanal	18.1
Cyclohexanone	27.6
Pentanal	28.4
Hexanal	34.1
Heptanal	35.0
Octanal	40.1
Nonanal	40.4
Decanal	44.1

*Adapted from Method 8315a, Determination Of Carbonyl Compounds By High Performance Liquid Chromatography (HPLC), and EPA Method 554, Revision 1.0, James W. Eichelberger, W.J. Bashe (Technology Applications, Incorporated), Environmental Monitoring Systems Laboratory, Office Of Research And Development, U. S. Environmental Protection Agency, Cincinnati, Ohio 45268

EPA Method 1664 Hexane Extractable Material (HEM)

UCT Product Number:
ECUNIOGXF (2000 mg endcapped C18, 83 mL cartridge)

August 2013

Procedure

1. Assemble

a) Assemble cartridge adapters on the vacuum manifold

b) Place **ECUNIOGXF** cartridge(s) on each vacuum station needed

c) Connect the manifold to a suitable trap and attach the trap to a vacuum system capable of attaining a minimum of 25" Hg (635 mm) of vacuum

d) Insert waste collection vial in manifold (optional)

2. Prepare Water Sample

a) Adjust the pH of the sample to less than 2 by adding 5 mL of 6N HCl or 2.5 mL of concentrated H_2SO_4. The pH of deionized water cannot be accurately determined using pH paper

b) If acid was added to the sample in the field, do not add more unless the pH is greater than 2

Note: Gloves are recommended as skin oils may affect final sample weight

3. Condition the Cartridge

a) Rinse the sides of the cartridge and bottle holder with 10 mL of hexane

b) Allow cartridge to soak for 1 minute

c) Draw the hexane through the cartridge using vacuum

d) Discard the hexane from the waste vial

e) Draw full vacuum through the cartridge for 2 minutes to dry

f) Add 10 mL of methanol to the cartridge

g) Slowly draw the methanol through leaving a layer on the cartridge frit

h) Soak for one minute

i) Draw methanol through the cartridge

j) Remove waste vial and discard methanol

k) Immediately, add 80 mL (fill cartridge) of DI water to the cartridge

l) Soak for 1 minute

m) Draw all of the water through the cartridge to waste

4. Sample Addition

a) Add the 1 liter water sample directly to the cartridge

b) Draw the sample through the cartridge under low vacuum. This may take several minutes depending on the solids in the sample. (Note 1) Increase vacuum pressure if necessary. Do not exceed 50 mL/minute for optimum recoveries. This is a fast drip, but not a stream

c) Remove the cartridge and tap any excess water from the bottom of the cartridge

d) Replace cartridge and allow to dry under full vacuum for 10 minutes

e) Remove any water remaining in the bottom support of the cartridge with a paper towel if necessary

5. Elution

a) Prepare an extract collection vial containing about 8 mm (0.3 inch) of anhydrous sodium sulfate

b) Place the vial in the manifold station under the cartridge

c) Add a thin layer of anhydrous sodium sulfate to the top of the cartridge

d) Rinse the water sample bottle with 10 mL of hexane

e) Add the hexane to the cartridge

f) Soak cartridge for 3 minutes. A slow drip of hexane is permissible

g) Turn on vacuum and slowly draw the hexane through the cartridge and into the collection vial

h) Turn off vacuum then repeat steps 5 d) – g) 2 additional times with 10 mL of hexane

i) Do not allow the solvent to splash into the collection vial

j) Add another 10 mL of hexane to the cartridge, rinsing the bottle holder

k) Soak cartridge for 3 minutes

l) Draw the hexane through the cartridge and collect

6. Dry the Extract

a) Remove the collection vial from the manifold and cover with a screw cap

b) If water is still present in the extract (no free moving sodium sulfate is visible) shake the extract to form a water/hexane emulsion and immediately pour the extract through a sodium sulfate funnel or column containing approximately 30 g of anhydrous sodium sulfate held in place with a glass wool plug or frit. **Do not use filter paper**

c) Collect the extract in a clean, pre-weighed vessel

d) Rinse the collection vial with hexane and add it to the sodium sulfate and collect. This will rinse the vial and the sodium sulfate. Poor rinsing of the sodium sulfate will result in low recoveries

7. Gravimetric analysis

a) Carefully evaporate the hexane using a nitrogen evaporator at 40° C until the extract just reaches dryness

Note: Do not over dry or low recoveries will result

b) Allow to cool to room temperature in a desiccator before weighing

c) Record this weight as the mass per unit volume of HEM and report as mg/L

Notes

1) If very high solids are present, add a small plug of glass wool to the cartridge prior to extraction to prevent clogging and improve flow. The glass wool must be thoroughly rinsed with hexane as part of the cartridge during the elution step.
2) Stearic acid must be in solution in the spiking solution or low recoveries will result. If small crystals are present in the spiking solution, sonicate or shake until dissolved.
3) If white crystals are present in the sample bottle after elution, the sample pH was not low enough prior to extraction. Repeat with lower pH
4) HCl will lose strength over time. Sulfuric acid is a good substitute
5) Any residue that does not rinse from the bottle or elute from the cartridge is not HEM
6) Placing a small amount of sodium sulfate on the top frit of the cartridge during the sorbent drying process can reduce the amount of water passed through the cartridge to the final extract

Solid-Phase Extraction and Determination of Organotin by Micro-Liquid Chromatography Electrospray Ion Trap MS
(Part A Water Samples)

UCT Product Number:
ECUNIC18 (C18 endcapped, 1100 mg/83 mL cartridge)

EPA Method 8323

March 2010

Analytes Determined Using This Method

Analyte	CAS No	LOD
Tributyltin chloride	1461-22-9	780 pg
Dibutyltin dichloride	683-18-1	970 pg
Monobutyltin trichloride	1118-46-3	1 ng
Triphenyltin chloride	668-34-8	NA
Diphenyltin dichloride	1135-99-5	920 pg
Monophenyltin trichloride	1124-19-2	NA

Note: Organotins can bond to glass surfaces, glassware must be specially treated. All glassware used in the extraction and analysis of organotins must be acid washed using the following procedure.

- Wash glassware in hot soapy water then rinse with DI water
- Prepare a pH 2 acid bath using 12 N HCl and soak glassware in acid for 24 hours
- Remove glassware from bath, then rinse with DI water followed by a methanol rinse
- Place in a 60°F oven until dry

Procedure

1. **Initial Preparation**
   a) Fill a 2 liter volumetric flask with sample water
   b) Adjust pH to 2.5 by adding about 600 µL of 12N HCl
   c) Stopper flask and invert several times to mix acid
2. **Cartridge Conditioning**
   a) Add 10 mL of methanol to the cartridge to activate

b) Briefly turn on vacuum to draw through a small amount to top of frit

c) Wait 1-2 minutes

d) Add 10 mL of a methanol/1% acetic acid solution

e) Draw about 2 mL through the cartridge then turn off vacuum

f) Let solution sit for 1-2 minutes then draw through

g) Add 10 mL of reagent water to cartridge and partially draw through

Note: Do not let the cartridge dry out after start of activation otherwise start over at step 2. a)

3. Sample Extraction

a) Add the 2 liter sample to the cartridge and draw through at approximately 50 mL/minute (fast drip)

b) Rinse volumetric flask and cartridge sides with 100 mL of reagent water and draw through

4. Elution

a) Dry cartridge by drawing full vacuum for 10 minutes

b) Place a clean, treated collection tube in the manifold

c) Add a **first** portion of 10 mL of methanol/1% acetic acid solution to the cartridge, rinsing the sides during addition, then slowly draw through cartridge

d) Add a **second** 10 mL portion of methanol/1% acetic acid solution to the cartridge, then slowly draw through

e) Add a **third** 10 mL portion of methanol/1% acetic acid solution to the cartridge, then slowly draw through

Micro-concentration by TurboVap® Nitrogen Evaporation

1. Place the concentrator tube in the TurboVap® or other analytical evaporator in a lukewarm water bath at 30° C
2. Evaporate the solvent volume to 0.5 mL using a gentle stream of clean, dry N_2
3. The internal wall of the tube must be rinsed down several times with the final solvent (methanol/1% acetic acid) during the evaporation
4. Do not allow the extract to become dry
5. Transfer the extract to a 2 mL glass vial with a PTFE-lined screw-cap or crimp-top vial and store refrigerated at 4° C
6. Sample is ready for μ-LC-ES-ITMS analysis

Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC) Aqueous Matrices

UCT Product Number:
ECDVB156 (500 mg DVB, 6 mL cartridge)

EPA Method 8330

September 2009

RCRA Compounds Using This Method
Table 1

Analyte	CAS	Abbreviation	% Recovery n=3
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	2691-41-0	HMX	100
Hexahydro-1,3,5-trinitro-1,3,5-triazine	121-82-4	RDX	110
1,3,5-Trinitrobenzene	99-35-4	1,3,5-TNB	100
1,3-Dinitrobenzene	99-65-0	1,3-DNB	100
1,4-Dinitrobenzene	10025-4	1,4-DNB	97
Methy-2,4,6-trinitrophenylnitramine	47945-8	Tetryl	85
Nitrobenzene	98-95-3	NB	100
2,4,6-Trinitrotoluene	118-96-7	TNT	94
4-Amino-2,6-dinitrotoluene	19406-51-0	4-Am-DNT	120
2-Amino-2,6-dinitrotoluene	35572-78-2	2-Am-DNT	110
2,4-Dinitrotoluene	121-14-2	2,4-DNT	98
2,6-Dinitrotoluene	606-20-2	2,6-DNT	110
2-Nitrotoluene	88-72-2	2-NT	90
3-Nitrotoluene	99-08-1	3-NT	91
4-Nitrotoluene	99-99-0	4-NT	92
Nitroglycerin	55-63-0	NG	100
Pentaerythritol tetranitrate	78-11-5	PETN	100
3,5-Dinitroaniline	618-87-1	3,5-DNA	68
1-Nitronaphthalene	86-57-7	NN	97
o-Dinitrobenzene	528-29-0	o-NB	100

Safety

- Extra caution that should be taken when handling the analytical standard neat material to prevent detonation

Interferences

- 2, 4-DNT and 2, 6-DNT elute at similar retention times on C18 columns using method separation conditions. If it is not apparent that both isomers are present or are not detected an isomeric mixture should be reported
- Tetryl is thermally labile (decomposed with heat at temperature above room temperature) and decomposes in methanol/water solutions. All aqueous samples expected to contain tetryl should be diluted with acetonitrile and acidified with sodium bisulfate to pH <3 prior to filtration
- Degradation products of tetryl appear as a shoulder on the 2,4,6-TNT peak when using C18 columns

Note: All samples should be stored at 2° to 4° C prior to extraction and should be extracted within 14 days of collection

Sample Preparation--Aqueous matrices, (e.g. water)
(from Method 3535)
Important Notes:

- Any particulate matter in the original sample must be included in the sample aliquot that is extracted.
- The sample container must be rinsed with solvent as the majority of organic analytes are hydrophobic and may adhere to the sample container surfaces.
- Do not concentrate explosives residue to dryness as they may DETONATE
- For explosives and nitramines or nitroaromatics the extraction pH should be as received in the sample
- Using a graduated cylinder, measure 1 liter of sample water. A smaller sample size may be used when analytical sensitivity is not a concern
- Add methanol (ACN if tetryl is being analyzed) so that the sample is 0.5% v/v. Add surrogate standards to all samples and blanks
- Add matrix spikes standards to representative sample replicates
- Adjustment of sample pH may result in precipitation or flocculation reactions and potentially remove analytes from the aqueous portion. Transfer the precipitate with rinses to the SPE extraction cartridge
- Do not let the cartridge dry out after cartridge conditioning with acetonitrile (ACN)

Glass Apparatus and SPE Cartridge Washing

Analyte	1st solvent wash	2nd solvent wash	3rd solvent wash
Explosives	5 mL acetone	15 mL isopropanol	15 mL methanol
Nitramines, Nitroaromatics	5 mL ACN	15 mL ACN	

1. **Cartridge Conditioning**
   a) Follow the 4 steps in the table below for solvent quantities and soak times

Analyte	Condition Step 1	Step 2	Step 3	Step 4
Explosives	20 mL ACN, 3 min*	20 mL ACN	50 mL DI water	50 mL DI water
Nitramines, Nitroaromatics	15 mL ACN, 3 min*	30 mL DI water	----	----

   b) Draw solvents through the cartridge under low vacuum

Do not let the cartridge dry out once cartridge is conditioned. This will affect analyte recovery

2. **Sample Extraction**
   a) Add the contents of the sample bottle to the cartridge
   b) Adjust vacuum to about 10-15 mm Hg to obtain a uniform flow rate of about 10 ml per minute.
   c) After all the sample is drawn through, draw air through the cartridge for 15 minutes to dry it
   d) Do not dry for longer than 20 minutes as lower recovery may result

3. **Cartridge Elution**
   a) Insert a collection tube in the base of the vacuum manifold

For Explosives

   b) Add 4 mL of ACN and soak for 3 minutes
   c) Draw through using gravity flow or very low vacuum into a collection tube
   d) Store extract in freezer until analysis

For Nitramines and Nitroaromatics

   b) Add 5 mL ACN, soak for 3 minutes
   c) Draw through using a gravity flow or very low vacuum into a collection tube
   d) Store extract in freezer until analysis

4. Extract Concentration (if necessary)

a) Concentrate the extract to 0.7 mL under a gentle stream of nitrogen in a warm bath at 40° C

b) Transfer the extract to a 1 mL volumetric flask

c) Add internal standard for an extract concentration of 5 µg/mL

d) Extract is now ready for analysis by HPLC

RP-HPLC Columns for the Analysis of Explosive Residues	
Primary Columns	C-18 reversed-phase HPLC column, 25-cm x 4.6-mm, 5 µm C8 reversed-phase HPLC column, 15-cm x 3.9-mm, 4 µm
Secondary Columns	CN reversed-phase HPLC column, 25-cm x 4.6-mm, 5 µm Luna Phenyl-Hexyl reversed-phase HPLC column, 25-cm x 3.0-mm, 5 µm

Injection volume: 100 µL
UV Detector: Dual 254 & 210 nm or Photodiode Array
Mobile phase: For C18 & CN column, 50:50 methanol:water
Flow Rate: 1.5 mL/minute

Retention Times and Capacity Factors

Analyte	LC-18 RT minutes	LC-CN RT minutes
HMX	2.44	8.35
RDX	3.78	6.15
1,3,5-TNB	5.11	4.05
1,3-DNB	6.16	4.18
3,5-DNA	6.90	NA
Tetryl	6.93	7.36
NB	7.23	3.81

NG	7.74	6.00
2,4,6-TNT	8.42	5.00
4-Am-DNT	8.88	5.10
2-Am-DNT	9.12	5.65
2,6-DNT	9.82	4.61
2,4-DNT	10.05	4.87
2-NT	12.26	4.37
4-NT	13.26	4.41
PETN	14.10	10.10
3-NT	14.23	4.45

*For complete details on Method 8330 "Nitroaromatics and Nitramines by High performance Liquid Chromatography" Revision 2 October 2006, the analyst is referred to: National Exposure Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, OH 45268 and Method 3550 Revision 0, December 1996

Alternative Test Procedure for the Measurement of Organochlorine Pesticides and Polychlorinated Biphenyls in Wastewater

UCT Part Numbers:
ECUNIC18 (1100 mg endcapped C18, 83 mL) or
EEC181M6 (1000 mg endcapped C18, 6 mL)

Optional:
ECSS15M6 (5000 mg Na_2SO_4, 6 mL)
ECCU01K (1 kg activated copper granules)
EUFLS1M6 (1000 mg PR Grade Florisil®, 6 mL)

EPA Method 608 ATP*

May 2013

This is a gas chromatographic (GC) method for determination of compounds listed below in municipal and industrial discharges. The EPA has approved the use of C18 cartridges for this method.

Analytes Recovered Using Method 608ATP

Analyte	CAS
Aldrin	309-00-2
α-BHC	319-84-6
β-BHC	319-85-7
γ-BHC (Lindane)	58-89-9
δ-BHC	319-86-8
α-chlordane	5103-71-9
γ-chlordane	5103-74-2
4,4'-DDD	72-54-8
4,4'-DDE	72-55-9
4,4'-DDT	50-29-3
Dieldrin	60-57-1
Endosulfan I	959-98-8
Endosulfan II	33213-65-9
Endosulfan sulfate	1031-07-8
Endrin	72-20-8
Endrin Aldehyde	7421-93-4
Endrin Ketone	53494-70-5
Heptachlor	76-44-8
Heptachlor epoxide	1024-57-3
Methoxychlor	72-43-5
Toxaphene	8001-35-2
PCB-1016	12674-11-2
PCB-1221	1104-28-2
PCB-1232	11141-16-5
PCB-1242	53469-21-9
PCB-1248	12672-29-6
PCB-1254	11097-69-1
PCB-1260	11096-82-5

Procedure

1. Condition Cartridge

a) Insert cartridge(s) into the manifold or automated extraction system

b) Wash with 10 mL of methylene chloride ($MeCl_2$)

c) Soak for 1 minute then draw through to waste

d) Draw air under full vacuum to dry cartridge

e) Add 10 mL of methanol (MeOH) then slowly draw through to top of frit

f) Soak for 1 minute

Note: Do not let the cartridge go dry after addition of methanol otherwise repeat at step1) e)

g) Rinse the cartridge with 10 mL of reagent water

h) Draw through leaving a thin layer on top of frit

2. Sample Extraction

a) Adjust 1 liter of sample pH to < 2 using sulfuric acid

b) If sample water is high in suspended solids, allow particulates to settle then slowly decant the water in the bottle. Once most of the water passes through the cartridge add the solids portion

c) Draw the sample water through the cartridge over a 20-30 minute time period (fast drip) by adjusting the vacuum

d) Dry the cartridge by drawing air under full vacuum through for 10 minutes

3. Extract Elution

a) Insert a collection tube into the vacuum manifold

b) Add 5 mL of acetone to the sample bottle then swirl

c) Add this to the cartridge

d) Soak for 1 minute and slowly collect eluate

e) Add 20 of methylene chloride to the sample bottle cover and shake. Add this to the cartridge

f) Soak for 2 minutes and slowly collect eluate

g) Rinse the inside walls of the sample bottle using 10 mL of methylene chloride then transfer solvent to the cartridge using a disposable pipette rinsing the inside of the cartridge

h) Soak for 2 minutes then collect eluate

4. Sample Drying

a) Pour the combined elutes together through a drying tube **ECSS15M6**. Alternatively, use 5 grams of sodium sulfate over a bed of glass wool in a funnel

b) Rinse the drying tube or sodium sulfate bed with 2 x 3 mL portions of 1 methylene chloride

c) Concentrate sample using a Kuderna-Danish (KD) concentrator while performing solvent exchange into hexane

d) Concentrate sample under a gentle stream of N_2 while gently heating in a water bath. **Other drying techniques may be used**

e) Rinse the inside walls of the concentrator tube two or three times with hexane during the evaporation

f) Adjust the final volume of the extract to 10 mL

Florisil PR® or Copper Granule Clean-up Procedure (if needed)

Clean-up procedures may not be needed for relatively clean samples. If required, the following procedure can be used to remove polar interferences from organochlorine pesticide and PCB extracts in hexane prior to analysis.

5. Florisil PR® Clean-Up

a) Place a cartridge in a vacuum manifold

b) Pre-rinse the Florisil® column with 10 mL of 90:10 hexane/acetone using gravity flow (a low vacuum may be necessary to start flow)

c) Discard solvent

d) Add a collection tube under the column

e) Add a 2 mL aliquot of the sample extract (in hexane) to the cartridge

f) Collect extract by gravity

g) Add 10 mL of 90:10 hexane/acetone to the cartridge

h) Continue to collect by gravity or low vacuum

i) Gently evaporate the extract to a volume of 1 mL

j) Adjust eluate to a final volume of 2 mL with hexane

k) Sample is now ready for analysis

6. Sulfur Clean-up

a) Place 4 grams of **ECCU01K** copper granules in a glass vial

b) Add 2 mL of liquid sample extract to the vial

c) Seal the glass vial and mix sample with copper for 2 minutes

d) Allow to stand for approximately 10 minutes

e) If sample contains high levels of sulfur, repeat process with 4 grams of fresh copper granules

Note: For the analysis of PCB type analytes, copper may reside in the extract

7. Analysis--GC/ECD

a) Transfer clean extract to autosampler vial

b) Sample is now ready for analysis

*The EPA has accepted the use of C18 bonded phases in packed cartridge format expanding the method from a disk only approach. For complete details on Method 607ATP, the analyst is referred to: "An alternative test procedure for the measurement of organochlorine pesticides and polychlorinated biphenyls in waste water", Federal register/Vol.60, No.148, August 2, 1995, Environmental Monitoring Systems Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, OH 45268

Florisil® is a registered trademark of U.S. Silica

Extraction of Metals

UCT Part Number:
EUTAX15Z (Tri-acetic Acid 500 mg/10 mL)

February 2009

Metals: Tin, Nickel, Mercury, Copper, Chromium, Ruthenium

Matrix: Water, Blood, Biological Fluids, Organic Solvents & Tissue Homogenates

1. Sample Pre-treatment

- It is important when using ion exchangers to adjust the pH of the analyte of interest so that it is totally ionized. Information about the analyte pKa is important

Aqueous or Organic Solvent Samples:

- Adjust the sample to pH 7 with 100 mM dibasic sodium phosphate buffer or ammonium hydroxide then vortex

Whole Blood, Serum or Plasma:

a) To 1 ml of sample add 4 ml of D.I. H20 and vortex

b) Let stand 5 minutes and centrifuge for 10 minutes at 2000 rpm and discard pellet

c) Adjust to pH 9.0 with 100 mM dibasic sodium phosphate buffer or ammonium hydroxide

2. Column Conditioning

a) Add 3 ml of methanol and draw to waste

b) Add 3 ml of water and draw to waste

c) Add 3 ml of buffer pH 7.0 and draw to waste leaving sorbent wet

3. Sample Application

a) Apply the sample to the column at a rate of 1 ml per minute. A faster rate of application may exceed the rate of ion-exchange

4. Analyte Purification

a) Wash the column with 2 ml of pH 7.0 buffer used in column equilibration.

5. Elution

a) Elute with 3 ml of acidic methanol (2% HCl, pH 2.0).

Alternative eluants:

- Elute with 3 ml of acidic methanol (Formic acid to pH 2.0).
- Elute with 3 ml of 0.1 M Nitric Acid (pH 2.0).

Ion Exchange Sorbents for Metals Extraction-Analysis & Sorbent Use Selection Guide

UCT Product Number:
UCT ENVIRO-CLEAN® (Ion-Exchange Cartridges)*

January 2010

The determination of trace metals in aqueous environmental samples or other matrices often require sample pretreatment and clean-up procedures prior to analysis by using specific ion-exchange sorbents. The sorbents are used to eliminate matrix interferences and achieve high concentrations of metal ions for good analytical accuracy. They are important when using such techniques as AA, IES and ICP-AES.

The use of ion-exchange sorbents for the preconcentration, separation, and determination of metal ions for trace analysis is well established in the literature. Selection of an appropriate sorbent ensures both high efficiency in metal chelating while minimizing the mass of sorbent required for a particular analytical task. A high efficiency sorbent means that a smaller bed mass may be used thereby reducing the quantity of solvent required for elution yielding greater analytical sensitivity.

Recommendations in this application note include the following metal ions:

Zinc (II)	Arsenic (V)	Tin (IV)	Selenous IV)
Mercury (II)	Chromium (III)	Copper (II)	Platinum (0)

Other metal ions may be extracted by the use of these ion-exchange sorbents

Sorbent Selection for Metals Extraction

Solid-phase sorbents have differing capacity and selectivity for various metal ions due to the specific nature of the ion-exchange functional group, the metal species and the valence state of the metal of interest. Depending on the specific metal ion of interest, elution of the cartridge may be most efficient using both the acid followed by the base elution procedure. This can be determined by looking at the following Extraction Protocol Tables. For example, when eluting Hg(II) from PSA the highest recovery is obtained using acid elution (green box) followed by base elution (yellow box).

Sample Analysis

1. Sample Extraction

a) Place a UCT ion exchange cartridge on a SPE manifold

Note: Cartridge selection will depend on the volume of sample or the concentration of metal to be extracted

b) Condition 1 mL cartridge by adding 3 mL of methanol. (Larger cartridges will require a larger volume of solvent and water wash volume in steps c) and d))

c) Add 3 mL of reagent water and allow to drip through the cartridge

Note: Do not allow the cartridge to dry out after addition of water, otherwise repeat step d)

d) Add 10-50 mL of sample water to the cartridge. A larger sample volume may be used depending on metal concentration or suspended solids content

e) Adjust vacuum setting so that the water flows at 1-3 mL/minute until sample has passed completely through the cartridge

f) Allow the cartridge to air dry for about 1 minute under full vacuum

2. Elution--Acid

a) Prepare a 100 mM nitric acid elution solution

b) Place a collection vial in the vacuum manifold

c) Add 3 mL of the nitric acid solution to the cartridge

d) Adjust flow rate for a flow of 1-3 mL/minute

e) Dilute eluant to an appropriate volume for detection using reagent water

f) Sample is ready for analysis

3. Elution--Base

a) Prepare a 100 mM triethylamine elution solution

b) Place a collection vial in the vacuum manifold

c) Add 3 mL of the triethylamine solution to the cartridge

d) Adjust flow rate for a flow of 1-3 mL/minute

e) Dilute eluant to an appropriate volume for detection using reagent water

f) Sample is ready for analysis

4. **Analysis**

a) Prepare calibration curves for use with atomic absorption (AA) or Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) using appropriate metallic ion standards

Extraction Protocol Tables

How to use these tables: When choosing an ion-exchange sorbent to capture arsenic (V) for example, all ion-exchange sorbents will capture a small quantity of metal ions, however, only a base extraction would elute metal ions from these sorbents. For extraction of zinc ions, all sorbents would have moderate to high capacity but elution could only occur from the sorbent using acidic elution conditions.

Acid Extraction Protocol

Sorbent	Cu (II)	Zn (II)	As (V)	Sn (IV)	Se (IV)	Hg (II)	Cr (III)	Pt (0)
PSA								
BCX-HL								
CCX								
TAX								
THX								
NAX								

Base Extraction Protocol

Sorbent	Cu (II)	Zn (II)	As (V)	Sn (IV)	Se (IV)	Hg (II)	Cr (III)	Pt (0)
PSA								
BCX-HL								
CCX								
TAX								
THX								
NAX								

Good to High Capacity
Moderate Capacity
Little or No Capacity

Ion-Exchange Sorbent Key

PSA	Primary secondary amine
BCX-HL	Benzene sulfonic acid –high load
CCX	Carboxylic acid
TAX	Triacetic acid
THX	Sulfhydryl (thiopropyl)
NAX	Aminopropyl

Primary Secondary Amine (PSA)

The PSA ion-exchange sorbent has a significant capacity for Hg(II) Se(IV) followed by a lesser capacity for Sn(IV), Cu(II), Zn(II) and Cr(III). Metal ions are readily eluted from PSA by the use of weak acid solutions such as 100 mM nitric acid solution. Additional recovery for selenium can be obtained by following the acid elution by the use of 100 mM triethylamine solution

Benzenesulfonic Acid-High Load (BCX-HL)

The BCX-HL ion-exchange sorbent is the least selective of all ion-exchange sorbents and has significant capacity for Hg(II) and Sn(IV) thus ensuring high extraction efficiency for trace analysis. It is also a strong sorbent for Cu(II), Zn(II), Cr(III) and small amounts of Pt. In most cases, metal ions are readily eluted from BCX-HL by the use of 100 mM nitric acid solution. Improvement in Hg(II) recovery yield and Sn(IV) can be achieved when eluting with 100 mM triethylamine solution.

Carboxylic Acid (CCX)

The CCX sorbents have high selectivity for Sn(IV) and Hg(II). Metal ions are readily eluted from CCX by the use of weak acid solutions such as 100 mM nitric acid solution. Sn(IV) is eluted using 100 mM triethylamine solution. Additional Hg(II) is released under basic elution.

Triacetic Acid (TAX)

TAX sorbents have the highest affinity for Sn(IV) and Hg(II) followed by lesser amounts of Cu(II) and Zn(II). Metal ions are readily eluted from TAX by the use of weak acid solutions such as 100 mM nitric acid solution. Sn(IV) is eluted using 100 mM triethylamine solution. Additional Hg(II) is released under basic elution.

Sulfhydryl THX (thiopropyl)

THX sorbents have the highest affinity for Hg(II) and Sn(IV), and approximately equal weights of Sn(IV) and Cu(II). Metal ions are readily eluted from THX by the use of weak acid solutions such as 100 mM nitric acid solution. Sn(IV), Se(IV) and Hg(II) are eluted using 100 mM triethylamine solution.

Aminopropyl (NAX)

The NAX ion-exchange sorbent has a significant capacity for Hg(II) followed by Se(IV). Metal ions are readily eluted from NAX by the use of weak acid solutions such as 100 mM nitric acid solution. Additional Hg(II) is released under basic elution.

*UCT ENVIRO-CLEAN® Ion-exchange cartridges are available in a variety of cartridge sizes, sorbent mass and particle size to most analytical requirements. For further information, contact UCT.

DCN-105001-181