

**Analysis of PCBs, Pesticides, and PAHs in  
Air and Precipitation Samples:  
Sample Preparation Procedures**

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**SOP #CH-PR-001.3**

**March 1995**

**Revision 3.0**



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### 1.0 Scope and Applications

- 1.1 This procedure details the sample preparation methods utilized at the ISWS, Office of Atmospheric Chemistry, Trace Organic Toxicants Lab as applied to the Lake Michigan Mass Balance (LMMB) and Lake Michigan Loading Study (LMLS) projects. The procedures apply to XAD-2 cartridge, filter, and XAD-2 precipitation samples. The following analytes are measured by this SOP:

#### Polychlorinated Biphenyls (PCBs) - Total and 105 congener peaks

congener (BZ)	CAS #
1	2051-60-7
3	2051-62-9
4+10	13029-08-8, 33146-45-1
6	25569-80-6
7+9	33284-50-3, 34883-39-1
8+5	34883-43-7, 16605-91-7
12	2974-92-7
13	2974-90-5
15+17	2050-68-2, 37680-66-3
16	28444-78-9
18	37680-65-2
19	39444-73-4
21	55702-46-0
22	38444-85-8
27	38444-76-7
25	55712-37-3
24	55702-45-9

**Polychlorinated Biphenyls (PCBs) Continued**

<b>congener (BZ)</b>	<b>CAS #</b>
26	38444-81-4
29	15862-07-4
31+28	16606-02-3, 7012-37-5
32	38444-77-8
33	38444-86-9
37	38444-90-5
40	8444-93-8
41+71	52663-59-9, 41464-46-4
42	36559-22-5
43	70362-46-8
44	41464-39-5
45	70362-45-7
46	41464-47-5
47	2437-79-8
48	70362-47-9
49	41464-40-8
51	68194-04-7
52	35693-99-3
53	41464-41-9
56+60	41464-43-1, 33025-41-1
63	74472-34-7
64	52663-58-8
66	32598-10-0
70+76	32598-11-1, 70362-48-0
74	32690-93-0
77	32598-13-3
81	70362-50-4
82	52663-62-4

**Polychlorinated Biphenyls (PCBs) Continued**

<b>congener (BZ)</b>	<b>CAS #</b>
83	60145-20-2
87	38380-02-8
89	73575-57-2
91	68194-05-8
92+84	52663-61-3, 52663-60-2
95	38379-99-6
97	41464-51-1
99	38380-01-7
100	39485-83-1
101	37680-73-2
107	70424-68-9
110	38380-03-9
114+131	74472-37-0, 61798-70-7
118	31508-00-6
119	56558-17-9
123+149	65510-44-3, 38380-04-0
128	38380-07-3
129	55215-18-4
130	52663-66-8
132+153+105	38380-05-1, 35065-27-1, 32598-14-4
134	52704-70-8
135+144	52744-13-5, 68194-14-9
136	38411-22-2
137+176	35694-06-5, 52663-65-7
141	52712-04-6
146	51908-16-8
151	52663-63-5
156	38380-08-4
157+200	69782-90-7, 52663-73-7
158	74472-42-7
163+138	74472-44-9, 35065-28-2

**Polychlorinated Biphenyls (PCBs) Continued**

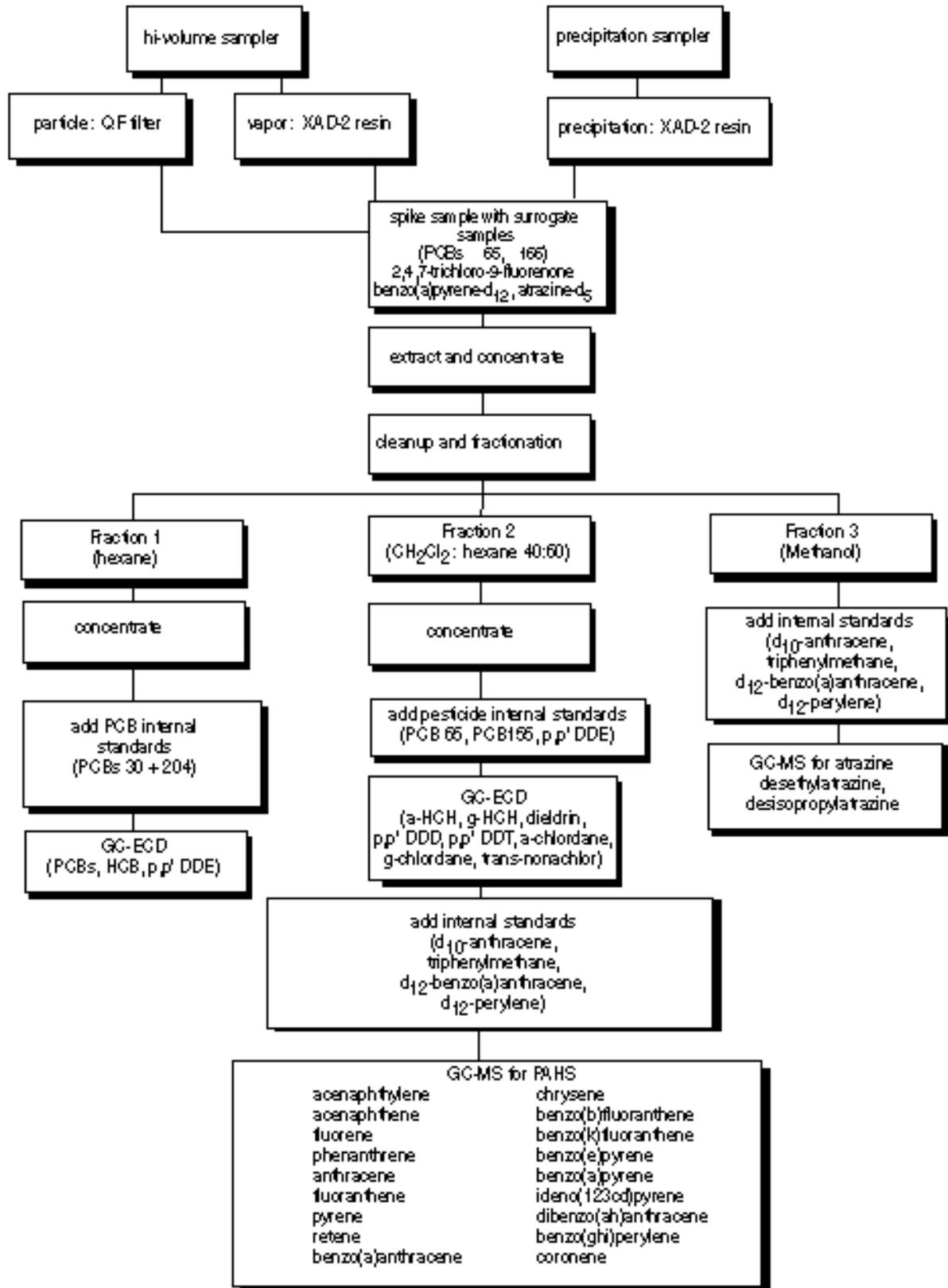
<b>congener (BZ)</b>	<b>CAS #</b>
167	52663-72-6
170+190	35065-30-6, 41411-64-7
174	38411-25-5
175	40186-70-7
177	52663-70-4
178	52663-67-9
180	35065-29-3
183	52663-69-1
185	52712-05-7
201	40186-71-8
202+171	2136-99-4, 52663-71-5
196	42740-50-1
203	52663-76-0
205	4472-53-0
206	40186-72-9
207	52663-79-3
208+195	52663-77-1, 52663-78-2
209	2051-24-3

<b>Pesticide</b>	<b>CAS #</b>
atrazine	1912-24-9
desethylatrazine (DEA)	6190-65-4
desisopropylatrazine (DIA)	1007-28-9
dieldrin	60-57-1
a-chlordane	5103-71-9
g-chlordane	5103-74-2
t-nonachlor	39765-80-5
a-hexachlorocyclohexane (a-HCH)	319-84-6
g-hexachlorocyclohexane (g-HCH)	58-89-9
hexachlorobenzene (HCB)	118-74-1
p,p'-DDD	72-54-8
p,p'-DDE	72-55-9
p,p'-DDT	50-29-3

<b>Polycyclic Aromatic Hydrocarbons (PAHs)</b>	<b>CAS #</b>
acenaphthene	83-32-9
acenaphthylene	208-96-8
anthracene	120-12-7
benzo(a)anthracene	56-55-3
benzo(a)pyrene	50-32-8
benzo(b)fluoranthene	205-99-2
benzo(e)pyrene	192-97-2
benzo(ghi)perylene	191-24-2
benzo(k)fluoranthene	207-08-9
chrysene	218-01-9
coronene	191-07-1
dibenzo(a,h)anthracene	53-70-3
fluoranthene	206-44-0
fluorene	86-73-7
indeno(123cd)pyrene	193-39-5
phenanthrene	85-01-8
pyrene	129-00-0
retene	483-65-8

- 1.2 Method detection limits (MDL) are defined in CFR, Vol 49, No. 209, October 26, 1984, Appendix B to Part 136. Matrix specific MDLs are determined by spiking 7-10 clean matrix samples with the analytes of interest and processing them through the entire extraction, cleanup, and analysis procedure.
  
- 1.3 The instrument detection limit (IDL) refers to the smallest signal above background noise that an instrument can reliably detect. The IDL is determined from a data set comprised of three separate chromatographic runs of a low level calibration standard; each run contains 7-10 analyses of the standard. The IDL equals the Student's *t* value (n-1) multiplied by the standard deviation of this data set.

1.4 Method Flow Diagram



## 2.0 Summary of Method

The analytes are extracted from XAD-2 resin or filter samples by Soxhlet extraction with hexane: acetone (50:50) followed by concentration by rotary evaporation. After extraction, interfering compounds are removed and analytes separated into different fractions with silica gel (3% deactivated). The first fraction (hexane) contains all PCBs and the pesticides HCB and DDE. The second fraction (40% DCM, 60% hexane) contains all PAHs and pesticides  $\alpha$  and  $\beta$  HCHs, dieldrin, DDD, DDT,  $\gamma$  chlordane,  $\delta$  chlordane, and t-nonachlor. Fraction three (methanol) contains atrazine and two metabolites (DEA, DIA). The samples are then concentrated to the desired volume with a slow stream of ultra-pure nitrogen. Final volumes depend on sample matrix, site, and date. Each sample is spiked with a known amount of internal standard. Subsamples are then transferred to autosampler microvials for capillary GC-ECD or GC-Ion Trap MS analysis.

## 3.0 Definitions

- 3.1 *Internal Standard (IS)* -- A pure analyte(s) added to a sample extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same solution.
- 3.2 *Surrogate Analyte (SA)* -- A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction or other processing, and is measured with the same procedures used to measure other sample components. The purpose of the SA is to monitor method performance with each sample.
- 3.3 All other terms are defined in the QAPjP, Revision 5, July 1995.

## 4.0 Interferences

Method interferences may be caused by contaminants in solvents, the sampling matrix, reagents, glassware, and other sample processing apparatus that lead to anomalous peaks or elevated baselines in gas chromatograms. Laboratory equipment and reagents will be monitored by the inclusion of quality control samples with each batch of samples prepared. Individual samples may contain interferences which will require additional sample preparations. All sample preparation details will be documented.

## 5.0 Safety

- 5.1 The toxicity or carcinogenicity of each chemical and reagent used in this method has not been precisely defined. However, each one must be treated as a potential health hazard, and exposure to these chemicals should be minimized. Some method analytes have been tentatively classified as known or suspected human or mammalian carcinogens. Pure standard materials and stock standard solutions of these compounds should be handled with suitable protection to skin, eyes, etc.

- 5.2 Chemists working in the laboratory should follow ISWS safety rules :
- 5.2.1 A lab coat is required when working in the lab.
  - 5.2.2 Eye protection with splash resistant safety glasses or safety goggles are required.
  - 5.2.3 Protective gloves should be used while handling samples or standards. Special solvent resistant gloves should be used while handling large amount of solvents.
  - 5.2.4 All solvent work should be done in fume hoods.
  - 5.2.5 Open shoes are not allowed in the laboratory.
  - 5.2.6 Particle mask is required when using dry silica.
  - 5.2.7 Avoid working alone in the laboratory. If work must be performed after hours or in the weekend inform the supervisor or other staff so that your presence is known and will be accounted for in case of an emergency.
  - 5.2.8 Chemicals and solvents are stored under the hoods. Acids must be separated from bases. A rubber bucket is required to transport any chemical.
  - 5.2.9 Gas cylinders should be well secured at all times. Flammable gases are stored in separate storage areas.
  - 5.2.10 Wash hands well after work.
  - 5.2.11 No food or drink is allowed in the laboratory.
  - 5.2.12 In case of minor spillage, get spillage kit to clean the area. A major spill requires the University of Illinois Fire Department to be contacted and the working area evacuated.
  - 5.2.13 MSDS sheets are stored in the laboratory and a copy placed on file with the office administrator.
  - 5.2.14 All chemicals and standards must be labeled with chemical name, date, and initials of person to contact.
  - 5.2.15 Empty chemical bottles should be flushed out with water, or, in case of liquid, allowed to evaporate under a hood before discarding.
- 5.3 Waste disposal
- 5.3.1 Solvents

Label waste containers, *Chlorinated Waste* and *Non-Chlorinated Waste*. Glass bottles used for waste are placed under hoods for convenience. When full, transfer waste to 10 L carboy containers in solvent cabinet. Contact the ISWS Waste Coordinator for removal.

#### 5.3.2 Silica

After solvent has evaporated, pour silica into a disposable glove and discard.

#### 5.3.3 Teflon Boiling Chips

Allow solvent to evaporate then discard.

#### 5.3.4 Glass

Place in 'Broken Glass Disposal Containers'. When containers are full, close according to directions on box and discard per university instructions.

#### 5.3.5 Aluminum Foil

Recycle

#### 5.3.6 Glass Wool

Allow solvent to evaporate then discard.

#### 5.3.7 XAD-2 and Filters

Leave XAD from air sample in Soxhlet under hood until solvent has evaporated then pour into container labeled *Used XAD-2*. Allow filter to dry in hood before discarding. XAD-2 (precip) is discarded.

## 6.0 Equipment and Supplies

### 6.1 Glassware -- General requirements

All glassware must be meticulously cleaned. Large glassware is thoroughly washed with laboratory detergent and hot water. Glassware with bad stains should be rinsed with MeOH or CH<sub>2</sub>Cl<sub>2</sub> before using the soap and water procedure. If still not clean, soak in H<sub>2</sub>SO<sub>4</sub>:HNO<sub>3</sub> (50:50) acid bath overnight, then wash thoroughly with soap and water. Volumetric pipettes used for standards *must* soak in acid bath overnight. Glassware is thoroughly rinsed with tap water, then with DI water and allowed to air dry. The glassware is foil wrapped and heated 450°C for four hours. If glassware is not clean after muffling at 450°C for four hours, muffle at 500°C for four hours. The glassware is cooled to ambient temperature and stored in a clean location.

Small glassware such as stoppers, vials, and disposables are wrapped in foil or placed into a beaker and covered with foil and heated to 450°C for four hours, cooled to ambient temperature,

and stored in a clean location. Vials are capped as soon as they are removed from the oven. Note: Always use dull side of foil towards glassware. Set initial temperature of furnace to 200°C if possible.

- 6.2 Sample vials and bottles -- amber glass vials with Teflon-lined screw caps. Amber colored glass is used for extract and standard storage since some of the method analytes are sensitive to light.
- 6.3 Volumetric flasks -- Various sizes.
- 6.4 Volumetric and graduated pipets -- Various sizes.
- 6.5 Forceps, spatulas, scissors and other stainless steel laboratory supplies. Metal supplies are washed with soap and water, rinsed with tap water, then rinsed with DI water and allowed to air dry. They are then rinsed with  $\text{CH}_2\text{Cl}_2$ , wrapped in foil, and stored in a clean location.  
  
**Note:** Always rinse with  $\text{CH}_2\text{Cl}_2$  immediately before use.
- 6.6 Micropipettor (Drummond or equiv.), glass capillaries -- Various sizes. Preclean capillaries with  $\text{CH}_2\text{Cl}_2$  prior to use.
- 6.7 Teflon stopcocks and Teflon lined caps. Stopcocks and caps are washed with laboratory detergent and hot water, rinsed with tap then DI water, and air dried on kimwipes. The stopcocks are stored in a clean jar or beaker and covered with foil. Caps are rinsed with hexane, air dried, then placed onto their associated bottle or vial.
- 6.8 Cork Rings
- 6.9 Muffle Oven
- 6.10 Drying Oven
- 6.11 Soxhlet extraction apparatus, glassware and heating assembly.
- 6.12 Desiccator
- 6.13 Analytical and top loading balances with check weights.
- 6.14 Rotary evaporator with aspirator pump and chiller circulator
- 6.15 Separatory funnel, various sizes
- 6.16 Round bottom flask and stoppers, various sizes
- 6.17 Chromatography column for silica cleanup - large columns for cartridge samples are 11 x 300 mm (Kimax # 1780011300) with removable PTFE stopcocks, replaceable large bore glass tips, and 100 mL reservoirs. Small columns for rain and filters samples are 11 x 300 mm (Kimax # 4205300214) with size 2 PTFE stopcock plug. A 22 x 155 mm joint (# 668500-1922) is added to the top of the column.

- 6.18 Misc. lab supplies including: Pasteur pipets, beakers, funnels, pipet bulbs, glass rods, rubber hammer
- 6.19 Ultrasonic bath
- 6.20 Pierce Reactitherm, Model 18800, with stainless steel needles
- 6.21 Autosampler vials, caps and inserts

## **7.0 Reagents and Standards**

- 7.1 Solvents - Pesticide quality or equivalent

Methylene Chloride (CH<sub>2</sub>Cl<sub>2</sub>, DCM)

Methanol (MeOH)

Acetone

Hexane

- 7.2 Reagents - Residue grade or equivalent

- 7.2.1 Organic free DI water

- 7.2.2 Glass Wool -- Cut glass wool into 2" pieces, place into a muffled beaker and cover with foil. Muffle at 450°C for four hours. Store in a clean location.

- 7.2.3 Teflon Boiling Chips -- Boiling chip cleanup requires a Soxhlet extraction step as follows:

Thoroughly rinse inside of condenser and outside of joint with methanol then CH<sub>2</sub>Cl<sub>2</sub> from wash bottles. Cover joint and exhaust tube with foil.

Add five or six boiling chips to flask. Add appropriate amount of CH<sub>2</sub>Cl<sub>2</sub> to flask.

Place glasswool plug at the siphon tube opening of the Soxhlet extractor using large tweezers.

Place new teflon boiling chips in Soxhlet extractor.

Assemble flask/Soxhlet apparatus.

Turn on heater to give proper boiling (set variac to 40-45).

Turn on chilled water for condenser.

Extract for 18 to 24 hours.

Turn heat off; let cool 15 to 30 minutes.

Turn off condenser water.

Drain as much solvent from Soxhlet as possible.

Remove boiling chips from Soxhlet and place in a 1 L beaker, cover loosely with foil.

Place boiling chips in a 70°C oven:

Every 10 to 15 minutes, shake beaker to accelerate solvent evaporation.

Let boiling chips remain in oven two to four hours, until dry.

*\*\*\*Warning: Beware of Solvent Fumes.\*\*\**

Place boiling chips in clean sample jar; cover with foil and lid.

Store on shelf.



- 7.2.4 Sodium Sulfate ( $\text{Na}_2\text{SO}_4$ ) -- Place  $\text{Na}_2\text{SO}_4$  into a clean muffled beaker and heat to  $450^\circ\text{C}$  for four hours or overnight, cool to  $100^\circ\text{C}$  in the oven. Place into a clean sample jar, cover with foil and cap. Store in a desiccator. If not used within two weeks, recondition in a  $100^\circ\text{C}$  drying oven overnight. Remove from oven; cover with foil and cap then store in desiccator.
- 7.2.5 Silica Gel (Davisil, grade 634, 100-200 mesh or equivalent)
- 7.3 Standards
- 7.3.1 PCB Stock Standards
- 7.3.1.1 LMMB PCB Intermediate PCB Stock Standard (provided by Mullin June 1994).
- Stock solution provided in sealed ampules with a total congener concentration of  $183\ \mu\text{g}/\text{mL}$ . (Aroclor 1232 =  $75\ \mu\text{g}/\text{mL}$ , Aroclor 1248 =  $54\ \mu\text{g}/\text{mL}$ , Aroclor 1262 =  $54\ \mu\text{g}/\text{mL}$ ). Per M. Mullin the PCB concentration of the intermediate PCB Stock Std is  $170.8\ \mu\text{g}/\text{mL}$  due to the presence of biphenyl and other components in the mix.
- 7.3.1.2 Custom PCB Standard (Ultra Scientific #CUS-937) for Method Detection Limit studies (provided by US EPA July 1994). Stock solution provided in sealed ampules with a certificate of analysis as follows: Lot # 0858
- PCB 1 =  $12.00\ \mu\text{g}/\text{mL}$   
PCB 6 =  $14.20\ \mu\text{g}/\text{mL}$   
PCB 29 =  $6.30\ \mu\text{g}/\text{mL}$   
PCB 49 =  $5.86\ \mu\text{g}/\text{mL}$   
PCB 101 =  $4.93\ \mu\text{g}/\text{mL}$   
PCB 141 =  $2.19\ \mu\text{g}/\text{mL}$   
PCB 180 =  $2.21\ \mu\text{g}/\text{mL}$   
PCB 194 =  $1.69\ \mu\text{g}/\text{mL}$   
PCB 206 =  $2.05\ \mu\text{g}/\text{mL}$   
PCB 209 =  $1.36\ \mu\text{g}/\text{mL}$
- 7.3.1.3 2-chlorobiphenyl (PCB 1), Ultra Scientific (RPC-0069) Stock Standard for enhancement of PCB 1 in the Ultra CUS-937 mix described above. Stock Solution provided by EPA in a sealed ampule with a concentration for PCB 1 =  $100\ \mu\text{g}/\text{mL}$  (Lot No. H 0039)
- 7.3.2 Pesticide and PAH Stock Standards
- Stock standard solutions are purchased from commercial sources (Ultra Scientific, Accustandard, Chem Service, Crescent Chemical) or are obtained from the USEPA repository. When stock solutions are not available, pesticides are purchased as the neat material and gravimetrically prepared in house.



### 7.3.3 Surrogate Standard Solutions

7.3.3.1 Surrogate standards are purchased from commercial sources (Aldrich Chemical, Cambridge Isotope) or are obtained from the USEPA repository. The following surrogate standards are utilized.

PCB 65 (PCB, HCB, DDE surrogate)  
PCB 166 (PCB surrogate)  
2,4,7-trichloro-9-fluorenone (pesticide surrogate)  
atrazine-d5 (atrazine surrogate)  
benzo-(a)pyrene-d12 (PAH surrogate)

7.3.3.2 If stock solutions are not commercially available, they are gravimetrically prepared from the neat material. Individual stock solutions are serially diluted in volumetric flasks to obtain the surrogate spike standard/s. A combined surrogate spiking standard may be prepared to save sample preparation time during the extraction procedure.

7.3.3.3 All samples are spiked with surrogate standards prior to extraction using volumetric pipets or a Drummond pipet and the spike volumes recorded on the sample preparation log.

### 7.3.4 Internal Standard Solutions (ISTDs)

7.3.4.1 Internal Standards are purchased commercially (Ultra Scientific) as a stock standard or as the neat material. The following ISTDs are utilized.

PCB 30 (PCB ISTD)  
PCB 204 (PCB ISTD)  
PCB 65 (Pesticide ISTD)  
PCB 155 (Pesticide ISTD)  
DDE (Pesticide ISTD)  
anthracene-d10 (PAH and atrazine ISTD)  
benzo(a)anthracene-d12 (PAH ISTD)  
perylene-d12 (PAH ISTD)  
triphenylmethane (PAH ISTD)

7.3.4.2 If stock solutions are not commercially available, they are gravimetrically prepared from the neat material. Individual stock solutions are serially diluted in volumetric flasks to obtain the ISTD spiking standard/s.

7.3.4.3 ISTDs are added to the appropriate sample fraction (PCBs in hexane, pesticides and PAHs in 40% DCM, and atrazine in MeOH) prior to GC-ECD or GC-MS analysis. A Drummond micropipet is used for ISTD addition.

### 7.3.5 Chromatographic Calibration Standards

Combined instrument calibration standards are prepared from the individual stock standards by volumetric dilution to obtain five concentration levels. The calibration standard concentrations bracket the expected analyte amounts in samples assayed and are within the working linear range of the detectors. Calibration mixes are prepared specifically for the appropriate instrument and fraction analyzed. The following calibration mixes are prepared.

PCBs, DDE, HCB in the hexane fraction, with surrogate and ISTDs  
chlorinated pesticides in the 40% DCM fraction, with surrogate and ISTDs  
PAHs in the 40% DCM fraction, with surrogate and ISTDs  
atrazine, DEA, and DIA in the MeOH fraction, with surrogate and ISTDs.

### 7.3.6 Matrix Spiking Solutions

7.3.6.1 Combined matrix spiking solutions are prepared from the individual stock standards by volumetric dilution. Combined matrix spike solutions are prepared for each analyte group. The following matrix spike mixes are prepared.

PCBs  
chlorinated pesticides  
PAHs  
atrazine, DEA, DIA

7.3.6.2 The matrix spike solutions will be added to clean sample matrix material prior to extraction to calculate the recovery of individual analytes. One matrix spike will be extracted with each batch of samples. The matrix spike will be added to the sample using a Drummond micropipet or a volumetric pipet and the spiking amounts reported in the sample preparation log.

### 7.3.7 Standard Evaluation

New working standards will be assayed prior to use by comparison with existing standards. Standards must agree within 10% prior to use.

## **8.0 Sample Collection, Preservation and Storage**

8.1 Sample collection, storage, and storage limits are defined in the QAPjP, Revision 5.0, July 1995.

8.2 Extracts are stored in amber vials at -10 to -20°C before and after GC analyses.

## **9.0 Quality Control/Quality Assurance (QC/QA)**

9.1 QA/QC requirements are described in the QAPjP, Revision 5.0, July 1995.

- 9.2 Quality control samples include: field and laboratory blanks, laboratory matrix spikes, laboratory surrogate spikes, and field and laboratory duplicate samples. The laboratory maintains all sample preparation and data records to document the quality of the data generated.

## **10.0 Calibration**

All instrument calibration and analysis are detailed in the following ISWS SOPs:

*Standard Operating Procedure for the Analysis of PAHs and Atrazine by GC/Ion Trap MS, July 1995.*

*Standard Operating Procedure for the Analysis of PCBs and Organochlorine Pesticides by GC-ECD, Revision 3.0, November 1995.*

## **11.0 Filter and XAD-2 Resin Precleaning Procedure**

### **11.1 XAD-2 Resin**

11.1.1 The following supplies are required:

Soxhlet extractor and condenser custom made by Crown Glass Company  
six 3 L round bottom flasks with 29/42 joint  
six glass stoppers (29/42 joint)  
one 1L beaker  
two 400 mL beakers  
heating mantle for 3 L flask  
variable autotransformer

11.1.2 Procedure for vapor sample cartridges

#### *Day 1*

- 1) Place approximately 1 kg XAD-2 in extractor plugged with glass wool.
- 2) Rinse XAD-2 with tap water many times, stirring to remove foam and small particles. Use kimwipes to remove foam.
- 3) Rinse with a small amount of methanol three times to remove water.
- 4) Add 2000 mL of methanol to 3 L flask.
- 5) Add about 20 boiling chips to flask.
- 6) Assemble flask/Soxhlet/condenser apparatus.
- 7) Turn on heater to give proper boiling (set variac to 60-65 for methanol).
- 8) Turn on chilled water for condenser.
- 9) Cover Soxhlet and flask with foil.
- 10) Extract with methanol for 24 hours.

#### *Day 2*

- 1) Turn off heater; cool 15 to 30 minutes.
- 2) Flush as much methanol from Soxhlet as possible.

- 3) Add 2000 mL acetone to 3 L flask.
- 4) Add about 20 boiling chips to flask.
- 5) Turn on heater (set variac to 45 for acetone).
- 6) Cover Soxhlet and flask with foil.
- 7) Extract with acetone for 24 hours.

*Day 3*

- 1) Turn off heater; cool 15 to 30 minutes.
- 2) Flush as much acetone from Soxhlet as possible.
- 3) Add 2000 mL hexane to 3 L flask.
- 4) Add five or six boiling chips to flask.
- 5) Turn on heater (set variac to 40-45 for hexane).
- 6) Cover Soxhlet and flask with foil.
- 7) Extract with hexane for 24 hours.

*Day 4*

- 1) Turn off heater; cool 15 to 30 minutes.
- 2) Flush as much hexane from Soxhlet as possible.
- 3) Add 2000 mL  $\text{CH}_2\text{Cl}_2$  to 3 L flask.
- 4) Add five or six boiling chips to flask.
- 5) Turn on heater (set variac to 40-50 for  $\text{CH}_2\text{Cl}_2$ ).
- 6) Cover Soxhlet and flask with foil.
- 7) Extract with  $\text{CH}_2\text{Cl}_2$  for 24 hours.

*Day 5*

- 1) Turn off heater; cool 15 to 30 minutes.
- 2) Flush as much  $\text{CH}_2\text{Cl}_2$  from Soxhlet as possible. Wait 15 minutes. Drain as much solvent as possible through stopcock (remove stopcock if necessary).
- 3) Add 300 mL hexane to the Soxhlet. Wait 15 minutes, then drain through stopcock. Repeat at least three times, until the level of the solvent in the siphon tube is the same as in the Soxhlet.
- 4) Add 2000 mL hexane to 3 L flask.
- 5) Add five or six boiling chips to flask.
- 6) Turn on heater (set variac to 40-45 for hexane).
- 7) Cover Soxhlet and flask with foil.
- 8) Extract with hexane for 24 hours. Flushing may need to be induced twice before it flushes on its own.

*Day 6*

- 1) Turn off heater; cool 15 to 30 minutes.
- 2) Flush as much hexane from Soxhlet as possible.
- 3) Add 2000 mL 50% acetone/50% hexane to 3 L flask.
- 4) Add five or six boiling chips to flask.
- 5) Turn on heater (set variac to 40-45 for acetone/hexane).
- 6) Cover Soxhlet and flask with foil.
- 7) Extract with acetone/hexane for 24 hours.



*Day 7*

- 1) Turn off heater; cool 15 to 30 minutes.
- 2) Flush as much acetone/hexane from Soxhlet as possible.
- 3) Pour XAD-2 in a beaker and dry overnight in 65°C oven.
- 4) Store in amber bottle in freezer at -20°C for up to three months.
- 5) Keep subsample in separate jar for use in preparation of lab blank and matrix spike.

11.1.3 Procedure for precipitation sample cartridges

*Day 1*

- 1) Place XAD-2 in Soxhlet plugged with glass wool.
- 2) Rinse XAD-2 with water many times, stirring to remove foam and small particles. Use kimwipes to remove foam.
- 3) Rinse with small amount of methanol 3 times to remove water.
- 4) Add 2000 mL methanol to 3 L flask.
- 5) Add about 20 boiling chips to flask.
- 6) Assemble flask/Soxhlet/condenser apparatus.
- 7) Turn on heater to give proper boiling (set variac at 60-65 for methanol).
- 8) Turn on chilled water for condenser.
- 9) Cover Soxhlet and flask with foil.
- 10) Extract for 24 hours.

*Day 2*

- 1) Turn off heater; cool 15 to 30 minutes.
- 2) Flush as much methanol from Soxhlet as possible.
- 3) Add 2000 mL acetone to 3 L flask.
- 4) Add about 20 boiling chips to flask.
- 5) Turn on heater (set variac to 40-45 for acetone).
- 6) Cover Soxhlet and flask with foil.
- 7) Extract with acetone for 24 hours.

*Day 3*

- 1) Turn off heater; cool 15 to 30 minutes.
- 2) Flush as much acetone from Soxhlet as possible.
- 3) Add 2000 mL hexane to 3 L flask.
- 4) Add about 20 boiling chips to flask.
- 5) Turn on heater (set variac to 40-45 for hexane).
- 6) Cover Soxhlet and flask with foil.
- 7) Extract with hexane for 24 hours.

*Day 4*

- 1) Turn off heater; cool 15 to 30 minutes.
- 2) Flush as much hexane from Soxhlet as possible.
- 3) Add 2000 mL CH<sub>2</sub>Cl<sub>2</sub> to 3 L flask.
- 4) Add about 20 boiling chips to flask.

- 5) Turn on heater (set variac to 40 for CH<sub>2</sub>Cl<sub>2</sub>).
- 6) Cover Soxhlet and flask with foil.
- 7) Extract with CH<sub>2</sub>Cl<sub>2</sub> for 24 hours.

*Day 5*

- 1) Turn off heater; cool 15 to 30 minutes.
- 2) Flush as much CH<sub>2</sub>Cl<sub>2</sub> from Soxhlet as possible. Wait 15 minutes. Drain as much solvent as possible through stopcock (remove stopcock if necessary).
- 3) Add 300 mL hexane mixture to the Soxhlet. Wait 15 minutes, then drain solvent through stopcock. Repeat at least three more times, until level of solvent in the siphon tube is the same as in the Soxhlet.
- 4) Add 2000 mL hexane to 3 L flask.
- 5) Add about 20 boiling chips to flask.
- 6) Turn on heater (set variac at 40-45 for hexane).
- 7) Cover Soxhlet and flask with foil.
- 8) Extract with hexane for 24 hours.

*Day 6*

- 1) Turn off heater; cool 15 to 30 minutes.
- 2) Flush as much hexane from Soxhlet as possible.
- 3) Add 2000 mL acetone to 3 L flask.
- 4) Add about 20 boiling chips to flask.
- 5) Turn on heater (set variac at 40-45 for acetone).
- 6) Cover Soxhlet and flask with foil.
- 7) Extract with acetone for 24 hours.

*Day 7*

- 1) Turn off heater; cool 15 to 30 minutes.
- 2) Flush as much acetone from Soxhlet as possible.
- 3) Add 2000 mL methanol to 3 L flask.
- 4) Add about 20 boiling chips to flask.
- 5) Turn on heater (set variac to 60-65 for methanol).
- 6) Cover Soxhlet and flask with foil.
- 7) Extract with methanol for 24 hours.

*Day 8*

- 1) Turn off heater; cool 15 to 30 minutes.
- 2) Turn off condenser water.
- 3) Flush as much methanol from Soxhlet as possible.
- 4) Rinse XAD-2 at least three times with organic-free DI water.
- 5) Store the clean XAD-2 in DI water in amber bottle in the refrigerator at 4°C. (The resin may be stored in this manner for up to three months.)
- 6) Vacuum filter about 50 gm of XAD-2 for use in the preparation of lab blank and matrix spike. Store it in a separate jar at 4°C.

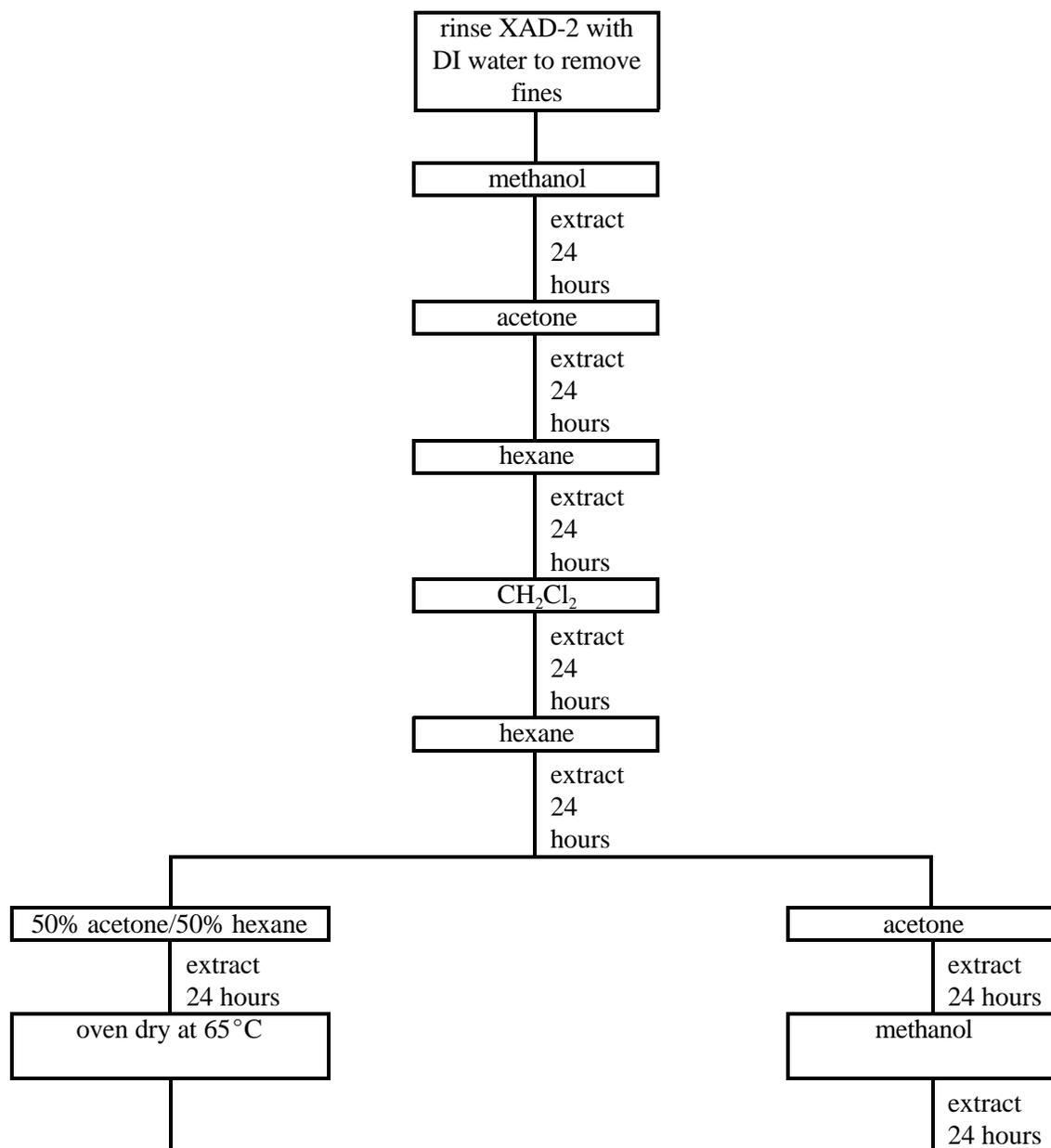
11.1.4 **Notes:** Settings may vary from autotransformer to autotransformer. Check that the solvent is boiling properly (nice rolling boil).

Solvent may not siphon well. Induce siphoning as many times as possible. Allow extra extraction time when improper syphoning occurs.

If XAD-2 is re-used after sample extraction, it is not necessary to rinse with DI water before extracting.

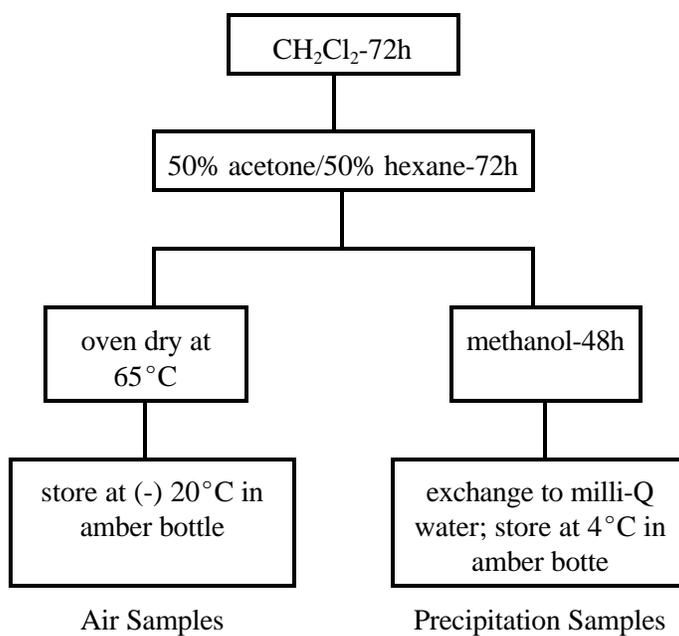
Extract used XAD with CH<sub>2</sub>Cl<sub>2</sub> and acetone:hexane (1:1) for three days each. XAD for precipitation collection requires an additional extraction in methanol for two days.

11.1.5 Flowchart of XAD-2 Precleaning Procedure





### 11.1.6 Flow Chart of Used XAD<sub>2</sub> Precleaning Procedure



### 11.2 Glass fiber (GFF) or Quartz fiber (QFF) Filters

Each filter is wrapped with aluminum foil separately, and muffled to 450°C for four hours. After returning to ambient temperature, about 25 are wrapped in aluminum foil and stored.

## 12.0 Sample Preparation - Extraction

### 12.1 Air Samples, Particulate and Vapor Phase (Filter and XAD-2 Cartridges)

12.1.1 Samples are extracted as a set. A sample set includes up to 12 samples (including one duplicate, one field blank, one lab blank, and one matrix spike). The matrix spike is spiked with known amount of PCBs, Pesticides, PAHs, and atrazine and is used to calculate the recovery of each analyte for that set. A batch code is assigned to each sample set based on the date of extraction (YY, MM, DD) and sample matrix, such as 951107C

(where C = cartridge). All information about the sample set will be recorded on sample preparation log sheets (see Appendix A & B).

#### 12.1.2 Sample extraction requires the following:

large Soxhlet extractor (55/50 and 24/40 joints)  
condenser (55/50 joint)  
500 mL round bottom flask (24/40 joint)  
glass stopper (24/40 joint)  
400 mL beaker

Remove spiking standards from freezer. *Standards must be at ambient temperature before using.* (Ambient temperature is achieved in about two hours.)

Thoroughly rinse inside of condenser and outside of joint with methanol then CH<sub>2</sub>Cl<sub>2</sub> from wash bottles. Cover joint and exhaust tube with foil.

Assemble supplies and samples under hood and/or utility cart. Label flasks.

Add five to six clean teflon chips into 500 mL round bottom flask.

Pour solvent into round bottom flask: 175 mL of acetone and 175 mL of hexane.

#### 12.1.3 Procedure for compositing XAD-2 samples.

Composite information is included on the Sample Log worksheet. Group the samples to be composited for each site on the lab cart.

Label a 400mL beaker with the same site, year and month as the individual samples with "00" in place of the day. eg. VH01C950300.

Check and record the balance calibration using a 50g and 10g weight. If off by greater than 0.1 g, recalibrate.

Tare the labelled beaker.

Weigh out approximately the same amount of each individual sample so the composite final weight is close to 40g.

Record the initial and final weights of the individual samples as well as the total weight of the composite sample on the sample prep. sheet.

Immediately cover beaker with aluminum foil.

#### XAD-2 Procedure:

Place glass wool plug at the siphon tube opening of the Soxhlet extractor using glass or metal rod.

Carefully pour XAD-2 into Soxhlet extractor. Rinse container with solvent (acetone/hexane 1:1) to remove all XAD-2; pour solvent rinse into Soxhlet.

Assemble flask/Soxhlet/condenser apparatus. Place on heating mantle.

#### 12.1.4 Procedure for Compositing Filters

Unwrap one filter at a time.

Trim off the black number at the corner with clean scissors.

Use two pairs of blunt tweezers to fold one filter; place in Soxhlet.

Repeat procedure for all filters in composite sample.  
Assemble flask/Soxhlet/condenser apparatus. Place on heating mantle.  
Rinse tweezers and scissors with  $\text{CH}_2\text{Cl}_2$ .

#### 12.1.5 Surrogate Standard Addition

Using a micropipette dispenser, spike each sample with the PCB, Pesticide, PAH, and atrazine surrogate standards. Record the amount spiked.

12.1.6 Matrix Spike (CMS)

Spike sample medium with the PCB, PAH, Pesticide and atrazine matrix standards. Add surrogate standards used in 12.1.5. Record the amounts added.

12.1.7 Lab Blank (LB)

Spike sample medium with surrogate standards (12.1.5). Record amount added.

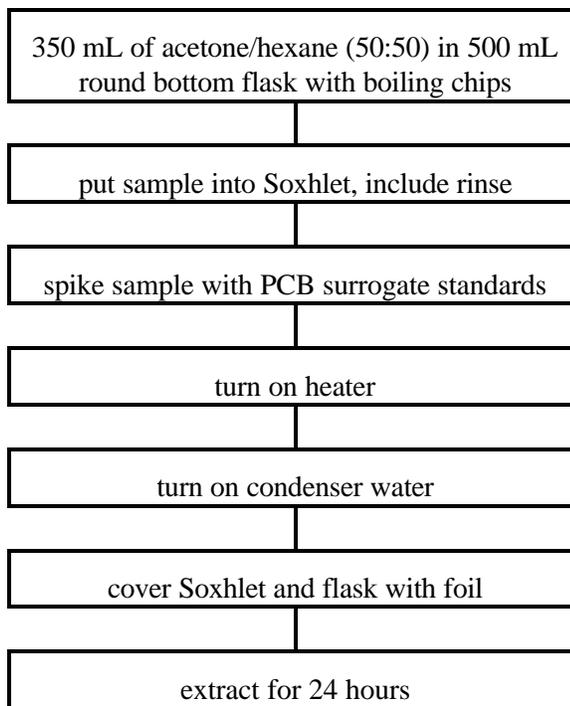
12.1.8 Assemble flask/Soxhlet/condenser unit. Place on heating mantle.

Turn on heating mantles: set Staco heating mantles to 45 or the multi-unit extraction heater to 5. Turn on condenser water. Cover Soxhlet and flask with foil. Extract for 24 hours.

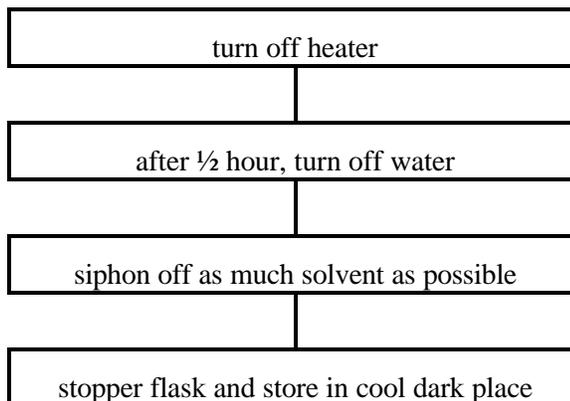
12.1.9 Turn heating mantle off. Let cool 15 to 30 minutes. Siphon off as much solvent from Soxhlet extractor into flask as possible. Detach the flask and insert stopper. Turn off condenser water. Store in cool dark place.

**Notes:** If XAD-2 gets into the flask, see Removing XAD-2 from flask (12.1.10.3). If condensation is a problem, wrap condensers with foil wrapped insulation or with kimwipes.

12.1.9.1 Flow Charts for Air Sample Extraction  
Setting-up extraction:



Taking down extraction:



12.1.10 Rotary Evaporation

12.1.10.1 Fill chamber with DI water. Turn on the chiller circulator.

Set bath temperature:

SOLVENT	TEMPERATURE (°C)
hexane	30-32
acetone	30-32
acetone/hexane	30-32
CH <sub>2</sub> Cl <sub>2</sub>	30
Methanol	40

Rinse joint of steam duct with CH<sub>2</sub>Cl<sub>2</sub>. Attach appropriate splash guard(s) to steam duct. Clamp each joint. Turn on and check vacuum system.

12.1.10.2 Evaporation

Remove boiling chips with large forceps. If XAD-2 is in flask, remove it as described in 12.1.10.3.

Attach flask to splash guard. Clamp joint.

Turn on motor to predetermined rotation speed (usually to the bottom of the indicator line, or about 50 rpm). Evaporation should begin in approximately one minute; solvent should *not* boil.

Evaporate sample down to approximately 2 mL (in a 500 mL round bottom flask, area of liquid should be about the size of a quarter).

Open stopcock of rotary evaporator to release vacuum.

Detach the flask

If exchanges are necessary, add specified amount of hexane from table below, then return flask to splash guard and clamp.

If additional exchanges are not necessary, stopper flask. Store flask under cabinet.

If vacuum unit get hot, turn on cold tap water and allow it to cycle through the bath.

Empty receiving flask into proper waste bottle as needed.

Rinse splash guard with CH<sub>2</sub>Cl<sub>2</sub> before using with a different sample. Splash guards should be washed and muffled after every set of samples.

	Fraction	Amount of hexane to add	# of exchanges	Total # of rotary evaporations	Final volume
After extraction		75 mL	2	3	2-5 mL
After column cleanup	hexane	-----	0	1	1 mL
	40%	25 mL	1	2	1 mL
	methanol	25 mL	2	3	1 mL

#### 12.1.10.3 Removing XAD-2 From Flask

Label another 500 mL flask with sample ID. Decant sample from original flask into clean flask. Hexane rinse the XAD-2 remaining in flask and add rinse to new flask. Rotary evaporate new flask using above procedures.

#### 12.1.10.4 Clean-up

Turn off heater and motor on rotary evaporator. Turn off chiller. Empty receiving flask into proper waste solvent bottle. Cover steam duct with foil. Turn off water supply to the vacuum unit, if used.

### 12.2 Precipitation Samples

#### 12.2.1 Sample extraction requires the following:

- large Soxhlet extractor (55/50 and 24/40 joints)
- condenser (55/50 joint)
- 500 mL round bottom flask
- glass stopper (24/40 joint)
- 200 mL (or larger) beaker

#### 12.2.2 Samples are extracted as a set. A sample set will include approximately 12 samples (including at least one duplicate sample, one field blank, one lab blank, and one matrix spike). All information about the sample set will be recorded on the sample preparation

log sheets (see Appendix A & B). An example of a set name is 941107P (year, month, day of sample extraction; P = precipitation sample).

- 12.2.3 Remove spiking standards from freezer. *Standards must be at ambient temperature before using.* (Ambient temperature is achieved in about two hours.)

Thoroughly rinse inside of condenser and outside of joint with methanol then  $\text{CH}_2\text{Cl}_2$  from wash bottles. Cover joint and exhaust tube with foil.

Assemble supplies and samples under hood and/or utility cart. Label flasks.

Add five to six clean teflon chips into 500 mL round bottom flask.

Measure 175 mL acetone in a beaker.

Place glass wool plug at the siphon tube opening of the Soxhlet extractor using glass or metal rod. Assemble Soxhlet extractor and flask.

Put XAD-2 sample into Soxhlet extractor. Rinse container with acetone from beaker; add this and remaining acetone from beaker to Soxhlet.

Add 175 mL hexane to top of Soxhlet.

- 12.2.4 Surrogate Standard Addition

Using micropipette dispenser, spike each sample with the PCB, Pesticide, PAH and Atrazine surrogate standards.

- 12.2.5 Matrix Spike (CMS)

Spike clean XAD-2 with the PCB, Pesticide, PAH, and Atrazine matrix standards. Add surrogate standards as in 12.2.4 above. Record the amount added.

- 12.2.6 Lab Blank (LB)

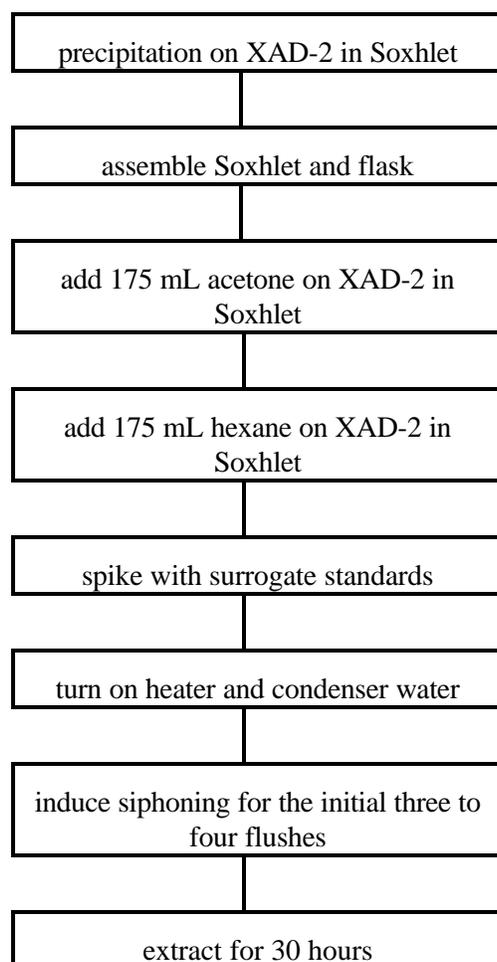
Spike clean matrix with the surrogate standards (12.2.4). Record the amount added.

- 12.2.7 Assemble flask/Soxhlet/condenser apparatus. Place on heating mantle. Turn on heating mantles: set Staco heating mantle to 45 or the multi-unit extraction heater to 5. Turn on condenser water. Cover Soxhlet and flask with foil. Extract for 30 hours.

**Note:** The sample has water in it, thus it may not siphon on its own the first two or three times depending on the amount of water present. Induce siphoning until the level of solvent in the Soxhlet and in the syphon tube are the same.

- 12.2.8 Turn heating mantle off. Let cool 15 to 30 minutes. Siphon off as much solvent from Soxhlet extractor into flask as possible. Detach the flask and insert stopper. Turn off condenser water. Store in cool dark place.

12.2.9 Flow Chart for the Extraction of Precipitation Samples



12.2.10 Rotary Evaporation

- 12.2.10.1 Fill chamber with DI water.  
Turn on the chiller circulator.  
Set bath temperature:

<b>SOLVENT</b>	<b>TEMPERATURE (°C)</b>
hexane	30-32
acetone	30-32
acetone/hexane	30-32
CH <sub>2</sub> Cl <sub>2</sub>	30

methanol	40
----------	----

Rinse joint of steam duct with  $\text{CH}_2\text{Cl}_2$ . Attach appropriate splash guard(s) to steam duct. Clamp each joint. Turn on and check vacuum system.

12.2.10.2 Evaporation

Remove boiling chips with large forceps. If XAD-2 is in flask, remove it as described in 12.2.10.3. Attach flask to splash guard. Clamp joint. Turn on motor of rotator to predetermined rotation speed (usually to the bottom of the indicator line, or about 50 rpm). Turn flask to start rotation. Evaporation should begin in approximately one minute; solvent should *not* boil. Evaporate sample until sample is at half the original volume. If vacuum unit gets hot, turn on cold tap water and allow it to cycle through the bath.

**Note:** If rate of evaporation slows down, *do not* continue. There is water in the sample.

12.2.10.3 Removing XAD-2 from the Flask.

Label another 500 mL flask with the sample ID. Decant sample from original flask into the clean flask; wash with 10 mL hexane twice. Rotary evaporate the new flask with rinses until evaporation begins to slow down.

12.2.10.4 Back Extraction and Solvent Exchanges

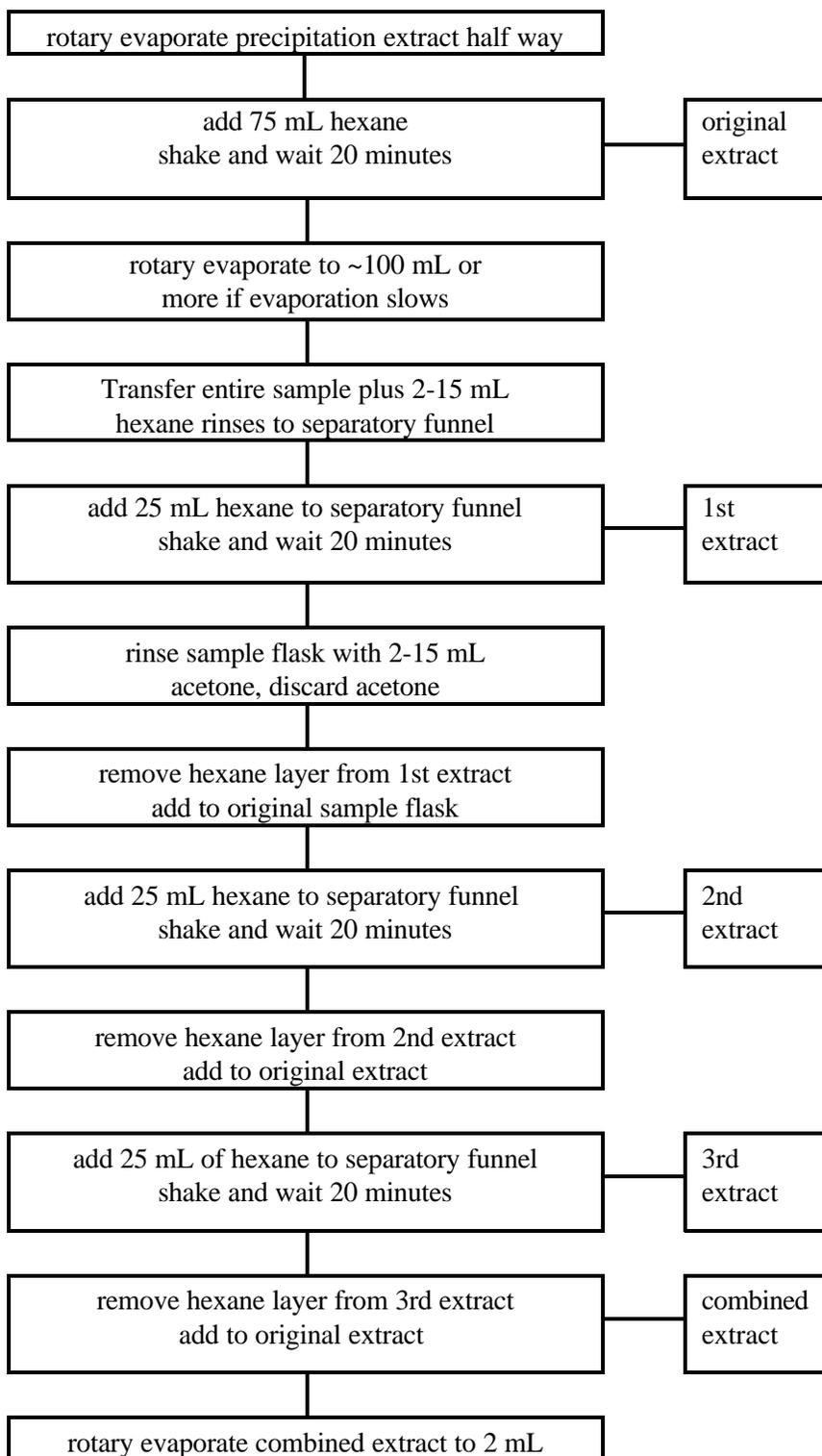
Add 75 mL hexane to sample flask. Shake vigorously; let stand *at least* 20 minutes. Rotary evaporate to a volume of approximately 100 mL or more if evaporation slows. Transfer entire sample plus 2-15 mL hexane rinses to a separatory funnel using a pipet. Rinse sample flask with 2-15 mL acetone and discard. Allow flask to dry. Add 25 mL hexane to separatory funnel. Add approximately 1 gm  $\text{Na}_2\text{SO}_4$ . Shake vigorously. Let stand *at least* 20 minutes then transfer the upper hexane layer back to original flask. Back extract the water layer twice more with hexane. Combine all hexane extracts.

12.2.10.5 Rotary evaporate the combined extract to 2 mL.

12.2.10.6 Clean-up

Turn off heater on rotary evaporator, motor on rotary evaporator, and chiller. Empty receiving flask into proper waste solvent bottle. Cover steam duct with foil.

12.2.10.7 Flow Chart of Rotary Evaporation and Back Extraction



## 13.0 Sample Preparation - Silica Cleanup

### 13.1 Glassware required:

columns  
 three 100 mL pear shaped flasks with 14/20 joints  
 three glass stoppers with 14/20 joints  
 Pasteur pipettes (9½ inch)  
 graduated cylinders: 50, 25, and 10 mL  
 funnel  
 100 mL beaker  
 250 mL beaker OR sample jar (need not be clean)  
 three 250 mL beakers  
 50 mL beakers

### 13.2 Column packing and elution amounts

Item	Air Particulate (filter)	Air Vapor (XAD-2)	Precipitation (XAD-2)
amount of silica to activate/deactivate	4-6 gms	8-10 gms	4-6 gms
column size	3½"	7"	3½"
amount of Na <sub>2</sub> SO <sub>4</sub>	½"	½"	1½"
elution volume (hexane)	23 mL	50 mL	23 mL
switching volume	4 mL	8 mL	4 mL
elution volume (40% DCM)	23 mL	50 mL	23 mL
DCM	15	30	15
switching volume	4	8	4
elution volume (methanol)	23	50	23

### 13.3 Silica gel activation

Place approximate amount of silica needed in a beaker. Cover beaker with foil. Place beaker in 100°C oven, turn thermostat to 300°C; keep in oven overnight.  
*Do Not Put Silica Into 300°C Oven!*

Turn oven temperature down to 100°C;

*Do Not Remove Silica From Oven.*

When oven has cooled to 100°C, remove beaker from oven; let cool on counter top until warm (approximately five to 10 minutes); place in desiccator.

When silica has reached ambient temperature (approximately two hours), deactivate it:

#### 13.4 Silica gel deactivation

Working quickly, weigh out desired amount of silica into a round bottom flask. Stopper flask *immediately* after pouring silica.

Add 3% weight/volume of DI water to silica, using the following equation:

$$\frac{\% \text{ deactivation}}{100 - \% \text{ deactivation}} = \frac{\text{mL DI water}}{\text{weight of silica (gm)}}$$

*Shake Well.* Shake flask until all clumps are broken-up.

Store in desiccator overnight for equilibration.

Use deactivated silica in desiccator within three days. Any unused silica may be reused after re-activating and re-deactivating.

#### 13.5 Preparation and packing of column(s)

Assemble stopcock(s) on column(s).

Stuff glass wool plug (approximately 1 cm) into lower end of the each column with 20" rod.

Measure and mark appropriate distance from top of glass wool plug for silica and Na<sub>2</sub>SO<sub>4</sub> with information from 13.2.

Clamp column(s) securely onto frame in ventilation hood. Place empty glass container under each column (100 mL minimum size; it need not be clean).

Close stopcock(s); fill column(s) half full with hexane.

Make a slurry of hexane and deactivated silica. Pour slurry into each *column*. *Do Not Allow Silica to Dry Out:* rinse column and beaker with hexane via Pasteur pipette. (Use of a funnel may facilitate process.) Open stopcock(s). Tap column(s) with rubber hammer to pack silica. Add silica/hexane as needed until desired length is loaded.

Cap column(s) with ½" Na<sub>2</sub>SO<sub>4</sub> for XAD-2 and filter samples, ½" Na<sub>2</sub>SO<sub>4</sub> for precipitation samples.

Wash column(s) with 25 or 50 mL hexane for equilibrium.

When hexane level reaches top of Na<sub>2</sub>SO<sub>4</sub>, close stopcock(s) to prevent further dripping. *Never Let Column Run Dry.*

If column(s) is/are not going to be used *immediately*, stopper column(s) and cover tip(s) of column(s) with foil.

#### 13.6 Cleanup procedure

13.6.1 Label one 100 mL pear-shaped flask for each fraction which is to be collected.

On a cart, assemble pear shaped flasks and remaining supplies.

Place sample flask in front of column.

Place a 50 or 100 mL beaker in front of sample flask.

Add hexane to 50 or 100 mL beaker; cover with foil (see 13.2 for hexane volume required).

### 13.6.2 Column chromatography

#### 13.6.2.1 First Fraction (hexane)

Sonicate sample flask before loading the sample onto the column to detach the particles adhering to the walls of the flask.

Remove stopper from sample flask. Assemble pipette and rubber bulb; place pipette in sample flask.

Place fraction #1 (hexane) pear shaped flask under the column.

Load sample into column with Pasteur pipette.

Set drip rate to approximately one drip per second. Add approximately 5 mL hexane to sample flask from the beaker. Swirl solvent in flask.

When sample has drained down to the top of the  $\text{Na}_2\text{SO}_4$  add the hexane from the sample flask to the column. Add an additional 5 mL hexane to the sample flask from the beaker. Swirl solvent in flask.

When solvent has drained down to the top of the  $\text{Na}_2\text{SO}_4$  add the second 5 mL hexane to the column. Add the remaining hexane from the beaker to the sample flask. Swirl solvent in sample flask.

When solvent has drained down to the top of the  $\text{Na}_2\text{SO}_4$  add the remaining hexane from the sample flask (If reservoir on top of the column cannot hold entire amount, add as much as possible, then refill as space becomes available).

**Note:** Stagger the timing of the column loadings such that the changing of the flasks are not concurrent.

#### 13.6.2.2 Second Fraction (40% $\text{CH}_2\text{Cl}_2$ /60% hexane)

While the hexane is eluting (from the first fraction), measure the hexane/ $\text{CH}_2\text{Cl}_2$  and put it into the appropriate containers. (See the following table.) Swirl the hexane/ $\text{CH}_2\text{Cl}_2$  in the sample flask.

column size (in)	hexane/ $\text{CH}_2\text{Cl}_2$ in beaker (mL)	switching volume in flask (mL)
3½	23	4
7	50	8

When the hexane level reaches the top of the  $\text{Na}_2\text{SO}_4$  add the switching volume hexane/ $\text{CH}_2\text{Cl}_2$  from the sample flask to the column. Transfer the hexane/ $\text{CH}_2\text{Cl}_2$  from the beaker to the sample flask. Swirl the solvent in the flask.

Place the appropriate pear shaped flask (labeled '40%' fraction) next to the flask under the column.

When the hexane/ $\text{CH}_2\text{Cl}_2$  level in the column is to the top of the  $\text{Na}_2\text{SO}_4$  quickly switch flasks and pour as much of the remaining hexane/ $\text{CH}_2\text{Cl}_2$  into the column as possible. Add hexane/ $\text{CH}_2\text{Cl}_2$  to the column as space permits.

Continue to monitor the rate of drip (approximately one drip per minute). Place the pear shaped flask from the first fraction on the supply cart. Stopper the flask.

DCM column conditioning: While the hexane/ $\text{CH}_2\text{Cl}_2$  is dripping, measure out 15 mL DCM for 3½" columns or 30 mL for 7" columns and put into beaker.

Place a waste jar next to the flask under the column.

When the hexane/ $\text{CH}_2\text{Cl}_2$  reaches the top of the  $\text{Na}_2\text{SO}_4$ , add the DCM to the column and quickly switch the flask and waste jar.

Stopper the second fraction flask and place on the supply cart.

### 13.6.2.3 Third Fraction (MeOH)

While the DCM is eluting, measure the methanol and put into the appropriate containers (See the following table).

column size (in)	methanol in large beaker	switching volume in small beaker
3½	23	4
7	50	8

When DCM reaches the top of  $\text{Na}_2\text{SO}_4$ , add the switching volume to the column.

Place the appropriate flask (labeled "MeOH fraction") next to the waste jar under the column.

When the methanol level in the column is to the top of the  $\text{Na}_2\text{SO}_4$ , quickly switch the flask and waste jar and pour the remaining methanol onto column.

Open the stopcocks fully so the methanol elutes as fast as possible.

Discard DCM from the waste jars.

Once the column has stopped dripping, remove flask and stopper it.

### 13.7 Clean-Up

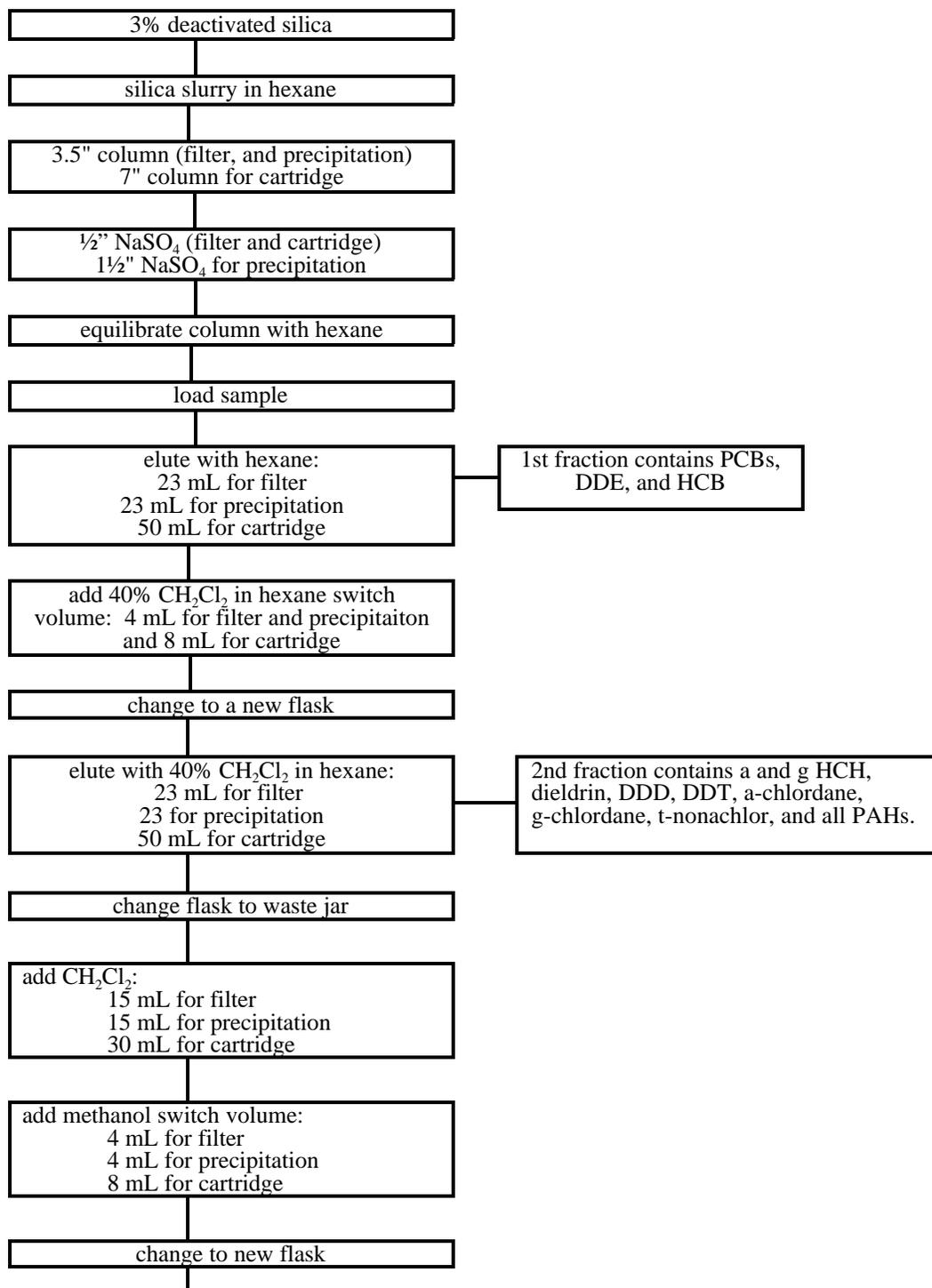
Remove stopcock from column.

Turn column upside down and secure it with clamps. Place container under column to catch  $\text{Na}_2\text{SO}_4$  and silica.

After column has dried out, use vacuum (air or water) to remove glass wool plug.

Pour silica and  $\text{Na}_2\text{SO}_4$  into used glove or foil before discarding into trash can.

13.8 Flow-Chart





Close amber vial tightly, place in vial file, and store in freezer. Label the vial file with sample set name, type of samples, and site of collection.

## 16.0 N<sub>2</sub> Blow Down

### 16.1 Set-up

Let N<sub>2</sub> flush the system for approximately five minutes. Ensure the N<sub>2</sub> cylinder pressure is >500 psi.

Turn heater on *Low*, 5.5 setting

Attach clean needle to each nozzle to be used.

### 16.2 Blow down

Place amber vials in heater block; adjust N<sub>2</sub> flow such that there are *gentle* (barely detectable) ripples in the vials.

Evaporate samples down to a final volume of 0.5 to 4.0mL according to sample site, matrix, and season. Document the actual amount on the sample preparation log sheet.

**Note:** Volumes may be changed as analyte amounts and/or interferences fluctuate.

### 16.3 Cleanup

Turn off N<sub>2</sub>.

Replace the nozzle caps.

Soak used needles in MeOH. Sonicate needles with CH<sub>2</sub>Cl<sub>2</sub> three times prior to reuse.

Store in a foil covered beaker.

## 17.0 Spiking Samples with ISTD

17.1 Remove ISTDs from freezer; equilibrate to ambient temperature (approximately two hours).

17.2 Clean micropipette

Remove glass tube used to cover plunger.

Rinse plunger with CH<sub>2</sub>Cl<sub>2</sub>. Allow to dry

Without touching glass tubes, insert plunger into new glass tube;

Rinse pipette tube:

- 1) Draw-up CH<sub>2</sub>Cl<sub>2</sub> into pipette and discard in solvent waste container.
- 2) Draw-up hexane into pipette and discard in solvent waste container. Repeat five times.
- 3) Vortex standard bottle to mix solution.
- 4) Draw standard into pipette and discard in solvent waste container. Repeat two times.

17.3 Spike sample vial (as described).

fraction	analyte group	ISTDs	color code
hexane	PCBs	PCB 30 PCB 204	red
40%	OC pesticides	DDE PCB 65 PCB 155	blue
40%	PAHs	anthracene-d10 benzo(a)anthracene-d12 perylene-d12 triphenylmethane	black
MeOH	atrazine	anthracene-d10	black

17.4 Mark each amber vial label with a appropriate color of dot (use a water-proof marker).

17.5 Rinse tip of micropipet with DCM and hexane, replace glass tube used to cover plunger. Store micropipette.

17.6 Label vial file with the following information (use same color of pen as dots on microvials):  
date microvials spiked fraction spiked initials of chemist spiking

17.7 Mix samples vigorously after spiking.

## **18.0 Preparing Samples for GC Analysis**

18.1 Glassware required  
disposable GC vials  
200 µL disposable inserts

18.2 Label GC vials with sample IDs. In addition, label an extra GC vial for hexane and the appropriate calibration and performance standards for every set of samples.  
Place inserts into the GC vials.  
Using a Pasteur pipette, remove approximately 200 µL of each sample and put into the appropriate vials. (The level of liquid should be at least half the volume of the insert.) Also place 200 µL of hexane and 200 µL of the appropriate standards into individual vials (See following chart for the appropriate standard).

fraction	target compounds	calibration standard
hexane	PCBs	PCB calibration standard with DDE and HCB
40%	PAHs	PAH standards
MeOH	atrazine	atrazine standards
40%	OC pesticides	mixed pesticide standard

Cap microvial.

Load microvials into autosampler.

## 19.0 References

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## **Appendix A.**

### **Sample Preparation Log Form Filter and Precipitation Samples**





LAB PROCEDURES	DATE PERFORMED	BY (INITIALS)	COMMENTS
Extraction			
Extract Concentration (hexane/acetone)			
Back Extraction (if Appl.)			
Silica Column Cleanup			
Concentration of Fraction			
hexane	_____	_____	
40%	_____	_____	
MeOH	_____	_____	
Nitrogen Blowdown			
hexane	_____	_____	
40%	_____	_____	
MeOH	_____	_____	

ADDITIONAL COMMENTS:

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## **Appendix B.**

### **Preparation Log Form Composited Cartridge Samples**





SAMPLE SET NAME: \_\_\_\_\_

LAB PROCEDURES	DATE PERFORMED	BY (INITIALS)	COMMENTS
Extraction			
Extract Concentration (hexane/acetone)			
Back Extraction (if Appl.)			
Silica Column Cleanup			
Concentration of Fraction			
hexane			
40%			
MeOH			

Nitrogen Blowdown  hexane  40%  MeOH			

ADDITIONAL COMMENTS:

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