2900

SAMPLING AND ANALYSIS PLAN FOR THE PPG MERCURY POND, NATRIUM, WEST VIRGINIA

Prepared for:

PPG INDUSTRIES, INC.
Natrium, West Virginia

By:

GERAGHTY & MILLER, INC.
Annapolis, Maryland

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1.0 Introduction

Section 265.92 of the U. S. Environmental Protection Agency Interim Status Standards for Owners and Operators of Hazardous Waste Treatment, Storage, and Disposal Facilities (FR 45:98, 33239), requires hazardous-waste facilities to undertake a ground-water monitoring program at all facilities being operated under "Interim Status". The requirement includes the installation of monitor wells, sampling of these wells, analysis of the water samples for selected water-quality parameters, and evaluation of the collected data.

To comply with these requirements at the PPG Industries, Natrium Plant, a monitoring network has been defined based upon data contained in the report, "Evaluation of Ground-Water Quality Impacts at the PPG Mercury Pond, Natrium, West Virginia". Additionally, this "Sampling and Analysis Plan" has been prepared to delineate sampling frequency and methods, and chemical parameters and analytical methods. A companion document, the "Ground-Water Quality Assessment Plan Outline" has been prepared to delineate data evaluation procedures, reporting requirements, and development of a detailed Ground-Water Quality Assessment Plan, if needed.

2.0 Sample Collection, Preservation, and Shipment

2.1 Frequency of Sample Collection

Table 2.1 presents 44 ground-water quality parameters which must be monitored at the mercury pond site on a quarterly basis during the first year of monitoring. The table includes all parameters required by EPA in Section 265.92 in addition to ground-water quality parameters suggested by the consultant. A map of the mercury pond site showing monitor well locations is presented in Figure 1. Monitor wells GM-1, GM-2, GM-6, and the PPG water-supply well will be sampled to determine the quality of ground water in the regional Ohio River alluvial aquifer.

2.2 Equipment

Sampling equipment needed for collecting representative samples of ground water are presented below.

1) 100-ft fiberglass or plastic measuring tape with weighted bottom (or) water level indicator ("m-scope") consisting of an ammeter, electrode and 100-ft cable;

2) Several gallons of distilled water and wash bottle;
3) Clean rags;
4) Plastic sheeting or large size garbage bags;
5) Bottom filling PVC bailer and 120-ft nautical rope (or) Middleburg pump;
6) Graduated bucket;
7) 7 sample bottles per sampling point;
8) Sample bottle labels, water-proof marking pen;
9) pH meter;
10) Thermometer;
11) Specific conductivity meter;
12) Preservatives for water samples;
13) Field data forms, clipboard, pen; and
14) Optional: ice chest and ice or freezer packs.

2.3 Sample Collection Method

2.3.1 Procedures for Measuring Water Levels

a) Place plastic sheeting around well to protect sampling equipment from potential contamination.

b) After unscrewing outer casing cap, measure the depth to water in the well. All measurements are made from top of metal casing.

- Using the M-scope, drop the probe down the center of the casing and allow cord to go untangled down the well. When ammeter indicates a closed electrical circuit, determine depth to water from top of outer metal casing. Record depth to water on field data form (Figure 2). Subtract this value from elevation at top of outer casing to find elevation of water level (see Figure 3 for elevation of top of casing).

(or)

- Using a fiberglass or plastic 100-ft tape with sandpaper backing on first five feet, drop weighted tape down center of casing. After water is encountered in well, record measurement of tape at top of casing, wind up tape and record the measurement where tape is wet. Subtract the "wet" measurement from the "held" measurement to determine the depth to water. Subtract this value from the elevation at top of outer casing to find elevation of water level.

- The water level measurements must be obtained at each sampling point every time water samples are collected. This information must be recorded and sent to the EPA Regional Administrator with the annual report (refer to the Assessment Plan for further information on reporting requirements).

c) Clean M-scope or tape bottom with distilled water and wipe dry with clean rag.

2.3.2 Procedures for Removing Standing Water in Wells

a) Remove at least one well volume of standing water using either the Middleburg pump or a hand bailer.

- To find the volume of standing water in the well, use the following calculation:

$$V = \pi r^2 h$$

where V = volume (ft^3)

π = 3.14

r = radius of monitor well casing (ft)

h = height or standing water in well (ft)

- The height of standing water in the well is found by subtracting the depth to water measurement from the total depth of the well (refer to Figure 3 for depth of monitor wells)

- It is generally recommended to remove three to five well volumes of water from the well to insure an accurate sample of ground-water quality but this may not be possible with the low yielding wells surrounding the mercury pond. At the least, the well should be pumped or bailed to dryness before sampling. Use graduated bucket to measure volume of work removed from the well.

. The "Procedures Manual for Ground Water Monitoring at Solid Waste Disposal Facilities", pp 220 to 270, should be consulted for further information concerning the amount of water to evacuate from the well, types of pumps or bailers to use in sampling ground water, and procedures to follow for using pumps or bailers. Another reference source is the U. S. Geological Survey (USGS) publication, "Guidelines for Collection and Field Analysis of Ground-Water Samples for Selected Unstable Constituents" pp 3 to 9.

b) Test each bailed portion of water or portions of pumped water for pH, temperature and specific conductance. Record values and discard sample.

c) Clean bailer or pump with distilled water before use in other wells to prevent possible cross contamination of ground water in the monitor wells. If the organic parameters are a major focus of concern, one should use teflon bailers and wash with acetone or hexane after sample collection.

2.3.3 Procedures for Sample Collection and Field Analyses

a) Allow well to recharge sufficiently to obtain samples. In some wells, this may require waiting a few minutes to a few hours; in other wells recovery time may be extremely slow and sampling may not be possible until after 24 hours. If the well is incapable of producing sufficient water required for analyses, composite sampling may be necessary where small quantities of samples are taken several days in a row.

b) Analyses of pH, temperature, and specific conductance should be made in the field at the time of sampling because these parameters change rapidly and a laboratory analysis might not be representative of the true ground-water quality. Remove enough water from well to determine

temperature of water, specific conductivity, and pH. Record values on field data sheet and discard water.

c) Rinse sample bottle with sampled ground water <u>except</u> coliform bacteria sample and the organic halogen/pesticides sample bottle (refer to Table 2.3.3).

d) Transfer water from well sampling device to sample bottles provided by the laboratory. Care should be taken not to agitate sample in order to limit amount of added oxygen to water sample. Minimize the number of containers used in order to limit the addition of outside contaminants. Sample bottles should be prepared as specified by future EPA regulations, the 1974 EPA "Manual of Methods for Chemical Analysis of Water and Wastes" (EPA 625/6-74-0030, or as specified within this plan.

e) Table 2.3.3 lists seven bottles which must be collected quarterly at each well during the first monitor year. These sample volumes may be increased as necessary based on laboratory needs and future EPA guidelines. The volumes listed below are based upon several EPA publications (EPA 625-16-74-003, EPA 600/4-76-049, and EPA/530/SW-611), and on the consultant's best judgement which is based upon publications and verbal communications with EPA support laboratories.

f) If there is insufficient water in the well to supply the necessary volumes for samples specified above, the sample collector should fill up as many bottles as possible, preserve and label as required, and continue sampling daily until the remaining bottles are filled. Table 2.3.4 provides data on maximum sample holding time for the ground-water quality parameters.

2.3.4 Procedures for Sample Preservation and Shipment

Many chemical parameters are unstable in water and may change drastically before analysis if the sample is not "fixed" or

preserved at the time of sampling. Table 2.3.4 presents information on methods of preservation and this table should be used in conjunction with the information on Table 2.3.3. The procedures for sample preservation and shipment are outlined below.

a) Add appropriate preservatives to sample bottles as listed on Table 2.3.4.

b) Seal sample bottle caps and label bottle. Labels should show sample number, date, sample source, preservative added, if any, and analysis to be performed. Refer to sample bottle tags in Figure 4.

c) Enter all pertinent information on field data sheets and chain of custody form.

d) Transfer samples to ice chest for shipment to laboratory.

e) Clean all equipment with distilled water and wipe with clean rags. Proceed to next sampling point.

f) Shipment of samples to laboratories to perform analyses outside PPG's capabilities should be performed with as few transfers as possible. All samples must remain cooled at 4°C during shipment. Additional information concerning sampling can be found in EPA 600/4-76-049, "Handbook for Sampling and Sample Preservation of Water and Waste Water".

3.0 Laboratory Analysis of Samples

During the first monitor year, PPG must sample ground water at the mercury pond site on a quarterly basis and perform laboratory analyses for the 44 parameters listed in Table 3.0. This table provides the currently accepted analytical procedures for each water quality parameter. The appropriate reference sources are listed on the table for detailed information related to the laboratory procedures. Appendix I and II provide methods of analysis for total organic halide and total organic carbon.

If no ground-water contamination is found during the first monitor year, PPG must collect ground-water samples during the second and subsequent years on an annual and semi-annual basis. Table 2.1 presents the list of ground-water quality parameters and the frequency of sample collection. Additional information is contained in the monitoring plan. The EPA Environmental Monitoring and Support Laboratory in Cincinnati, Ohio or EPA Region III should be contacted concerning specific questions on analytical procedures, quality control, and frequency of sampling should the references mentioned above not provide adequate information to laboratory personnel.

4.0 Chain of Custody

PPG must demonstrate the reliability of data by proving the chain of possession and custody of any ground-water samples collected at the mercury pond site. There are two steps in the chain of custody procedure; 1) the transfer of bulk samples to outside laboratories. In general, a sample is in custody if it is in someone's actual physical possession, in view after being in physical possession, or in physical possession and locked up. Figure 5 presents a sample chain of custody record form to be used when transferring bulk samples to a laboratory. PPG personnel should consult EPA-600/4-76-049 "Handbook for Sampling and Sample Preservation of Water andd Wastewater" or the EPA Region III personnel for specific questions concerning chain of custody requirements. At the time of report preparation, no specific steps or procedures have been required by EPA for chain of custody control. A general practice of minimal transfers of sample bottles and good record keeping should provide adequate chain of custody control.

Bibliography

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TABLE 2.1: GROUND-WATER QUALITY PARAMETERS AND FREQUENCY OF SAMPLE COLLECTION

Ground-Water Quality Parameter	Ground-Water Sampling Frequency: First Monitor Year	Second Monitor Year
Ground-Water Contamination Indicators		
pH	Quarterly	at least Semi-Annually
Specific Conductance	Quarterly	Semi-Annually
Total Organic Carbon	Quarterly	Semi-Annually
Total Organic Halogen	Quarterly	Semi-Annually
	(4 replicate measurements must be obtained for each sample from PPG water-supply well)	
Ground-Water Quality Parameters		
Chloride	Quarterly	at least Annually
Iron[1]	Quarterly	Annually
Manganese	Quarterly	Annually
Phenols	Quarterly	Annually
Sodium	Quarterly	Annually
Sulfate	Quarterly	Annually
Drinking Water Supply Parameters		
Arsenic	Quarterly	-
Barium	Quarterly	-
Cadmium	Quarterly	-
Chromium (VI[2] and total)	Quarterly	-
Fluoride	Quarterly	-
Lead	Quarterly	-
Mercury (dissolved[2] and total)	Quarterly	Semi-Annually[2]
Nitrate (N)	Quarterly	-
Selenium	Quarterly	-
Silver	Quarterly	-
Endrin	Quarterly	-
Lindane	Quarterly	-
Methoxychlor	Quarterly	-
Toxaphene	Quarterly	-

Ground- Water Quality Parameter	First Monitor Year	Second Monitor Year
2,4 -D	Quarterly	-
2,4,5 -TP Silvex	Quarterly	-
Radium	Quarterly	-
Gross Alpha	Quarterly	-
Gross Beta	Quarterly	-
Turbidity	Quarterly	-
Coliform Bacteria	Quarterly	-
Additional Parameters[2]		
Alkalinity (as HCO_3 and $CaCO_3$)	Quarterly	-
Calcium	Quarterly	-
Color	Quarterly	-
Copper	Quarterly	-
Magnesium	Quarterly	-
pH, field	Quarterly	Semi-Annually[2]
Specific Conductance, field	Quarterly	Semi-Annually[2]
Potassium	Quarterly	-
Total Dissolved Solids	Quarterly	Semi-Annually[2]
Zinc	Quarterly	-

[1]All metals are Total metals (not dissolved) unless otherwise specified.
[2]Additional parameters recommended by consultant, not required by EPA.

TABLE 2.3.3: LIST OF SAMPLE BOTTLE SIZE AND SAMPLE PRESERVATION

(1) Use a 500 ml clean plastic or glass sample bottle for the following parameters:

pH (laboratory)[1]
specific conductance (laboratory)[1]
chloride[2]
iron[2]
sulfate[2]
fluoride[3]
turbidity[3]
alkalinity (as HCO_3 and $CaCO_3$)[4]
calcium[4]
color[4]
mercury, dissolved[4]
potassium[4]
total dissolved solids[4]

Cool bottle at 4^0C.

(2) Use a 500 ml clean glass sample bottle washed with nitric acid for the following parameters:

manganese[2]
sodium[2]
arsenic[3]
barium[3]
cadmium[3]
chromium, hexavalent[4] and total[3]
lead[3]
mercury, total[3]
selenium[3]
silver[3]
copper[4]
magnesium[4]
zinc[4]

Acidify samples with HNO_3 to pH <2; cool at 4^0C. All metals are total metals unless otherwise specified.

(3) Use a 500 ml clean glass sample bottle for the following parameters:

total organic carbon[1]
nitrate (as N)[3]

Acidify sample with H_2SO_4 to pH <2; cool at 4^0C.

(4) Use a 500 ml clean glass sample bottle for:

phenols[2]

Acidify with H_3PO_4 to pH <4; cool at 4 ^{0}C.

(5) Use a 500 ml clean, glass sample bottle, solvent washed, with teflon-lined caps for the following parameters:

total organic halogen[1]
endrin[3]
lindane[3]
methoxychlor[3]
toxaphene[3]
2,4-D[3]
2,4,5-TP Silvex[3]

DO NOT RINSE SAMPLE BOTTLE WITH WATER SAMPLE BEFORE SAMPLING.
Cool bottles at 4 ^{0}C.

(6) Use a 100 ml sterile glass sample bottle and sterile cap for:

coliform bacteria

Cool at 4 ^{0}C.

(7) Use a 100 ml clean glass sample bottle cleaned with nitric acid and rinsed with double distilled water for the following parameters:

radium[3]
gross alpha[3]
gross beta[3]

---

[1]Ground-Water Contamination Indicators

[2]Ground-Water Quality Parameters

[3]Drinking Water Supply Parameters

[4]Additional Parameters Recommended by Consultant for First Year of Monitoring

TABLE 2.3.4: SAMPLE BOTTLE PRESERVATION

WATER QUALITY PARAMETER	CONTAINER	METHOD OF PRESERVATION[1]	HOLDING TIME
Ground-Water Contamination Indicators			
pH	P, G[4]	Cool 4°C	6 hrs
Specific Conductance	P, G	Cool 4°C	24 hrs
Total Organic Carbon	P, G	H_2SO_4 to pH<2; Cool 4°C	24 hrs
Total Organic Halogen	G	(6)	(6)
Ground-Water Quality Parameters			
Chloride	P, G	none	7 days
Iron, total	P, G	HNO_3 to pH<2	6 mos
Manganese, total	P, G	HNO_3 to pH<2	6 mos
Phenols	G	H_3PO_4 to pH<4; Cool 4°C	24 hrs
Sodium, total	P, G	HNO_3 to pH<2; Cool 4°C	6 mos
Sulfate	P, G	Cool 4°C	7 days

WATER QUALITY PARAMETER	CONTAINER	METHOD OF PRESERVATION[1]	HOLDING TIME
Drinking Water Supply Parameters			
Arsenic, total	P, G	HNO_3 to pH<2	6 mos
Barium, total	P, G	HNO_3 to pH<2	6 mos
Cadmium, total	P, G	HNO_3 to pH<2	6 mos
Chromium, hexavalent[2]	P, G	HNO_3 to pH<2	24 hrs
Chromium, total	P, G	HNO_3 to pH<2	6 mos
Fluoride, total	P, G	Cool 4°C	7 days
Lead, total	P, G	HNO_3 to pH<2	6 mos
Mercury, dissolved[2]	G	Filter; HNO_3 to pH<2	38 days
Mercury, total	G	HNO_3 to pH<2	38 days
Nitrate (N)	P, G	H_2SO_4 to pH<2; Cool 4°C	24 hrs
Selenium, total	G	HNO_3 to pH<2	6 mos
Silver, total	G	HNO_3 to pH<2	6 mos
Endrin[3]	G[5]	none [5]	(6)
Lindane[3]	G[5]	none [5]	(6)
Methoxychlor[3]	G[5]	none [5]	(6)
Toxaphene[3]	G[5]	none [5]	(6)
2,4-D[3]	G[5]	none [5]	(6)

WATER QUALITY PARAMETER	CONTAINER	METHOD OF PRESERVATION[1]	HOLDING TIME
Drinking Water Supply Parameters (Cont)			
2,3,5-TP Silvex[3]	G[5]	none [5]	(6)
Radium	G	(6)	(6)
Gross Alpha	G	(6)	(6)
Gross Beta	G	(6)	(6)
Turbidity	P, G	Cool 4°C	7 days
Coliform Bacteria, total	G	Cool 4°C	24 hrs
Additional Parameters[2]			
Alkalinity (as HCO_3 and $CaCO_3$)	P, G	Cool 4°C	24 hrs
Calcium, total	P, G	Cool 4°C	6 mos
Color	G	Cool 4°C	24 hrs
Copper, total	G	HNO_3 to pH<2	6 mos
Magnesium, total	P, G	HNO_3 to pH<2	6 mos
pH, field	P, G	determine on site	-
Specific Conductance, field	P, G	determine on site	-

WATER QUALITY PARAMETER	CONTAINER	METHOD OF PRESERVATION[1]	HOLDING TIME
Additional Parameter[2] (Cont)			
Potassium, total	P	Cool 4°C	6 mos
Total Dissolved Solids (TDS)	P, G	Cool 4°C	7 days
Zinc, total	G	HNO_3 to pH<2	6 mos

[1] Primary data sources: p. viii, EPA-625/6-74-003 "Methods for Chemical Analysis of Water and Wastes" and Chapter 10, EPA-600/4-76-049, "Handbook for Sampling and Sample Preservation of Water and Wastewater."

[2] Additional parameters recommended by consultant, not required by EPA.

[3] Also refer to "Methods for Chlorinated Phenoxy Acid Herbicides in Industrial Effluents" MDQARL, EPA, Cincinnati, Ohio, November 28, 1973 and "Method for Organochloride Pesticides in Industrial Effluents" MDQARL, EPA, Cincinnati, Ohio, November 28, 1973.

[4] P = Polyethylene bottles
G = Glass bottles

[5] Do NOT rinse container with ground water before sample collection.

[6] Refer to EPA guidelines and regulations for more information.

TABLE 3.0: ANALYTICAL PROCEDURES

WATER QUALITY PARAMETERS	ANALYTICAL PROCEDURES[1]	REFERENCES (page number)		
		1974 EPA METHODS	14th EDITION STANDARD METHODS	1975 Part 31 ASTM
Ground-Water Contamination Indicators				
pH	Electrometric measurement Field analysis preferred	239	460	178
Specific Conductance	Wheatston bridge conductimetry	275	71	120
Total Organic Carbon	Combustion - infrared method	236	532	467
Total Organic Halogen	Microcoulometric-titration detection method. Refer to Method 450.1 included in the appendix	-	-	-
Ground-Water Quality Parameters				
Chloride	Silver nitrate; mercuric nitrate; or automated colorimetric-ferricyanide	29; 31	303; 304; 613	267; 625
Iron, total	Digestion followed by atomic absorption; or colorimetric (Phenanthroline)	110	148; 208	345; 328
Manganese, total	Digestion followed by atomic absorption; or colorimetric (Persulfate or periodate)	116	148; 225; 227	345
Phenols	Colorimetric (4AAP)	241	582	545
Sodium, total	Digestion followed by atomic absorption; or flame photometric	147	250	403
Sulfate	Gravimetric; turbidimetric; or automated colorimetric (barium chloranilate)	277; 279	493; 496	424; 425

WATER QUALITY PARAMETERS	ANALYTICAL PROCEDURES[1]	REFERENCES (page number)		
		1974 EPA METHODS	14th EDITION STANDARD METHODS	1975 Part 31 ASTM
Drinking Water Supply Parameters				
Arsenic, total	Digestion followed by silver diethyldithiocarbamate; or atomic absorption	9; 95	285; 283; 159	-
Barium, total	Digestion followed by atomic absorption	97; 98	152	-
Cadmium, total	Digestion followed by atomic absorption; or colorimetric (Dithizone)	101	148; 182	345
Chromium, hexavalent[2]	Extraction and atomic absorption; colorimetric (Diphenylcarbazide)	89; 105	192	-
Chromium, total	Digestion followed by atomic absorption; or colorimetric (Diphenylcarbazide)	105	148; 192	345; 286
Fluoride, total	Distillation followed by ion electrode; SPADNS; or automated complexone	65; 59; 61	389; 391; 393 614	307; 305
Lead, total	Digestion followed by atomic absorption; or colorimetric (Dithizone)	112	148; 215	345
Mercury, dissolved[2]	Filter with 0.45 micron paper followed by the referenced method for total maganese			
Mercury, total	Flameless atomic absorption	118	156	338
Nitrate (N)	Cadmium reduction; brucine sulfate; automated cadmium or hydrazine reduction	201; 197; 207	423; 427; 620 620	358
Selenium, total	Digestion followed by atomic absorption;	145	159	-
Silver, total	Digestion followed by atomic absorption; or colorimetric (Dithizone)	146	148; 243	-

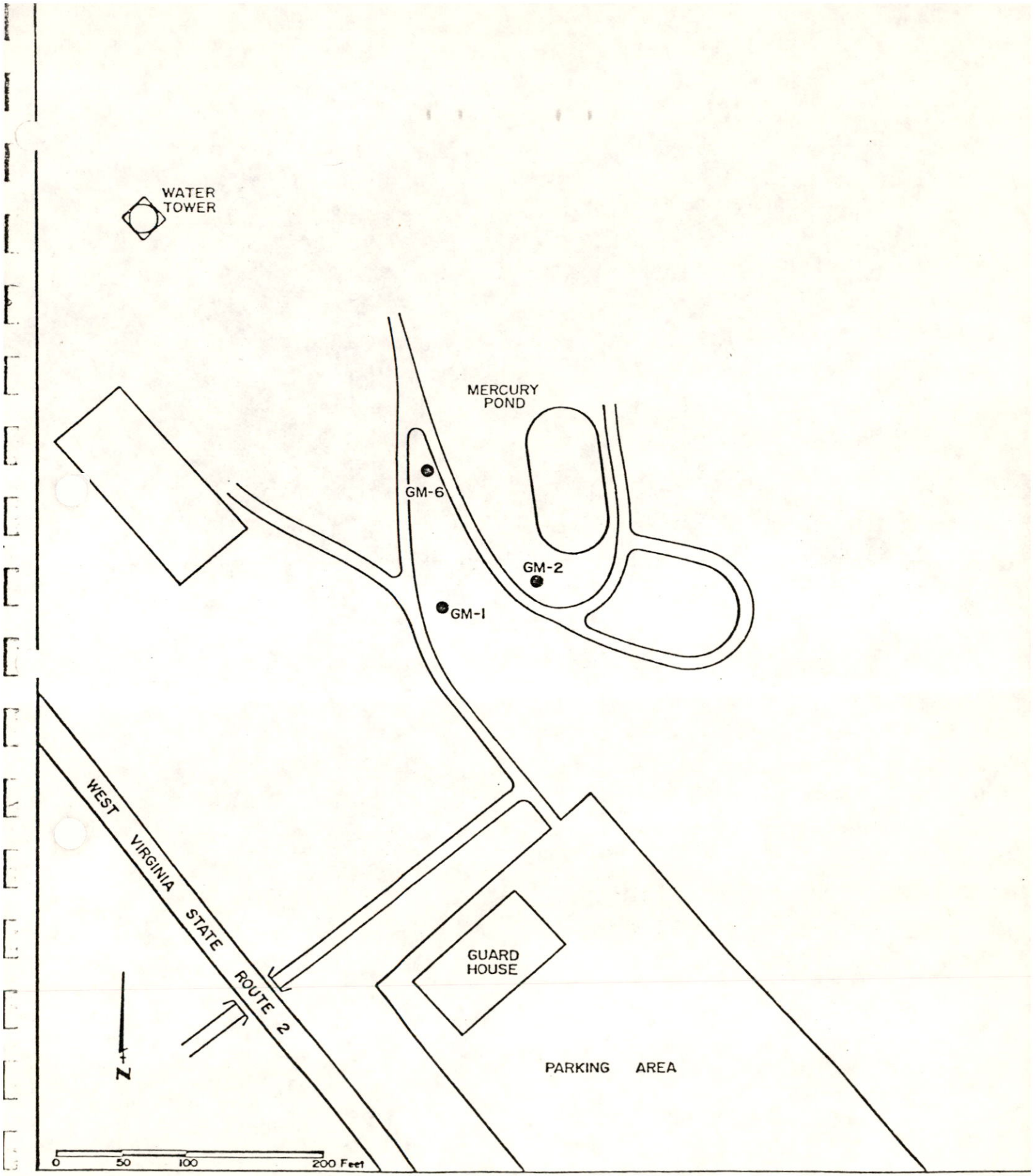
WATER QUALITY PARAMETERS	ANALYTICAL PROCEDURES[1]	REFERENCES (page number)		
		1974 EPA METHODS	14th EDITION STANDARD METHODS	1975 Part 31 ASTM
Drinking Water Supply Parameters				
Endrin[3]	EPA Method 625; Gas chromotography	December 3, 1979 Federal Register	555	-
Lindane[3]	EPA Method 625; Gas chromotography	December 3, 1979 Federal Register	555	-
Methoxychlor[3]	Gas Chromotograph	-	555	-
Toxaphene[3]	EPA Method 625; Gas chromotography	December 3, 1979 Federal Register	555	-
2,4-D[3]	Gas Chromotography	-	555	-
2,4,5-TP Silvex[3]	Gas Chromotography	-	555	-
Radium	Proportional counter; scintillation counter	-	661	661
Gross Alpha	Proportinal counter; scintillation counter	-	648	591
Gross Beta	Proportional counter	-	648	601
Turbidity	Nephelometric method	295	132	223
Coliform Bacteria, total	Most Probable Number (MPN): membrane filter	916; 928	-	35

WATER QUALITY PARAMETERS	ANALYTICAL PROCEDURES[1]	REFERENCES (page number)		
		1974 EPA METHODS	14th EDITION STANDARD METHODS	1975 Part 31 ASTM
Additional Parameters[2]				
Alkalinity (as $CaCO_3$ and HCO_3)	Electrometric titration (only to pH 4.5) manual or automated, or equivalent automated methods	3; 5	278	111
Calcium, total	Digestion followed by atomic absorption; or EDTA titration	103	148; 189	345
Color	Colorimetric; Spectrophotometric; or ADMI procedure	36; 39	64; 69	-
Copper, total	Digestion followed by atomic absorption; or colorimetric (Neocuproine)	108	148; 196	345; 293
Magnesium, total	Digestion followed by atomic absorption; orgravimetric	114	148; 221	345
pH, field	Portable pH meter. Refer to operating instructions with meter	239	460	178
Specific conductance (field)	Portable conductivity meter. Refer to operating instructions with meter	275	71	120
Potassium, total	Digestion followed by atomic absorption; colorimetric (Cobaltinitrite); or flame photometric	143	235; 234	403
Total Dissolved Solids (TDS)	Glass fiber filtration, 180°C	266	92	-
Zinc, total	Digestion followed by atomic absorption; or colorimetric (Dithizone)	155	148; 265	345

1 Primary data source: EPA, Table 1 "List of Approved Test Procedures", draft copy from 1979 EPA methods manual.

2 Additional parameters recommended by consultant, not required by EPA.

3 Also refer to "Methods for Chlorinated Phenoxy Acid Herbicides in Industrial Effluents" MDQARL, EPA, Cincinnati, Ohio, November 28, 1973 and "Method for Organochloride Pesticides in Industrial Effluents" MDQARL, EPA, Cincinnati, Ohio, November 28, 1973.



EXPLANATION

● GM-2 Monitor well and number

FIGURE 1: MONITOR WELL LOCATION MAP

FIGURE 2. GROUND WATER SAMPLING DATA FORM

Date: _____

Spring/Well Number: _____ Time: _____ to _____

Sampled by: _____ Weather: _____

A. GROUND-WATER ELEVATION

(1) Length of Tape Held at Top of Outer Casing: _____ (or) m-scope reading _____

(2) Length of Tape Wet: _____

(3) Depth to Water (1 minus 2): _____

(4) Depth to Well Bottom: _____

(5) Height to Water Column, h (4 minus 3): _____

B. WATER SAMPLING DATA

(1) Volume of water in well = $\pi r^2 h$ = $(3.14)(.083\ ft)^2\ (h)$ =

_____

(2) Amount of water removed from well:

(3) Was well pumped dry? _____

C. FIELD ANALYSES AND REMARKS

(1) Temperature: _____

(2) Specific Conductance: _____

(3) pH: _____

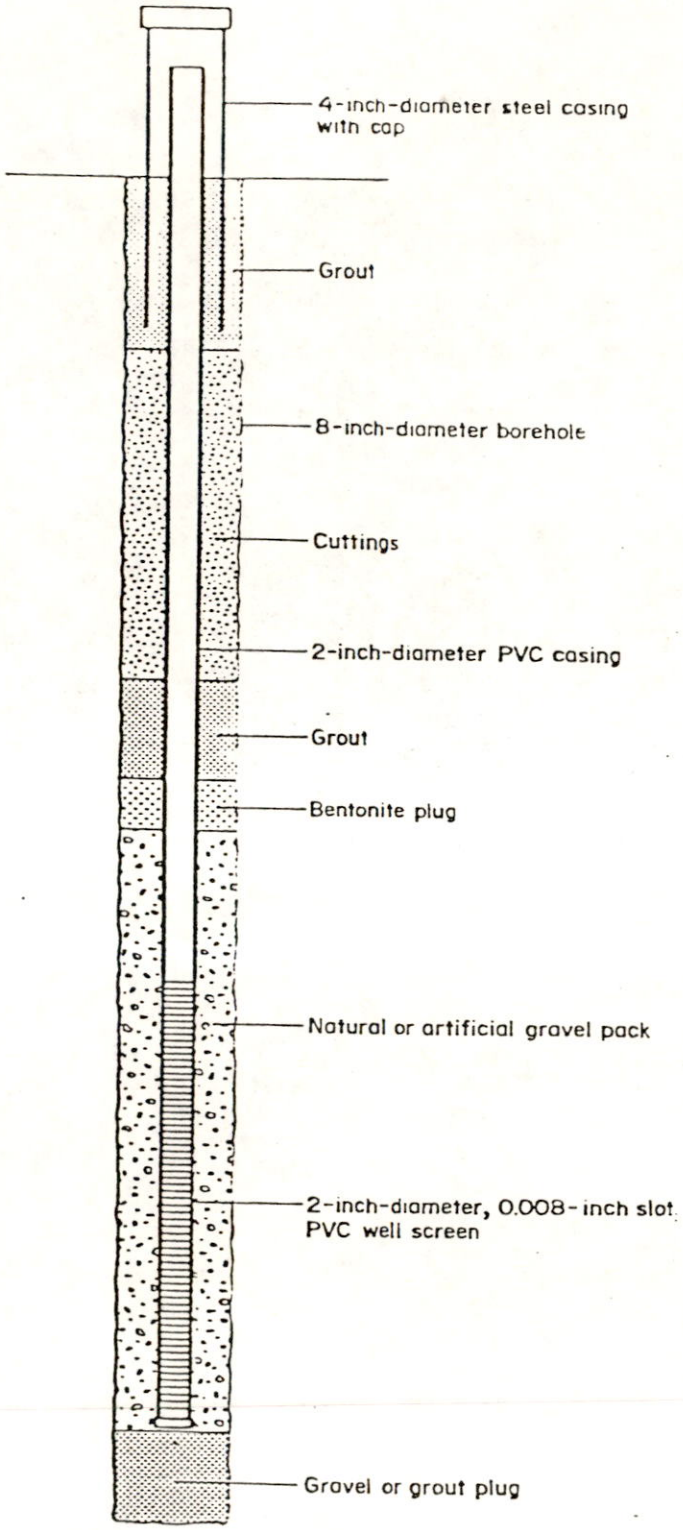
(4) Physical Appearance: _____

(5) Number & Type of Samples Collected: _____

_____

(6) Remarks _____

_____



Well Number	Elevation* (ft)	Total Depth* (ft)
GM-1	693.10	99
GM-2	709.88	102
GM-6	696.90	78

* Measurement from top of outer casing.

FIGURE 3: ELEVATION AND DEPTH OF MONITOR WELLS

FIGURE 4.
CHAIN OF CUSTODY RECORD - BOTTLE SAMPLE TAG

PPG MERCURY POND: GROUND-WATER MONITORING

SAMPLE # _____ COLLECTION DATE _____ TIME _____

SAMPLE SOURCE _____ PRESERVATIVE _____

SAMPLE COLLECTOR (signature) _____

REMARKS (analysis required, etc.) _____

_____

FRONT

Sample relinquished from:	Sample received:	Date/Time
Sample relinquished from:	Sample received:	Date/Time
Sample relinquished from:	Sample received:	Date/Time
Method of shipment:		

BACK

FIGURE 5. CHAIN OF CUSTODY RECORD

SAMPLE COLLECTOR'S NAME:

DATE	TIME	SAMPLE #	SAMPLE SOURCE	SAMPLE VOLUME	# OF CONTAINERS	ANALYSIS REQUIRED

Relinquished by:(signature)	Received by:(signature)	Date/Time
Relinquished by:(signature)	Received by:(signature)	Date/Time
Relinquished by:(signature)	Received by:(signature)	Date/Time
Dispatched by:(signature)	Date/Time:	Method of Shipment:
Received at Laboratory	Date/Time:	

APPENDIX I

TOTAL ORGANIC HALIDE

Method 450.1

Interim

U S. Environmental Protection Agency
Office of Research and Development
Environmental Monitoring and Support Laboratory
Physical and Chemical Methods Branch
Cincinnati, Ohio 45268

November 1980

TOTAL ORGANIC HALIDE

Method 450.1

1. Scope and Application

   1.1 This method is to be used for the determination of Total Organic Halides as Cl^- by carbon adsorption, and requires that all samples be run in duplicate. Under conditions of duplicate analysis, the reliable limit of sensitivity is 5 µg/L. Organic halides as used in this method are defined as all organic species containing chlorine, bromine and iodine that are adsorbed by granular activated carbon under the conditions of the method. Fluorine containing species are not determined by this method.

   1.2 This is a microcoulometric-titration detection method applicable to the determination of the compound class listed above in drinking and ground waters, as provided under 40 CFR 265.92.

   1.3 Any modification of this method, beyond those expressly permitted, shall be considered as major modifications subject to application and approval of alternate test procedures under 40 CFR 260.21.

   1.4 This method is restricted to use by, or under the supervision of, analysts experienced in the operation of a pyrolysis/microcolumeter and in the interpretation of the results.

2. Summary of Method

   2.1 A sample of water that has been protected against the loss of volatiles by the elimination of headspace in the sampling container, and is free of undissolved solids, is passed through a column containing 40 mg of activated carbon. The column is washed

to remove any trapped inorganic halides, and is then pyrolyzed to convert the adsorbed organohalides to a titratable species that can be measured by a microcoulometric detector.

3. Interferences

3.1 Method interferences may be caused by contaminants, reagents, glassware, and other sample processing hardware. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running method blanks.

3.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by treating with chromate cleaning solution. This should be followed by detergent washing in hot water. Rinse with tap water and distilled water, drain dry, and heat in a muffle furnace at 400°C for 15 to 30 minutes. Volumetric ware should not be heated in a muffle furnace. Glassware should be sealed and stored in a clean environment after drying and cooling, to prevent any accumulation of dust or other contaminants.

3.1.2 The use of high purity reagents and gases help to minimize interference problems.

3.2 Purity of the activated carbon must be verified before use. Only carbon samples which register less than 1000 ng/40 mg should be used. The stock of activated carbon should be stored in its granular form in a glass container with a Teflon seal. Exposure to the air must be minimized, especially during and after milling and sieving the activated carbon. No more than a two-week supply

should be prepared in advance. Protect carbon at all times from all sources of halogenated organic vapors. Store prepared carbon and packed columns in glass containers with Teflon seals.

3.3 This method is applicable to samples whose inorganic-halide concentration does not exceed the organic-halide concentration by more than 20,000 times.

4. Safety

The toxicity or carcinogenicity of each reagent in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current-awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material-handling data sheets should also be made available to all personnel involved in the chemical analysis.

5. Apparatus and Materials (All specifications are suggested. Catalog numbers are included for illustration only).

5.1 Sampling equipment, for discrete or composite sampling

5.1.1 Grab-sample bottle - Amber glass, 250-mL, fitted with Teflon-lined caps. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The container must be washed and muffled at 400°C before use, to minimize contamination.

5.2 Adsorption System

5.2.1 Dohrmann Adsorption Module (AD-2), or equivalent, pressurized, sample and nitrate-wash reservoirs.

5.2.2 Adsorption columns - pyrex, 5 cm long X 6-mm OD X 2-mm ID.

5.2.3 Granular Activated Carbon (GAC) - Filtrasorb-400, Calgon-APC, or equivalent, ground or milled, and screened to a 100/200 mesh range. Upon combustion of 40 mg of GAC, the apparent-halide background should be 1000-mg Cl^- equivalent or less.

5.2.4 Cerafelt (available from Johns-Manville), or equivalent - Form this material into plugs using a 2-mm ID stainless-steel borer with ejection rod (available from Dohrmann) to hold 40 mg of GAC in the adsorption columns. CAUTION: Do not touch this material with your fingers.

5.2.5 Column holders (available from Dohrman).

5.2.6 Volumetric flasks - 100-mL, 50-mL.

A general schematic of the adsorption system is shown in Figure 1.

5.3 Dohrmann microcoulometric-titration system (MCTS-20 or DX-20), or equivalent, containing the following components:

5.3.1 Boat sampler.

5.3.2 Pyrolysis furnace.

5.3.3 Microcoulometer with integrator.

5.3.4 Titration cell.

A general description of the analytical system is shown in Figure 2.

5.4 Strip-Chart Recorder.

6. Reagents

6.1 Sodium sulfite - 0.1 M, ACS reagent grade (12.6 g/L).

6.2 Nitric acid - concentrated.

6.3 Nitrate-Wash Solution (5000 mg NO_3^-/L) - Prepare a nitrate-wash solution by transferring approximately 8.2 gm of potassium nitrate into a 1-litre volumetric flask and diluting to volume with reagent water.

6.4 Carbon dioxide - gas, 99.9% purity.

6.5 Oxygen - 99.9% purity.

6.6 Nitrogen - prepurified.

6.7 70% Acetic acid in water - Dilute 7 volumes of acetic acid with 3 volumes of water.

6.8 Trichlorophenol solution, stock (1 µL = 10 µg Cl^-) - Prepare a stock solution by weighing accurately 1.856 gm of trichlorophenol into a 100-mL volumetric flask. Dilute to volume with methanol.

6.9 Trichlorophenol solution, calibration (1 µL = 500 ng Cl^-) - Dilute 5 mL of the trichlorophenol stock solution to 100 mL with methanol.

6.10 Trichlorophenol standard, instrument-calibration - First, nitrate wash a single column packed with 40 mg of activated carbon as instructed for sample analysis, and then inject the column with 10 µL of the calibration solution.

6.11 Trichlorophenol standard, adsorption-efficiency (100 µg Cl^-/L) - Prepare a adsorption-efficiency standard by injecting 10 µL of stock solution into 1 liter of reagent water.

6.12 Reagent water - Reagent water is defined as a water in which an

interferent is not observed at the method detection limit of each parameter of interest.

6.13 Blank standard - The reagent water used to prepare the calibration standard should be used as the blank standard.

7. Calibration

7.1 Check the adsorption efficiency of each newly-prepared batch of carbon by analyzing 100 mL of the adsorption-efficiency standard, in duplicate, along with duplicates of the blank standard. The net recovery should be within 5% of the standard value.

7.2 Nitrate-wash blanks (Method Blanks) - Establish the repeatability of the method background each day by first analyzing several nitrate-wash blanks. Monitor this background by spacing nitrate-wash blanks between each group of eight pyrolysis determinations.

7.2.1 The nitrate-wash blank values are obtained on single columns packed with 40 mg of activated carbon. Wash with the nitrate solution as instructed for sample analysis, and then pyrolyze the carbon.

7.3 Pyrolyze duplicate instrument-calibration standards and the blank standard each day before beginning sample analysis. The net response to the calibration-standard should be within 3% of the calibration-standard value. Repeat analysis of the instrument-calibration standard after each group of eight pyrolysis determinations, and before resuming sample analysis after cleaning or reconditioning the titration cell or pyrolysis system.

8. Sample Preparation

8.1 Special care should be taken in the handling of the sample to

minimize the loss of volatile organohalides. The adsorption procedure should be performed simultaneously on duplicates.

8.2 Reduce residual chlorine by the addition of sulfite (1 mL of 0.1 M per liter of sample). Addition of sulfite should be done at the time of sampling if the analysis is meant to determine the TOX concentration at the time of sampling. It should be recognized that TOX may increase on storage of the sample. Samples should be stored at $4^{o}C$ without headspace.

8.3 Adjust pH of the sample to approximately 2 with concentrated HNO_3 just prior to adding the sample to the reservoir.

9. Adsorption Procedure

9.1 Connect two columns in series, each containing 40 mg of 100/200-mesh activated carbon.

9.2 Fill the sample reservoir, and pass a metered amount of sample through the activated-carbon columns at a rate of approximately 3 mL/min. NOTE: 100 mL of sample is the preferred volume for concentrations of TOX between 5 and 500 µg/L; 50 mL for 501 to 1000 µg/L, and 25 mL for 1001 to 2000 µg/L.

9.3 Wash the columns-in-series with 2 mL of the 5000-mg/L nitrate solution at a rate of approximately 2 mL/min to displace inorganic chloride ions.

10. Pyrolysis Procedure

10.1 The contents of each column is pyrolyzed separately. After rinsing with the nitrate solution, the columns should be protected from the atmosphere and other sources of contamination until ready for further analysis.

10.2 Pyrolysis of the sample is accomplished in two stages. The volatile components are pyrolyzed in a CO_2-rich atmosphere at a low temperature to assure the conversion of brominated trihalomethanes to a titratable species. The less volatile components are then pyrolyzed at a high temperature in an O_2-rich atmosphere.

NOTE: The quartz sampling boat should have been previously muffled at 800°C for at least 2 to 4 minutes as in a previous analysis, and should be cleaned of any residue by vacuuming.

10.3 Transfer the contents of each column to the quartz boat for individual analysis.

10.4 If the Dohrmann MC-1 is used for pyrolysis, manual instructions are followed for gas flow regulation. If the MCT-20 is used, the information on the diagram in Figure 3 is used for gas flow regulation.

10.5 Position the sample for 2 minutes in the 200°C zone of the pyrolysis tube. For the MCTS-20, the boat is positioned just outside the furnace entrance.

10.6 After 2 minutes, advance the boat into the 800°C zone (center) of the pyrolysis furnace. This second and final stage of pyrolysis may require from 6 to 10 minutes to complete.

11. Detection

The effluent gases are directly analyzed in the microcoulometric-titration cell. Carefully follow manual instructions for optimizing cell performance.

12. Breakthrough

Because the background bias can be of such an unpredictable nature, it can be especially difficult to recognize the extent of breakthrough of organohalides from one column to another. All second-column measurements for a properly operating system should not exceed 10-percent of the two-column total measurement. If the 10-percent figure is exceeded, one of three events can have happened. Either the first column was overloaded and a legitimate measure of breakthrough was obtained - in which case taking a smaller sample may be necessary; or channeling or some other failure occurred - in which case the sample may need to be rerun; or a high, random, bias occurred and the result should be rejected and the sample rerun. Because knowing which event has occurred may not be possible, a sample analysis should be repeated often enough to gain confidence in results. As a general rule, any analyses that is rejected should be repeated whenever sample is available. In the event that the second-column measurement is equal to or less than the nitrate-wash blank value, the second-column value should be disregarded.

13. Quality Control

13.1 Before performing any analyses. the analyst must demonstrate the ability to generate acceptable accuracy and precision with this procedure by the analysis of appropriate quality-control check samples.

13.2 The laboratory must develop and maintain a statement of method accuracy for their laboratory. The laboratory should update the accuracy statement regularly as new recovery measurements are made.

13.3 It is recommended that the laboratory adopt additional quality-assurance practices for use with this method. The specific practices that would be most productive will depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to monitor the precision of the sampling technique. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance-evaluation studies.

14. Calculations

OX as Cl^- is calculated using the following formula:

$$\frac{(C_1 - C_3) + (C_2 - C_3)}{V} = \mu g/L \text{ Total Organic Halide}$$

where:

C_1 = µg Cl^- on the first column in series

C_2 = µg Cl^- on the second column in series

C_3 = predetermined, daily, average, method-blank value (nitrate-wash blank for a 40-mg carbon column)

V = the sample volume in L

15. Accuracy and Precision

These procedures have been applied to a large number of drinking-water samples. The results of these analysis are summarized in Tables I and II.

16. Reference

Dressman, R., Najar, G., Redzikowski, R., paper presented at the Proceedings of the American Water Works Association Water Quality Technology Conference, Philadelphia, Dec. 1979.

TABLE I

PRECISION AND ACCURACY DATA FOR MODEL COMPOUNDS

Model Compound	Dose µg/L	Dose as µg/L Cl	Average % Recovery	Standard Deviation	No. of Replicates
$CHCl_3$	98	88	89	14	10
$CHBrCl_2$	160	106	98	9	11
$CHBr_2Cl$	155	79	86	11	13
$CHBr_3$	160	67	111	8	11
Pentachlorophenol	120	80	93	9	7

TABLE II

PRECISION DATA ON TAP WATER ANALYSIS

Sample	Avg. halide ug Cl/L	Standard Deviation	No. of Replicates
A	71	4.3	8
B	94	7.0	6
C	191	6.1	4

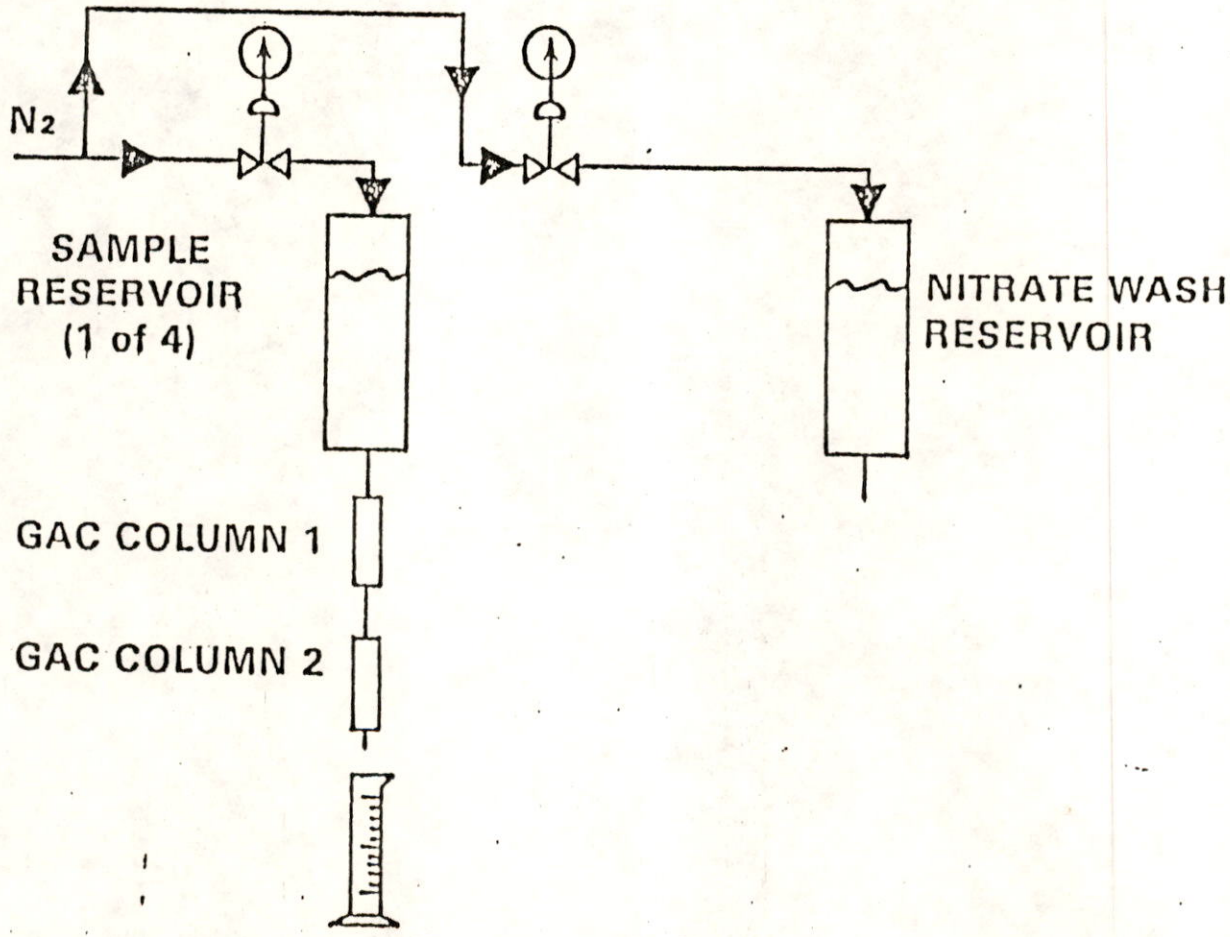


Figure 1. Adsorption Schematic

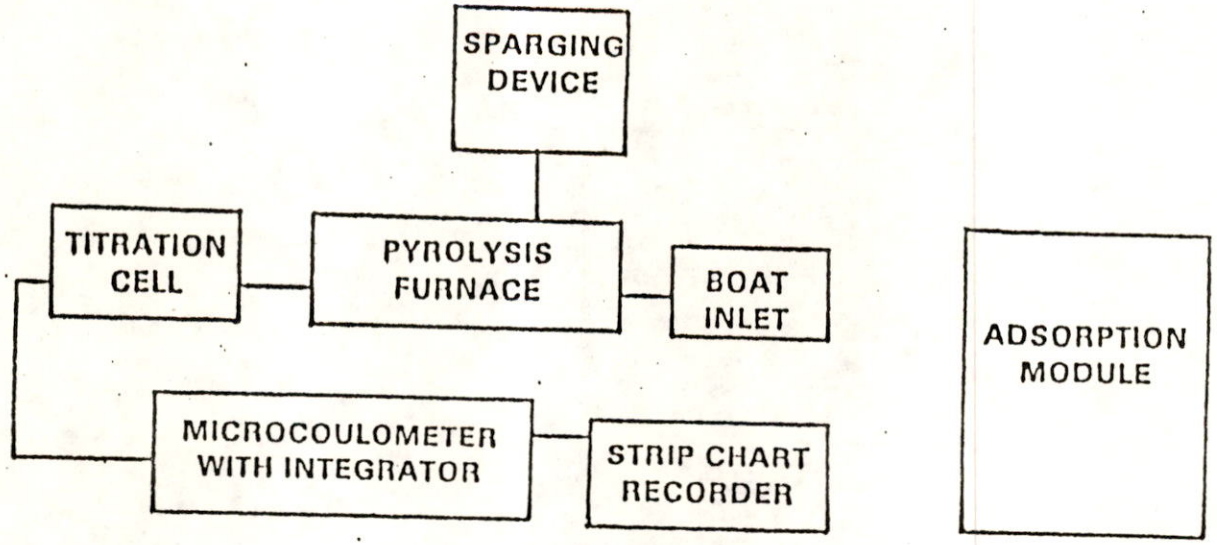


Figure 2. CAOX Analysis System Schematic

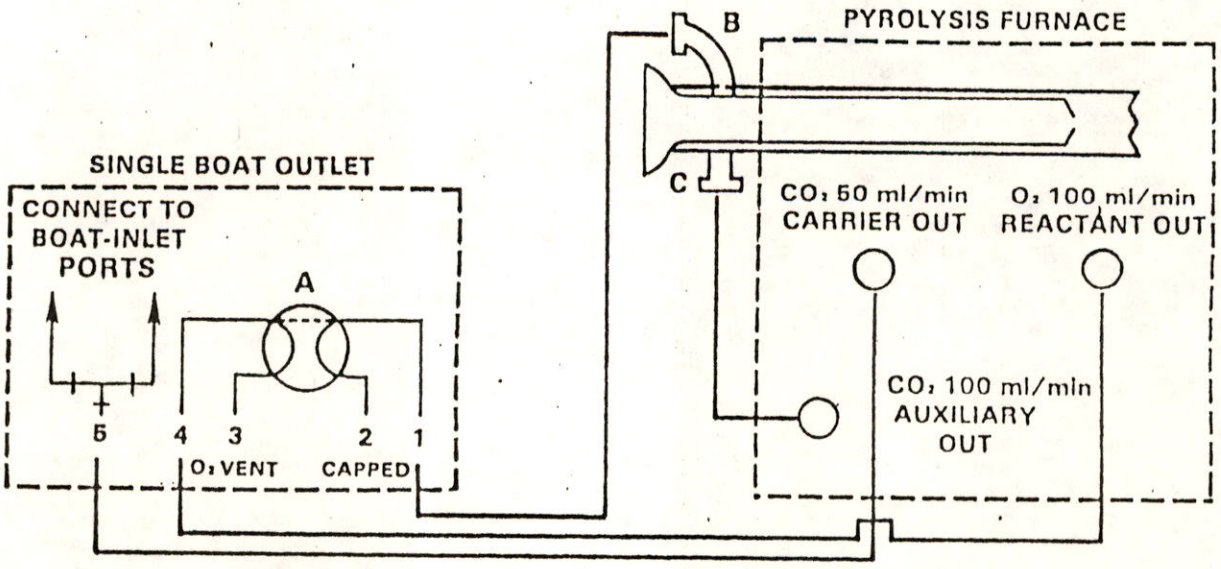


Figure 3. Rear view plumbing schematic for MCTS-20 system. Valve A is set for first-stage combustion, O_2 venting (push/pull valve out). Port B enters inner combustion tube; Port C enters outer combustion tube.

APPENDIX II

TOTAL ORGANIC CARBON, low level
(UV promoted, persulfate oxidation method)

STORET NO.
LOW LEVEL TOTAL

1. Scope and Application

1.1 This method covers the determination of total organic carbon in drinking water and other waters subject to the limitations in 1.3 and 5.1.

1.2 This instrument is designed for a two-step operation to distinguish between purgeable and nonpurgeable organic carbon. These separate values are not pertinent to this method.

1.3 This method is applicable only to that carbonaceous matter which is either soluble or has a particle size of 0.2 mm or less.

1.4 The applicable range is from approximately 50 ug/l to 10 mg/l. Higher concentrations may be determined by sample dilution.

2. Summary of Method

A sample is combined with 1 ml of acidified persulfate reagent and placed in a sparger. The sample is purged with helium which transfers inorganic CO_2 and purgeable organics to a CO_2 scrubber. The CO_2 is removed with at least 99.9% efficiency with a 2.5-minute purge. The purgeable organics proceed through a reduction system where the gas stream is joined by hydrogen and passed over a nickel catalyst which converts the purgeable organic carbon to methane. The methane is measured by a flame ionization detector. The detector signal is integrated and displayed as the concentration of purgeable organic carbon.

The sample is then transferred to a quartz ultraviolet reaction coil where the nonpurgeable organics are subjected to intense ultraviolet illumination in the presence of the acidified persulfate reagent. The nonpurgeables are converted to CO_2 and transferred to a second sparger where a helium purge transfers the CO_2 to the reduction system and into the detector. The signal is integrated, added to the purgeable organic carbon value, and displayed as the concentration of total organic carbon.

3. Definitions

3.1. Total organic carbon measured by this procedure is the sum of the purgeable organic carbon and the nonpurgeable organic carbon as defined in 3.2 and 3.3.

3.2 Purgeable organic carbon is the organic carbon matter that is transferred to the gas phase when the sample is purged with helium and which passes through the CO_2 scrubber. The definition is instrument condition dependent.

3.3 Nonpurgeable organic carbon is defined as that which remains after removal of the purgeable organic carbon from the sample containing acidified persulfate reagent and which is converted to CO_2 under the instrument conditions.

3.4 The system blank is the value obtained in 8.2 for an irradiated, recirculated reagent distilled water sample.

4. Sample Handling and Preservation

4.1 Sampling and storage of samples must be done in glass bottles. Caution: Do not leave any headspace in the sample bottle as this may contribute to loss of purgeable organics.

4.2 Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the lapse of time between collection of samples and start of analysis should be kept to a minimum. Also, samples should be kept cool (4°C) and protected from sunlight and atmospheric oxygen.

4.3 When analysis cannot be performed within two hours from time of sampling, the sample should be acidified to pH 2 with H_2SO_4. Note: HCl should not be used because it is converted to chlorine during the analysis. This causes damage to the instrument.

5. Interferences

5.1 If a sample is homogenized to reduce the size of the particulate matter, the homogenizing may cause loss of purgeable organic carbon, thus yielding erroneously low results.

6. Apparatus

6.1 Apparatus for blending or homogenizing samples: a household blender or similar device that will reduce particles in the sample to less than 0.2 mm.

6.2 Apparatus for Total Organic Carbon: The essential components for the apparatus used in this method are: A sparge assembly, flow switching valves, a pyrolysis furnace, quartz ultraviolet reactor coil, reducing column, flame ionization detector, electrometer and integrator. This method is based on the Dohrmann Envirotech DC-54 Carbon Analyzer. Other instruments having similar performance characteristics may be used.

6.3 Sampling Devices - Any apparatus that will reliably transfer 10 ml of sample to the sparger. A 50 ml glass syringe is recommended when analyzing samples with easily purgeable organics so as to minimize losses.

7. Reagents

7.1 Reagent Distilled Water: Distilled water used in preparation of standards and for dilution of samples should be ultra-pure to reduce the magnitude of the blank. Carbon dioxide-free, double distilled water is recommended. The water should be distilled from permanganate or be obtained from a system involving distillation and carbon treatment. The reagent distilled water value must be compared to a system blank determined on a recirculated distilled water sample. The total organic carbon value of the reagent distilled water should be less than 60 ug/l. Purgeable organic carbon values of the reagent distilled water should be less than 4 ug/l.

7.2 Potassium hydrogen phthalate, stock solution, 500 mg carbon/liter: Dissolve 1.063 g of potassium hydrogen phthalate (Primary Standard Grade) in reagent distilled water (7.1) and dilute to 1 liter.

7.3 Potassium hydrogen phthalate (2 mg/l): Pipet 4 ml of potassium hydrogen phthalate stock solution (7.2) into a one liter volumetric flask and dilute to the mark with reagent distilled water (7.1).

7.4 Potassium hydrogen phthalate (5 mg/l): Pipet 1 ml of potassium hydrogen phthalate stock solution (7.2) into a 100 ml volumetric flask and dilute to the mark with reagent distilled water (7.1).

7.5 Potassium hydrogen phthalate (10 mg/l): Pipet 2 ml of potassium hydrogen phthalate stock solution (7.2) into a 100 ml volumetric flask and dilute to the mark with reagent distilled water (7.1).

7.6 Acidified Persulfate Reagent - Place 100 ml of reagent distilled water (7.1) in a container. Add 5 g of potassium persulfate. Add 5 g (3 ml) of concentrated (85%) phosphoric acid.

7.7 Carbonate-bicarbonate, stock solution, 1000 mg carbon/liter: Place 0.3500 g of sodium bicarbonate and 0.4418 g of sodium carbonate in a 100 ml volumetric flask. Dissolve with reagent distilled water (7.1) and dilute to the mark.

7.8 Carbonate-bicarbonate, standard solution 50 mg/l: Place 5 ml of the carbonate-bicarbonate stock solution in a 100 ml volumetric flask and dilute to the mark with reagent distilled water (7.1).

8. Procedure

8.1 Allow at least 30 minutes warm-up time. Leave instrument console on continuously when in daily use, except for the ultraviolet light source, which should be turned off when not in use for more than a few hours.

8.2 Adjust all gas flows, temperatures and cycle times to manufacturer's specifications. Perform the "System Cleanup and Calibration" procedure in the manufacturer's specifications each day. Recirculate a sample of irradiated distilled water until two consecutive readings within 10% of each other are obtained. Record the last value for the system blank. This value is a function of the total instrument operation and should not vary significantly from previous runs. Reasons for significant changes in the value should be identified.

8.3 Check the effectiveness of the CO_2 scrubber by analyzing the carbonate-bicarbonate standard solution (7.8). Add 1 ml of acidified persulfate reagent (7.6) to 50 ml of the solution. Transfer 10 ml of the solution-with-reagent to the first sparger and start the analysis cycle. No response, or a very minor reading, should be obtained from this solution.

8.4 Add 1 ml of acidified persulfate reagent (7.6) to 50 ml of reagent distilled water (7.1) blank, standards 7.3, 7.4, and 7.5 and the samples.

8.5.1 Run the reagent distilled water (7.1) and 5.0 mg/l standard (7.4):

Transfer 10 ml of the solution-with-reagent to the first sparger and start analyzer cycle

Ignore the meter reading for the first cycle

Transfer a second 10 ml of the solution-with-reagent to the first sparger and start the analysis cycle

Record the meter reading (see 9.1) of the final carbon value for each of the reagent distilled water (7.1) and the standard (7.4).

If the meter reading is more than 25% above or below the calculated value of standard 7.4, reanalyze the standard and set the calibration within 25% (8.5.4), reanalyze the system blank, and then begin 8.5.1 again. If the meter reading (see 9.1) is within 25% of the calculated value, continue to next step. The calculated value is defined in 8.5.2.

8.5.2 Calculate the factor for the deviation of the instrument reading (see 9.1) for the standard (7.4) from the calculated value by:

$$\frac{\text{standard reading} - \text{calculated value}}{\text{calculated value}} = \text{FACTOR}$$

where the calculated value is that value obtained by using the weight of potassium hydrogen phthalate and does not include the carbon contributed by the reagent distilled water (7.1) with which it has been diluted.

8.5.3 Calculate the adjusted reading by:

calculated value + (RDW -(FACTOR X RDW)) = ADJUSTED READING.

where RDW = mean reagent distilled water (7.1) value.

8.5.4 Push in CALIBRATE button after READY light comes on and adjust the SPAN control to the ADJUSTED READING calculated in 8.5.3.

8.6 Analyze the standards 7.3 and 7.5 in order to check the linearity of the instrument at least once each day:

Transfer 10 ml of the solution-with-reagent to the first sparger and start analyzer cycle

Ignore the meter reding for the first cycle

Transfer a second 10 ml of the solution-with-reagent to the first sparger and start the analyzer cycle

Record the meter reading (see 9.1) of the final carbon value for each of the standards 7.3 and 7.5.

The range of concentration used for calibrating the instrument and checking the lineararity of the instrument should be ascertained from a knowledge of the range of concentrations expected from the samples. Standards for lower ranges can be prepared by diluting standards 7.2, 7.3, and 7.4.

8.7 Analyze the samples. Transfer 10 ml of sample with reagent to the first sparger and start the analysis cycle.

Transfer 10 ml of the solution-with-reagent to the first sparger and start analyzer cycle

Ignore the meter reading for the first cycle

Transfer a second 10 ml of the solution-with-reagent to the first sparger and start the analyzer cycle

Record the meter reading (see 9.1) of the final carbon value for each of the samples.

9. Calculations

9.1 The values are read off the final digital readout in ug/l. The system blank reading obtained in 8.2 must be subtracted from all reagent distilled water, standard and sample readings.

10. Precision and Accuracy

10.1 In a single laboratory (MERL), using raw river water, centrifuged river water, drinking water, and the effluent from a carbon column which had concentrations of 3.11, 3.10, 1.79, and 0.07 mg/l total organic carbon respectively, the standard deviations from ten replicates were $\pm$0.13, $\pm$0.03, $\pm$0.02, and $\pm$0.02 mg/l, respectively.

10.2 In a single laboratory (MERL), using potassium hydrogen phthalate in distilled water at concentrations of 5.0 and 1.0 mg/l total organic carbon, recoveries were 80% and 91%, respectively.

11. References

11.1 Proposed Standard Method for Purgeable and Nonpurgeable Organic Carbon in Water (UV-promoted, persulfate oxidation method). ASTM Committee D-19, Task Group 19.06.02.03 (Chairman R. J. Joyce), January 1978.

11.2 Operating Instruction Dohrmann Envirotech, 3420 Scott Boulevard, Santa Clara, California 95050.

11.2 Takahashi, Y., "Ultra Low Level TOC Analysis of Potable Waters." Presented at Water Quality Technology Conference, AWWA, Dec. 5-8, 1976.

METHOD FOR CHLORINATED HYDROCARBONS IN WATER AND WASTEWATER

1. Scope and Application

1.1 This method covers the determination of various organochlorine pesticides and heptachlor epoxide in water and wastewater.

1.2 The following pesticides may be determined individually by this method:

Parameter	Storet No.
Aldrin	39330
BHC	----
Captan	39640
Chlordane	39350
DDD	39360
DDE	39365
DDT	39370
Dichloran	----
Dieldrin	39380
Endosulfan	39388
Endrin	39390
Heptachlor	39410
Lindane	39782
Methoxychlor	39480
Mirex	39755
PCNB	39029
Strobane	----
Toxaphene	39400
Trifluralin	39030

1.3 The following chlorinated organic compound may be determined individually by this method:

Compound	Storet No.
Heptachlor epoxide	----

2. Summary

2.1 The method offers several analytical alternatives, dependent on the analyst's assessment of the nature and extent of interferences and/or the complexity of the pesticide mixtures found. Specifically, the procedure describes the use of an effective co-solvent for efficient sample extraction; provides, through use of column chromatography and liquid-liquid partition, methods for elimination of non-pesticide interferences and the pre-separation of pesticide mixtures. Identification is made by selective gas chromatographic separations and may be corroborated through the use of two or more unlike columns. Detection and measurement is accomplished by electron capture, microcoulometric or electrolytic conductivity gas chromatography. Results are reported in micrograms per liter.

2.2 Confirmation of the identity of the compounds should be made by GC-MS when a new or undefined sample type is being analyzed and the concentration is adequate for such determination.

2.3 This method is recommended for use only by experienced pesticide analysts or under the close supervision of such qualified persons.

3. Interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines, causing misinterpretation of gas chromatograms.

All of these materials must be demonstrated to be free from interferences under the conditions of the analysis. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Refer to Appendix I.

3.2 The interferences in industrial effluents are high and varied and often pose great difficulty in obtaining accurate and precise measurement of organochlorine pesticides. Sample clean-up procedures are generally required and may result in the loss of certain organochlorine pesticides. Therefore, great care should be exercised in the selection and use of methods for eliminating or minimizing interferences. It is not possible to describe procedures for overcoming all of the interferences that may be encountered in industrial effluents.

3.3 Polychlorinated Biphenyls (PCBs) - Special attention is called to industrial plasticizers and hydraulic fluids such as the PCBs, which are a potential source of interference in pesticide analysis. The presence of PCBs is indicated by a large number of partially resolved or unresolved peaks which may occur throughout the entire chromatogram. Particularly severe PCB interference will require special separation procedures (1, 2).

3.4 Phthalate Esters - These compounds, widely used as plasticizers, respond to the electron capture detector and are a source of interference in the determination of organochlorine pesticides using this detector. Water leaches these materials from plastics, such as polyethylene bottles and tygon tubing.

The presence of phthalate esters is implicated in samples that respond to electron capture but not to the microcoulometric or electrolytic conductivity halogen detectors or to the flame photometric detector.

3.5 Organophosphorus Pesticides - A number of organophosphorus pesticides, such as those containing a nitro group, e.g., parathion, also respond to the electron capture detector and may interfere with the determination of the organochlorine pesticides. Such compounds can be identified by their response to the flame photometric detector (3).

4. Apparatus and Materials

4.1 Gas Chromatograph - Equipped with glass lined injection port.

4.2 Detector Options:

4.2.1 Electron Capture - Radioactive (tritium or nickel-63)

4.2.2 Microcoulometric Titration

4.2.3 Electrolytic Conductivity

4.3 Recorder - Potentiometric strip chart (10 in.) compatible with the detector.

4.4 Gas Chromatographic Column Materials:

4.4.1 Tubing - Pyrex (180 cm long X 4 mm ID)

4.4.2 Glass Wool - Silanized

4.4.3 Solid Support - Gas-Chrom-Q (100-120 mesh)

4.4.4 Liquid Phases - Expressed as weight percent coated on solid support.

4.4.4.1 OV-1, 3%

4.4.4.2 OV-210, 5%

4.4.4.3 OV-17, 1.5% plus QF-1 or OV-210, 1.95%

4.4.4.4 QF-1, 6% plus SE-30, 4%

4.5 Kuderna-Danish (K-D) Glassware

4.5.1 Snyder Column - three-ball (macro) and two-ball (micro)

4.5.2 Evaporative Flasks - 500 ml

4.5.3 Receiver Ampuls - 10 ml, graduated

4.5.4 Ampul Stoppers

4.6 Chromatographic Column - Chromaflex (400 mm long x 19 mm ID) with coarse fritted plate on bottom and Teflon stopcock; 250-ml reservoir bulb at top of column with flared out funnel shape at top of bulb - a special order (Kontes K-420540- 9011).

4.7 Chromatographic Column - pyrex (approximately 400 mm long x 20 mm ID) with coarse fritted plate on bottom.

4.8 Micro Syringes - 10, 25, 50 and 100 µl.

4.9 Separatory funnels - 125 ml, 1000 ml and 2000 ml with Teflon stopcock.

4.10 Blender - High speed, glass or stainless steel cup.

4.11 Graduated cylinders - 100 and 250 ml.

4.12 Florisil - PR Grade (60-100 mesh); purchase activated at 1250°F and store in the dark in glass containers with glass stoppers or foil-lined screw caps. Before use, activate each batch overnight at 130°C in foil-covered glass container. Determine lauric-acid value (See Appendix II).

5. Reagents, Solvents, and Standards

5.1 Sodium Chloride - (ACS) Saturated solution in distilled water

(pre-rinse NaCl with hexane).

5.2 Sodium Hydroxide - (ACS) 10 N in distilled water.

5.3 Sodium Sulfate - (ACS) Granular, anhydrous (conditioned at 400 C for 4 hrs.).

5.4 Sulfuric Acid - (ACS) Mix equal volumes of conc. H_2SO_4 with distilled water.

5.5 Diethyl Ether - Nanograde, redistilled in glass, if necessary.

5.5.1 Must be free of peroxides as indicated by EM Quant test strips. (Test strips are available from EM Laboratories, Inc., 500 Executive Blvd., Elmsford, N.Y. 10523.)

5.5.2 Procedures recommended for removal of peroxides are provided with the test strips.

5.6 Acetonitrile, Hexane, Methanol, Methylene Chloride, Petroleum Ether (boiling range 30-60°C) - nanograde, redistill in glass if necessary.

5.7 Pesticide Standards - Reference grade.

6. Calibration

6.1 Gas chromatographic operating conditions are considered acceptable if the response to dicapthon is at least 50% of full scale when $\lesssim$ 0.06 ng is injected for electron capture detection and $\lesssim$ 100 ng is injected for microcoulometric or electrolytic conductivity detection. For all quantitative measurements, the detector must be operated within its linear response range and the detector noise level should be less than 2% of full scale.

6.2 Standards are injected frequently as a check on the stability of operating conditions. Gas chromatograms of several standard

pesticides are shown in Figures 1, 2, 3 and 4 and provide reference operating conditions for the four recommended columns.

6.3 The elution order and retention ratios of various organochlorine pesticides are provided in Table 1, as a guide.

7. Quality Control

7.1 Duplicate and spiked sample analyses are recommended as quality control checks. Quality control charts (4) should be developed and used as a check on the analytical system. Quality control check samples and performance evaluation samples should be analyzed on a regular basis.

7.2 Each time a set of samples is extracted, a method blank is determined on a volume of distilled water equivalent to that used to dilute the sample.

8 Sample Preparation

8.1 The sample size taken for analysis is dependent on the type of sample and the sensitivity required for the purpose at hand. Background information on the pesticide levels previously detected at a given sampling site will assist in determining the sample size required, as well as the final volume to which the extract needs to be concentrated. A 1-liter sample is usually taken for drinking water and ambient water analysis to provide a detection limit of 0.050to 0.100 μg/l. One-hundred milliliters is usually adequate to provide a detection limit of 1 μg/l for industrial effluents.

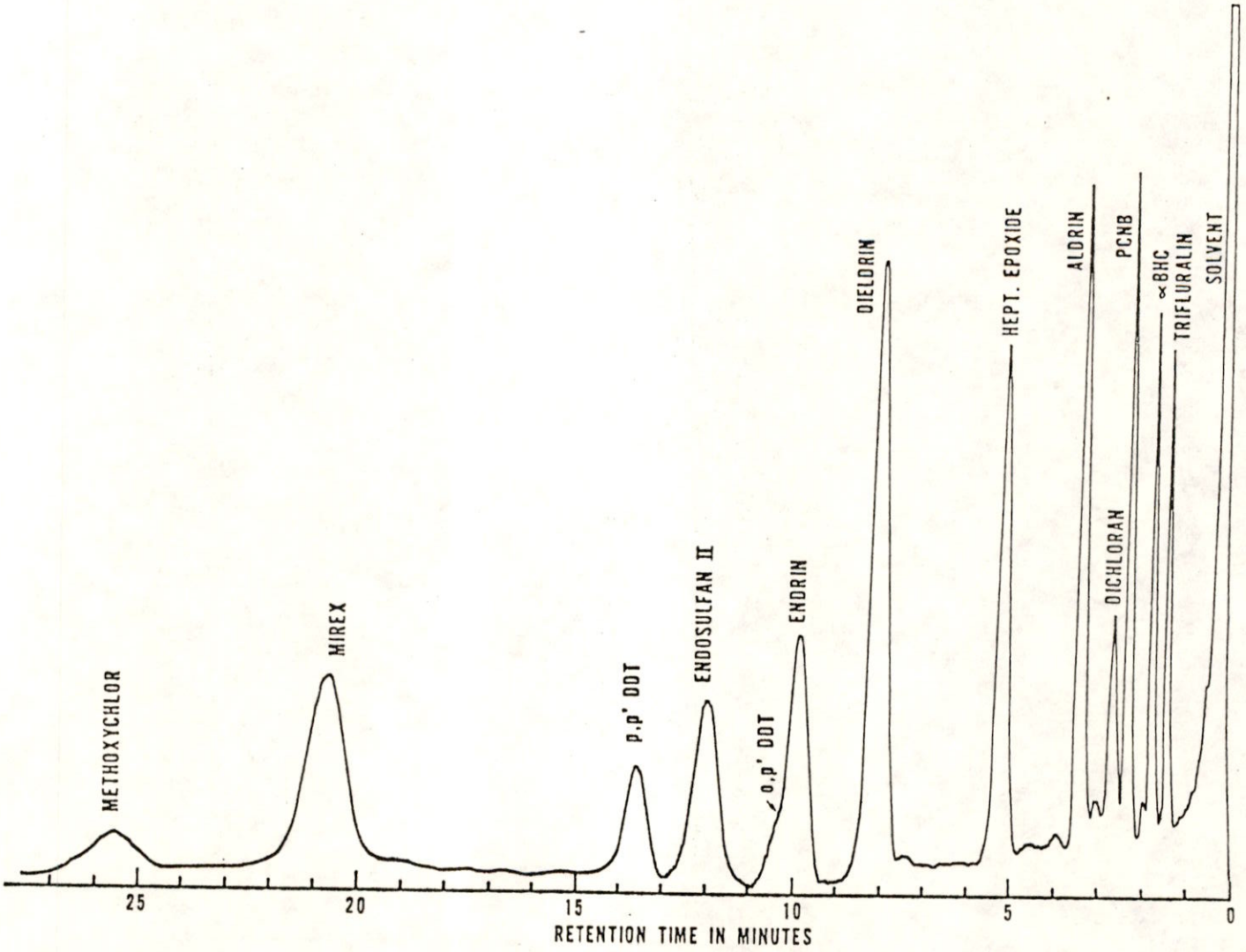


Figure 1. Column Packing: 1.5% OV-17 + 1.95% QF-1, Carrier Gas: Argon/Methane at 60 ml/min, Column Temperature: 200 C, Detector: Electron Capture.

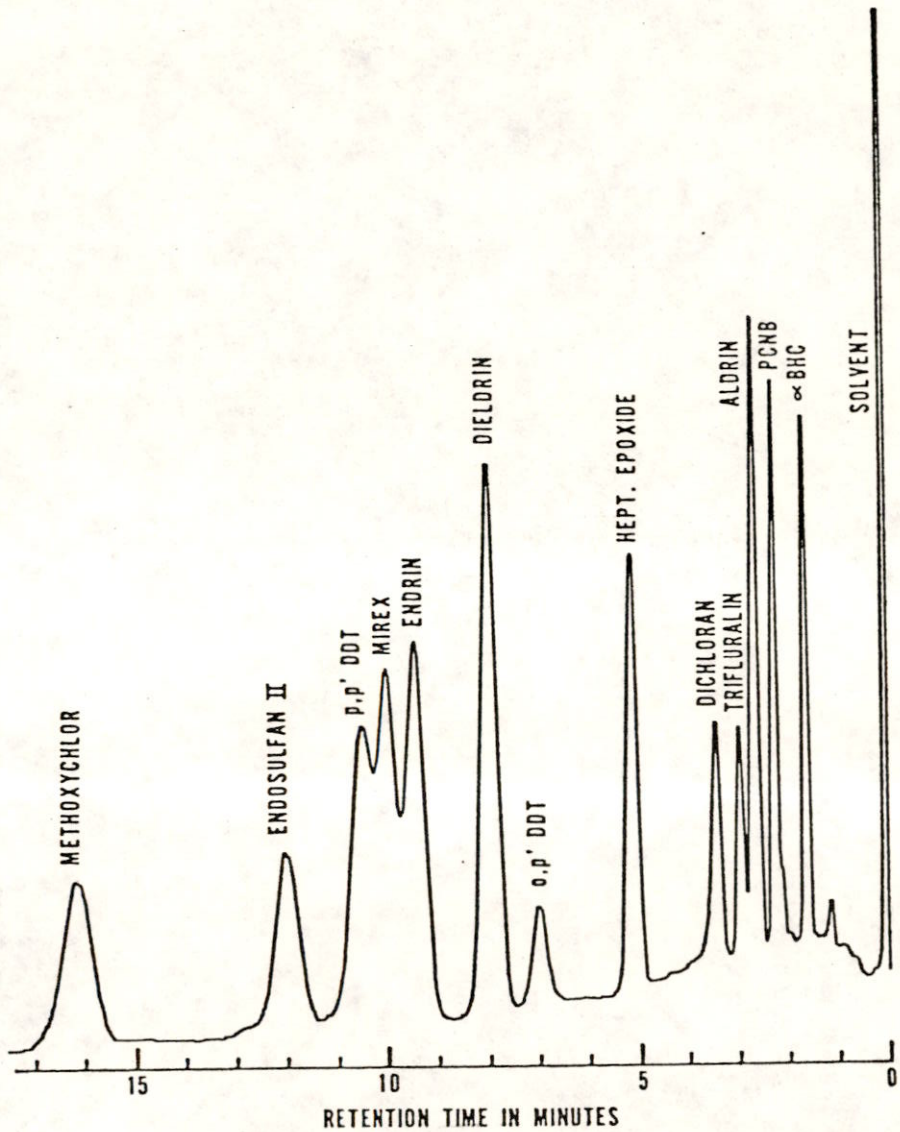


Figure 2. Column Packing: 5% OV-210, Carrier Gas: Argon/Methane at 70 ml/min, Column Temperature: 180 C, Detector: Electron Capture.

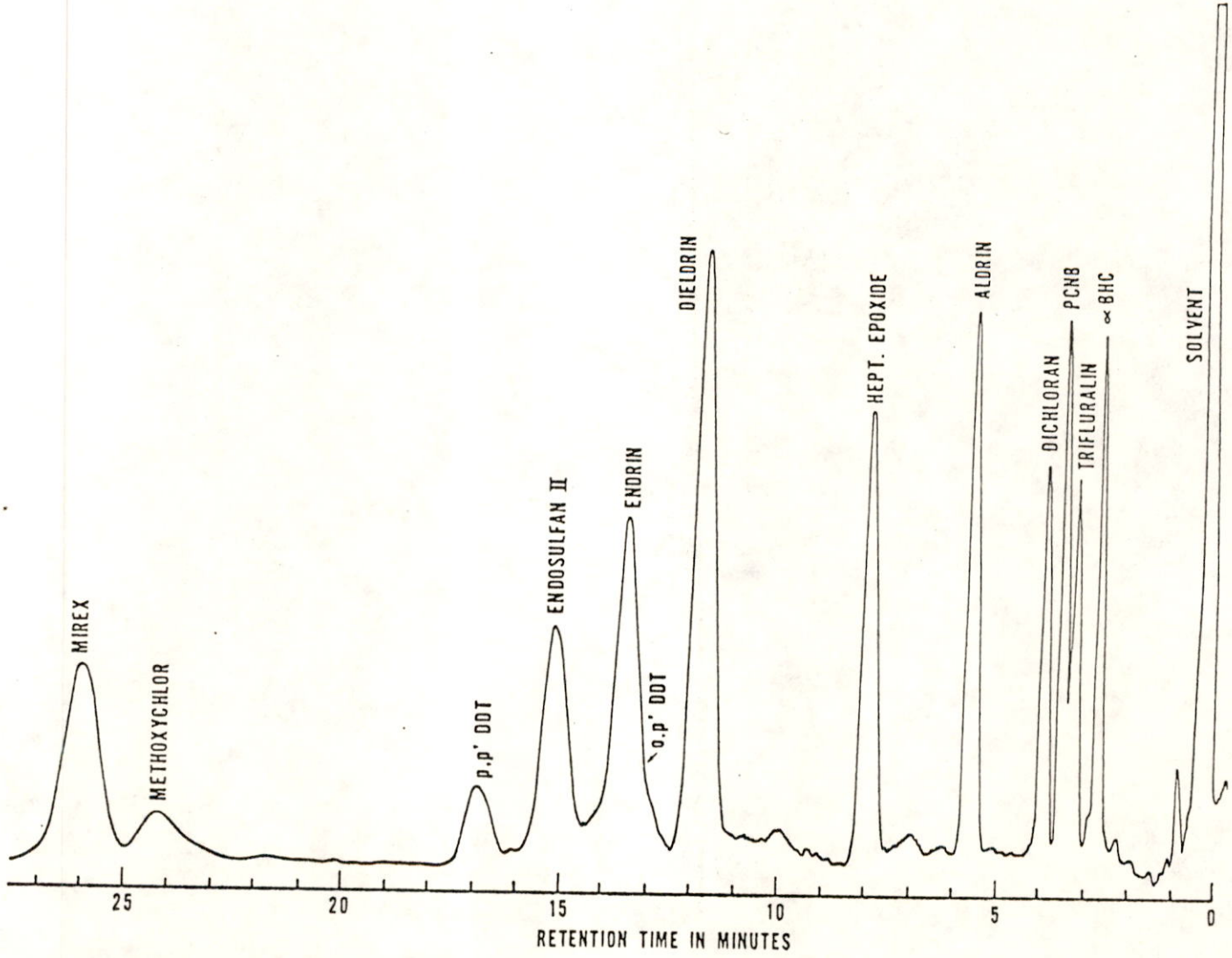


Figure 3. Column Packing: 6% QF-1 + 4% SE-30, Carrier Gas: Argon/Methane at 60 ml/min, Column Temperature: 200 C, Detector: Electron Capture.

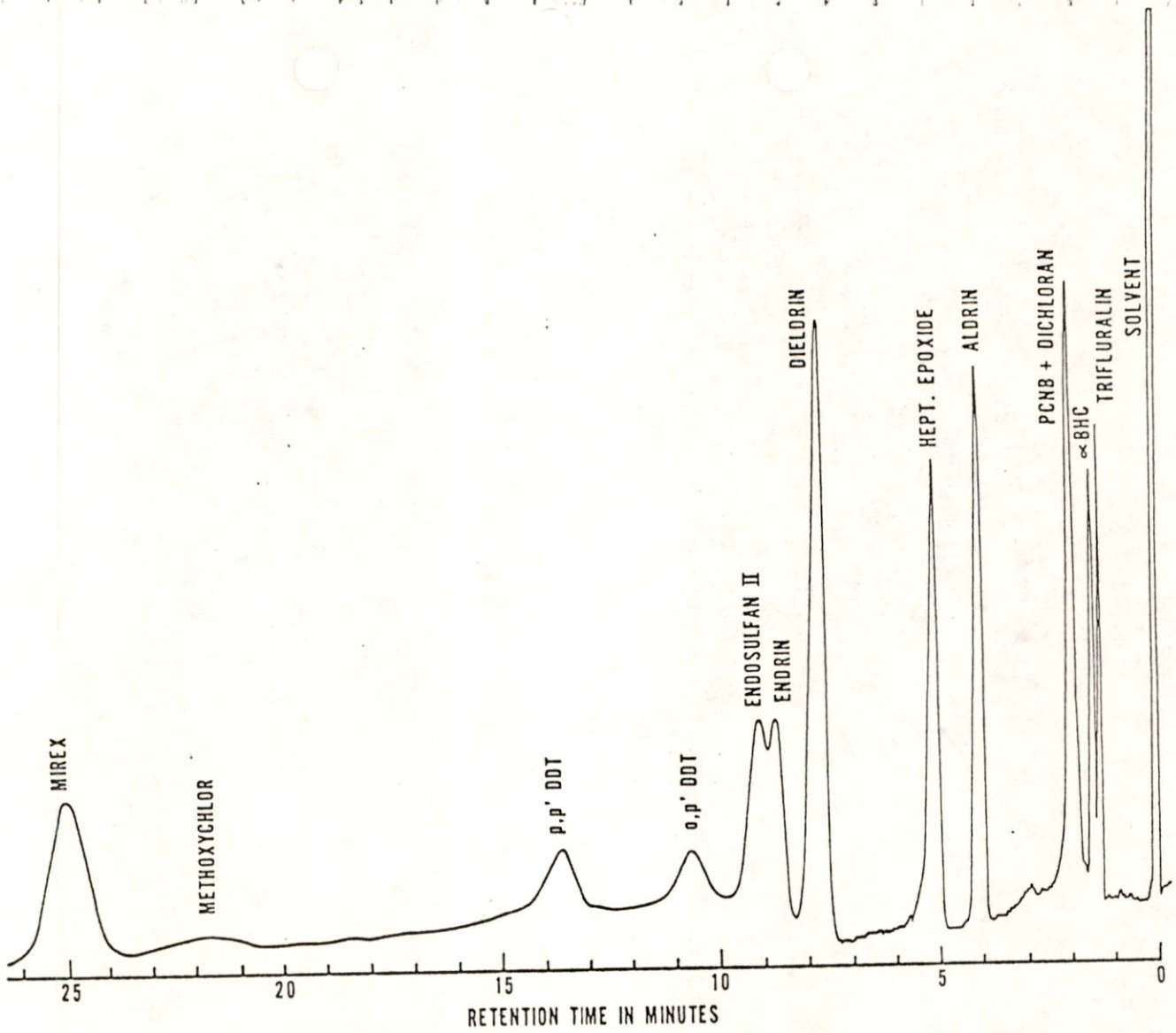


Figure 4. Column Packing: 3% OV-1, Carrier Gas: Argon/Methane at 70 ml/min, Column Temperature: 180 C, Detector: Electron Capture.

Table 1
RETENTION RATIOS OF VARIOUS ORGANOCHLORINE PESTICIDES RELATIVE TO ALDRIN

Liquid Phase[1]	1.5% OV-17 + 1.95% QF-1[2]	5% OV-210	3% OV-1	6% QF-1 + 4% SE-30
Column Temp.	200 C	180 C	180 C	200 C
Argon/Methane Carrier Flow	60 ml/min	70 ml/min	70 ml/min	60 ml/min
Pesticide	RR	RR	RR	RR
Trifluralin	0.39	1.11	0.33	0.57
α-BHC	0.54	0.64	0.35	0.49
PCNB	0.68	0.85	0.49	0.63
Lindane	0.69	0.81	0.44	0.60
Dichloran	0.77	1.29	0.49	0.70
Heptachlor	0.82	0.87	0.78	0.83
Aldrin	1.00	1.00	1.00	1.00
Heptachlor Epoxide	1.54	1.93	1.28	1.43
Endosulfan I	1.95	2.48	1.62	1.79
p,p'-DDE	2.23	2.10	2.00	1.82
Dieldrin	2.40	3.00	1.93	2.12
Captan	2.59	4.09	1.22	1.94
Endrin	2.93	3.56	2.18	2.42
o,p'-DDT	3.16	2.70	2.69	2.39
p,p'-DDD	3.48	3.75	2.61	2.55
Endosulfan II	3.59	4.59	2.25	2.72
p,p'-DDT	4.18	4.07	3.50	3.12
Mirex	6.1	3.78	6.6	4.79
Methoxychlor	7.6	6.5	5.7	4.60
Aldrin (Min. absolute)	3.5	2.6	4.0	5.6

[1]All columns glass, 180 cm x 4 mm ID, solid support Gas-Chrom Q (100/120 mesh)
[2]OV-210 also may be used

8.2 Quantitatively transfer the proper aliquot of sample from the sample container into a two-liter separatory funnel. If less than 800 ml is analyzed, dilute to one liter with interference free distilled water.

9. Extraction

9.1 Add 60 ml of 15% methylene chloride in hexane (v:v) to the sample in the separatory funnel and shake vigorously for two minutes.

9.2 Allow the mixed solvent to separate from the sample, then draw the water into a one-liter Erlenmeyer flask. Pour the organic layer into a 100 ml beaker and then pass it through a column containing 3-4 inches of anhydrous sodium sulfate, and collect it in a 500 ml K-D flask equipped with a 10 ml ampul. Return the water phase to the separatory funnel. Rinse the Erlenmeyer flask with a second 60-ml volume of solvent; add the solvent to the separatory funnel and complete the extraction procedure a second time. Perform a third extraction in the same manner.

.3 Concentrate the extract in the K-D evaporator on a hot water bath.

9.4 Analyze by gas chromatography unless a need for cleanup is indicated (See Section 10).

10. Clean-up and Separation Procedures

10.1 Interferences in the form of distinct peaks and/or high background in the initial gas chromatographic analysis, as well as the physical characteristics of the extract (color, cloudiness, viscosity) and background knowledge of the sample will indicate

whether clean-up is required. When these interfere with measurement of the pesticides, or affect column life or detector sensitivity, proceed as directed below.

10.2 Acetonitrile Partition - This procedure is used to isolate fats and oils from the sample extracts. It should be noted that not all pesticides are quantitatively recovered by this procedure. The analyst must be aware of this and demonstrate the efficiency of the partitioning for specific pesticides. All of the pesticides listed in Scope (1.2) with the exception of mirex are efficiently recovered.

10.2.1 Quantitatively transfer the previously concentrated extract to a 125-ml separatory funnel with enough hexane to bring the final volume to 15 ml. Extract the sample four times by shaking vigorously for one minute with 30-ml portions of hexane-saturated acetonitrile.

10.2.2 Combine and transfer the acetonitrile phases to a one-liter separatory funnel and add 650 ml of distilled water and 40 ml of saturated sodium chloride solution. Mix thoroughly for 30-45 seconds. Extract with two 100-ml portions of hexane by vigorously shaking about 15 seconds.

10.2.3 Combine the hexane extracts in a one-liter separatory funnel and wash with two 100-ml portions of distilled water. Discard the water layer and pour the hexane layer through a 3-4 inch anhydrous sodium sulfate column into a 500-ml K-D flask equipped with a 10-ml

ampul. Rinse the separatory funnel and column with three 10-ml portions of hexane.

10.2.4 Concentrate the extracts to 6-10 ml in the K-D evaporator in a hot water bath.

10.2.5 Analyze by gas chromatography unless a need for further cleanup is indicated.

10.3 Florisil Column Adsorption Chromatography

10.3.1 Adjust the sample extract volume to 10 ml.

10.3.2 Place a charge of activated Florisil (weight determined by lauric-acid value, see Appendix II) in a Chromaflex column. After settling the Florisil by tapping the column, add about one-half inch layer of anhydrous granular sodium sulfate to the top.

10.3.3 Pre-elute the column, after cooling, with 50-60 ml of petroleum ether. Discard the eluate and just prior to exposure of the sulfate layer to air, quantitatively transfer the sample extract into the column by decantation and subsequent petroleum ether wash- ings. Adjust the elution rate to about 5 ml per minute and, separately, collect up to three eluates in 500-ml K-D flasks equipped with 10-ml ampuls (see Eluate Composition 10.4.). Perform the first elution with 200 ml of 6% ethyl ether in petroleum ether, and the second elution with 200 ml of 15% ethyl ether in

petroleum ether. Perform the third elution with 200 ml of 50% ethyl ether - petroleum ether and the fourth elution with 200 ml of 100% ethyl ether.

10.3.4 Concentrate the eluates to 6-10 ml in the K-D evaporator in a hot water bath.

10.3.5 Analyze by gas chromatography.

10.4 Eluate Composition - By using an equivalent quantity of any batch of Florisil, as determined by its lauric acid value, the pesticides will be separated into the eluates indicated below:

6% Eluate

Aldrin	DDT	Mirex
BHC	Heptachlor	PCNB
Chlordane	Heptachlor Epoxide	Strobane
DDD	Lindane	Toxaphene
DDE	Methoxychlor	Trifluralin

15% Eluate

Endosulfan I
Endrin
Dieldrin
Dichloran

50% Eluate

Endosulfan II
Captan

Certain thiophosphate pesticides will occur in each of the above fractions as well as the 100% fraction. For additional information regarding eluate composition, refer to the FDA Pesticide Analytical Manual (5).

11. Calculation of Results

11.1 Determine the pesticide concentration by using the absolute calibration procedure described below or the relative calibration procedure described in Appendix III.

(1) Micrograms/liter = $\frac{(A)\ (B)\ (V_t)}{(V_i)\ (V_s)}$

$A = \frac{\text{ng standard}}{\text{Standard area}}$

B = Sample aliquot area
V_i = Volume of extract injected (µl)
V_t = Volume of total extract (µl)
V_s = Volume of water extracted (ml)

12. Reporting Results

12.1 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

ITEM 6

OUTLINE OF GROUNDWATER QUALITY ASSESSMENT PROGRAM

GROUND-WATER ASSESSMENT PLAN OUTLINE FOR THE PPG MERCURY POND, NATRIUM, WEST VIRGINIA

Prepared for:

PPG INDUSTRIES, INC.
Natrium, West Virginia

By:

GERAGHTY & MILLER, INC.
Annapolis, Maryland

April, 1981

1.0 Introduction

Section 265.93(a) of the U. S. Environmental Protection Agency, Interim Status Standards for Owners and Operators of Hazardous Waste Treatment, Storage and Disposal Facilities (FR, 45:98, 33241) specifies that by November 19, 1981, PPG Industries, Natrium Plant must prepare and have on file an "outline of a ground-water quality assessment program" for facilities under "Interim Status". This document has been prepared for compliance with that requirement and is applicable to the "mercury pond".

While this document outlines information and procedures not specifically required to be contained in accordance with Section 265.93(a), it is felt that a clear understanding of all of these requirements is necessary to assure proper initiation of the "ground-water assessment program" as needed. This outline has been prepared from requirements contained in Sections 265.92, 265.93 and 265.94 of the subject regulations to include the procedures to be followed by PPG to assure proper evaluation of water-quality samples collected from the mercury-pond monitor-well network, compliance with reporting procedures, and institution of the ground-water quality assessment plan.

2.0 First-year Water-Quality Analysis (Section 265.92)

2.1 Sample Collection and Analysis

(See Ground-Water Sampling and Analysis Plan for details.)

2.1.1 Ground-Water Contamination Indicators
2.1.2 Ground-Water Quality Parameters
2.1.3 Drinking-Water Supply Parameters
2.1.4 Additional Parameters

2.2 Ground-Water Contamination Indicators - Initial Background Mean and Variance (Section 265.92(c)(2))

On a quarterly basis sample the well and make four replicate analyses for the Ground-Water Contamination Indicators. Pool the data for the respective parameters and determine the Initial Background Arithmetic Mean and variance of each parameter. This section may be followed for all downgradient monitor wells (GM-1, GM-2, and GM-6) but must be followed for the upgradient well (PPG water-supply well).

2.3 Water-Level Measurements (Section 265.92(e))

2.3.1 Determine water-level elevations in all monitor wells each time a water-sample is collected.

2.3.2 At least once during the year evaluate the water-level data to assure that the existing network properly monitors downgradient movement of fluid. If significant change in direction of ground-water flow is determined, install monitor wells, as needed, to ensure continued downgradient monitoring. Report results of the evaluation in accordance with 2.4.2.

2.4 Reporting (Section 265.94(a)(2))

2.4.1 Report to EPA Regional Administrator within 15 days after quarterly sampling:

(1) Results of analyses for Drinking-Water Supply Parameters; and
(2) Each well found to produce water in excess of EPA Interim Primary Drinking Water Standards (See Sampling and Analysis Plan).

2.4.2 Report concentrations or values for the Ground-Water Contamination Indicators and Initial Background Mean and variance at end of first-year monitoring. Also report results of water-level elevation evaluation and describe the water-level response.

3.0 Second (and Subsequent) Year Water Quality Analysis

3.1 Semi-Annual Sample Collection and Analysis (Section 265.92(b))

(See Grond-Water Sampling and Analysis Plan for details.)

3.1.1 Ground-Water Contamination Indicators

3.1.2 Drinking-Water Supply Parameters

3.1.3 Additional Parameters

3.2 Preparation of Mean and Variance (Section 265.93(b))

3.2.1 Semi-annually for each monitor well (GM-1, GM-2, GM-6, and PPG water-supply well),

calculate the arithmetic mean and variance for each Ground-Water Contamination Indicator based on at least four replicates.

3.2.2 Compare the results of 3.2.1 for each downgradient well (GM-1, GM-2, and GM-6) with the Initial Background Arithmetic Mean for the upgradient well (PPG water-supply well) to determine if a statistically significant increase (decrease in the case of pH) in the level of any parameter has occurred.

3.2.3 Statistical significance shall be determined using the Student's t-test at the 0.01 level of significance.

3.3 <u>If Statistical Significance is Determined (Section 265.93(c))</u>

3.3.1 If the results of 3.2.2 indicate a significant change for the upgradient well (PPG water-supply well), report results to EPA Regional Administrator in accordance with 3.6.2.

3.3.2 If the results of 3.2.2 indicate a significant change for any downgradient well (GM-1, GM-2, or GM-6), immediately collect additional water samples from the affected well. Split sample in two and reanalyze to determine whether the significance is the result of laboratory error.

3.3.3 If significance is proven to be a result of laboratory error, resume following normal Ground-Water Sampling and Analysis Plan.

3.3.4 If significance is proven to be result of actual change in water quality, provide written notice to EPA Regional Administrator within 7 days of confirmation.

3.3.4.1 Within 15 days of notification to EPA Regional Administrator, develop and submit specific Ground-Water Quality Assessment Plan. Plan must be based on Section 4.0 and must contain:

(1) Number, location, and depth of additional monitor wells,

(2) Sampling and analytical methods for hazardous-waste constituents;
(3) Data evaluation procedures including any previous data gathering; and
(4) Schedule of implementation.

3.3.4.2 The plan must be certified by a qualified geologist or geotechnical engineer.

3.4 Annual Sample Collection and Analysis (Section 265.92(b))

(See Ground-Water Sampling and Analysis Plan for details.)

3.4.1 Ground-Water Quality Parameters

3.5 Water-Level Measurements (Section 265.93(f))

3.5.1 At least once annually evaluate water-level evaluation data collected at the time of sampling to determine direction of ground-water flow.

3.5.2 If significant change in direction of ground-water flow is determined, install monitor wells, as needed, to ensure continued down-gradient monitoring.

3.6 Reporting and Record Keeping (Section 265.94(a))

3.6.1 Annually report to EPA Regional Administrator, concentrations or values for the Ground-Water Contamination Indicators and results of evaluations.

3.6.2 Annually report to EPA Regional Administrator, statistically significant changes in quality of upgradient well.

3.6.3 Annually report to EPA Regional Administrator results of water-level elevation evaluation and describe the water-level response.

3.6.4 All records of analyses and evaluations made as a part of this Section must be maintained throughout the life and post-closure care period of the facility.

4.0 Preliminary Ground-Water Quality Assessment Plan (Section 265.93(a))

PPG may have to have prepared and to submit a Ground-Water Quality Assessment Plan, if normal sampling

indicates a statistically significant change for any of the Ground-Water Contamination Indicators in any downgradient monitor well (GM-1, GM-2, or GM-6). This section contains an outline of the basic steps which PPG should follow to carry-out that Plan and should be used with appropriate amplification to prepare it. Due to the many uncertainities with regard to specific wells which might show affects of contamination, and because the type of "Rate and Extent" study requested by EPA is a very iterative process, most of the details regarding location and type of future monitoring points must be left very sketchy.

4.1 Hazardous-Waste Confirmation Monitoring (Section 265.93(d))

4.1.1 If results of Section 3.3.2 prove that a statistically significant change in any Ground-Water Contamination Indicator has occurred, institute a water-sampling program to confirm presence of hazardous-waste constitutents.

4.1.2 To confirm presence of hazardous-waste constitutes sample daily for one week:

(1) discharge to mercury pond,
(2) discharge from mercury pond to carbon filter,
(3) upgradient well (PPG water-supply well), and
(4) downgradient monitor wells (GM-1, GM-2, and GM-6).

(Sampling shall be made in accordance with the Sampling and Analysis Plan.)

4.1.3 Analyze samples collected in accordance with 4.1.2 to determine levels of the hazardous-waste constitutents and other parameters listed below. These parameters have been selected as most representative of the waste currently entering the mercury pond. If the waste stream character changes, appropriate modification of this list is necessary.

(1) pH,
(2) Specific conductance,
(3) Total dissolved solids,
(4) Sodium,
(5) Chloride,

(6) Sulfate,
(7) Barium,
(8) Cadmium,
(9) Chromium (total),
(10) Mercury,
(11) Lead,
(12) Total organic carbon, and
(13) Total organic halogens.

(Follow Sampling and Analysis Plan for these analyses.)

4.1.4 Compare results of analyzes of samples from downgradient wells made during this week of sampling with data collected during the first year of sampling (and subsequent years when available) for the downgradient wells and with data collected from the mercury pond and the upgradient well. Using the Student's t-test or equivalent, determine if the statistically significant change previously determined for the Ground-Water Contamination Indicator is the result of hazardous waste or hazardous-waste constituents from the mercury pond.

4.1.4.1 If the mercury pond cannot be identified as the cause of the statistically significant change, report results to EPA Regional Administrator within 15 days of determination and request resumption of normal Ground-Water Sampling and Analysis Plan.

4.1.4.2 If statistically significant change is determined, institute Rate and Extent Monitoring Program contained in 4.2.

4.2 Rate and Extent Monitoring Program

4.2.1 Additional monitor wells must be installed; the location and configuration of which will be related to the determination of which downgradient well(s) is contaminated.

4.2.1.1 If well GM-2 or GM-6 is contaminated, additional monitor wells should be installed on either side of the affected well. In addition, monitor wells should be insalled downgradient from the affected well (s). It may be necessary to install several sets of these downgradient wells to define the extent of contamination (see Figure 1 for potential locations).

4.2.1.2 If well GM-1 is contaminated, additional monitor wells should be installed on either side of it. In addition, monitor wells should be installed on either side of GM-2, and one or more lines of monitor wells should be installed parallel to the terrace face and at least 20 feet west of GM-1. If more than one line of wells is installed west of GM-1 the wells fronts should be at least 20 feet apart (see Figure 1 for potential locations).

4.2.1.3 The exact number and location of the additional monitor wells must be determined by the geologist or geotechnical engineer preparing the final Ground-Water Assessment Plan.

4.2.2 The hollow-stem auger drilling method shall be used to install 2-inch I.D. PVC monitor wells. Ten-foot well screens should be installed across the water table and above the top of consolidated bedrock. The estimated depth to the top of the screen will be approximately 80 feet. Soil samples should be collected during construction of the borehole. The annular space around the screen should be gravel packed. A bentonite plug shall be set above the screen and the remaining annulus shall be filled with bentonite or grout.

4.2.3. Via laboratory tests or pumping tests determine the permeability (hydraulic conductivity) of the earth material above and in the aquifer. The data will be needed to calculate ground-water flow rates.

4.2.4 Determine the elevation of water in all wells and prepare a map of the water table depicting the direction of ground-water movement and hydraulic gradient.

4.2.5 Following the Sampling and Analysis Plan, collect water samples from all existing monitor wells (GM-1, GM-2, and GM-6), the upgradient well (PPG water-supply well), the mercury pond, and newly installed wells. Determine the levels of the following constituents in each sample:

(1) pH
(2) Specific conductance,
(3) Total dissolved solids,
(4) Sodium,
(5) Chloride,
(6) Sulfate,
(7) Barium,
(8) Cadmium,
(9) Chromium (total),
(10) Mercury,
(11) Lead,
(12) Total organic carbon, and
(13) Total organic halogens

4.2.6 Map results of water-quality analyses to determine the extent of ground-water contamination. Show concentration distributions of the quality of the contaminated zone for critical hazardous-waste constituents.

4.2.7 Using available data on flow direction, hydraulic conductivity, hydraulic gradient, or other factors predicate the rate of movement of the contamination.

4.3 Schedule of Implementation (Section 265.93(d))

4.3.1 Within 15 days of the determination that ground water is contaminated by hazardous constituents (Section 4.1.4.2) begin installation of additional monitor wells.

4.3.2 Within 60 days of initiation of installation of additional monitor wells, have results of all analyses completed and prepare a report defining the Rate and Extent of contamination.

4.3.3 Within 15 days of completion of the report defining the Rate and Extent of contamination, report results to EPA Regional Administration.

4.4 Reprediction (Section 265.93(d))

4.4.1 On a quarterly basis determine:

(1) The rate and extent of migration of hazardous waste or hazardous-waste constituents in ground-water, and
(2) The concentrations of the hazardous waste or hazardous-waste constituent.

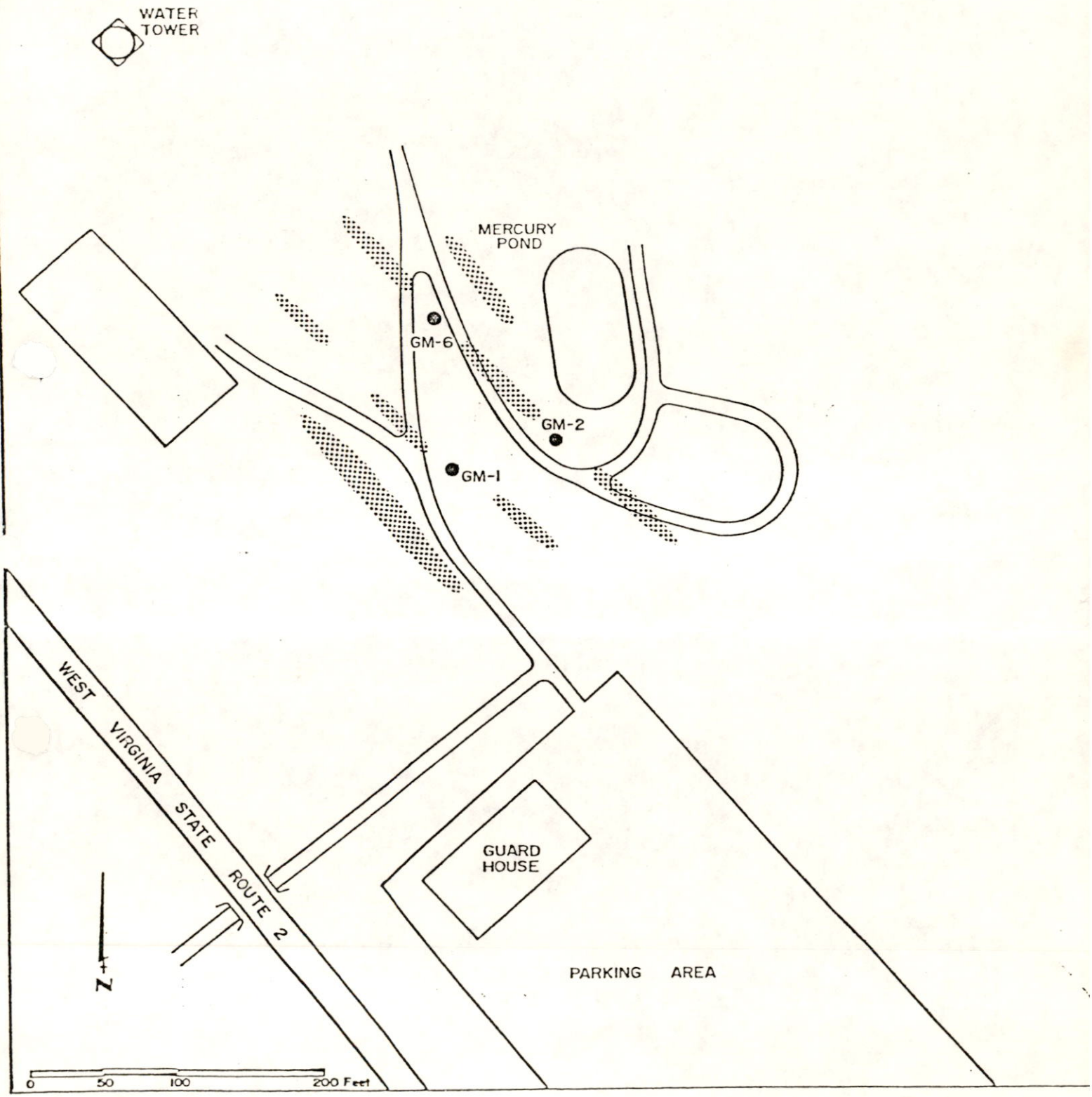
4.4.2 Repredications must be made until the facility is closed.

4.4.3 As needed, install additional monitor to assure the ability to comply with Section 4.4.1.

4.5 Reporting and Record Keeping (Section 265.94(a))

4.5.1 Annually report to the EPA Regional Administrator the results of the quarterly reprediction contained in Section 4.4.

4.5.2 Maintain all records during life of facility and through the post-closure case period.



EXPLANATION

GM-2 Monitor well and number

Potential location of additional monitor wells

Figure 1. Future Monitor-Well Locations