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TRINITY RIVER BOTTOM SEDIMENT RECONNAISSANCE STUDY, PHASE I, PL--ETC(U)
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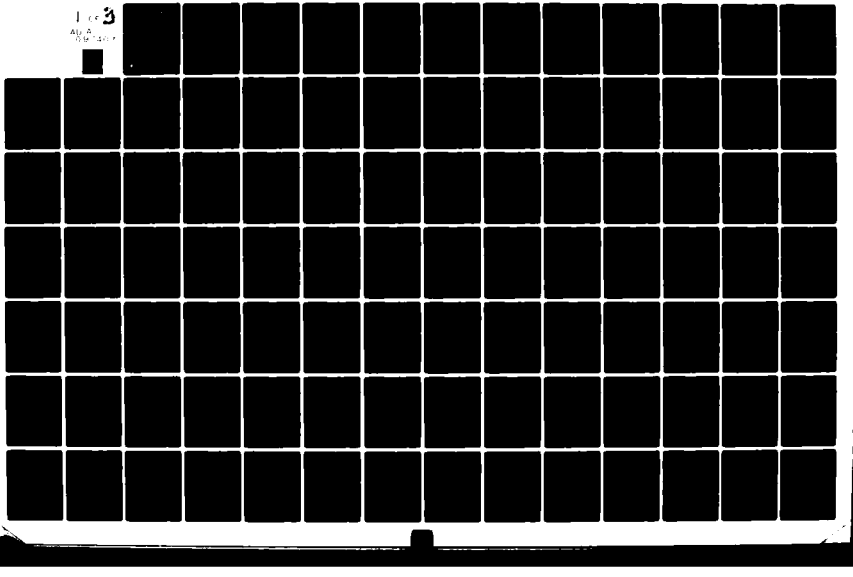

APPENDICES

To

FINAL REPORT

TRINITY RIVER BOTTOM SEDIMENT RECONNAISSANCE STUDY

PHASE I – PLAN OF WORK

To

FORT WORTH DISTRICT CORPS OF ENGINEERS
FORT WORTH, TEXAS

Prepared Under Contract No. DACW 63-76-C-0140

By

Syed R. Qasim,
Vern H. Sorgee, and
Andrew T. Armstrong

November 30, 1976

Contributors

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and Saiid Derbendi

THE UNIVERSITY OF TEXAS AT ARLINGTON
Arlington, Texas 76019

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TEXAS WATER QUALITY BOARD

WASTE CONTROL ORDERS AND POINTS OF ENTRY INTO THE TRINITY RIVER

APPENDIX A

TEXAS WATER QUALITY BOARD

WASTE CONTROL ORDERS AND POINTS OF ENTRY INTO THE TRINITY RIVER

The Waste Control Order data presented in this appendix was obtained from the Texas Water Quality Board computer printout. The waste control orders (WCO s) were arranged numerically by segment numbers (See Table A-1). These data were later transferred to county maps for the purpose of obtaining point-of-entry into the Trinity River. The data was used in Table 1 for site selection.

The basic method by which the following data were compiled was as follows:

1. Known discharge points and their location were obtained from TWQB.
2. The point sources were then pin-pointed on county by county topographical maps, made available from the Texas Highway Department.
3. The point source discharge was then traced along its tributary of entry to the point at which it finally entered the river.
4. The point of entry into the river was then referenced by latitude and longitude for exact location (See Table A-2).

NOTE: All point sources are latest available from TWQB as of August, 1976.

TABLE A-1: ARRANGEMENT OF WCO s BY TWQB SEGMENT NUMBER
(These segment numbers relate to Main Stems of the Trinity River)

WCO	PG	NAME	PLANT OR OUTFALL NAME	DST CTY BSN SGMT TR	FLOW-AVG GAL/DAY	RE-TAINED	TYPE WCO	TYPE OWNER	TYPE ESTAB	EFF DATE MO-DA-YR
10060	05	DALLAS CITY OF	ELM FORK WTP-OUTFALL NO. 001	04 057 08 0822 Y	5,000,000	NO	2	10	93494	03-25-75
ADDRESS			MUNICIPAL BLDG.,500 S. ERVAY	DALLAS TEXAS	ZIP 75201 NON-PRIMARY					
10060	07	DALLAS CITY OF	BACHMAN STORMWATER CONTROL STA	04 057 08 0822 Y	3,000,000	NO	3	10	93495	11-26-74
ADDRESS			MUNICIPAL BLDG.,500 S.ERVAY	DALLAS, TEXAS	ZIP 75201 NON-PRIMARY					
10662	01	LEWISVILLE CITY OF	MUN. STP	04 061 08 0822 Y	9,000,000	NO	3	10	93495	10-22-74
ADDRESS			151 WEST CHURCH STREET	LEWISVILLE TEXAS	ZIP 75067 PRI-MAILING					
10805	02	DALLAS COUNTY PARK CITIES MUD	OUTLET NO 2	04 057 08 0822	15,000	NO	1	10	93494	02-24-66
ADDRESS			8527 HINES BOULEVARD	DALLAS TEXAS	ZIP 75235 PRI-MAILING					
11321	01	FLOWER MOUND MUD NO C)		04 061 08 0822 Y	700,000	NO	3	13	93495	08-27-74
ADDRESS			P. O. BOX 31705	DALLAS, TEXAS	ZIP 75231 PRI-MAILING					
11543	01	ADDISON CITY OF	NORTH SEWAGE TREATMENT PLT.	04 057 08 0822 Y	15,000	NO	3	10	93495	02-27-74
ADDRESS			P. O. BOX 144	ADDISON, TEXAS	ZIP 75001 PRI-MAILING					

WCO	PG	NAME	PLANT OR OUTFALL NAME	DST CTY BSN SGMT TR	FLOW-AVG GAL/DAY	RE-TAINED	TYPE WCO	TYPE OWNER	TYPE ESTAB	EFF DATE MO-DA-YR
10028	01	FORNEY CITY OF	STP	04 129 08 0819 Y	400,000	NO	3	10	93495	10-22-74
			P O BOX 826	FORNEY TEXAS	ZIP 75126 PRI-MAILING					
10060	03	DALLAS CITY OF	EAST SIDE WTP-OUTFALL 001	04 057 08 0819 Y	7,000,000	NO	2	10	93494	03-25-75
ADDRESS			MUNICIPAL BLDG.,500 S. ERVAY	DALLAS TEXAS	ZIP 75201 NON-PRIMARY					
10090	01	GARLAND CITY OF	DUCK CREEK PLANT	04 057 08 0819 Y	10,000,000	NO	3	10	93495	03-16-72
ADDRESS			P O BOX 189	GARLAND TEXAS	ZIP 75040 PRI-MAILING					
10221	01	NORTH TEXAS MUN WATER DISTRICT	CITY OF MESQUITE STP	04 057 08 0819 Y	5,500,000	NO	3	13	93495	01-28-75
ADDRESS			P.O. DRAWER C	WYLIE, TEXAS	ZIP 75098 PRI-MAILING					
10570	01	SEAGOVILLE CITY OF	MUN STP	04 057 08 0819 Y	1,200,000	NO	3	10	93495	11-26-74
ADDRESS			110 WEST ELM STREET	SEAGOVILLE TEXAS	ZIP 75159 PRI-MAILING					
10834	01	CRANDALL CITY OF	MUN. STP	04 129 08 0819 Y	300,000	NO	3	10	93495	02-27-74
ADDRESS			P. O. BOX 278	CRANDALL TEXAS	ZIP 75114 PRI-MAILING					
11209	01	ROCKWALL ESTATES INC	SUBDIV SEWERAGE SYS	04 199 08 0819	125,000	NO	1	01	93495	06-18-71
ADDRESS			ROUTE 1 BOX 26-A	ROCKWALL, TEXAS	ZIP 75087 PRI-MAILING					

WCD PG	NAME	PLANT OR OUTFALL NAME	DST CTY BSN SGMT TR	FLOW-AVG GAL/DAY	RE-TAINED	TYPE WCD	TYPE OWNER	TYPE ESTAB	EFF DATE MO-DA-YR
00367 01	BELL HELICOPTER CO	HURST PLANT-OUTFALL NO.001	04 220 08 0805 Y	350,000	NL	2	01	37210	04-22-75
ADDRESS		P. O. BOX 482	FORT WORTH TEXAS	ZIP 76101			PRI-MAILING		
00579 01	WINSTON REFINING CO.	PETROLEUM RFY-OUTFALL 001	04 220 08 0805	43,200	NO	2	01	29110	10-22-74
ADDRESS		P. O. BOX 1508	FORT WORTH, TEXAS	ZIP 76101			PRI-MAILING		
01248 01	DALLAS P L L CO	DALLAS PWR PLT-OUTFALL 001	04 057 08 0805 Y	600,000	NO	2	01	49110	03-25-75
ADDRESS		1506 COMMERCE ST	DALLAS TEXAS	ZIP 75201			NON-PRIMARY		
01248 02	DALLAS P L L CO	DALLAS PWR PLT-OUTFALL 002	04 057 08 0805 Y	200,000	NO	2	01	49110	03-25-75
ADDRESS		1506 COMMERCE ST	DALLAS TEXAS	ZIP 75201			NON-PRIMARY		
01251 01	DALLAS P L L CO	PARKDALE PWR PLT-OUTFALL 001	04 057 08 0805 Y	50,000	NO	2	01	49110	05-27-7
ADDRESS		1506 COMMERCE ST	DALLAS TEXAS	ZIP 75201			NON-PRIMARY		
01251 02	DALLAS P L L CO	PARKDALE PWR PLT-OUTFALL 002	04 057 08 0805 Y	800,000	NO	2	01	49110	05-27-75
ADDRESS		1506 COMMERCE ST	DALLAS TEXAS	ZIP 75201			NON-PRIMARY		
01251 03	DALLAS P L L CO	PARKDALE PWR PLT-OUTFALL 003	04 057 08 0805 Y	30,000	NO	2	01	49110	05-27-7
ADDRESS		1506 COMMERCE ST	DALLAS TEXAS	ZIP 75201			NON-PRIMARY		
01251 04	DALLAS P L L CO	PARKDALE PWR PLT-OUTFALL 004	04 057 08 0805 Y	500,000	NO	2	01	49110	05-27-75
ADDRESS		1506 COMMERCE ST	DALLAS TEXAS	ZIP 75201			NON-PRIMARY		
01474 01	DRESSER INDUSTRIES, INC	OUTFALL NO. 001	04 057 08 0805 Y	50,000	NO	2	01	35330	05-27-75
ADDRESS	PETROLEUM & MINING GROUP	P.O. BOX 718	DALLAS, TEXAS	ZIP 75221			PRI-MAILING		
10060 01	DALLAS CITY OF	CENTRAL STP	04 057 08 0805 Y	93,800,000	NO	3	10	93495	12-16-74
ADDRESS		MUNICIPAL BLDG..500 S. ERVAY	DALLAS TEXAS	ZIP 75201			PRI-MAILING		
10060 06	DALLAS CITY OF	SOUTHSIDE SEWAGE TREAT PLANT	04 057 08 0805	7,000,000	NO	3	10	93495	01-28-75
ADDRESS		MUNICIPAL BLDG..500 S. ERVAY	DALLAS TEXAS	ZIP 75201			NON-PRIMARY		
10061 01	DALLAS CO WCID NO 6	STP	04 057 08 0805 Y	600,000	NO	3	13	93495	11-26-74
ADDRESS		2000 HICKORY TREE ROAD	BALCH SPRINGS, TEXAS	ZIP 75149			PRI-MAILING		
10103 01	HALTOM CITY CITY OF	MUNICIPAL STP	04 220 08 0805 Y	1,200,000	NO	3	10	93495	10-22-74
ADDRESS		P O BOX 14246	FORT WORTH TEXAS	ZIP 76117			PRI-MAILING		
10192 01	HUTCHINS CITY OF		04 057 08 0805	180,000	NO	3	10	93495	11-26-74
ADDRESS		P.O.BOX AE	HUTCHINS TEXAS	ZIP 75141			PRI-MAILING		
10216 01	MANSFIELD CITY OF	MUNICIPAL STP	04 220 08 0805 Y	320,000	NO	3	10	93495	11-26-74
ADDRESS		P O BOX 403	MANSFIELD TEXAS	ZIP 76063			PRI-MAILING		
10239 01	NORTH TARRANT CO MUN WTR DIST	KELLER STP	04 220 08 0805 Y	135,000	NO	3	13	93495	06-25-74
ADDRESS		P O BOX 363	KELLER TEXAS	ZIP 76248			PRI-MAILING		
10303 01	TRINITY RIVER AUTH OF TEXAS	CENTRAL PLANT	04 057 08 0805 Y	30,000,000	NO	3	11	93495	02-25-76
ADDRESS		P O BOX 1196	GRAND PRAIRIE TEXAS	ZIP 75050			PRI-MAILING		
10316 01	WILMER CITY OF	STP	04 057 08 0805 Y	122,000	NO	3	10	93495	11-26-74
ADDRESS		P.O. BOX 248	WILMER TEXAS	ZIP 75172			PRI-MAILING		
10348 01	MIDLOTHIAN CITY OF	MUNICIPAL STP	04 070 08 0805 Y	900,000	NO	3	10	93495	11-26-74
ADDRESS									
10488 03	GRAPEVINE CITY OF	SOUTHWEST PLT.	04 220 08 0805 Y	200,000	NO	3	[illegible]	[illegible]	
ADDRESS		P C BOX 307	GRAPEVINE TEXAS	ZIP 76051			NON-PRIMARY		
10494 01	FORT WORTH CITY OF	RIVERSIDE PLANT NORTH OUTFALL	04 220 08 0805	19,200,000	NO	3	10	[illegible]	11-26-74
ADDRESS		P O BOX 870	FORT WORTH TEXAS	ZIP 76101			PRI-MAILING		
10494 02	FORT WORTH CITY OF	RIVERSIDE PLANT SOUTH OUTFALL	04 220 08 0805	13,100,000	NO	3	10	93495	11-26-74
ADDRESS		P O BOX 870	FORT WORTH TEXAS	ZIP 76101			NON-PRIMARY		

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WCO	PG	NAME	PLANT OR OUTFALL NAME	DST CTY BSN SGMT TR	FLOW-AVG GAL/DAY	RE-TAINED	TYPE WCO	TYPE OWNER	TYPE ESTAB	EFF DATE MO-DA-YR
10494	13	FORT WORTH CITY OF	VILLAGE CREEK PLANT	04 220 08 0805	45,000,000	NO	3	10	93495	11-26-74
ADDRESS		1000 THROCKMORTON ST	PO BOX 870	FORT WORTH TEXAS		ZIP 76101		NON-PRIMARY		
10494	14	FORT WORTH CITY OF	INTERNATIONAL AIRPORT STP	04 220 08 0805	500,000	NO	3	10	93495	11-26-74
ADDRESS		1000 THROCKMORTON ST	PO BOX 870	FORT WORTH TEXAS		ZIP 76101		NON-PRIMARY		
10594	01	PALMER CITY OF	STP	04 070 08 0805 Y	71,000	NO	3	10	93495	11-26-74
ADDRESS			301 JEFFERSON	PALMER TEXAS		ZIP 75152		PRI-MAILING		
10605	01	SAGINAW PARK UTIL CO	BLUE MOUND PLANT	04 220 08 0805 Y	240,000	NO	3	01	93495	02-25-75
ADDRESS			1601 BELE AVE	FORT WORTH TEXAS		ZIP 76131		PRI-MAILING		
10883	01	VENUS CITY OF	MUN. STP	04 126 08 0805 Y	75,000	NO	3	10	93495	11-26-74
ADDRESS			CITY HALL-P.O. BOX 380	VENUS TEXAS		ZIP 76084		PRI-MAILING		
10886	01	POLY WEBB MOBILE PARK		04 220 08 0805 W	12,000	NO	3	03	93495	04-22-75
ADDRESS		C/O JIMMIE E. DVORAK	1800 WEST POLY WEBB ROAD	ARLINGTON TEXAS		ZIP 76016		PRI-MAILING		
10984	01	TRINITY RIVER AUTH OF TEXAS	TEN MILE CREEK STP	04 057 08 0805 Y	6,780,000	NO	3	11	93495	11-26-74
ADDRESS			P. O. BOX 5768	ARLINGTON TEXAS		ZIP 76011		PRI-MAILING		
11002	01	MCCARTY JUNE	L E W MOBILE HOME PARK	04 220 08 0805 Y	9,000	NO	3	03	93495	02-25-75
ADDRESS			4921 WHITE SETTLEMENT ROAD	FORT WORTH TEXAS		ZIP 76114		PRI-MAILING		
11009	01	NISCHER DEVELOPMENT INC	ROYAL COACH MOBILE PK	04 220 08 0805 Y	100,000	NO	3	01	93495	04-22-75
ADDRESS			2501 POLY WEBB ROAD	ARLINGTON, TEXAS		ZIP 76016		PRI-MAILING		
11032	01	KELLER MOBILE HOME ESTATES		04 220 08 0805 Y	8,000	NO	3	03	93495	02-25-75
ADDRESS			P O BOX C	KELLER TEXAS		ZIP 76248		PRI-MAILING		
11039	01	GOODMAN LEE JR	GREEN VALLEY MOBILE HOME PK	04 220 08 0805 Y	15,000	NO	3	03	93495	01-28-75
ADDRESS			1513 COMMERCE STREET	FORT WORTH, TEXAS		ZIP 76102		PRI-MAILING		
11102	01	KUYKENDALL, JAMES E.	MOUNTAIN VIEW ESTATES	04 126 08 0805 Y	13,000	NO	3	08	93495	02-25-75
ADDRESS			2622 W. DIVISION	ARLINGTON, TEXAS		ZIP 76012		PRI-MAILING		
11106	01	STOLL HARRY J	FOREST ACRES PARK	04 220 08 0805 Y	9,400	NO	3	03	93495	02-25-75
ADDRESS			3205 FORREST DRIVE	ARLINGTON TEXAS		ZIP 76010		PRI-MAILING		
11110	01	TUMBLEWEED MOBILE HOME PARK		04 220 08 0805 Y	64,000	NO	3	00	93495	02-25-75
ADDRESS		C/O JOHN MADDUX	2120 RIDGMAR BLVD	FORT WORTH TEXAS		ZIP 76116		PRI-MAILING		
11114	01	COMMUNICATION APPARATUS CORP		04 220 08 0805	000	YES	1	01	93495	07-31-70
ADDRESS			P O BOX 426	KELLER TEXAS		ZIP 76248		PRI-MAILING		
11117	01	KAWITZ RAYMOND A	MOBILE HOME PK SEWAGE SYSTEM	04 070 08 0805	24,000	YES	1	03	93495	08-28-70
ADDRESS			13111 MITCHMIN ROAD	DALLAS TEXAS		ZIP 75234		PRI-MAILING		
11119	01	RED OAK CITY OF		04 070 08 0805 Y	100,000	NO	3	10	93495	02-25-75
ADDRESS			P O BOX 393	RED OAK TEXAS		ZIP 75151		PRI-MAILING		
11168	01	GREEN TOP MOBILE HOME ESTATES		04 057 08 0805 Y	25,000	NO	3	03	93495	02-25-75
ADDRESS		ATTN: ALLEN W. GRAVES	2870 DOWDY FERRY ROAD	DALLAS TEXAS		ZIP 75217		PRI-MAILING		
11175	01	MCNARY, JOHN	DBA OAK LEAF MOBILE HOME PARK	04 220 08 0805 W	14,500	NE	3	03	93495	02-25-75
ADDRESS			1245 HURSTVIEW DRIVE	HURST, TEXAS		ZIP 76053		PRI-MAILING		
11297	01	MICKS FIELD SEWER CORP		04 220 08 0805 Y	53,000	NO	3	01	93495	01-21-75
ADDRESS			P. O. BOX 1227	FORT WORTH, TEXAS		ZIP 76101		PRI-MAILING		
11338	01	INTL LINGUISTICS CENTER INC	STP	04 057 08 0805 Y	10,000	NO	3	01	93495	03-25-75
ADDRESS			901 ROSS AVE	DALLAS, TEXAS		ZIP 75202		PRI-MAILING		

TABLE A-1 (Cont'd.)

WCD	PG	NAME	PLANT OR OUTFALL NAME	DST CTY BSN SGMT TR	FLOW-AVG GAL/DAY	RE-TAINED	TYPE WCD	TYPE OWNER	TYPE ESTAB	EFF DATE MO-DA-YR
11691	01	DALLAS CITY OF-WATER UTIL DEPT	FOX CREEK STP	04 057 08 0805 Y	100,000	NO	3	10	93495	08-26-75
		ADDRESS	508 SOUTH ERVAY	DALLAS, TEXAS		ZIP 75201	NON-PRIMARY			
12702	01	SKY INC.	OUTFALL 001	04 220 08 0805 Y	125,000	NE	4	01	93495	09-23-75
		ADDRESS	4301 OLD DENTON ROAD	FORT WORTH, TEXAS		ZIP 76117	PRI-MAILING			
11703	01	IRVING, CITY OF	STP	04 057 08 0805 Y	24,000	NE	3	10	93495	10-28-75
		ADDRESS	835 W. IRVING BLVD.	IRVING, TEXAS		ZIP 75060	PRI-MAILING			
01250-01		Dallas, P & L Co.	Mountain Ck. Sta. 1506 Commerce St.	08 805	48.PMGD	No	1	01	49110	
10324-01		Arlington City of	P. O. Box 231	04 057 08 805	6.5MGD	No	3	10	93495	
10554-01		Dallas Co WCID No. 7	Stp	04 057 08 805	500,000	No	3	13	93495	
11036-01		High Chaparral Mobile Home	Route 2, Box 276-B	04 220 08 805Y	6,000	No	3	03	93495	
11244-01		Wilson Joe H.	Mobile Home Park 1801 Crest Haven	04 220 08 805Y	4,000	No	3	03	93495	
11585-01		Ryan Management Co.	Bunsey States Devel. 611 Ryan Plaza Dr.	04 220 08 805Y	250,000	No	3	01	93495	

TABLE A-1 (Cont'd.)

WCO	PG	NAME	PLANT OR OUTFALL NAME	DST CTY BSN SGMT TR	FLOW-AVG GAL/DAY	RE-TAINED	TYPE WCO	TYPE OWNER	TYPE ESTAB	EFF DATE MO-DA-YR
00967	01	TEXAS POWER AND LIGHT CO	TRINIDAD STEAM ELEC STA	05 107 08 0804	20,160	NO	1	01	49110	06-27-66
ADDRESS			P E BOX 6331	DALLAS TEXAS	ZIP 75222		NON-PRIMARY			
01029	01	NIPAK INC	TRINITY RIVER PLT-OUTFALL 001	04 175 08 0804 N	267,000	NO	2	01	28730	11-26-7-
ADDRESS			PO DRAWER A	KERENS TEXAS	ZIP 75144		PRI-MAILING			
01288	01	HANKS JOT PROCESSING PLANT		05 001 08 0804	1,000	NO	1	03	20130	02-27-69
ADDRESS			RT 2 BOX 275 B	PALESTINE TEXAS	ZIP 75801		PRI-MAILING			
01444	01	GLASS CONTAINER CORPERATION	OUTFALL NO. 001	05 001 08 0804 Y	160,000	NO	2	01	32210	05-27-75
ADDRESS			P E BOX 800	PALESTINE TEXAS	ZIP 75801		PRI-MAILING			
01911	01	J C W REFINING, INC	PETROLEUM RFY-OUTFALL 001	05 001 08 0804 Y	32,000	NO	2	01	29110	03-25-75
ADDRESS			P.C. BOX 828	PALESTINE, TEXAS	ZIP 75801		PRI-MAILING			
01911	02	J C W REFINING, INC	PETROLEUM RFY-OUTFALL 002	05 001 08 0804 Y	32,000	NO	2	01	29110	03-25-75
ADDRESS			P.C. BOX 828	PALESTINE, TEXAS	ZIP 75801		NON-PRIMARY			
01911	03	J C W REFINING, INC	PETROLEUM RFY-OUTFALL 003	05 001 08 0804 Y	32,000	NO	2	01	29110	03-25-75
ADDRESS			P.O. BOX 828	PALESTINE, TEXAS	ZIP 75801		NON-PRIMARY			
10022	01	BUFFALO CITY OF		03 145 08 0804 Y	200,000	NO	3	10	93495	11-26-74
ADDRESS			P. O. BOX 219	BUFFALO TEXAS	ZIP 75831		PRI-MAILING			
10143	02	ATHENS CITY OF	WEST PLANT	05 107 08 0804	920,000	NO	3	10	93495	08-27-74
ADDRESS			P. O. DRAWER C	ATHENS TEXAS	ZIP 75751		NON-PRIMARY			
ADDRESS			P.O. BOX [illegible]							
10147	01	CENTERVILLE CITY OF	MUN. STP	03 145 08 0804 Y	105,000	NO	3	10	93495	08-26-75
ADDRESS			P O BOX 273	CENTERVILLE TEXAS	ZIP 75833		PRI-MAILING			
10154	01	CROCKETT CITY OF	PLANT NO 1	06 113 08 0804 Y	1,000,000	NO	3	10	93495	11-26-74
ADDRESS			P E BOX 550	CROCKETT TEXAS	ZIP 75835		PRI-MAILING			
10168	01	FAIRFIELD CITY OF	WALNUT CREEK PLANT	03 081 08 0804 Y	200,000	NO	3	10	93495	01-28-75
ADDRESS			P O BOX 87	FAIRFIELD TEXAS	ZIP 75840		PRI-MAILING			
10168	02	FAIRFIELD CITY OF	NIMS CREEK PLANT	03 081 08 0804 Y	200,000	NO	3	10	93495	01-28-75
ADDRESS			P E BOX 87	FAIRFIELD TEXAS	ZIP 75840		NON-PRIMARY			
10244	01	PALESTINE CITY OF	TOWN CREEK PLANT	05 001 08 0804 Y	800,000	NO	3	10	93495	11-26-74
ADDRESS			P. O. DRAWER 2	PALESTINE TEXAS	ZIP 75801		PRI-MAILING			
10500	02	YEAGUE CITY OF	PLANT NO 2 NORTH PLT	03 081 08 0804 Y	105,000	NO	3	10	93495	11-26-74
ADDRESS			521 MAIN STREET	YEAGUE TEXAS	ZIP 75860		NON-PRIMARY			
10467	02	TRINIDAD TOWN OF	MUNICIPAL STP	05 107 08 0804 Y	150,000	NO	3	10	93495	07-22-75
ADDRESS			P E BOX 345	TRINIDAD TEXAS	ZIP 75163		NON-PRIMARY			
10551	01	WORTHAM CITY OF	MUNICIPAL STP	03 081 08 0804 Y	195,000	NO	3	10	93495	11-26-74
ADDRESS			P.O. BOX 186	WORTHAM TEXAS	ZIP 76693		PRI-MAILING			
10551	03	WORTHAM CITY OF	WTP-OUTFALL 001	03 081 08 0804 Y	600	NO	2	10	93496	05-27-75
ADDRESS			P.O. BOX 186	WORTHAM TEXAS	ZIP 76693		NON-PRIMARY			
10576	01	LAKEVIEW METHODIST ASSEMBLY	SEWERAGE SYSTEM	05 001 08 0804 Y	90,000	NO	3	00	93495	02-25-75
ADDRESS			ROUTE 5	PALESTINE TEXAS	ZIP 75801		PRI-MAILING			
10586	01	OAKWOOD CITY OF	MUN. STP	03 145 08 0804 Y	75,000	NO	3	10	93495	05-27-75
ADDRESS			P O BOX 96	OAKWOOD TEXAS	ZIP 75855		PRI-MAILING			
10735	01	ELKHART CITY OF	MUNICIPAL STP	05 001 08 0804 Y	123,000	NO	3	10	93495	10-22-74
ADDRESS			P.O. BOX 137	ELKHART TEXAS	ZIP 75839		PRI-MAILING			

WCO	PG	NAME	PLANT OR OUTFALL NAME	DST CTY BSN SGMT TR	FLOW-AVG GAL/DAY	RE-TAINED	TYPE WCO	TYPE OWNER	TYPE ESTAB	EFF DATE MO-DA-YR
10750	01	MALAKOFF CITY OF		05 107 08 0804 Y	216,000	NO	3	10	93495	04-22-75
ADDRESS			P O BOX 0	MALAKOFF TEXAS	ZIP 75148 PRI-MAILING					
10745	01	KERENS CITY OF	MUNICIPAL STP	04 175 08 0804 Y	140,000	NO	3	10	93495	10-22-74
ADDRESS			100 S.E. 4TH	KERENS TEXAS	ZIP 75144 PRI-MAILING					
10823	01	TEXAS DEPT OF CORRECTIONS	COFFIELD UNIT STP	05 001 08 0804 Y	240,000	NO	3	08	93495	04-22-75
ADDRESS			P.O. BOX 99	HUNTSVILLE, TEXAS	ZIP 77340 NON-PRIMARY					
10933	01	TUCKER WATER SUPPLY CORP	WWTP-OUTFALL NO. 001	05 001 08 0804 Y	300	NO	2	01	93494	05-27-75
ADDRESS			ROUTE 5	PALESTINE TEX	ZIP 75801 PRI-MAILING					
11176	01	TEXAS DEPT OF CORRECTIONS	FERGUSON UNIT	03 157 08 0804 Y	180,000	NO	3	08	93495	05-27-75
ADDRESS			P.O. BOX 32	HUNTSVILLE TEXAS	ZIP 77340 NON-PRIMARY					
11181	01	TEXAS DEPT OF CORRECTIONS	EASTHAM UNIT	06 113 08 0804	242,000	NO	3	08	93495	02-25-75
ADDRESS			P O BOX 99	HUNTSVILLE TEXAS	ZIP 77340 NON-PRIMARY					
11577	01	BAILEY, BILL H. JR.	TRUCK STOP STP	03 145 08 0804 Y	3,000	NO	3	03	93495	06-26-7
ADDRESS			706 EAST RUSK ST.	JACKSONVILLE, TEXAS	ZIP 75766 PRI-MAILING					
11578	01	CARR OIL CO.		03 081 08 0804 Y	10,000	NO	3	01	93495	07-23-74
ADDRESS			801 S. SE. LOOP 323	TYLER, TEXAS	ZIP 75701 PRI-MAILING					
11586	01	DYER VOCATIONAL TRAINING CNTR		03 145 08 0804	12,000	NO	3	01	93495	07-23-74
ADDRESS			P. O. BOX 57	LEONA, TEXAS	ZIP 75850 PRI-MAILING					
11627	01	TEXAS PARKS & WILDLIFE DEPT	FAIRFIELD LAKE PARK AREA II	03 081 08 0804 Y	22,000	NO	3	08	93495	10-
ADDRESS			JOHN H. REAGAN BLDG	AUSTIN, TEXAS	ZIP 78701 NON-PRIMARY					
11629	01	TEXAS PARKS & WILDLIFE DEPT	FAIRFIELD LAKE PARK AREA III	03 081 08 0804 Y	40,000	NO	3	08	93495	10-
ADDRESS			JOHN H. REAGAN BLDG	AUSTIN, TEXAS	ZIP 78701 NON-PRIMARY					
10471-01		Streetman City of	WtPoutfall 001	03 081 08 804Y	3,000	No	2	10	93494	
10871-01		Houston Co. WCID No. 1	WTP Outfall No. 001	06 113 08 804Y	60,000	No	2	13	93494	

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WCO	PG	NAME	PLANT OR OUTFALL NAME	DST CTY BSN SGMT TR	FLOW-AVG GAL/DAY	RE-TAINED	TYPE WCO	TYPE OWNER	TYPE ESTAB	EFF DATE MO-DA-YR
01896	01	RALSTON-PURINA CO., INC.	OUTFALL 001 MUSHROOM PRODN PLT	03 157 08 0803 Y	100,000	NO	2	01	20330	02-25-75
ADDRESS			BOX W	MADISONVILLE, TEXAS	ZIP 77864		PRI-MAILING			
10154	02	CROCKETT CITY OF	PLANT NO 2	06 113 08 0803 Y	250,000	NC	3	10	93495	11-26-74
ADDRESS			PO BOX 550	CROCKETT, TEXAS	ZIP 75835		NON-PRIMARY			
10215	01	MADISONVILLE CITY OF	STP	03 157 08 0803 Y	400,000	NC	3	10	93495	11-26-74
ADDRESS			216 WEST MAIN ST	MADISONVILLE TEXAS	ZIP 77864		PRI-MAILING			
10356	01	NORMANGEE CITY OF		03 145 08 0803 Y	50,000	NO	3	10	93495	06-25-74
ADDRESS			P O BOX E	NORMANGEE TEXAS	ZIP 77871		PRI-MAILING			
10556	01	GROVETON CITY OF	MUN. STP	06 228 08 0803 Y	70,000	NO	3	10	93495	03-25-75
ADDRESS			P O BOX 37	GROVETON TEXAS	ZIP 75845		PRI-MAILING			
10734	01	LOVELADY CITY OF		06 113 08 0803 Y	50,000	NO	3	10	93495	08-27-74
ADDRESS		COMMERCE ST	P O BOX 83	LOVELADY TEXAS	ZIP 75851		PRI-MAILING			
10781	01	HUNTSVILLE CITY OF	NORTH STP	06 236 08 0803 Y	2,100,000	NC	3	10	93495	11-26-74
ADDRESS			P. O. DRAWER 891	HUNTSVILLE TEXAS	ZIP 77340		PRI-MAILING			
10997	01	MITCHELL DEVELPMNT CORP OF SW	CAPE ROYALE SUBDIV. STP	06 204 08 0803	100,000	NC	3	01	93495	09-24-74
ADDRESS			ROUTE 1, BOX 20-E	COLDSPRING, TEXAS	ZIP 77331		PRI-MAILING			
11100	01	BRIDGEPORT, INC.	STP	06 187 08 0803 N	15,000	NO	3	01	93495	03-25-75
ADDRESS			P.O. BOX 446	LAKE LIVINGSTON, TEXAS	ZIP 77351		PRI-MAILING			
11147	01	MEMORIAL POINT UTILITY DIST		06 187 08 0803	400,000	NO	3	13	93495	08-27-74
ADDRESS		C/O VINSON, ELKINS ETAL	FIRST CITY NATIONAL BANK BLDG	HOUSTON TEXAS	ZIP 77002		PRI-MAILING			
11180	01	TEXAS DEPT OF CORRECTIONS	ELLIS UNIT STP	06 236 08 0803 Y	155,000	NO	3	08	93495	05-27-75
ADDRESS			P O BOX 99	HUNTSVILLE TEXAS	ZIP 77340		NON-PRIMARY			
11197	01	BEACON BAY	PARK SEWERAGE SYSTEM	06 187 08 0803 N	10,000	NO	3	03	93495	03-25-75
ADDRESS			ROUTE 1, BOX 249F	LIVINGSTON, TEXAS	ZIP 77351		PRI-MAILING			
11290	01	TRINITY RIVER AUTH OF TEXAS	UMALAKA WASTEWATER TRTMT PLT	06 187 08 0803 Y	150,000	NO	3	11	93495	05-2
ADDRESS			P. O. BOX 5768	ARLINGTON, TEXAS	ZIP 76011		NON-PRIMARY			
11300	01	WESTWOOD SHORES MUN UTIL DIST	LAKE LIVINGSTON	06 228 08 0803 N	30,000	NO	3	13	93495	03-2
ADDRESS		C/O VINSON, ELKINS, ET AL	2100 FIRST CITY NATIONAL BANK	HOUSTON, TEXAS	ZIP 77002		PRI-MAILING			
11310	01	TRINITY RIVER AUTH OF TEXAS	LAKE LIVINGSTON-PARK SITE 2	06 204 08 0803 N	25,000	NC	3	11	93495	05-2
ADDRESS			P. O. BOX 5678	ARLINGTON, TEXAS	ZIP 76011		NON-PRIMARY			
11325	01	TEXAS HIGHWAY DEPT-DISTRICT 17	WALKER CO. REST AREA IH-45 SO.	06 236 08 0803 Y	3,000	NC	3	08	93495	05-27-75
ADDRESS			P.O. BOX 3249	BRYAN, TEXAS	ZIP 77801		PRI-MAILING			
11326	01	TEXAS HIGHWAY DEPT-DISTRICT 17	WALKER CO. REST AREA IH-45 NO.	06 236 08 0803 Y	3,000	NC	3	08	93495	05-27-75
ADDRESS			P.O. BOX 3249	BRYAN, TEXAS	ZIP 77801		NON-PRIMARY			
11350	01	GALLOWAYS, DOC INC	DBA GALLOWAY'S MARINA	06 228 08 0803 Y	12,000	NO	3	01	93495	03-25-75
ADDRESS		C/O RICHARD BYSHOP	P.O. BOX 607	TRINITY, TEXAS	ZIP 75862		PRI-MAILING			
11465	01	MOORE, THERON L.								
ADDRESS			MALITA POINT SUBDIV. STP	06 187 08 0803 N	15,000	NO	3	03	93495	04-22-75
			3403 MARQUART	HOUSTON, TEXAS	ZIP 77027		PRI-MAILING			
11930	01	POLK COUNTY FWSD NO. 1	OAK TERRACE ESTATES STP	06 187 08 0803 N	75,000	NO	3	13	93495	06-26-7
ADDRESS			ROUTE 1, BOX 731	LIVINGSTON, TEXAS	ZIP 77351		PRI-MAILING			
11621	01	LAKE WATER SUPPLY CORP	INDIAN HILL HARBOR STP	06 187 08 0803 N	15,000	NC	3	01	93495	10-.
ADDRESS			P.O. BOX 246	LIVINGSTON, TEXAS	ZIP 77351		PRI-MAILING			
11644	01	GREATER HOUSTON AREA YMCA	LAKE LIVINGSTON YMCA CAMP STP	06 228 08 0803 Y	10,000	NO	3	00	93495	12-16-74
ADDRESS			1600 LOUISIANA	HOUSTON, TEXAS	ZIP 77002		PRI-MAILING			
11722	01	TEXAS PARKS & WILDLIFE DEPT	LAKE LIVINGSTON STATE PARK STP	06 187 08 0803 N	35,000	NO	3	08	93495	01-28-75
ADDRESS			JOHN H. REAGAN BLDG	AUSTIN, TEXAS	ZIP 78701		NON-PR			

1061 01 Trinity City of Mun. Stp. P. O. Box 305 06 228 08 803 250,000 No 3 10 93495

TABLE A-1 (Cont'd.)

WCO	PG	NAME	PLANT OR OUTFALL NAME	DST CTY BSN SGMT TR	FLOW-AVG GAL/DAY	RE-TAINED	TYPE WCO	TYPE OWNER	TYPE ESTAB	EFF DATE MO-DA-YR
10208	01	LIVINGSTON CITY OF		06 187 08 0802 Y	720,000	NO	3	10	93495	08-27-74
ADDRESS			P O BOX 867	LIVINGSTON TEXAS	ZIP 79339 PRI-MAILING					
10495	80	HOUSTON CITY OF	CWA TRINITY RIVER PUMP STA	07 146 08 0802 Y	2,000	NO	3	10	93495	12-16-74
ADDRESS			900 BRAZOS	HOUSTON, TEXAS	ZIP 77002 NON-PRIMARY					
10564	0	DAYTON CITY OF	NORTHEAST STP	07 146 08 0802	200,000	NO	3	10	93495	07-23-74
ADDRESS			111 W. CHURCH ST.	DAYTON TEXAS	ZIP 77535 PRI-MAILING					
11139	01	MOSCOW WATER SUPPLY CORP	STP	06 187 08 0802 Y	40,000	NO	3	01	93495	02-25-75
ADDRESS			P O BOX 357	CORRIGAN TEXAS	ZIP 75939 PRI-MAILING					
11223	01	POLK COUNTY	SOUTHLAND PARK	06 187 08 0802 N	3,000	NO	3	09	93495	02-25-75
ADDRESS		C/O COUNTY JUDGE	POLK COUNTY COURTHOUSE	LIVINGSTON, TEXAS	ZIP 77331 PRI-MAILING					
11277	01	HARDIN CITY OF		07 146 08 0802	150,000	NO	1	10	93495	04-2
ADDRESS			CITY HALL	HARDIN, TEXAS	ZIP 77561 PRI-MAILING					
11288	01	HARPRINER EDUCATION & TRNG INC	W.E.T. STP	06 187 08 0802 Y	23,060	NO	3	01	93495	02-2
ADDRESS			105 E. HOUSTON	CLEVELAND, TEXAS	ZIP 77327 PRI-MAILING					
11377	01	TARKINGTON IND SCHOOL DISTRICT		07 146 08 0802 Y	30,000	NO	3	12	93495	02-25-75
ADDRESS			ROUTE 1,BOX 130	CLEVELAND, TEXAS	ZIP 77327 PRI-MAILING					
11380	01	SHEPHERD, CITY OF		06 204 08 0802	200,000	NO	3	10	93495	09-24-74
ADDRESS			P. O. BOX 246	SHEPHERD, TEXAS	ZIP 77371 PRI-MAILING					
11520	01	OLD RIVER COUNTRY MUD	OLD RIVER COUNTRY SUBDIV STP	07 036 08 0802 Y	70,000	NO	3	13	93495	06-26-
ADDRESS			P. O. BOX 245	MONT BELVIEW, TEXAS	ZIP 77580 PRI-MAILING					
11524	01	WOODHARBOR MUD UTILITY DIST.	WOODHARBOR MUD STP	06 087 08 0802 N	50,000	NO	3	13	93495	05-22-
ADDRESS		C/O FULBRIGHT, CROOKER, ET AL	910 TRAVIS STREET	HOUSTON, TEXAS	ZIP 77002 PRI-MAILING					
11697	01	LAKESIDE VILLAGE WATER, INC.	STP	06 187 08 0802 Y	30,000	NO	3	01	93495	08-26-75
ADDRESS			P.O. BOX 90	LIVINGSTON, TEXAS	ZIP 77351 PRI-MAILING					

TABLE A-1 (Cont'd.)

WCO	PG	NAME	PLANT OR OUTFALL NAME	DST CTY BSN SGMT TR	FLOW-AVG GAL/DAY	RE-TAINED	TYPE WCO	TYPE OWNER	TYPE ESTAB	EFF DATE MO-DA-YR
00952	01	TEXASGULF, INC	MOSS BLUFF DOME-OUTFALL 001	07 146 08 0801	41,000	NO	2	01	14770	08-27-74
ADDRESS			811 RUSK AVE, SUITE 1803	HOUSTON, TEXAS	ZIP 77002		PRI-MAILING			
00952	02	TEXASGULF, INC	MOSS BLUFF DOME-OUTFALL 002	07 146 08 0801	4,500,000	NO	2	01	14770	08-27-74
ADDRESS			811 RUSK AVE-SUITE 1803	HOUSTON, TEXAS	ZIP 77002		NON-PRIMARY			
01969	01	ARJAY, INC.	OUTFALL NO. 001	07 146 08 0801 Y	5,800	NO	2	01	28430	10-28-75
ADDRESS			P.O. BOX 45045	HOUSTON, TEXAS	ZIP 77045		PRI-MAILING			
564	02	DAYTON CITY OF	SOUTHEAST STP	07 146 08 0801	353,000	NO	3	10	93495	11-26-74
ADDRESS			111 N. CHURCH ST.	DAYTON TEXAS	ZIP 77535		NON-PRIMARY			
10108	01	LIBERTY CITY OF	MAIN STP	07 146 08 0801	656,000	NO	3	10	93495	02-25-75
ADDRESS			1829 SAM HOUSTON ST	LIBERTY TEXAS	ZIP 77575		PRI-MAILING			
10108	03	LIBERTY CITY OF	TREE TOP SUBDIVISION PLT	07 146 08 0801	36,400	NO	1	10	93495	06-30-65
ADDRESS			1829 SAM HOUSTON ST	LIBERTY TEXAS	ZIP 77575		NON-PRIMARY			
11030	01	BARBERS HILL IND SCHOOL DIST	HIGH SCHOOL SEWERAGE SYS.	07 036 08 0801 Y	7,500	NO	3	12	93495	02-25-75
ADDRESS			P O BOX R	MONT BELVIEU TEXAS	ZIP 77580		PRI-MAILING			
11109	01	HARRINGTON R K SR		07 036 08 0801 Y	6,000	NO	3	03	93495	01-28-75
ADDRESS			RT 2 BOX 169	BAYTOWN TEXAS	ZIP 77520		PRI-MAILING			
11449	01	DUTTON & GRAY	COVE MOBILE HOME PARK	07 036 08 0801 Y	6,000	NO	3	02	93495	02-2
ADDRESS			ROUTE 2, BOX 175C	BAYTOWN, TEXAS	ZIP 77520		PRI-MAILING			
11720	01	GRAY, EDDIE V.	WOODLAND ACRES STP	07 036 08 0801 Y	13,200	NO	4	03	93495	01-28-7
ADDRESS			P.O. BOX 638	BAYTOWN, TEXAS	ZIP 77520		PRI-MAILING			

TABLE A-2: COUNTY BY COUNTY POINT OF ENTRY OF EFFLUENT SOURCES (WCO'S) INTO THE TRINITY RIVER WITH RESPECT TO CORPS RIVER MILES

COUNTY: Anderson County, Texas

Map Number	TWQB WCO Number	Point of Entry Into Trinity River				
		Corp. River Mile	Latitude		Longitude	
			Deg.	Min.	Deg.	Min.
1	10823-01	337	31	46	95	54
2	01288-01	323	31	42	95	50
3	01911-01	314	31	39	95	47
	01911-02	314	31	39	95	47
	01911-03	314	31	39	95	47
4	10933-01	314	31	39	95	47
5	10244-01	317	31	42	95	47
6	01444-01	317	31	42	95	47
7	10578-01	302	31	38	95	43
8	10735-01	293	31	33	95	43

COUNTY: Chambers County, Texas

Map Number	TWQB WCO Number	Point of Entry Into Trinity River				
		Corp. River Mile	Latitude		Longitude	
			Deg.	Min.	Deg.	Min.
1	11449-01	T.B.*	29	48	94	44
2	11109-01	T.B.	29	48	94	44
3	11030-01	T.B.	29	48	94	44
4	11720-01	T.B.	29	48	94	44

TABLE A-2 (Cont'd.)

COUNTY: Dallas & Rockwall Counties, Texas

Map Number	TWQB WCO Number	Point of Entry Into Trinity River				
		Corp. River Mile	Latitude		Longitude	
			Deg.	Min.	Deg.	Min.
1	10324-01	517	32	47	97	01
2	10303-01	509	32	47	96	56
3	01250-01	M.C.L.*	32	47	96	55
4	01474-01	487	32	41	96	42
5	01248-01&02	501	32	47	96	49
6	10060-01	495	32	44	96	46
7	01251-01&04	493	32	43	96	44
8	10192-01	487	32	41	96	42
9	11166-01	484	32	38	96	41
10	10060-06	481	32	39	96	39
11	10061-01	462	32	31	96	30
12	10554-01	462	32	31	96	30
13	10316-01	471	32	35	96	35
14	10984-01	471	32	35	96	35
15	10805-02	505	32	48	96	54
16	10060-07	505	32	48	96	54
17	10060-05	505	32	48	96	54
18	11209-01	460	32	30	96	30
19	10221-01	460	32	30	96	30
20	10370-01	460	32	30	96	30
						continued

*Mountain Creek Lake

TABLE A-2 (Cont'd.)

COUNTY: Dallas & Rockwall Counties, Texas; Cont'd.

Map Number	TWQB WCO Number	Point of Entry Into Trinity River				
		Corp. River Mile	Latitude		Longitude	
			Deg.	Min.	Deg.	Min.
21	11543-01	W.R.L.**	32	43	96	44
22	11338-01	M.C.L.*	32	47	96	55
23	11703-01	510	32	47	96	56
24	11691-01	M.C.L.*	32	47	96	56

COUNTY: Denton County, Texas

Map Number	TWQB WCO Number	Point of Entry Into Trinity River				
		Corp. River Mile	Latitude		Longitude	
			Deg.	Min.	Deg.	Min.
1	11321-01	506	33	01	97	02
2	10662-01	E.R.*	33	03	96	58

COUNTY: Ellis County, Texas

Map Number	TWQB WCO Number	Point of Entry Into Trinity River				
		Corp. River Mile	Latitude		Longitude	
			Deg.	Min.	Deg.	Min.
1	10348-01	MCL*	32	30	97	01
2	11118-01	457	32	23	96	
3	11119-01	457				
4	10594-01	457	32	38	96	38

*Mountain Creek Lake
**White Rock Lake

TABLE A-2 (Cont'd.)

COUNTY: Freestone County, Texas

Map Number	TWQB WCO Number	Point of Entry Into Trinity River				
		Corp. River Mile	Latitude		Longitude	
			Deg.	Min.	Deg.	Min.
1	10551-01	347	31	49	96	58
2	10551-03	347	31	49	96	58
3	10471-01	347	31	49	96	58
4	10300-02	347	31	49	96	58
5	10168-02	273	31	23	95	42
6	10168-01	347	31	49	96	58
7	11627-01	FL*	31	49	96	58
8	11629-01	FL*	31	49	96	58
9	11578-01	273	31	23	95	42

COUNTY: Henderson County, Texas

Map Number	TWQB WCO Number	Point of Entry Into Trinity River				
		Corp. River Mile	Latitude		Longitude	
			Deg.	Min.	Deg.	Min.
1	00947-01	387	32	07	96	07
2	10467-02	385	32	05	96	05
3	10738-01	385	32	05	96	05
4	10143-02	385	32	05	96	05

*Fairfield Lake

TABLE A-2 (Cont'd.)

COUNTY: Houston County, Texas

Map Number	TWQB WCO Number	Point of Entry Into Trinity River				
		Corp. River Mile	Latitude		Longitude	
			Deg.	Min.	Deg.	Min.
1	11181-01	200	30	56	95	32
2	10154-01	266	31	21	95	39
3	10154-02	169	30	55	95	16
4	10734-01	169	30	55	95	16
5	10871-01	266	31	21	95	39

COUNTY: Kaufman County, Texas

Map Number	TWQB WCO Number	Point of Entry Into Trinity River				
		Corp. River Mile	Latitude		Longitude	
			Deg.	Min.	Deg.	Min.
1	10090-01	460	32	30	96	30
2	10060-03	460	32	30	96	30
3	10028-01	460	32	30	96	30
4	10834-01	460	32	30	96	30

COUNTY: Leon County, Texas

Map Number	TWQB WCO Number	Point of Entry Into Trinity River				
		Corp. River Mile	Latitude		Longitude	
			Deg.	Min.	Deg.	Min.
1	10356-01	208	30	56	95	37
2	10147-01	241	31	08	95	46
3	11577-01	273	31	23	95	42
4	11586-01	287	31	30	95	44
5	10022-01	273	31	23	95	42

TABLE A-2 (Cont'd.)

COUNTY: Liberty County, Texas

Map Number	TWQB WCO Number	Point of Entry Into Trinity River				
		Corp. River Mile	Latitude		Longitude	
			Deg.	Min.	Deg.	Min.
1	10564-01	29	29	58	94	48
2	10564-02	29	29	58	94	48
3	01969-01	29	29	58	94	48
4	10495-80	26	29	57	94	48
5	00952-01&02	8	29	52	94	44
6	10108-01	32	30	00	94	48
7	10108-03	32	30	00	94	48
8	11277-01	47	30	06	94	49
9	11377-01	72	30	17	94	57

COUNTY: Madison County, Texas

Map Number	TWQB WCO Number	Point of Entry Into Trinity River				
		Corp. River Mile	Latitude		Longitude	
			Deg.	Min.	Deg.	Min.
1	10215-01	208	30	56	95	37
2	01896-01	208	30	56	95	37
3	11176-01	208	30	56	95	37

COUNTY: Navarro County, Texas

Map Number	TWQB WCO Number	Point of Entry Into Trinity River				
		Corp. River Mile	Latitude		Longitude	
			Deg.	Min.	Deg.	Min.
1	10745-01	388	32	06	96	07
2	1029-01	394	32	09	96	07

TABLE A-2 (Cont'd.)

COUNTY: Polk County, Texas

Map Number	TWQB WCO Number	Point of Entry Into Trinity River				
		Corp. River Mile	Latitude		Longitude	
			Deg.	Min.	Deg.	Min.
1	11100-01	L. R.*	30	49	95	07
2	11298-01	L. R.	30	47	95	06
3	11147-01	L. R.	30	42	95	04
4	11197-01	L. R.	30	41	95	02
5	11223-01	124	30	38	95	01
6	11288-01	118	30	34	94	57
7	11722-01	118	30	34	94	57
8	11139-01	118	30	34	94	57
9	10208-01	118	30	34	94	57
10	11465-01	L. R. *	30	44	95	03

COUNTY: San Jacinto County, Texas

Map Number	TWQB WCO Number	Point of Entry Into Trinity River				
		Corp. River Mile	Latitude		Longitude	
			Deg.	Min.	Deg.	Min.
1	10997-01	L. R. *	30	39	95	05
2	11380-01	98	30	27	94	52
3	11310-01	L. R. *	30	39	95	09

*Livingston Reservoir

TABLE A-2 (Cont'd.)

COUNTY: Tarrant County, Texas

Map Number	TWQB WCO Number	Point of Entry Into Trinity River				
		Corp. River Mile	Latitude		Longitude	
			Deg.	Min.	Deg.	Min.
1	11032-01	510	32	47	96	57
2	10235-01	510	32	47	96	57
3						
4	11035-01	510	32	47	96	57
5	11175-01	510	32	47	96	57
6	10486-03	510	32	47	96	57
7	10605-01	543	32	47	97	14
8	00570-01	553	32	47	97	19
9	10103-01	543	32	47	97	14
10	10494-13	534	32	46	97	09
11	00367-01	534	32	46	97	09
12	10494-14	525	32	49	97	04
13	10494-01	551	32	45	97	17
14	10494-02	551	32	45	97	17
15	11036-01	534	32	47	97	09
16	11244-01	534	32	47	97	09
17	11106-01	534	32	47	97	09
18	11110-01	534	32	47	97	09
19	11009-01	534	32	47	97	09
20	10886-01	534	32	47	97	09

continued

TABLE A-2 (Cont'd.)

COUNTY: Tarrant County, Texas; Cont'd.

Map Number	TWQB WCO Number	Point of Entry Into Trinity River				
		Corp. River Mile	Latitude		Longitude	
			Deg.	Min.	Deg.	Min.
21	11002-01	534	32	47	97	09
22	10216-01	MCL*	32	47	96	55
23	11585-01	510	32	47	96	57

COUNTY: Trinity County, Texas

Map Number	TWQB WCO Number	Point of Entry Into Trinity River				
		Corp. River Mile	Latitude		Longitude	
			Deg.	Min.	Deg.	Min.
1	11300-01	170	30	55	95	16
2	11350-01	170	30	55	95	16
3	10556-01	L.R.*	30	50	95	05
4	10617-01	170	30	55	95	16
5	11644-01	170	30	55	95	16

COUNTY: Walker County, Texas

Map Number	TWQB WCO Number	Point of Entry Into Trinity River				
		Corp. River Mile	Latitude		Longitude	
			Deg.	Min.	Deg.	Min.
1	11326-01	198	30	56	95	31
2	11325-01	198	30	56	95	31
3	10781-01	L.R.*	30	52	95	26
4	11180-01	L.R.	30	53	95	26

*Mountain Creek Lake

APPENDIX B

TEXAS WATER QUALITY BOARD

MONITORING PROGRAM

AND SEDIMENT QUALITY DATA

FOR THE TRINITY RIVER

APPENDIX B

TEXAS WATER QUALITY BOARD MONITORING PROGRAM AND SEDIMENT QUALITY DATA FOR THE TRINITY RIVER

The Texas Water Quality Board currently operates seven sediment monitoring stations on the Trinity River within the reaches of this study. The sediment data for the water year October 1, 1974 to September 30, 1975 has been tabulated in this appendix.

TEXAS WATER QUALITY BOARD

The Texas Water Quality Board monitoring program began with the Board's first operations in 1967. As the chief water quality agency in the State, the purposes of its monitoring program include determining where pollution problems exist, measuring the effect of pollution abatement actions over a period of time, and enforcement.

Since 1967 the program has increased greatly in stations, parameters, and frequency. The following table and Figure 1 represent the program as of April 1974. Only the designations of "Types of Record" should require explanation, as follows:

C = Chemical

a. Dissolved oxygen, temperature, pH, turbidity, and conductivity - monthly
b. Chlorides, sulphates, and total dissolved solids (calculated from conductivity) - at nontidal stations only - quarterly
c. Fecal coliform - at nonestuarine stations only - quarterly
d. Total coliform - at estuarine stations only - quarterly
e. Total phosphate, ortho-phosphate, ammonia nitrogen, nitrate nitrogen, and chlorophyll "a", total organic carbon, total suspended solids, volatile suspended solids, dissolved oxygen, temperature, pH, turbidity, conductivity - quarterly
f. Streamflow - at time of monthly sampling (will use USGS flow data where available)
g. Tidal measurements - quarterly in conjunction with estuarine monitoring (will use Corps of Engineers tide stage data if possible)

P = Pesticides

a. Herbicides in water - annually
   2, 4 - D
   2, 4, 5 - T
   Silvex
b. Insecticides in water - annually
   Heptachlor
   Heptachlor epoxide
   Lindane
   Malathion
   Methoxychlor
   Parathion
c. PCB - occasionally

B = Biological

a. Benthic macroinvertebrate communities - quarterly

S = Sediment

The following parameters are measured in sediments annually:

a. Arsenic
b. Barium
c. Boron
d. Cadmium
e. Copper
f. Chromium (total)
g. Lead
h. Manganese
i. Mercury
j. Nickel
k. Herbicides
   Silvex
l. Selenium
m. Silver
n. Zinc
o. Total phosphate
p. Chemical oxygen demand
q. Kjeldahl nitrogen
r. Volatile solids
s. Oil and grease
t. Total organic carbon
u. PCB
v. Insecticides

Aldrin	Endrin
Chlordane	Heptachlor
Chlorthion	Heptachlor epoxide
DDD	Lindane
DDE	Methoxychlor
DDT	Methyl Parathion
Diazinon	Parathion
Dieldrin	Toxaphene

TEXAS WATER QUALITY BOARD MONITORING
TRINITY RIVER BASIN

Location	Station Number	Type of Record
Trinity River at IH 10 south of Liberty	0801.01	CBSP
Trinity River at US 90 in Liberty	0802.01	CBS
Trinity River at US 59 south of Goodrich	0802.02	CP
Lake Livingston at US 190 north of Pointblank	0803.01	C
Trinity River (Lake Livingston) at SH 19 north of Riverside	0804.01	CS
Harmons Creek at Lake Falls Estates	0800.01	C
Bedias Creek at FM 247 northwest of Huntsville	0800.02	C
Trinity River (Lake Livingston) at SH 21 north of Midway	0804.02	CB
Trinity River at SH 7 west of Crockett	0804.03	CP
Houston County Lake at mid-lake	0813.01	C
Trinity River at US 79 northeast of Oakwood	0804.04	CBS
Town Creek at FM 645 southwest of Palestine	0800.04	C
Tehuacana Creek at FM 488 northeast of Fairfield	0800.03	C
Chambers Creek at SH 31 east of Corsicana	0814.01	CB
Bardwell Reservoir at mid-lake near dam	0815.01	C
Lake Waxahachie at mid-lake near dam	0816.01	C
Richland Creek at IH 45 north of Richland	0800.05	C
Navarro Mills Reservoir at mid-lake near dam	0817.01	C
Trinity River at US 287 west of Cayuga	0804.05	C
Trinity River at SH 31 west of Trinidad	0804.06	CBS
Cedar Creek Reservoir at mid-lake	0818.01	C
Cedar Creek Reservoir at Kings Creek Arm at SH 274 south of Kemp	0818.02	CS
Trinity River at SH 34 southwest of Rosser	0805.01	CBP
East Fork Trinity River at US 175 northwest of Crandall	0819.01	CBS

Lake Ray Hubbard at mid-lake near dam	0820.03	C
Lake Ray Hubbard at Rowlett Creek Arm	0820.01	CS
Lake Ray Hubbard at East Fork Arm	0820.02	C
Lake Lavon at mid-lake near dam	0821.03	C
Lake Lavon at Pilot Grove Arm	0821.02	C
Lake Lavon at East Fork Arm	0821.01	CS
Trinity River at Belt Line Road east of Wilmer	0805.02	C
Trinity River at South Loop SH 12 south of Dallas	0805.03	CBS
White Rock Lake at mid-lake near dam	0827.01	C
Trinity River at Commerce Street in Dallas	0805.04	C
Elm Fork Trinity River at SH 356 at Dallas	0822.01	CB
Elm Fork Trinity River at Carrollton Dam west of Carrollton	0822.02	C
Denton Creek at SH 121 west of Lewisville	0825.01	C
Grapevine Reservoir at mid-lake near dam	0826.01	C
Lake Lewisville at mid-lake near dam	0823.03	C
Lake Lewisville at Hickory Creek Arm	0823.01	C
Lake Lewisville at Elm Fork Arm	0823.02	CS
Elm Fork Trinity River at FM 455 northeast of Sanger	0824.01	CPB
West Fork Trinity River at Belt Line Road in Grand Prairie	0805.05	CBS
Lake Arlington at mid-lake near dam	0828.01	CS
West Fork Trinity River at Randol Mill Road south of Richland Hills	0805.06	C
West Fork Trinity River at Beach Street in Fort Worth	0805.07	CBS
West Fork Trinity River at East Northside Drive in Fort Worth	0806.01	C
Clear Fork Trinity River at Bryant-Irvin Street in Fort Worth	0829.01	CB
Benbrook Reservoir at mid-lake near dam	0830.01	C
Clear Fork Trinity River at US 377 southeast of Aledo	0831.01	CP
Lake Weatherford at mid-lake near dam	0832.01	C
Clear Fork Trinity River at FM 51 northeast of Weatherford	0833.01	C
West Fork Trinity River at River Oaks Blvd. (SH 183) in Fort Worth	0806.02	C
Lake Worth at midlake near dam	0807.01	C
Lake Worth at Ten Mile Bridge Road in Fort Worth	0808.01	C
Eagle Mountain Reservoir at mid-lake near dam	0809.01	C
West Fork Trinity River at FM 730 northeast of Boyd	0810.01	CB
Lake Amon G. Carter at mid-lake near dam	0834.01	C
Lake Bridgeport at mid-lake near dam	0811.01	C
West Fork Trinity River at SH 59 northeast of Jacksboro	0812.01	CP

TEXAS WATER QUALITY BOARD MONITORING ON TRINITY RIVER

Trinity River Reach a: Beach Street Bridge in Fort Worth downstream to the confluence of the East fork of the Trinity River.

TWQB Station	Location	Type of Record
805.07*	West Fork Trinity River at Beach Street Fort, Worth, Texas	CBS
805.06	West Fork Trinity River at Randol Mill Road South of Richland Hills	C
805.05*	West Fork Trinity River at Beltline Road in Grand Prairie	CBS
805.04	Trinity River at Commerce Street in Dallas	C
805.03*	Trinity River at South Loop SH12 South of Dallas	CBS
805.02	Trinity River at Beltline Road East of Wilmer, Texas	C

Trinity River Reach b: East Fork Confluence downstream to Highway 31 Bridge at Trinidad, Texas.

805.01	Trinity River at SH34 Southwest of Rosser, Texas	CBP
804.06*	Trinity River at SH31 West of Trinidad	CBS

Trinity River Reach c: From Hwy. 31 Bridge at Trinidad downstream to the Headwaters of Lake Arlington.

804.05	Trinity River at US287 West of Cayuga, Texas	C
804.04*	Trinity River at US79 Northeast of Oakwood, Texas	CBS
804.03	Trinity River at SH7 West of Crockett, Texas	CP
804.02	Trinity River - (Lake Livingston) at SH21 North of Midway, Texas	CB

Trinity River Reach d: Lake Livingston Dam downstream to River Mile 0.0

802.2	Trinity River at US59 South of Goodrich, Texas	CP
802.01*	Trinity River at US90 in Liberty, Texas	CBS
801.01*	Trinity River at IH10 South of Liberty, Texas	CBSP

*Data on bottom sediments are included in this Appendix.

TRINITY RIVER REACH (a):

TWQB STATION 805.07 BOTTOM SEDIMENT DATA ONLY

Chemical Tests Bottom Deposits	Quantity MG/KG as Element Dry Wt.	Date
Metals:		
1. Arsenic	6.30	July 9, 1975
2. Barium	78.00	"
3. Boron	0.72	"
4. Cadmium	1.20	"
5. Copper	15.50	"
6. Chromium	14.20	"
7. Lead	323.00	"
8. Manganese	301.00	"
9. Mercury	21.00	"
10. Nickel	13.30	"
11. Selenium	2.58	"
12. Silver	1.70	"
13. Zinc	57.80	"

Insecticides:	ug/kg dry solids	Date
1. Aldrin	No	
2. Chlordane	Data	
3. Chlorthion	Available	
4. DDD	As of	
5. DDE	May 1976	
6. DDT		
7. Diazinon		
8. Dieldrin		
9. Endrin		
10. Heptachlor		
11. Heptachlor Epoxide		
12. Lindane		
13. Methoxychlor		
14. Methyl Parathion		
15. Parathion		
16. Toxaphene		
17. PCB's		

TRINITY RIVER REACH a:

TWQB STATION 805.05 BOTTOM SEDIMENT DATA ONLY

Chemical Tests Bottom Deposits	Quantity MG/KG as Element Dry Wt.	Date
Metals:		
1. Arsenic	.74	October 1, 1975
2. Barium	1715.00	"
3. Boron	5.30	"
4. Cadmium	1.67	"
5. Copper	41.80	"
6. Chromium	23.20	"
7. Lead	39.40	"
8. Manganese	979.00	"
9. Mercury	0.00	"
10. Nickel	35.20	"
11. Selenium	0.90	"
12. Silver	1.70	"
13. Zinc	86.40	"

Insecticides:	ug/kg dry solids	Date
1. Aldrin	No	
2. Chlordane	Data	
3. Chlorthion	Available	
4. DDD	As of	
5. DDE	May 1976	
6. DDT		
7. Diazinon		
8. Dieldrin		
9. Endrin		
10. Heptachlor		
11. Heptachlor Epoxide		
12. Lindane		
13. Methoxychlor		
14. Methyl Parathion		
15. Parathion		
16. Toxaphene		
17. PCB's		

TRINITY RIVER REACH a :

TWQB STATION 805.03 BOTTOM SEDIMENT DATA ONLY

Chemical Tests Bottom Deposits	Quantity MG/KG as Element Dry Wt.	Date
Metals:		
1. Arsenic	0.23	September 9, 1975
2. Barium	152.20	"
3. Boron	19.70	"
4. Cadmium	2.87	"
5. Copper	62.70	"
6. Chromium	43.90	"
7. Lead	37.30	"
8. Manganese	110.40	"
9. Mercury	0.10	"
10. Nickel	13.70	"
11. Selenium	3.03	"
12. Silver	1.80	"
13. Zinc	67.46	"
Insecticides:	ug/kg dry solids	Date
1. Aldrin	.00	August 7, 1975
2. Chlordane	---	
3. Chlorthion	---	
4. DDD	.10	"
5. DDE	.20	"
6. DDT	.00	"
7. Diazinon	---	
8. Dieldrin	.50	"
9. Endrin	---	
10. Heptachlor	.00	"
11. Heptachlor Epoxide	.00	"
12. Lindane	.00	"
13. Methoxychlor	.00	"
14. Methyl Parathion	---	
15. Parathion	---	
16. Toxaphene	---	
17. PCB's	4.00	"

TRINITY RIVER REACH b :

TWQB STATION 804.06 BOTTOM SEDIMENT DATA ONLY

Chemical Tests Bottom Deposits	Quantity MG/KG as Element Dry Wt.	Date
Metals:		
1. Arsenic	0.27	October 2, 1975
2. Barium	635.00	"
3. Boron	10.50	"
4. Cadmium	0.89	"
5. Copper	34.90	"
6. Chromium	9.50	"
7. Lead	14.00	"
8. Manganese	181.00	"
9. Mercury	0.00	"
10. Nickel	10.20	"
11. Selenium	0.21	"
12. Silver	1.30	"
13. Zinc	69.80	"

Insecticides:	ug/kg dry solids	Date
1. Aldrin	No	
2. Chlordane	Data	
3. Chlorthion	Available	
4. DDD	As of	
5. DDE	May 1976	
6. DDT		
7. Diazinon		
8. Dieldrin		
9. Endrin		
10. Heptachlor		
11. Heptachlor Epoxide		
12. Lindane		
13. Methoxychlor		
14. Methyl Parathion		
15. Parathion		
16. Toxaphene		
17. PCB's		

TRINITY RIVER REACH c ;

TWQB STATION 804.04 BOTTOM SEDIMENT DATA ONLY

Chemical Tests Bottom Deposits	Quantity MG/KG as Element Dry Wt.	Date
Metals:		
1. Arsenic	2.60	July 30, 1975
2. Barium	---	"
3. Boron	---	"
4. Cadmium	0.50	"
5. Copper	6.70	"
6. Chromium	12.00	"
7. Lead	8.30	"
8. Manganese	160.00	"
9. Mercury	0.00	"
10. Nickel	13.00	"
11. Selenium	---	"
12. Silver	0.50	"
13. Zinc	32.00	"

Insecticides:	ug/kg dry solids	Date
1. Aldrin	0.00	July 30, 1975
2. Chlordane	---	"
3. Chlorthion	---	"
4. DDD	0.00	"
5. DDE	0.00	"
6. DDT	0.00	"
7. Diazinon	---	"
8. Dieldrin	0.00	"
9. Endrin	0.00	"
10. Heptachlor	0.00	"
11. Heptachlor Epoxide	0.00	"
12. Lindane	---	"
13. Methoxychlor	0.00	"
14. Methyl Parathion	---	"
15. Parathion	---	"
16. Toxaphene	0.00	"
17. PCB's	0.00	"

TRINITY RIVER REACH d :

TWQB STATION 802.01 BOTTOM SEDIMENT DATA ONLY

Chemical Tests Bottom Deposits	Quantity MG/KG as Element Dry Wt.	Date
Metals:		
1. Arsenic	0.0	July 3, 1974
2. Barium	5.20	Nov.12, 1975
3. Boron	---	
4. Cadmium	1.00	Nov. 12,1975
5. Copper	1.00	"
6. Chromium	1.00	"
7. Lead	2.50	"
8. Manganese	30.20	"
9. Mercury	0.10	"
10. Nickel	2.10	"
11. Selenium	---	"
12. Silver	1.00	"
13. Zinc	3.10	"
Insecticides:	ug/kg dry solids	Date
1. Aldrin	.00	July 3, 1974
2. Chlordane	---	
3. Chlorthion	---	
4. DDD	.00	July 3, 1974
5. DDE	.00	"
6. DDT	2.00	"
7. Diazinon	---	
8. Dieldrin	.00	"
9. Endrin	.00	"
10. Heptachlor	.00	"
11. Heptachlor Epoxide	.00	"
12. Lindane	2.00	"
13. Methoxychlor	.00	"
14. Methyl Parathion	---	
15. Parathion	---	
16. Toxaphene	.00	"
17. PCB's	0.00	"

B-12

TRINITY RIVER REACH d:

TWQB STATION 801.01 BOTTOM SEDIMENT DATA ONLY

Chemical Tests Bottom Deposits	Quantity MG/KG as Element Dry Wt.	Date
Metals:		
1. Arsenic	0.00	July 3, 1974
2. Barium	1.00	Oct. 1, 1975
3. Boron	---	
4. Cadmium	1.00	"
5. Copper	2.70	"
6. Chromium	4.90	"
7. Lead	2.50	"
8. Manganese	249.20	"
9. Mercury	0.10	"
10. Nickel	6.50	"
11. Selenium	---	
12. Silver	1.00	"
13. Zinc	18.50	"

Insecticides:	ug/kg dry solids	Date
1. Aldrin	.00	July 3, 1974
2. Chlordane	---	
3. Chlorthion	---	
4. DDD	.00	"
5. DDE	.00	"
6. DDT	2.00	"
7. Diazinon	---	"
8. Dieldrin	.00	"
9. Endrin	.00	"
10. Heptachlor	.00	"
11. Heptachlor Epoxide	.00	"
12. Lindane	2.00	"
13. Methoxychlor	.00	"
14. Methyl Parathion	---	"
15. Parathion	---	"
16. Toxaphene	0.00	"
17. PCB's	0.00	

APPENDIX C

INSECTICIDES AND HERBICIDES

EVALUATION

ALONG TRINITY RIVER BASIN

APPENDIX C

INSECTICIDES AND HERBICIDES EVALUATION ALONG TRINITY RIVER BASIN*

An assessment of the insecticides and herbicides that are used within the counties in the watershed is a good indication of the relative amounts of these pesticides polluting various regions of the river. Studies have shown a high correlation between insecticide application and insecticide concentrations in the river waters and sediments.

Pesticide concentration in river sediments are directly dependent on watershed characteristics such as land use patterns, surface erodability, rainfall patterns, and soil compositon of the treated acreage. The fate of pesticides carried into the river depends upon the type of sediment with which they become associated.

Finer textured sediments have a proportionately greater concentration of pesticides and thus the pesticides are easily transported down stream. As the flow decreases, the load capacity decreases allowing pesticide-containing sediments to be deposited in regions of low velocity flow. It is not unusual to find that pesticide contents in silt and clay deposits exceeding river water content by several hundred times. The largest user of insecticides and herbicides are the counties bordering the river for approximately 200 miles downstream of Dallas. This distance would include Kaufman, Ellis, Navarro, Henderson, Anderson, and Freestone counties (See Tables C-1, C-2, C-3). According to U.S.G.S. data, the concentrations of pesticides and herbicides in river sediments are increasing considerably (See Table C-4). Evidence from studies indicates that industrial waste

discharge from pesticide manufacturers and surface runoff from areas which have received pesticide applications are responsible for the largest percentage of pesticide contamination of waters.

McCullough and Champ collected and analyzed Trinity River sediments during 1972-73.* A total of 49 samples were collected and the results of their findings are given in Table C-5. From the studies of McCullough and Champ, there is a high correlation between organics concentration and pesticide concentration. Therefore, the heavy organic loading from the Fort Worth-Dallas area could furnish a mechanism for the transport of pesticides. The domestic and industrial discharges from the Metropolitan Area may be one of the major sources of pesticides in the Trinity River sediments.

*"Status Report of Environmental Evaluations, Main Text", Corps of Engineers, 1975, pp. 150-162.

TABLE C-1

CUMULATIVE ACREAGE TREATED WITH INSECTICIDES IN 1970-71

Sampling Station	River Mile	Adjacent Counties	Cumulative Acreage* Treated
Rosser	454	Ellis	414,000
		Kaufman	119,000
Highway 85	430	Henderson	14,900
		Navarro	49,100
Cayuga	370	Anderson	43,427
		Freestone	9,000
Fairfield	308	Anderson (both counties included above) Freestone	
Highway 7	266	Leon	10,000
		Houston	48,000
Highway 21	231	Leon (both counties included above) Houston	

*The term "cumulative" refers to total acres treated per year, although the same acreages may have been treated more than once, or with more than one insecticide.

Data Source: Texas A. & M. Extension Service, Texas A. & M., College Station, Texas.

TABLE C-2

ESTIMATED INSECTICIDE USAGE IN SELECTED COUNTIES, DALLAS TO TRINITY BAY, TEXAS, 1968-1971

	Pounds of Insecticide Used per Year			
	1968	1969	1970	1971
Anderson County				
Carbaryl	4,730	6,581	23,111	-
DDT	2,250	2,700	1,840	-
Diazinon	580	160	1,280	-
Guthion	37	-	1,260	-
Malathion	1,110	730	4,313	-
Methyl parathion	328	393	643	-
Parathion	464	780	3,990	-
Toxaphene	1,875	2,533	1,533	-
Chambers County				
Carbofuran	-	-	-	15,500
Dallas County - no entries				
Ellis County				
Carbaryl	-	-	-	1,200
DDT	-	-	-	600,000
Malathion	-	-	-	450
Parathion	-	-	-	1,425
Toxaphene	-	-	-	400,000
Freestone County				
Carbaryl	8,430	13,256	14,231	-
DDT	-	900	2,700	-
Guthion	2,100	3,412	2,940	-
Malathion	1,305	2,048	1,974	-
Methyl parathion	-	131	418	-
Parathion	1,708	2,633	2,583	-
Toxaphene	11	750	2,383	-

(continued)

TABLE C-2 (Continued)

	Pounds of Insecticide Used per Year			
	1968	1969	1970	1971
Henderson County				
Carbaryl	6,271	49,352	10,202	-
DDT	150	450	450	-
Diazinon	750	500	700	-
Guthion	105	105	105	-
Malathion	1,494	4,776	1,751	-
Methyl parathion	59	65	65	-
Parathion	756	6,119	1,168	-
Toxaphene	125	2,875	625	-
Houston County				
Carbaryl	-	-	-	32,850
DDT	-	-	-	45,000
Malathion	-	-	-	7,327
Parathion	-	-	-	16,548
Toxaphene	-	-	-	30,000
Kaufman County				
Carbaryl	-	-	-	29,700
DDT	-	-	-	150,000
Malathion	-	-	-	5,200
Parathion	-	-	-	8,550
Toxaphene	-	-	-	100,000
Leon County				
Carbaryl	-	-	-	1,500
DDT	-	-	-	12,000
Diazinon	-	-	-	200
Malathion	-	-	-	375
Parathion	-	-	-	150
Toxaphene	-	-	-	8,000
Liberty County				
Carbofuran	-	-	-	25,000
DDT	-	-	-	6,000
Toxaphene	-	-	-	94,000

(continued)

TABLE C-2 (Continued)

	Pounds of Insecticide Used per Year			
	1968	1969	1970	1971
Navarro County				
Carbaryl	10,525	13,975	28,009	-
DDT	60,000	60,000	22,650	-
Diazinon	50	50	100	-
Guthion	840	1,050	-	-
Malathion	1,088	706	2,838	-
Methyl parathion	8,750	8,750	3,303	-
Parathion	2,696	2,048	4,800	-
Toxaphene	50,030	50,083	20,041	-
Polk County				
Carbaryl	-	-	-	37
Malathion	-	-	-	100
Methyl parathion	-	-	-	6
Parathion	-	-	-	450
San Jacinto County - no entries				
Trinity County				
Malathion	-	-	-	57
Parathion	-	-	-	258
Walker County				
Malathion	-	-	-	50
Parathion	-	-	-	225

Data Source: Individual County Agents.

(-) indicates information not available.

TABLE C-3

HERBICIDE USAGE IN SELECTED COUNTIES,
DALLAS TO TRINITY BAY, TEXAS, 1970-1971

	Total Gallons Used per Year		
	2,4-D		2,4,5-T
Counties	1970	1971	1971
Anderson	1,622	-	-
Chambers	-	-	-
Dallas	-	288	0
Ellis	-	-	-
Freestone	782	-	-
Henderson	5,100	-	-
Houston	-	6,999	205
Kaufman	-	3,10[illegible]	0
Leon	-	6,09[illegible]	227
Liberty	-	-	-
Navarro	6,529	-	-
Polk	-	1,001	133
San Jacinto	-	0	0
Trinity	-	115	11
Walker	-	7,831	1,550

- No entries provided.

Data Source: Texas Department of Agriculture

TABLE C-4

MAXIMUM PESTICIDE-HERBICIDE CONCENTRATIONS*

	1967-1968	1969-1970	1970-1971	1971-1972
Heptachlor	0.00	0.00	0.00	0.00
Heptachlor epoxide	0.00	0.00	0.00	0.00
Lindane	0.01	0.05	0.04	0.03
2,4-D	0.17	1.6	0.23	0.29
2,4,5-T	0.05	0.10	0.06	0.06
Silvex	0.00	0.01	0.00	0.00
Aldrin	-	0.00	0.00	0.00
DDT	-	0.14	0.10	0.02
DDE	-	0.00	0.00	0.03
DDD	-	0.04	0.02	0.00
Dieldrin	-	0.25	0.05	0.04
Endrin	-	0.00	0.00	0.00
Chlordane	-	0.41	0.3	0.3
Diazinon	-	0.00	0.44	0.37
Methyl Parathion	-	0.00	0.46	0.00
Parathion	-	0.00	0.00	0.00
Malathion	-	-	1.0	0.05
Toxaphene	-	-	0.0	-

*micrograms per liter detected in the Trinity River at the USGS Rosser water quality sampling station

TABLE C-5

PESTICIDE CONCENTRATIONS IN BOTTOM SEDIMENTS
1972 AVERAGE CONCENTRATIONS AT GAGING STATIONS
(µg/kg)

Pesticide	* -	Rosser RM 454	Hwy 85 RM 430	Cayuga RM 370	Fair-field RM 308	Hwy 7 RM 266	Hwy 21 RM 231
LINDANE	25	1.60	.44	.64	.40	.28	.05
ALDRIN	12	.62	0.00	1.31	.02	0.00	.02
CHLORDANE	92	127.02	49.69	22.41	12.09	9.75	25.16
HEPTACHLOR	41	5.07	.80	.56	.11	.05	.12
o p' DDE	78	3.85	2.36	1.10	.50	.65	.91
o p' DDT	16	0.00	0.00	.88	.12	.67	.52
MIREX	4	0.00	0.00	.17	0.00	.18	0.00
ENDRIN	10	1.89	0.00	.45	0.00	0.00	0.69
DIELDRIN	8	.40	.42	.61	0.00	0.00	0.00
METHOXYCHLOR	-	0.00	0.00	0.00	0.00	0.00	0.00

*Percent of Samples Containing Measurable Quantities

Data Source: McCullough and Champ (1973)

APPENDIX D

LAND USE AND GEOLOGICAL FORMATIONS OF THE TRINITY RIVER BASIN

APPENDIX D

LAND USE AND GEOLOGICAL FORMATIONS OF THE TRINITY RIVER BASIN

This appendix was compiled from basic data obtained from the Status Report of Environmental Evaluations. Surrounding land uses and underlying formations were referenced to channel miles. These are approximate ranges for the noted formations and land uses and should be noted as such.

River Mile	Channel Mile	River Channel Soil	Surrounding Area Soil**	Underlying Formations***	Percent Land Utilization
0-50	0-47	Mixed Alluvial Soils	Vertisols	Beaumont FM	40% Pasture & range 40% Forest 10% Crop 5% Urban 5% Other
50-120	47-95	Mixed Alluvial Soils	Alfisols	*47-65 Beaumont FM *65-75 Bentley FM *75-85 Willis FM *85-95 Fleming FM	24% Pasture & range 74% Forest 1% Crop .5% Urban .5% Other
120-156	95-115	Mixed Alluvial Soils	Alfisols & Utisols	*95-110 Fleming FM *110-115 Catahoula FM	20% Pasture & range 70% Forest 4% Crop 3% Urban 3% Other
156-422	115-280	Mixed Alluvial Soils	Alfisols	*115-130 Catahoula FM *130-135 Whitsett Sand *135-145 Manning FM *145-150 Wellborn FM *150-172 Yegua FM *172-190 Cook Mtn. FM *190-195 Sparta Sand *195-220 Queen City Sand *220-225 Reklew FM *225-265 Wilcox Group *265-280 Wills Pt. FM	43% Pasture & range 32% Forest 20% Crop 4% Urban 2% Other

continued

*Channel Miles
**For Soil Definitions, See page D-8
***For Formation Data, See Table D-1

River Mile	Channel Mile	River Channel Soil	Surrounding Area Soil**	Underlying Formations***	Percent Land Utilization
422-493	280-327	Mixed Alluvial Soils	Vertisols	*280-289 Nacatoch Sand *289-300 Neylandville FM & Marlbrook Marl *300-305 Wolf City Sand *305-315 Ozan FM *315-327 Austin Chalk	41% Pasture & range 3% Forest 46% Crop 6% Urban 4% Other
493-503	327-337	Mollisols	Mollisols	*327-334 Austin Chalk *334-337 Eagle Ford Shale	28% Pasture & range 7% Forest 43% Crop 14% Urban 8% Other
503-520	337-349	Vertisols	Vertisols	*337-345 Eagle Ford Shale *345-349 Woodbine FM	28% Pasture & range 6% Forest 40% Crop 16% Urban 10% Other
520-551	349-370	Alfisols	Alfisols	*349-355 Woodbine FM *355-370 Lower Cretacous Limestones & Clays	35% Pasture & range 7% Forest 35% Crop 15% Urban 8% Other

*Channel Miles

**For soil definitions, see page D-8

***For formation data, see Table D-1

TABLE D-1

GENERAL DESCRIPTION OF STRATIGRAPHIC UNITS

System	Series	Group	Stratigraphic Units	Approx. Thickness (feet)	Physical Characteristics of Rock Units
Quaternary	Recent		Alluvium		Unconsolidated clay, silt, sand and gravel deposits.
	Recent or late Pleisto-cene		Deweyville Formation	0-50+	Unconsolidated clay, silt, sand and gravel deposited at a level slightly above present floodplain.
	Pleisto-cene		Fluviatile Terrace Deposits	0-80	Unconsolidated clay, silt, sand and gravel terrace deposits in river valley. Three distinct terraces are recognized and may be in part correlative to Beaumont Formation.
			Beaumont Formation	100±	Unconsolidated clay, silt and sand.
			Montgomery Formation (Upper Lissie)	100±	Clay, silt, sand and some siliceous gravel; locally calcareous.
			Bentley Formation (Lower Lissie)	100±	Clay, silt, sand, and minor amounts of gravel.
			Willis Formation	100±	Clay, silt, sand, and some siliceous gravel.
Tertiary	Pliocene		Goliad Sand	0-500	Sand, gravel, calcareous sandstone; interbedded clay.
	Miocene		Fleming Formation	1,300-1,450	Clay, silt, and sand; clays commonly calcareous.
			Catahoula Formation	250-300	Mudstone and sand, tuffaceous. Lower portion of formation quartz sand. Fossil wood abundant.

	Eocene or Oligocene		Whitsett	30-70	Quartz sand, fine to medium grained, tuffaceous, lignitic.
Tertiary	Eocene	Jackson	Manning Formation	250±	Quartz sand and clay, lignitic. Fossil wood abundant.
			Wellborn Formation	50-150	Quartz sand, fine to very fine grained, glauconitic and lignitic, with interbeds of lignitic clay. Locally marine megafossils.
			Caddell Formation	50-150	Quartz sand and clay; clay, sandy and lignitic; sand, glauconitic.
		Claiborne	Yegua Formation	600-1000	Clay, quartz sand and lignite. Upper portion of formation mostly clay, lower portion mostly sand. Marine megafossils.
			Cook Mt. Formation Stone City Formation	450-470	Clay, marl and sand; lignitic, glauconitic with some limestone lentils.
			Sparta Sand	200±	Quartz sand, fine to very fine grained with lignitic clay and silt partings.
			Weches Formation	50-90	Glauconite, glauconitic marl and quartz sand. Marine megafossils.
			Queen City Sand	425±	Quartz sand, fine grained, with interbeds of clay, clay ironstone beds, and concretions common.
			Reklaw Formation	30-130	Marquez member: clay and silts; carbonaceous, glauconitic, clay ironstone with imprints of marine megafossils. Newby member: glauconite, quartz sand, clay; marine megafossils.
			Carrizo Sand	60-150	Quartz sand; upper portion fine grained with some clay and silt interbeds; lower portion fine to medium grained.
		Wilcox	Undivided	2000±	Quartz sand, silt, clay, carbonaceous clays and lignite; fossil wood.

TABLE D-1 (cont'd)

Tertiary	Eocene	Midway	Wills Point Formation	500±	Clay and silt; silt increases upward, local occurrences of lignite and calcareous concretions. Formation becomes glauconitic near base.
			Kincaid Formation	180±	Clay; glauconitic, calcareous, silty or sandy. Phosphatic near base, and some thin limestones occurring near top of formation.
Upper Cretaceous	Gulf	Navarro	Kemp Clay and Corsicana Marl	Undivided 550±	Clay and marl; silty, sandy, calcareous, glauconitic, locally gypsiferous.
			Nacatoch Sand	200±	Sand and sandy shale; locally cemented to form calcareous sandstone; glauconitic marine megafossils.
			Neylandville Formation	140±	Clay; calcareous, locally sandy, glauconitic and fossiliferous. Some concretionary beds.
		Taylor	Marlbrook Marl (Upper Taylor marl)	400±	Marl and clay; chalky.
			Wolf City Formation	250±	Alternating sandy, calcareous clay; marly sand and thin beds of calcareous sandstone
			Ozan Formation (Lower Taylor marl)	550±	Marl and clay; sandy, calcareous.
		Austin	Austin Chalk	700±	Limestone; basal 150 feet of formation consists of massive chalk layers separated by thin shaly layers. Middle portion 250 feet, characterized by thick shaly limestone layers. The uppermost portion contains more shale and less chalk.
		Eagle Ford	Arcadia Park Shale	100±	Clay, shale and limestone. Basal portion clay, separated from upper shaly portion by thin limestone flags. Numerous calcareous concretions in upper portion.

Upper Cretaceous	Gulf	Eagle Ford	Britton Shale	320±	Clay, marl and shale with some limestone seams, calcareous concretions, and bentonite seams. Lower 20 feet (Tarrant Member) consists of sandy clay, limestone and calcareous concretions.
		Woodbine	Lewisville Formation	250±	Sandstone, sandy clay and clay.
			Dexter	100±	Sandstone, sand and clay; fossil plant remains.
Lower Cretaceous	Comanche	Washita	Grayson Marl	75±	Shale and marl with thin limestone layers in upper portion of formation. Marine megafossils.
			Main Street Formation	30±	Limestone, chalky, massive to medium beds separated by thin shale layers. Marine megafossils.
			Pawpaw Formation	20±	Shale, calcareous, sandy near base. Thin, sandy limestone layers present in the basal beds.
			Weno Limestone	55±	Limestone predominant in upper half of formation, shale in lower half. Locally poor to abundant marine megafossils.
			Denton Clay	35±	Clay, calcareous, locally sandy or silty. Marine megafossils.
			Fort Worth Limestone	30±	Limestone; chalky, limestone beds separated by thin layers of calcareous shale. Marine megafossils.
			Duck Creek Limestone	50±	Upper 2/3 of formation consists of marl & calcareous shale interbedded with limestone. Lower 1/3 massive limestone.
		Fredericksburg	Kiamichi Clay	30-50	Clay, silty, calcareous, minor amounts of thin limestone lentils. Marine megafossils.
			Goodland Limestone	120±	Limestone with alternating marl & clay beds. Marine megafossils.
		Trinity	Paluxy Formation	95-105	Sandstone & mudstone. Sandstone commonly crossbedded. Mudstone, sandy, massive. Sandy, fossiliferous limestone beds locally in upper 50 feet.
			Glen Rose Formation	40-200	Limestone, distinctly bedded with alternating units of clay, marl and sand.
			Twin Mountain Formation	150±	Upper part, claystone; middle part sandstone above claystone; lower part, mostly sandstone with some claystone & conglomerate. Locally crossbedded.
Permian	Wolfcamp				Mudstone & sandstone. Massive to thick-bedded. Sandstone in part conglomeratic.
	Cisco				Red sandy shale with some sandstone & thin limestone beds.
Pennsylvanian	Canyon				Massive limestones with thick-bedded sandy shales & some sandstone.

Data Source: Bureau of Economic Geology, University of Texas at Austin

SOIL DEFINITIONS

MIXED ALLUVIAL SOILS:

Soils formed at various locations and transported to their present position by water.

VERTISOLS:

Clay soils that shrink and develop wide cracks during dry seasons followed by expansion or swelling on rewetting during moist seasons. This characteristic movement can break plant roots, pipes, building foundations, and complicate the design, construction, and maintenance of highways and streets. Vertisols have a high capacity for holding plant nutrients and water, but when moist they are slowly permeable to water and air. Commonly they are dark colored from the surface down to as much as 3 to 6 feet. They have gradually changing wavy boundaries between layers of little contrast except in organic matter content and associated changes in soil color. Micro-mounds and micro-depressions, called "gilgai" micro-relief develop on undisturbed surfaces.

MOLLISOLS:

Soils that are dark colored in the surface layer, soft, granular, and generally do not set hard when dry. They form under limited leaching in subhumid and semiarid regions. Parent materials are high in bases, especially calcium, in contact with decomposing organic matter in rather than on the soil.

ALFISOLS:

Soils usually light colored in the plow layer with deeper layers more clayey and higher in bases than the plow layer. These soils are moderately leached in the upper layers, but usually become more

basic with depth. Layers high in carbonates, or other salts may occur deep in the soil. Commonly the plow layers are thin and loamy over very clayey and slowly permeable subsoil, making many alfisols very drouthy for plants. Some alfisols are sources of trouble in construction.

ULTISOLS:

Light colored sandy and loamy acid soils of humid regions commonly with yellowish brown or mottled soil below the plow layer which is less clayey. These soils have a low base status accounted for by parent sediments low in bases and by leaching. The return of bases to the surface is largely limited to the cycle through tree vegetation. These soils are very deficient in plant nutrients. Its layers are well developed, highly contrasting in color and texture.

APPENDIX E

UNITED STATES GEOLOGICAL SURVEY

TIME-OF-TRAVEL

STUDIES

APPENDIX E

UNITED STATES GEOLOGICAL SURVEY TIME-OF-TRAVEL STUDIES

The United States Geological Survey, in cooperation with the United States Corps of Engineers and the Trinity River Authority of Texas, conducted time-of-travel studies in the Trinity River Basin in three different time periods. These periods are:

1. July 31 to August 14, 1972
2. September 19 to September 23, 1973
3. July 23 to August 1, 1974

In these studies, the time-of-travel of solutes was determined by injecting a flourescent dye at a known point upstream and measuring the time to maximum concentration downstream. The velocities obtained were utilized in Table 1 as one rationale for the selection of sampling sites.

TIME OF TRAVEL OF SOLUTES, FIELD OBSERVATIONS OF WATER QUALITY, AND SUSPENDED-SEDIMENT DATA FOR STREAM REACHES IN THE TRINITY RIVER BASIN, TEXAS, JULY 31 TO AUGUST 14,1972

The U.S. Geological Survey, in cooperation with the Corps of Engineers and the Trinity River Authority, conducted a time-of-travel study and collected water-quality data in the Trinity River Basin during the period July 31 to August 14, 1972. Studies were made on the reach of the West Fork Trinity River between Fort Worth and Dallas and on two reaches of the main stem, one from Dallas to the upper end of Livingston Reservoir and the other from below Livingston Dam to Liberty, a combined distance of 368.4 river miles.

The purpose of this study was to provide low-flow time-of-travel for solutes, water quality, and sediment data for the Corps of Engineers. Data collected will also be used by the Trinity River Authority as input in a water-quality model that is being developed for a comprehensive water-quality management plan for the Trinity River Basin.

Time-of-travel was determined by injecting a fluorescent dye (Rhodamine WT, 20-percent solution) as a tracer material into the stream and observing the downstream travel by fluorometric analysis at selected sampling sites. Measurements of the dispersion and concentration of dyes give insight to the behavior of contaminants that may be introduced to a stream. The methods and equipment used were similar to those described by Wilson (1968).

The data presented in table 1 summarize the results of the time-of-travel studies. Figure 1 shows the streambed profile and the average velocity of the dye cloud in the reaches studied.

The part of the river system studied was divided into seven reaches, and dye was injected upstream from the upstream end of each reach. table 1 shows the seven reaches and the sites where the dye cloud was measured as it traveled through the reach. The arrival times of the leading edge, the peak, and the trailing edges of the dye cloud were determined at each site

The end of the trailing edge was defined as that concentration value equal to 10 percent of the peak concentration.

Streamflow conditions for all except two reaches were relatively stable when the dye clouds were measured. The two exceptions were in reaches 1 and 7. The original dye injection for reach 1 was made on July 31, but channel construction downstream from the injection site resulted in streamflow of only 2 cfs (cubic feet per second). On August 7 a second dye injection for reach 1 was made further downstream below the channel construction. After the dye cloud had passed the first measuring site at Precinct Line Drive, it was caught by a release from Benbrook Lake before it arrived at the next measuring site at the Arlington sewage treatment plant. The resulting increased discharge in reach 1 (34 cfs to 326 cfs) made the time-of-travel determinations downstream from Precinct Line Drive to be in error.

The dye injection for reach 7 below Livingston Dam, was made on August 2. A discharge of 870 cfs was sustained for 26 hours after the dye injection and before reduction to approximately 400 cfs. The reduction in discharge explains the lower velocities in the subreach from F.M. 162 to U.S. 90.

Water-quality sampling was conducted at each site in conjunction with the time-of-travel studies. Water sampling and subsequent water-quality determinations were made by the U.S. Geological Survey and the Trinity River Authority. The results of these determinations are given in tables 2 and 3.

REFERENCE CITED

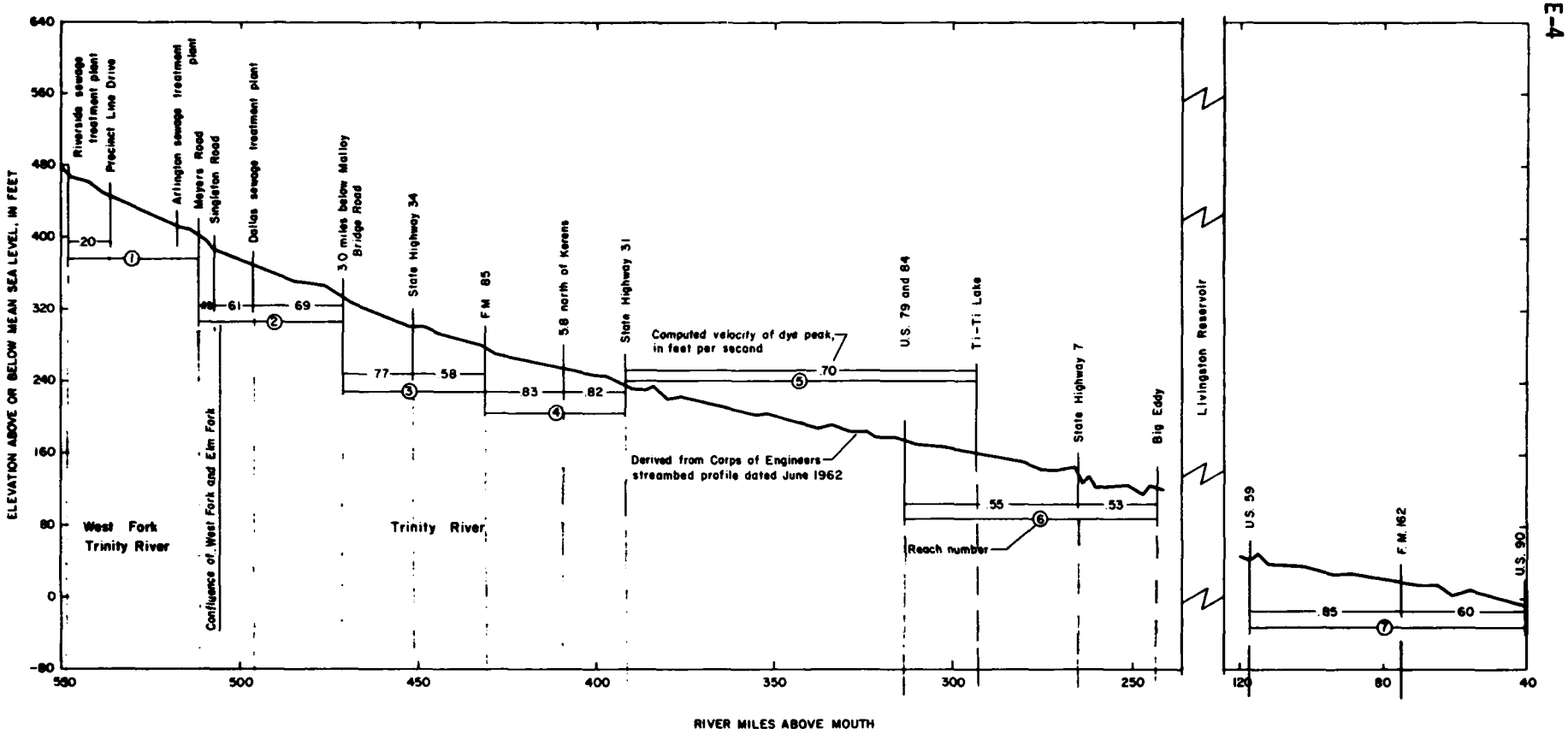
Wilson, J. F., Jr., 1968, Fluorometric procedures for dye tracers: U.S. Geol. Survey, Techniques of water resources investigation, book 3, ch. A12, 31 p.

TABLE 1.--SUMMARY OF DYE STUDIES, JULY 31 TO AUGUST 14, 1972

Reach			Subreach			Streamflow		Dye cloud						
								Leading edge		Peak		Trailing edge		
No. [a]	Description	Distance [b] (river miles)	From	To	Distance [b] (river miles)	Q (cfs)	Duration [c] (percent)	Travel time from previous site (hr)	Average velocity (fps)	Travel time from previous site (hr)	Average velocity (fps)	Travel time from previous site (hr)	Average velocity (fps)	Dye recovery (percent)
1	Riverside sewage treatment plant in Fort Worth to Meyers Rd. in Grand Prairie	34.9	Riverside sewage treatment plant	Precint Line Drive	11.4	[d] 30	99	70.39	0.24	84.20	0.20	99.14	0.17	68
			Precinct Line Drive	Arlington sewage treatment plant	18.5	[d] 85 [e]	99	--	--	--	--	--	--	--
			Arlington sewage treatment plant	Meyers Rd.	5.0	[f] 90	98	--	--	--	[e] .40 to .50			-
2	Meyers Rd. in Grand Prairie to 3 miles downstream from Malloy Bridge Rd. near Ferris	40.7	Meyers Rd.	Singleton Rd.	4.3	[d] 115	95	11.30	.56	12.77	.49	17.07	.36	80
			Singleton Rd.	Dallas sewage treatment plant	10.9	[d] 150	98	23.67	.68	26.33	.61	27.83	.58	66
			Dallas sewage treatment plant	Malloy Bridge Rd.	25.5	[d] 340	95	52.17	.72	54.17	.69	55.50	.68	65
3	3.0 miles downstream from Malloy Bridge Rd. near Ferris to F.M. 85 near Ennis	36.9	Malloy Bridge Rd.	State Hwy. 34	19.1	320	98	32.65	.86	36.67	.77	40.48	.69	91
			State Hwy. 34	F.M. 85	17.8	[d] 327	98	41.00	.64	45.00	.58	49.62	.53	83
4	F.M. 85 near Ennis to 0.9 mile downstream from State Hwy. 31 at Trinidad	40.3	F.M. 85	5.8 miles north of Kerens	22.1	[d] 332	98	32.90	.99	39.10	.83	46.22	.70	86
			5.8 miles north of Kerens	0.9 mile downstream from State Hwy. 31	18.2	336	98	31.33	.85	32.50	.82	33.18	.80	66
5	0.9 mile downstream from State Hwy. 31 at Trinidad to Ti-Ti Lake 19.8 miles downstream from U.S. 79 and U.S. 84 near Oakwood	96.7	None	None	96.7	[d] 392	98	186.62	.76	201.62	.70	214.10	.66	68
6	U.S. 79 and U.S. 84 near Oakwood to Big Eddy	67.3	U.S. 79 and U.S. 84	State Hwy. 7	47.3	425	97	112.50	.62	125.40	.55	137.97	.50	70
			State Hwy. 7	Big Eddy	20.0	[d] 425	97	49.25	.60	55.00	.53	61.83	.48	70
7	U.S. 59 near Goodrich to U.S. 90 at Liberty	71.4	U.S. 59	F.M. 162	41.4	[d] 520	--	62.92	.97	71.50	.85	84.67	.72	37
			F.M. 162	U.S. 90	30.0	[f] 450	--	61.42	.72	73.83	.60	75.00	.59	37

[a] Number of reach corresponds to the reaches number on figure 2.
[b] Data provided by the Trinity River Authority.
[c] Based on most recent 5 years of record available (1967-71) because of increasing effluents sustaining low flows.
[d] Using a nearby continuous gage-height record, the average flow at downstream site was computed for the period the dye cloud was in the subreach.
[e] Rise, caused by release, began about 1:00 p.m. on Aug. 13, 1972 (results not usable).
[f] Estimated.

FIGURE 1.-AVERAGE VELOCITY OF THE DYE CLOUD IN RELATION TO THE STREAMBED PROFILE



TIME OF TRAVEL OF SOLUTES, FIELD OBSERVATIONS OF WATER QUALITY, AND SUSPENDED-SEDIMENT DATA FOR STREAM REACHES IN THE TRINITY RIVER BASIN, TEXAS, JULY 31 TO AUGUST 14, 1972

By
Ralph H. Ollman

1973

TIME-OF-TRAVEL OF SOLUTES IN THE TRINITY RIVER BASIN, TEXAS SEPTEMBER 1973 AND JULY-AUGUST 1974

The U.S. Geological Survey, in cooperation with the U.S. Army Corps of Engineers and the Trinity River Authority of Texas, conducted time-of-travel studies in the Trinity River basin during a period of low flow September 19-23, 1973, and during a period of moderate flow July 23-August 1, 1974. The purpose of these two studies was to provide data that could be used by the Trinity River Authority as part of the basic input to a mathematical water-quality model of the river. The model is being developed as part of a comprehensive water-quality management plan for the basin.

The time-of-travel of solutes in the Trinity River and West Fork Trinity River was determined by injecting a fluorescent dye (Rhodamine WT, 20-percent solution) that could be detected by fluorometric analysis of water samples collected at selected downstream sites. Plots of observed dye concentration versus time were made for each injection and sampling site, and a smooth curve was drawn. The resulting curves were then used to determine arrival times of the leading edge, the peak, and the trailing edge of the dye cloud. The trailing edge was defined as the concentration value equal to 10 percent of the peak concentration.

Measurements of the concentration and dispersion of the dye provide information on the probable behavior of soluble contaminants that might be introduced in the reaches studied. The methods and equipment used in these studies were similar to those described by Wilson (1968).

The study in September 1973 was conducted on the West Fork Trinity River between Fort Worth and Dallas. The discharge during the study period has been equaled or exceeded about 75 percent of the time during the 11-year period (1963-73) at the gaging station West Fort Trinity River at Grand Praire. The river reach under study was divided into two subreaches to reduce the time required to complete the study. The data given in table 1 summarize the results of the study.

The study in July and August 1974 included parts of the West Fork Trinity and Trinity Rivers. This study reach was divided into five subreaches, and the dye injections were made in downstream order. The discharge during this period has been equaled or exceeded about 24 percent of the time in subreach 1, about 50 percent of the time in subreach 2, about 56 percent of the time in subreach 3, about 60 percent of the time in subreach 4, and about 66 percent of the time in subreach 5. These percentages apply to 11 years of records (1963-73) at gaging stations near the upper ends of the five subreaches.

The data given in table 2 summarize the results of the study.

The subdivision and injection pattern was designed to keep time requirements to a minimum and to allow the release-augmented flow to stabilize within a subreach before the dye injection was made. The augmentation of flow was accomplished by a constant release of water from Benbrook Lake, which is operated by the Corps of Engineers. The release of about 230 cubic feet per second (6.5 cubic metres per second) was designed to approximate the amount of sewage effluent that would be flowing from the Fort Worth metropolitan area in about 10 to 15 years.

Streamflow conditions were stable during both study periods. Small diurnal variations in flow were caused by the discharge of effluents from sewage-treatment plants located upstream from and within the reaches studied.

Previous time-of-travel data and water-quality data were obtained in the Trinity River basin during an extreme low-flow period in July 1972 (Oliman, 1973). These data were obtained for approximately the same river reaches used in the moderate-flow study of July-August 1974.

TABLE 1.-SUMMARY OF LOW-FLOW STUDY, SEPTEMBER 19-23, 1973

Reach No a/	Reach Description	Subreach From	Subreach To	Distance b/ (river miles)	Stream-flow (ft^3/s) c/	Dye cloud: Leading edge Travel time from upstream site (hours)	Leading edge Average velocity (ft/s)	Peak Travel time from upstream site (hours)	Peak Average velocity (ft/s)	Trailing edge Travel time from upstream site (hours)	Trailing edge Average velocity (ft/s)
1	Riverside sewage-treatment plant in Fort Worth to Precinct Line Drive	--	--	11.4	58	43.58	.18	51.22	.33	60.67	.28
2	Precinct Line Drive to Singleton Road	Precinct Line Drive	Arlington sewage-treatment plant	18.5	115	44.05	.59	52.88	.51	58.76	.46
		Arlington sewage-treatment plant	Meyers Road	5.0	119	10.33	.71	11.52	.61	12.20	.59
		Meyers Road	Singleton Road	4.3	160	8.83	.71	9.75	.65	12.62	.50

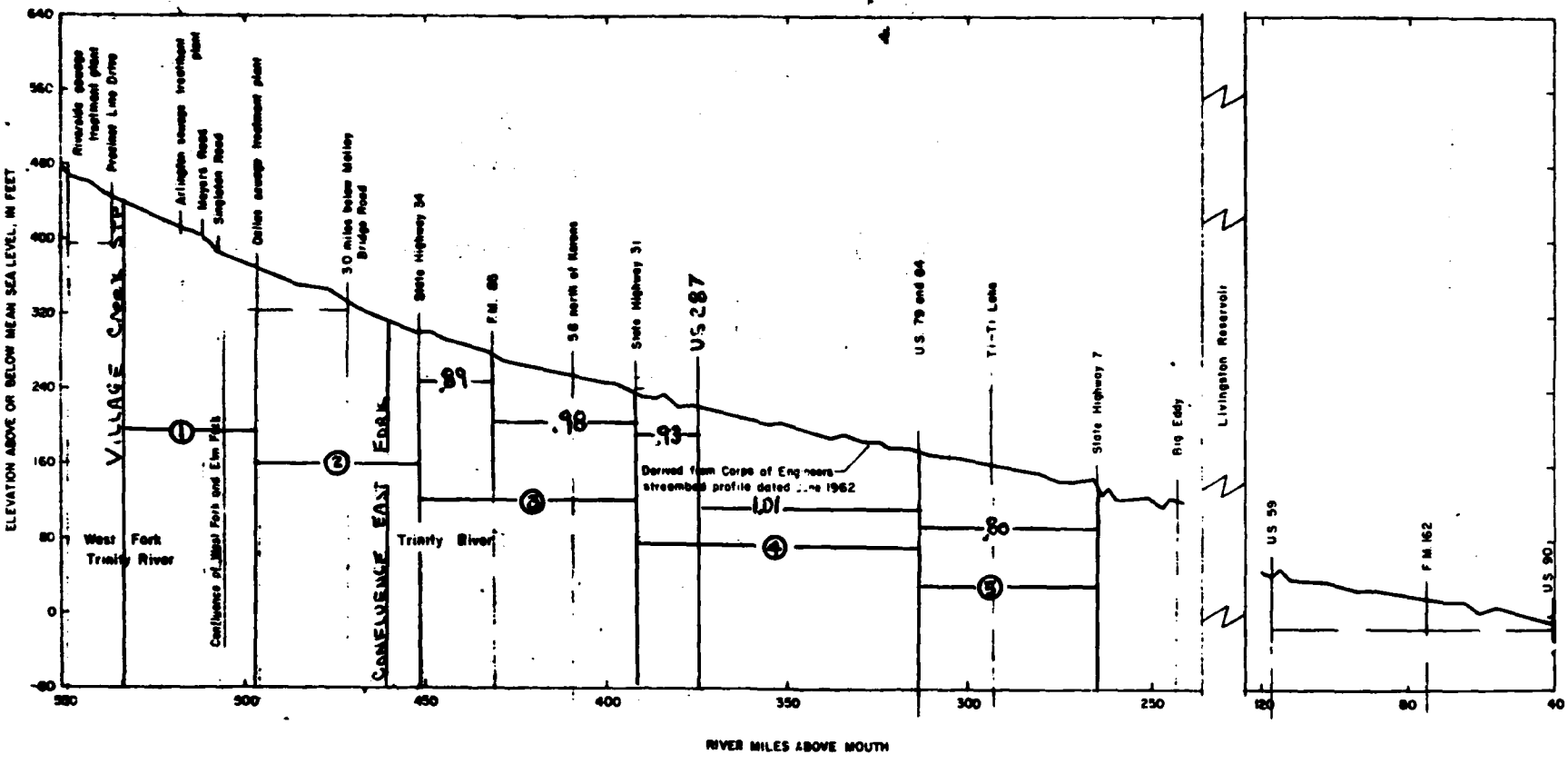
a/ Number of reach corresponds to the reach number on figure 1.
b/ Data provided by Trinity River Authority.
c/ The average flow at each site for the period the dye cloud was in the subreach was computed from instantaneous measurements and the record of a nearby continuous-record gaging station.

TABLE 2.-SUMMARY OF MODERATE-FLOW STUDY, JULY 23 TO AUGUST 1, 1974

Reach No a/	Reach Description	Subreach From	Subreach To	Distance (river miles) b/	Stream-flow (ft^3/s) c/	Dye cloud: Leading edge Travel time from upstream site (hours)	Leading edge Average velocity (ft/s)	Peak Travel time from upstream site (hours)	Peak Average velocity (ft/s)	Trailing edge Travel time from upstream site (hours)	Trailing edge Average velocity (ft/s)
1	Village Creek sewage-treatment plant near Fort Worth to Dallas sewage-treatment plant at Dallas	Village Creek sewage-treatment plant	Arlington sewage-treatment plant	15.6	340	18.88	1.21	21.35	1.07	23.98	.96
		Arlington sewage-treatment plant	Gifford-Hill Co. private bridge	7.7	345	8.25	1.37	8.83	1.28	9.50	1.19
		Gifford-Hill Co. private bridge	Commerce St. viaduct	8.4	390	10.25	1.20	10.92	1.13	11.42	1.08
		Commerce St. viaduct	Dallas sewage-treatment plant	4.1	400	5.00	1.21	5.25	1.15	5.58	1.08
2	Dallas sewage treatment plant at Dallas to S.H. 34 near Rosser	Dallas sewage-treatment plant	Dowdy-Ferry Road	13.4	580	12.32	1.60	13.52	1.46	15.02	1.31
		Dowdy-Ferry Road	So. Belt Line Road	5.0	581	8.02	.92	9.05	.81	10.25	.72
		So. Belt Line Road	Malloy Bridge Road	4.1	582	5.92	1.02	6.50	.93	7.00	.86
		Malloy Bridge Rd.	Confluence East Fork Trinity River	13.7	583	17.15	1.16	17.92	1.12	18.87	1.07
		Confluence East Fork Trinity River	S.H. 34 near Rosser	8.4	618	10.95	1.13	11.05	1.12	11.05	1.12
3	S.H. 34 near Rosser to 0.9 mile downstream from S.H. 31 at Trinidad	S.H. 34 near Rosser	F.M. 85	17.8	640	25.95	1.01	29.35	.89	34.17	.77
		F.M. 85 near Rosser	0.9 mile downstream from S.H. 31 at Trinidad	40.3	696	55.67	1.06	60.42	.98	64.42	.92
4	0.9 mile downstream from S.H. 31 at Trinidad to U.S. Hwy 79-84 near Oakwood	0.9 mile downstream from S.H. 31 at Trinidad	U.S. Hwy. 287	17.1	698	23.27	1.08	27.12	.93	31.28	.80
		U.S. 287	U.S. 79-84 near Oakwood	59.8	700	82.42	1.07	86.75	1.01	91.23	.96
5	U.S. 79-84 near Oakwood to S.H. 7 near Crockett	U.S. 79-84 near Oakwood	S.H. 7 near Crockett	47.2	800	79.58	.87	87.20	.80	97.72	.71

a/ Number of reach corresponds to the reach number on figure 2.
b/ Data provided by Trinity River Authority.
c/ The average flow at each site for the period the dye cloud was in the subreach was computed from instantaneous measurements and the record of a nearby continuous-record gaging station.

FIGURE 2.-AVERAGE VELOCITY OF THE DYE CLOUD IN RELATION TO THE STREAMBED PROFILE



JULY 23 TO AUGUST 1, 1974

APPENDIX F

UNITED STATES CORPS OF ENGINEERS

FORT WORTH DISTRICT

PROPOSED MULTIPURPOSE CHANNEL

LOCK AND DAM SITES

APPENDIX F

UNITED STATES CORPS OF ENGINEERS
FORT WORTH DISTRICT
PROPOSED MULTIPURPOSE CHANNEL
LOCK AND DAM SITES

This data was obtained from the Status Report of Environmental Evaluations, Appendix A (See Plates 28.1 through 28.10). Table F-1 summarizes the locks.

NOTE: Trinity River Authority river miles do not match Corps of Engineers river miles; therefore, mileage in all reports will be with respect to Corps of Engineers River Miles.

TABLE F-1: CORPS OF ENGINEER, FORT WORTH DISTRICT
PROPOSED MULTIPURPOSE CHANNEL LOCK & DAM SITES
FOR THE TRINITY RIVER

Proposed Multipurpose Channel Lock & Dam Sites	Corp. River Mile	Channel Mile
1 Wallisville L & D	4	28.3
3	63	60.5
4	97	75.8
5A	123	98.0
5B	128	99.2
6	200	147.9
7	268.5	197.5
9	309	216.4
10A	341	234.6
10B	342.5	235.9
12	422	280.5
13	444	292.6
16	466	306.6
17	480.5	317.8
18	499	331.3
19	510	342.65
20	525	352.1
21	536	360.0
Proposed Tennessee Colony Dam (Recommended Site No. 2A)	343	235.9

APPENDIX G

UNITED STATES GEOLOGICAL SURVEY

STREAM GAUGING PROGRAM

APPENDIX G

UNITED STATES GEOLOGICAL SURVEY

STREAM GAUGING PROGRAM

The United States Department of the Interior Geological Survey currently operates eleven streamflow gauging stations between Fort Worth, Texas and Liberty, Texas on the Trinity River. The USGS Station numbers and their locations are listed in Table G-1; and, in addition, the stage-discharge relation curves for each station have been obtained.

These rating curves will be utilized to obtain the flow rate in the respective section of the river when each sample is gathered.

INDEX OF SURFACE-WATER STATIONS IN TEXAS

OCTOBER 1972

The U.S. Geological Survey's investigations of the water resources of Texas are conducted in cooperation with the Texas Water Development Board, Texas Highway Department, river authorities, cities, U.S. Corps of Engineers, Bureau of Sport Fisheries and Wildlife, Environmental Protection Agency, U.S. Soil Conservation Service, and others.

Investigations are under the general direction of I. D. Yost, District Chief, Water Resources Division. The Texas District Office is located in the Federal Building, 300 East 8th Street, Austin, Texas 78701. Copies of basic data prior to publication and other unpublished records may be obtained upon request.

Information regarding provisional records of discharge prior to publication and other hydrologic data collected within their respective areas may also be obtained from any of the five subdistrict offices located in Fort Worth, Houston, San Angelo, San Antonio, and Wichita Falls. Requests for information from subdistrict offices should be directed to the following:

J. H. Montgomery, Subdistrict Chief
U.S. Geological Survey, WRD
Fort Worth Federal Center, Bldg. 23
Fort Worth, Texas 76104

R. E. Smith, Subdistrict Chief
U.S. Geological Survey, WRD
2320 LaBranch Street, Room 174
Houston, Texas 77004

E. S. Denison, Subdistrict Chief
U.S. Geological Survey, WRD
1409 Knickerbocker Road
San Angelo, Texas 76901

A. E. Hulme, Subdistrict Chief
U.S. Geological Survey, WRD
7077 San Pedro, Room 116
San Antonio, Texas 78216

J. O. Joerns, Subdistrict Chief
U.S. Geological Survey, WRD
318-320A Federal Building
Wichita Falls, Texas 76301

This index shows the station number and name, type of record collected, and the office at which the basic data are permanently filed. A permanent numerical designation for gaging stations has been adopted on a nationwide basis; stations are numbered and listed in downstream order. In this report, in a downstream direction along the main stem, all stations on a tributary entering above a main-stem station are listed before that station. A tributary entering between two main-stem stations is listed between them. A similar order is followed in listing stations on first rank, second rank, and other ranks of tributaries. To indicate the rank of any tributary on which a gaging station is situated and the stream to which it is an immediate tributary, each indention in the listing of gaging stations represents one rank. This downstream order and system of indention show which gaging stations are on tributaries between any two stations on a main stem and the rank of the tributary on which each gaging station is situated.

As of October 1, 1972, 487 streamflow, 75 reservoir-content, 14 stage, 110 low-flow partial-record, 185 crest-stage partial-record, 11 periodic water-quality, 3 miscellaneous, 27 tide-level, 111 chemical-quality, 25 continuous-recording water-quality, 87 periodic chemical-quality, 143 periodic organic-quality, 105 pesticides, 10 sediment, 37 periodic sediment, 32 periodic biological, and 55 reservoir-inventory stations were in operation (plate 1).

At each STREAMFLOW STATION, a permanent gage is maintained from which a daily record of stage is obtained. Actual measurements of discharge are made to develop stage-discharge relation curves. Discharge records, showing the mean daily discharge in cubic feet per second, peak discharges for the major floods of each year, and total monthly and yearly runoff expressed in acre-feet, are computed from basic hydrologic data on the basis of the water year ending September 30.

At each RESERVOIR-CONTENT STATION, a daily record of stage is obtained.

PARTIAL-RECORD STATION. Because the number of streams for which information is desired far exceeds the number of stations feasible to operate at one time, the Geological Survey collects limited streamflow data at sites other than streamflow stations. When limited streamflow data are collected on a systematic basis over a period of years for use in hydrologic analyses, the site at which the data are collected is called a PARTIAL-RECORD STATION. There are two kinds of partial-record stations: (1) Those operated for the purpose of defining annual minimum discharges, low-flow partial-record stations; and (2) those operated for the purpose of defining annual maximum discharges, crest-stage partial-record stations.

At each CHEMICAL-QUALITY STATION, samples are collected for chemical analyses. At most stations, daily samples are collected and the temperature is measured. At daily stations where discharge records are available, discharge-weighted average concentrations of the chemical constituents are computed for each water year.

At PERIODIC BIOLOGICAL STATIONS, densities (colonies per 100 milliliters) of coliforms, fecal coliforms, and fecal streptococci are determined from 6 to 12 times per year.

At each PERIODIC CHEMICAL-QUALITY STATION, a sample for chemical analysis is collected at about 1-month intervals. An attempt is made to collect samples over as wide a range in discharge as possible. Periodic chemical-quality stations are operated in conjunction with a streamflow station or a partial-record station.

At PERIODIC ORGANIC-QUALITY STATIONS, from 6 to 12 samples per year are collected for analyses. The analysis includes biochemical oxygen demand (BOD), dissolved oxygen (DO), pH, and nitrogen and phosphorus species. At each of these stations, samples are also collected for chemical analyses.

At PESTICIDE STATIONS, samples are collected from 4 to 12 times per year for analyses. Bottom deposit samples are collected at selected stations for pesticide analyses 4 times a year.

SEDIMENT STATIONS are maintained to determine the quantity of sediment transported by streams. Samples are collected on a daily, weekly, or periodic schedule for determinations of suspended load, particle-size distribution of suspended load and bed material, or unmeasured sediment discharge.

In addition to streamflow information collected at the regular gaging stations and the partial-record stations, measurements of flow and water-quality data have been collected for specific purposes at various other locations in the State. Many of these measurements show the peak discharge for the greatest flood that has been known to occur at that site. Others show minimum flows or channel losses experienced in various streams.

Water-Supply Papers and other reports containing special detailed information on flood discharges, rainfall intensities, hydrology of small watersheds, and other related data have been prepared by the Geological Survey. In addition to published reports, records not yet published and file copies of special reports on floods and other investigations are available for examination in the District and Subdistrict offices of the Geological Survey in Texas.

UNITED STATES GEOLOGICAL SURVEY

Stream Gauging Stations on Trinity River

Trinity River Reach a: -- Beach Street Bridge in Fort Worth downstream to the confluence of the East Fork

USGS Station	Location
8048000	Located in Fort Worth, Texas at latitude 32°45', longitude 97°19' on the left bank 980 feet downstream from North Main viaduct.
8049500	Located in Grand Prairie, Texas at latitude 32°45', longitude 96°59' on the left bank on the upstream side of bridge on Belt Line Road.
8057000	Located in Dallas, Texas at latitude 32°46', longitude 96°49' on the left bank on downstream side of left pier of Commerce Street viaduct.
8057410	Located in South Dallas, Texas at latitude 32°42', longitude 96°44' on the left bank at downstream side of bridge on South Loop 12.

Trinity River Reach b: -- East Fork Confluence downstream to SH 31

8062500	Located southwest of Rosser, Texas at latitude 32°25', longitude 96°27' on left bank at downstream side of left pier on bridge on State Highway 34.
80627	Located west of Trinidad, Texas at latitude 32°08', longitude 96°06' on left bank at pumping station of Texas Power and Light 0.9 miles downstream of bridge on State Highway 31.

Trinity River Reach c: -- From Highway 31 downstream to the headwaters of Livingston Reservoir

8065000	Located northeast of Oakwood, Texas at latitude 31°38',

longitude 95°47' on left bank on downstream side of bridge on U.S. 79 and U.S. 84.

8065350 Located west of Crockett, Texas at latitude 31°20', longitude 95°39' on right bank 30 feet downstream from bridge on State Highway 7.

Trinity River Reach d: -- From the dam on Livingston Reservoir downstream to River Mile 0.0

8066250 Located south of Goodrich, Texas at latitude 30°34', longitude 94°56' on the left bank 40 feet downstream from the downstream side of bridge on U.S. 59.

8066500 Located near Romayor, Texas at latitude 30°25', longitude 94°51' near the right bank on downstream side of pier on S.H. 105.

8067000 Located west of Liberty, Texas at latitude 30°03', longitude 94°49' near center of the channel at upstream side of upstream bridge on U.S. 90.

APPENDIX H

CLIMATOLOGICAL STATIONS

APPENDIX H

CLIMATOLOGICAL DATA

At the time of sampling, meteorological conditions will be noted. These conditions include:

1) Time of day
2) Sky cover
3) Precipitation conditions on the day of sampling and during the past six days
4) Air and water temperatures

Precipitation records pertaining to that portion of the Trinity River Basin associated with the particular sampling site will be obtained by contacting the recording stations as listed in Climatological Data* (See Table H-1).

*"Climatological Data of Texas", Department of Commerce, Environmental Data Service, January 1976.

TABLE H-1

CLIMATOLOGICAL STATIONS & OBSERVERS BY COUNTY

County	Station	Observer
Henderson	1. Athens 3 SSE 2. Mabank 4 SW 3. Trinidad Power Plant	Dr. Dwight A. Jones City of Mabank Texas Power & Light Co.
Freestone	1. Long Lake 5 SW	Noyl Anders
Anderson	1. Palestine	Mrs. Jimmie Dale Trezise
Leon	1. Buffalo 2. Centerville 3. Jewell	Henry M. Harris Royce Wilson Mrs. Elna E. Leazar
Houston	1. Crockett 2. Lovelady	James H. Gibbs Lester Jones
Madison	1. Madisonville	Ross Madole
Trinity	1. Groveton	T. P. Walton, Jr.
Walker		
Liberty	1. Cleveland 2. Liberty	Chester V. Ellisor Mrs. Vera E. Garner
Chambers	1. Anahuac TBCD	Anahuac TBCD
San Jacinto	1. Coldspring 5 SSW	Leroy S. Dibney
Tarrant	1. Arlington 2. Benbrook Dam 3. Dal-FtW Reg. WSMO AP 4. Ft. Worth, Meacham WSO AP 5. Ft. Worth Fed'l. Bldg. 6. Grapevine Dam 7. Kennedale 6 SSW	Charles I. Hawkes Pro Eng. Benbrook Proj. Weather Service Met. Obs'y. National Weather Service National Weather Service US Corps of Engineers Mark M. Malone
Dallas	1. Carrollton 2 N 2. Dallas FAA AP 3. Richardson	Mrs. Betty L. Sumner FAA Flight Service Station City of Richardson

continued

TABLE H-1 (Continued

County	Station	Observer
Ellis	1. Avalon	Herschel H. Smith
	2. Barowell Dam	Corps of Engineers
	3. Ennis	S. L. Brunson
	4. Midlothian 2	Inactive 1/1/75
	5. Red Oak	William H. Brown
	6. Waxahachie	Waxahachie Fire Dept.
Kaufman	1. Crandall	Mrs. Vallie Sue Sorrells
	2. Kaufman 3 SE	Mrs. Frankle M. Fair
	3. Rosser	Mrs. Opal L. Taliaferro
	4. Terrell	Finis G. Eppler
Navarro	1. Corsicana	Radio Station KAND
	2. Frost	Cotheo I.Thompson
	3. Navarro Mills Dam	US Corps of Engineers

APPENDIX I

FIELD SAMPLING, ELUTRIATION, AND SEDIMENT ANALYSIS EQUIPMENT

APPENDIX I

FIELD SAMPLING, ELUTRIATION, AND SEDIMENT ANALYSIS EQUIPMENT

The following equipment or equivalent will be used during field samplings, elutriation and sediment analysis:

Standard Wildco-Eckman Dredge

Chamber Dimensions 9" x 9"

Empty Weight, 15 lbs.

Page 9A Wildco Catalog 74A

Ponar Grab Dredge

Chamber Dimensions 9" x 9"

Empty weight, 15 lbs.

Page 11 Wildco Catalog 74A

Alpha Style - Vertical PVC Bottle with Semi-Rigid Ends

Volume 4.3 l

OD $4\frac{1}{2}$"

Length 23-3/4"

End Seal, Neoprene

Empty Weight, 10 lbs.

Sample Storage Bottles

Wide mouth glass jars, one gallon capacity with Teflon liner, screw-top lid

Possible source Cincinnati Container Corporation, Cincinnati, Ohio

Teflon Sheet

0.02 mich thick

Possible source, Cadillac Plastic, Cincinnati, Ohio

Boat

Aluminum fishing boat 12 to 16 feet; light weight, $7\frac{1}{2}$ hp motor, removable; speed 10 mph

Ph, Eh Measurement

Direct reading, portable, battery operated expanded scale, unit for field measurement. (Sargent-Welch, Model PBX, page 497, Catalog 124.)

DO Meter

Oxygen, polaragraphic cell, Portable YSI Model 54

Current Meter

1. Teledyne-Gurley Price, for deep water
2. Pigmy Price, for shallow water

Velocity determination from rating tables for each instrument. Teledyne-Gurley meter with a magnetic on-off switch activated at every ten revolutions of the current meter wheel. The Pigmy current meter with direct flow on-off switch for every ten revolutions.

Photographic Equipment

1. 35 mm slide and camera
2. 8 mm movie camera

Membrane Filter Assembly

1. 0.45 micron membrane filter
2. Suction apparatus
3. Container and holder

Centrifuge

Large, International Equipment Co.; Model CS

Centrifuge, cont'd.

1. Timer, brake, adjustable speed

2. Top speed = 3200 RPM

Shaka

1. 1/3 hp electric motor, Dayton Electric Manufacturing Co., 1725 rpm. Type KS

   18" x 10" x $7\frac{1}{2}$ box, adjustable seat, 120 excursions per minute

APPENDIX J

LABORATORY PROCEDURES FOR ANALYSIS OF WATER, STANDARD ELUTRIATE AND BOTTOM SEDIMENTS

TABLE OF CONTENTS

APPENDIX J

LABORATORY PROCEDURES FOR ANALYSIS OF WATER, STANDARD ELUTRIATE AND BOTTOM SEDIMENTS

Residue in Water and Standard Elutriate*

Scope and Application

STORET No. 70300

This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

The practical range of the determination is 10 mg/l to 20,000 mg/l.

Summary of Method

A well-mixed sample is filtered through a standard glass fiber filter. The filtrate is evaporated and dried to constant weight at 103°C.

Definitions

Filterable solids are defined as those solids capable of passing through a standard glass fiber filter (0.45 membrane filter) and dried to constant weight at 103°C.

Sample Handling and Preservation

Preservation of the sample is not practical; analysis should begin as soon as possible.

Interferences

Highly mineralized waters containing significant concentrations of calcium, magnesium, chloride and/or sulfate may be hygroscopic and will require prolonged drying, desiccation and rapid weighing.

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* Adapted from "Manual of Methods for Chemical Analysis of Water and Wastes", EPA-625-/6-74-003, 1974; page 266, with modification.

Samples containing high concentrations of bicarbonate will require careful and possibly prolonged drying at 103°C to insure that all the bicarbonate is converted to carbonate.

Too much residue in the evaporating dish will crust over and entrap water that will not be driven off during drying. Total residue should be limited to about 200 mg.

Apparatus

(See elutriation section for membrane filter assembly)

Evaporating dishes, porcelain, 100 ml volume. (Vycor or platinum dishes may be substituted).

Steambath

Drying oven, 103°C ± 2°C.

Desiccator

Analytical balance, 200 g capacity, capable weighing to 0.1 mg.

Procedure

Transfer 100 ml (or a larger volume) of the filtrate to a weighed evaporating dish and evaporate to dryness on a steam bath.

Dry the evaporate sample for at least one hour at 103°C. Cool in a desiccator and weigh. Repeat the drying cycle until a constant weight is obtained or until weight loss is less than 0.5 mg.

Calculation

Calculate filterable residue as follows:

$$\text{Filt. residue, mg/l} = \frac{(A-B) \times 1000}{C}$$

where:

A = weight of dried residue + dish
B = weight of dish
C = volume of filtrate used

Volatile Solids in Water and Elutriate*

STORET No. 00505

Scope and Application

This method determines the weight of solid material combustible at 550°C.

The test is useful in obtaining a rough approximation of the amount of organic matter present in the solid fraction of sewage, activated sludge, industrial wastes, or bottom sediments.

Summary of Method

The residue obtained from the determination of total filterable residue is ignited at 550°C in a muffle furnace. The loss of weight on ignition is reported as mg/l volatile residue.

Comments

The test is subject to many errors due to loss of water of crystallization, loss of volatile organic matter prior to combustion, incomplete oxidation of certain complex organics, and decomposition of mineral salts during combustion.

The results should not be considered an accurate measure of organic carbon in the sample, but may be useful in the control of plant operations.

The principal source of error in the determination is failure to obtain a representative sample.

Sample Handling and Preservation

Preservation of sample is not practical; analysis should begin as soon as possible.

---

*Adapted from "Manual of Methods for Chemical Analysis of Water and Wastes", EPA-625-/6-74-003, 1974, page 272.

Solids - Total and Volatile in Bottom Sediments*

General Discussion

Principle: The sample is dried in a weighed dish in an oven at 103-105°C to constant weight. The increase in weight over that of the empty dish represents the total solids.

The volatile solids are determined by placing the oven-dried sample from above in the muffle furnace for one hour at 600°C. The decrease in weight of residue after ashing represents the volatile solids.

Minimum detectable concentration: Dependent on the sensitivity of the analytical balance used for weighing.

Apparatus

Drying oven

Muffle Furnace

Porcelain Crucibles

Porcelain Evaporating Dishes

Analytical Balance

Procedure

Wash dishes and number with heat-resistant marking pencil.

Place evaporating dishes in a muffle furnace at a temperature of 600-650°C for one hour.

Remove evaporating dishes from the furnace and allow them to cool for

*Adapted from "Chemistry Laboratory Manual, Bottom Sediments," compiled by Great Lake Region, Committee on Analytical Method, 1969; page 85.

for 1-2 minutes in air, but not more than 3-4 minutes. Then place them in a dessicator for 1 hour.

Weigh and record this weight as the tare weight.

Weigh 10 grams of bottom sediment to the nearest 0.01 grams in the tared evaporating dishes.

Place the sample in the oven at 103-105°C overnight.

Remove samples from the oven and place then in a dessicator for 1 hour.

Weigh and record this weight as the oven-dry weight.

Place the oven dried sample in the muffle furnace at 600°C for 1 hour.

Remove samples from the furnace and allow them to cool for 1-2 minutes in air, but not more than 3-4 minutes. Afterwards, place them in a dessicator for 1 hour.

Weigh and record this weight as the furnace weight.

Calculation

$$\frac{\text{Oven dry weight}}{\text{Init. wt. of sample}} \times 100 = \% \text{ total solids}$$

$$\frac{(\text{Oven dry weight} - \text{furnace weight})}{\text{Oven dry weight}} \times 100 = \% \text{ volatile solids}$$

Nitrogen, Ammonia - Water and Elutriate*

STORET No. 00610

1. Scope and Application

1.1 This distillation method covers the determination of ammonia-nitrogen exclusive of total Kjeldahl nitrogen, in drinking, surface, and saline waters, domestic and industrial wastes. It is the method of choice where economics and sample load do not warrant the use of automated equipment.

1.2 The method covers the range from about 0.05 to 1.0 mg/l NH_3-N/l for the colorimetric procedures, from 1.0 to 25 mg/l for the titrimetric procedure.

1.3 This method is described for macro glassware.

2. Summary of Method

2.1 The sample is buffered at a pH of 9.5 with a borate buffer in order to decrease hydrolysis of cyanates and organic nitrogen compounds, and is then distilled into a solution of boric acid. The ammonia in the distillate can be determined colorimetrically by nesslerization. For higher concentrations, nesslerization can be done by dilution of samples with distilled water. For very high concentration, titrimetric procedure can, however, be adopted.

3. Sample Handling and Preservation

3.1 Samples may be preserved with 2 ml of concentrated H_2SO_4 or 40 mg. $HgCl_2$ per liter and stored at 4°C.

*Adapted from "Manual of Methods for Chemical Analysis of Water and Wastes", EPA-625-/6-74-003, 1974; page 159, with modification.

4. Interferences

4.1 A number of aromatic and aliphatic amines, as well as other compounds both organic and inorganic, will cause turbidity upon the addition of Nessler reagent, so direct nesslerization (i.e., without distillation), has been discarded as an official method.

4.2 Cyanate, which may be encountered in certain industrial effluents, will hydrolyze to some extent even at the pH of 9.5 at which distillation is carried out. Volatile alkaline compounds, such as certain ketones, aldehydes, and alcohols, may cause an off-color upon nesslerization method. Some of these, such as formaldehyde, may be eliminated by boilding off at a low pH (approximately 2 to3) prior to distillation and nesslerization.

4.3 If the sample has been preserved with a mercury salt, the mercury ion must be complexed with sodium thiosulfate (0.2 g) prior to distillation.

5. Apparatus

5.1 An all-glass distilling apparatus with an 800-1000 ml flask.

5.2 Spectrophotometer or filter photometer for use at 425 nm and providing a light path of 1 cm or more.

5.3 Erlenmeyer flasks: The distillate is collected in 500 ml glass-stoppered flasks. These flasks should be marked at the 350 and the 500 ml volumes. With such marking, it is not necessary to transfer the distillate to volumetric flasks.

6. Reagents (prepared as in reference.)

6.1 Distilled water should be free of ammonia.

6.2 Ammonium chloride, stock solution.

6.3 Ammonium chloride, standard solution.

6.4 Boric acid solution (20g/l).

6.5 Mixed Indicator: Mix 2 volumes of 0.2% methyl red in 95% ethyl alcohol with 1 volume of 0.2% methylene blue in 95% ethyl alcohol. This solution should be prepared fresh every 30 days.

NOTE: Specially denatured ethyl alcohol conforming to Formula 3A or 30 of the US Bureau of Internal Revenue may be substituted for 95% ethanol.

6.6 Nessler reagent.

6.7 Borate buffer.

6.8 Sulfuric acid, standard solution.

6.9 Sodium hydroxide.

6.10 Dechlorinating reagents.

7. Procedure

7.1 Preparation of equipment: Add 500 ml of distilled water to an 800 ml Kjeldahl flask. The addition of boiling chips which have been previously treated with dilute NaOH will prevent bumping. Steam out the distillation apparatus until the distillate shows no trace of ammonia with Nessler reagents.

7.2 Sample preparation: Remove the residual chlorine in the sample by adding dechlorinating agent equivalent to the chlorine residual. To 400 ml of sample add 1 N NaOH, (6.9), until the pH is 9.5, checking the pH during addition with a pH meter or by use of a short range pH paper.

7.3 Distillation: Transfer the sample, the pH of which has been adjusted to 9.5, to an 800 ml Kjeldahl flask and add 25 ml of the borate buffer (6.7).

Distill 300 ml at the rate of 6-10 ml/min. into 50 ml of 2% boric acid (6.4) contained in a 500 ml Erlenmeyer flask.

NOTE: The condenser tip or an extention of the condenser tip must extend below the level of the boric acid solution.

Dilute the distillate to 500 ml with distilled water and nesslerize an aliquot to obtain an approximate value of the ammonia-nitrogen concentration. For concentration of above 1 mg/l to 2 mg/l nesslerization can be accomplished by diluting the distillate. For concentrations higher than 2 mg/l, ammonia should be determined titrimetrically.

7.4 Determination of ammonia in distillate: Determine the ammonia content of the distillate titrimetrically, colorimetrically, as described below.

7.4.1 Titrimetric determination: Add 3 drops of the mixed indicator to the distillate and titrate the ammonia with the 0.02 N H_2SO_4, matching the end point against a blank containing the same volume of distilled water and H_3BO_3 solution.

7.4.2 Determine the ammonia in the distillate by nesslerizing 50 ml or an aliquot diluted to 50 ml and reading the optical density at 425 nm against the blank. Ammonia-nitrogen content is read from the standard curve.

8. Calculations

8.1 Titrimetric

$$\text{mg/l } NH_3 - N = \frac{A \times 0.28 \times 1000}{S}$$

where:

A = ml 0.02 N H_2SO_4 used.

S = ml sample

8.2 Spectrophotometric

$$mg/l\ NH_3 - N = \frac{A \times 1000}{D} \times \frac{B}{C}$$

where:

A = mf NH_3 - N read from standard curve.

B = ml total distillate collected, including boric acid and dilution.

C = ml distillate taken for nesslerization.

D = ml of original sample taken.

Nitrogen, Kjeldahl, Total*

STORET No. 00625

1. Scope and Application

1.1 This method covers the determination of total Kjeldahl nitrogen in drinking, surface, and saline waters, domestic and industrial wastes. The procedure converts nitrogen components of biological origin such as amino acids, proteins and peptides to ammonia, but may not convert the nitrogenous compounds of some industrial wastes such as amines, nitro compounds, hydrazones, oximes, semi-carbazones and some refractory tertiary amines.

1.2 Two alternatives are listed for the determination of ammonia after distillation: the titrimetric method which is applicable to concentrations above 2 mg N/liter; the Nesslerization method which is applicable to concentrations below 2 mg N/liter (for concentrations above 1 mg/l to 2 mg/l, Nesslerization is accomplished by diluting the distillate two times).

1.3 This method is described for macro glassware systems.

2. Definitions

2.1 Total Kjeldahl nitrogen is defined as the sum of free-ammonia and organic nitrogen compounds which are converted to ammonium sulfate $(NH_4)_2SO_4$, under the conditions of digestion described below.

2.2 Organic Kjeldahl nitrogen is defined as the difference obtained by subtracting the free-ammonia value from the total Kjeldahl nitrogen

*Adapted from "Manual of Methods for Chemical Analysis of Water and Wastes", EPA-625-/6-74-003, 1974, page 175, with modification.

value. This may be determined directly by removal of ammonia before digestion.

3. Summary of Method

3.1 The sample is heated in the presence of concentrated sulfuric acid, K_2SO_4 and $HgSO_4$ and evaporated until SO_3 fumes are obtained and the solution becomes colorless or pale yellow. The residue is cooled, diluted, and is treated and made alkaline with a hydroxide-thiosulfate solution. The ammonia is distilled and determined after distillation by Nesslerization or titrimetry.

4. Sample Handling and Preservation

4.1 Samples may be preserved by addition of 2 ml of concentrated H_2SO_4 or 40 mg $HgCl_2$ per liter and stored at 4°C. Even when preserved in this manner, conversion of organic nitrogen to ammonia may occur. preserved samples should be analyzed as soon as possible.

5. Apparatus

5.1 Digestion apparatus: A Kjeldahl digestion apparatus with 800 ml flasks and suction takeoff to remove SO_3 fumes and water.

5.2 Distillation apparatus: The macroKjeldahl flask is connected to a condenser and an adaptor so that the distillate can be collected.

5.3 Spectrophotometer for use at 400 to 425 nm with a light path of 1 cm or longer.

6. Reagents

6.1 Distilled water should be free of ammonia.

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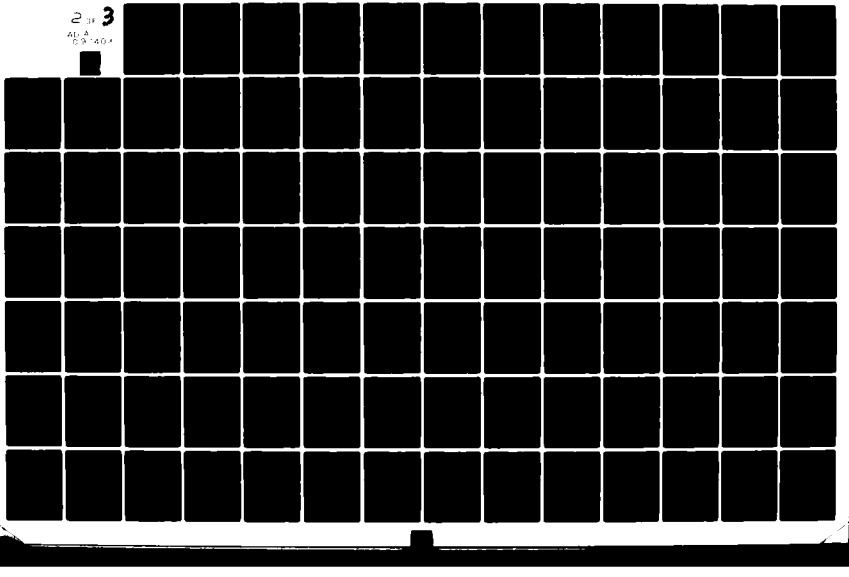

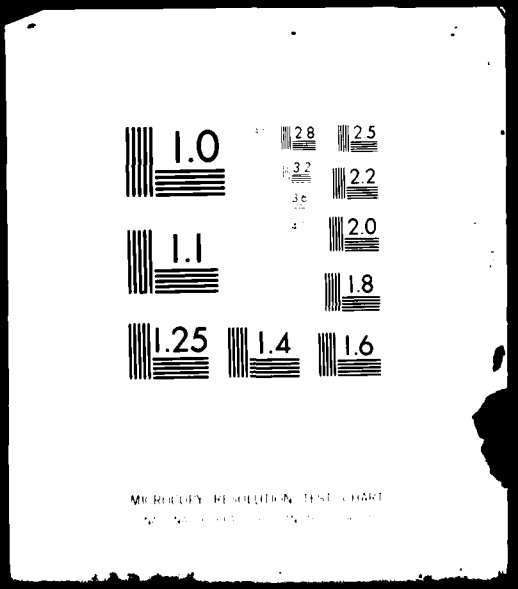

6.2 Mercuric sulfate solution.

6.3 Sulfuric acid-mercuric sulfate-potassium sulfate solution.

6.4 Sodium hydroxide-sodium thiosulfate solution.

6.5 Phenolphthalein indicator solution.

6.6 Mixed indicator.

6.7 Boric acid solution.

6.8 Sulfuric acid, standard solution.

6.9 Ammonium chloride, stock solution.

6.10 Ammonium chloride, standard solution.

6.11 Nessler reagent.

7. Procedure

7.1 The distillation apparatus should be pre-steamed before use by distilling a 1:1 mixture of distilled water and sodium hydroxide-sodium thiosulfate solution (6.4) until the distillate is ammonia-free. This operation should be repeated each time the apparatus is out of service long enough to accumulate ammonia (usually 4 hours or more).

7.2 Macro Kjeldahl system

7.2.1 Place a measured sample into an 800 ml Kjeldahl flask. The sample size can be determined from the following table:

Kjeldahl Nitrogen in Sample, mg/l	Sample Size ml
0 - 5	500
5 - 10	250
10 - 20	100
20 - 50	50.0
50 - 500	25.0

Dilute the sample, if required, to 500 ml with distilled water, and add 100 ml sulfuric acid-mercuric sulfate-potassium sulfate solution (6.3) and evaporate the mixture in the Kjeldahl apparatus until SO_3 fumes are given off and the solution turns colorless or pale yellow. Continue heating for 30 additional minutes. Cool the residue and add 300 ml distilled water.

7.2.2 Make the digestate alkaline by careful addition of 100 ml of sodium hydroxide-thiosulfate solution (6.4) without mixing.

NOTE: Slow addition of the heavy caustic solution down the tilted neck of the digestion flask will cause heavier solution to underlay the aqueous sulfuric acid solution without loss of free-ammonia. Do not mix until the digestion flask has been connected to the distillation apparatus.

7.2.3 Connect the Kjeldahl flask to the condenser with the tip of condenser (or an extension of the condenser tip) below the level of the boric acid solution (6.7) in the receiving flask.

7.2.4 Distill 300 ml at the rate of 6-10 ml/min., into 50 ml of 2% boric acid (6.7) contained in a 500 ml Erlenmeyer flask.

7.2.5 Dilute the distillate to 500 ml in the flask. These flasks should be marked at the 350 and the 500 ml volumes. With such marking, it is not necessary to transfer the distillate to volumetric flasks. For concentrations above 2 mg/l.,

the ammonia can be determined titrimetrically. For concentrations below this value, it is determined colorimetrically by nesslerization (Dilute the distillate two times with ammonia free distilled water, for samples of concentration 1 to 2 mg/l.).

7.3 Determination of ammonia in distillate: Determine the ammonia content of the distillate titrimetrically, colorimetrically, as described below.

7.3.1 Titrimetric determination: Add 3 drops of the mixed indicator (6.6) to the distillate and titrate the ammonia with the 0.02 N H_2SO_4, (6.8), matching the endpoint against a blank containing the same volume of distilled water and H_3BO_3 (6.7) solution.

7.3.2 Nesslerization: Determine the ammonia in the distillate by nesslerizing 50 ml or an aliquot diluted to 50 ml and reading the optical density at 425 nm against the blank. Ammonia content is read from the standard curve.

8. Calculation

8.1 If the titrimetric procedure is used calculate Total Kjeldahl Nitrogen, in mg/l, in the original sample as follows:

$$\text{Total Kjeldahl nitrogen, mg/l} = \frac{(A-B)N \times F \times 1000}{S}$$

where:

A = Milliliters of standard 0.020 N H_2SO_4 solution used in titrating sample.

B = milliliters of standard 0.020 N H_2SO_4 solution used in titrating blank.

N = normality of sulfuric acid solution.

F = milliequivalent weight of nitrogen (14 mg).

S = milliliters of sample digested.

If the sulfuric acid is exactly 0.02 N the formula is shortened to:

$$\text{TKN, mg/l} = \frac{(A-B) \times 280}{S}$$

8.2 If the Nessler procedure is used, calculate the Total Kjeldahl Nitrogen, in mg/l, in the original sample as follows:

$$\text{TKN, ml/g} = \frac{A \times 1000}{\text{ml sample}} \times \frac{B}{C}$$

where:

A = mg NH_3-N read from curve.

B = ml total distillate collected including the H_3BO_3.

C = ml distillate taken for Nesslerization.

8.3 Calculate Organic Kjeldahl Nitrogen in mg/l, as follows:

Organic Kjeldahl Nitrogen = TKN - (NH_3 - N.)

Nitrogen, Ammonia, in Bottom Sediments - Distillation*

1. General Discussion

1.1 Principle: Free ammonia nitrogen can be recovered by distillation of a sample at pH 7.4. Since natural waters exhibit varying pH values and buffering properties, a phosphate buffer is applied to maintain the required pH during the distillation process. The free ammonia distillate is collected in boric or sulfuric acid solutions to minimize ammonia losses.

Samples containing high ammonia concentrations (5-10 mg/l) should be analyzed following the procedure described in "Standard Methods for Examination of Water and Wastewater", 12th Ed., 1965, Method A, page 191, Sec. 4.4.

The concentration of ammonia in the distillate determines the final method for measurement.

If the sample contains from 0.01 to 0.2 mg/l ammonia nitrogen, the distillate from 500 ml of sample is collected in 0.02N H_2SO_4. The acid solution is concentrated on a steam bath to 50 ml producing a 10:1 concentration. The ammonia in the concentrated solution is then reacted with Nessler's reagent to form a characteristic yellow-brown color which is measured at a wave length of 425mμ.

Samples which contain from 0.2 to 1.0 mg/l are distilled into dilute boric acid solution. The acid distillates are diluted to the

*Adapted from "Chemistry Laboratory Manual, Bottom Sediments", Compiled by Great Lakes Region Committee on Analytical Methods, EPA, Dec. 1969.

original 500 ml volume and a 50 ml aliquot is taken for Nesslerization as outlined above.

Samples that contain more than 1.0 mg/l ammonia nitrogen are distilled into boric acid and can then be titrated with standard sulfuric acid using an appropriate indicator.

1.2 Interference: Ammonia recovery will be low on water samples containing more than 250 mg/l calcium unless the treatment prescribed in Sec. 4.2 is followed. The calcium and the phosphate buffer react to precipitate calcium phosphate, releasing hydrogen ions and lowering the pH. A number of aliphatic and aromatic amines, organic chloramines, acetone, aldehydes, and alcohols, and other undefined organic compounds, cause trouble in direct nesslerization. Compounds of this type have been found to yeild a yellowish or greenish off color or a turbidity following the addition of nessler reagent to distillates collected from chlorinated samples.

The titration procedure is also subject to amine interference because the standard acid can react with such alkaline bodies. However, the titration procedure is free of interference from neutral organic compounds. Sulfide has also been reported to cause turbidity following nesslerization, a condition which may be avoided by adding lead carbonate to the flask prior to distillation. Volatile substances such as formaldehyde can be removed by

boiling at low pH, after which the sample can be distilled and nesslerized in the normal manner.

2. Apparatus

2.1 Distillation apparatus: A glass flask of 800 ml capacity attached to a vertical condenser is so arranged that the distillate falls directly into the collecting glassware.

2.2 Digestion apparatus: Provided with a suction take-off to remove water vapor and sulfur trioxide fumes.

2.3 Colorimetric equipment: A spectrophotometer for use at 400 to 425mμ, providing a light path of 1 inch or longer.

3. Reagents

3.1 Ammonia-free water.

3.2 Phosphate Buffer Solution pH 7.4: Dissolve 14.3 g anhydrous potassium dihydrogen phosphate, KH_2PO_4, and 68.8 g anhydrous dipotassium hydrogen phosphate, K_2HPO_4, and dilute 1 liter with ammonia-free water.

3.3 Boric Acid Solution: Dissolve 20 g anhydrous boric acid H_3BO_3 in ammonia-free water and dilute to 1 liter.

3.4 Sodium Hydroxide-Sodium Thiosulfate reagent: Dissolve 500 g NaOH and 25 g $Na_2S_2O_3 \cdot 5H_2O$ in ammonia-free water and dilute to 1 liter.

3.5 Phenalphthalein Indicator Solution: Dissolve 5 g phenalphthalein in 500 ml 95% ethyl alcohol and add 500 ml distilled water. Then add

0.02N NaOH dropwise until a faint pink color appears.

3.6 Mixed Indicator: Mix 2 volumes of 0.2 percent methyl red in 95% alcohol with 1 volume of 0.2 percent methylene blue in 95% ethyl alcohol. This solution must be made fresh every 30 days.

3.7 Standard Sulfuric Acid Titrant 0.02N: In this strength 1.00 ml equals 0.28 mg N.

3.8 Nessler reagent: Dissolve 100 g mercuric iodide, HgI_2 and 70 g potassium iodide, KI, in a small quantity of ammonia-free water, and add this mixture slowly, with stirring, to a cool solution of 160 g NaOh in 500 ml ammonia-free water. Dilute to 1 liter and store in dark pyrex bottle out of sunlight. Stable about one year. (Caution - Toxic)

3.9 Standard Ammonium Solution: Dissolve 3.819 g anhydrous ammonium chloride, NH_4Cl, dried at 100°C in ammonia-free water and dilute to 1,000 ml: 1 ml = 1.0 mg N - (1.22 mg NH_3). Then dilute 10.0 ml stock ammonium chloride solution to 1,000 ml with ammonia-free water. 1 ml = 10.00 µg N (12.2µg NH_3).

3.10 Standard Organic Nitrogen Solution: Dissolve 1.0503 g of glutamic acid dried at 100°C in ammonia-free water and dilute to 1,000 ml = 1 ml = 0.1 mg N.

4. Procedure

4.1 Add 500 ml distilled water, 10 ml phosphate buffer solution and a few boiling chips to an 800 ml flask and steam out the entire distillation apparatus until the distillate shows no trace of ammonia.

4.2 Place a previously prepared acid sample in a 800 ml kjeldahl flask and add 500 ml of ammonia-free distilled water. (Boil to remove H_2S, if present.) Neutralize to about pH 6.6 using a pH meter if necessary then add 10 ml phosphate buffer solution. Add a few boiling chips.

4.3 Distillation: Distill over 300 ml at the rate of 6-10 ml/min. collecting the distillate in 50 ml of 0.02N H_2SO_4. (Boil to remove H_2S if present.) Place distillate in a glass stoppered 500 ml graduate cylinder and bring up to 500 ml with ammonia-free water and mix.

4.4 Color Development: Place 50 ml portion of the distillate in a 50 ml nessler tube. Add 1 ml of nessler reagent and mix thoroughly by inverting the tube six times. Allow to stand 20 minutes and read at 425mμ.

4.5 A standard and blank should also be run in the same manner as the sample.

5. Calculation

5.1 Wet Basis:

$$\text{mg/kg} = \frac{\text{mg in Std.}}{\text{O. D. Std.}} \times \frac{\text{O. D. Sample}}{\text{(g Sample in aliquot)}} \times 1000$$

5.2 Dry Basis:

$$\text{mg/k} = \frac{\text{mg/kg wet basis}}{\text{\% Solids (decimal fraction)}}$$

Nitrogen, Total Kjeldahl in Bottom Sediments*

Organic nitrogen may be determined by digestion of the sample after removal of free ammonia, with subsequent distillation and titration with standard acid or as the difference between the value obtained for total kjeldahl nitrogen and that for free ammonia.

1. General Discussion

1.1 Principle: The kjeldahl method, using mercuric sulfate as a catalyst, converts organically bound nitrogen in the trinegative state to ammonium bisulfate by digestion with sulfuric acid to which potassium sulfate has been added to raise the boiling point to 345° - 370°C. The temperature should not exceed 382° or loss of nitrogen will result. After dilution, the solution is made alkaline with sodium hydroxide and the ammonia is distilled into 0.2N H_2SO_4 or boric acid solution. If distillate is collected in 0.02N H_2SO_4 acid the ammonia nitrogen should be determined by nesslerization and if distillate is collected in 2% boric acid, the ammonia nitrogen should be determined by titration with 0.02N H_2SO_4, using a mixed indicator.

1.2 Interference: In the presence of large quantities of nitrogen-free organic matter, it is necessary to add an additional 50 ml of sulfuric acid-mercuric sulfate-potassium sulfate solution for each gram of solid material in the sample.

*Adapted from "Chemistry Laboratory Manual, Bottom Sediments". Compiled by Great Lakes Region Committee on Analytical Methods, EPA, Dec. 1969.

1.3 Storage: Because organic nitrogen in unsterilized sewage and sludge is continually ammonified, the determination must be made on a freshly collected sample. If the analysis cannot be made at once, the sample must be preserved with sufficient sulfuric acid to obtain a concentration of 1,500 mg/l H_2SO_4 or more (.8 ml/l).

2. Apparatus

2.1 Digestion apparatus, provided with a suction take-off to remove water vapor and sulfur trioxide fumes.

2.2 Distillation apparatus: See Nitrogen (Ammonia), Standard Methods for the Examination of Water and Wastewater, p. 187-193.

3. Reagents

3.1 Ammonia-free water.

3.2 Sodium Sulfate (low in nitrogen).

3.3 Mercuric Sulfate.

3.4 Litmus Paper.

3.5 Sodium hydroxide-sodium thiosulfate solution: Dissolve 500 g NaOH and 25 g $Na_2S_2O_3 \cdot 5H_2O$ in distilled water and dilute to 1 liter.

3.6 Phenolphthalein indicator solution: Either the aqueous (a) or alcoholic (b) solution may be used.

a. Dissolve 5 g phenolphthalein disodium salt in distilled water and dilute to 1 liter. If necessary, add 0.02N NaOH dropwise until a faint pink color appears.

b. Dissolve 5 g phenolphthalein in 500 ml 95% ethyl alcohol or isopropyl alcohol and add 500 ml distilled water. Then add 0.02N NaOh dropwise until a faint pink color appears.

3.7 Mixed indicator: Mix 2 volumes of 0.2 percent methyl red in 95% alcohol with 1 volume of 0.2 percent methylene blue in 95% ethyl alcohol. This solution must be made fresh every 30 days.

3.8 Standard sulfuric acid titrant, 0.02N. In this strength, 1.00 ml = 0.28 mg N. Other strengths of standard acid may be used.

3.9 Sulfuric acid, concentrated

3.10 Dissolve 20 g anhydrous boric acid, H_3BO_3, in ammonia-free water and dilute to 1 liter.

3.11 Antifoam.

4. Procedure

4.1 Take either the residue from the free ammonia analysis for organic nitrogen or a new sample for total kjeldahl nitrogen (1 or 2 g).

4.2 Add 35 ml of conc. H_2SO_4 plus 15 g Na_2SO_4, plus 3 g mercuric sulfate and a little antifoam and allow to boil until white fumes appear.

4.3 After fumes appear, allow to digest for 30 minutes turning the flask from time to time. Cool to room temperature.

4.4 To cooled sample, add 500 ml of ammonia-free water, 0.3 ml (1 dropper full) of phenolphthalein or litmus paper, and then add 50 to 75 ml of 50% NaOH-thiosulfate solution being careful not to

mix. Place on distillation rack and mix. If the solution is not red or litmus paper is not blue, add more NaOH until a red color appears or litmus is blue.

4.5 Distill over 300 ml collecting the distillate in 50 ml of 2% boric acid. To this add 10 drops of mixed indicator and titrate with 0.02N H_2SO_4 which has been standardized against 0.02N Na_2CO_3.

4.6 Blanks and standards should be run in the same manner as the samples.

5. Calculation

5.1 Wet basis (titration)

$$mg/kg = \frac{\text{ml of 0.02 } NH_2SO_4 \text{ x } 0.28}{\text{g sample}} \text{ x } 1000$$

5.2 Dry Basis

$$mg/kg = \frac{\text{mg/kg wet basis}}{\text{\% solids (decimal fraction)}}$$

5.3 Wet Basis (colorimetric)

$$mg/kg = \frac{\text{mg in Std}}{\text{O.D. Std.}} \text{ x } \frac{\text{O.D. Sample}}{(\text{g sample in aliquot})} \text{ x } 1000$$

5.4 Dry basis

$$mg/kg = \frac{\text{mg/kg wet basis}}{\text{\% solids (decimal fraction)}}$$

6. Nitrogen (Total Kjeldahl) - (Bottom Sediments)

Total kjeldahl nitrogen includes ammonia and organic nitrogen, but does not include nitrite and nitrate nitrogen. The method is the same as that for organic nitrogen, except that the ammonia removal step is omitted. The procedure therefore begins with Sec. 4. Place an appropriate aliquot of a well-mixed sample in an 800 ml kjeldahl flask. (1 or 2 g)

Total Phosphorus in Water Elutriate*

The total phosphorus content of the sample includes all of the orthophosphates and condensed phosphates, both soluble and insoluble, and organic and inorganic species. To release phosphate from combination with organic matter, a digestion is called for. Persulfate Digestion Method can be considered most conveniently applicable.

Following digestion, the liberated orthophosphate is determined colorimetrically by Ascorbic Acid Method.

I. Persulfate Digestion Method

1. Apparatus

1.1 Hot plate: A 30 x 50 cm heating surface is adequate.

1.2 Autoclave: An autoclave or pressure cooker capable of developing 15 to 20 psi may be used in place of a hot plate.

2. Reagents

2.1 Phenolphthalein indicator solution.

2.2 Sulfuric acid solution: Carefully add 300 ml conc. H_2SO_4 to approximately 600 ml distilled water and then dilute to 1 liter with distilled water.

2.3 Potassium persulfate solution: Dissolve 5 g $K_2S_2O_8$ in 100 ml distilled water. Prepare daily.

2.4 Sodium hydroxide, 1N.

*Adopted from "Standard Methods", for the Examination of Water and Wastewater, 14th Ed., 1975, with modification.

3. Procedure

3.1 Take 100 ml or a suitable aliquot of thoroughly mixed sample. To each 100 ml sample or aliquot diluted to 100 ml, add 1 drop (0.05 ml) phenolphthalein indicator solution. If a red color develops, add sulfuric acid solution dropwise to just discharge the color. Then add 1 ml sulfuric acid solution and 15 ml potassium persulfate solution.

3.2 Boil gently for at least 90 minutes, adding distilled water to keep the volume between 20 and 50 ml. Alternatively, heat for 30 minutes in an autoclave or pressure cooker at 15 - 20 psi. Cool, add 1 drop (0.05 ml) phenolphthalein indicator solution, and neutralize to a faint pink color with sodium hydroxide solution. Restore the volume to 100 ml with distilled water. Determine the phosphorus present using Ascorbic Acid Method.

II. Ascorbic Acid Method for Determination of Total Phosphorous, Colorimetrically

1. General Discussion

1.1 Principle: Ammonium molybdate and potassium antimonyl tartrate react in an acid medium with dilute solutions of orthophosphate to form a heteropoly acid -- phosphomolybdic acid-- which is reduced to the intensely colored molybdenum blue by ascorbic acid.

1.2 Interference: Arsenates react with the molybdate reagent to produce a blue color similar to that formed with phosphate. Concentrations as low as 0.10 mg/l arsenic interfere with the phosphate determination. Hexavalent chromium and nitrite interfere to give results about 3% low at concentrations of 1.0 mg/l and 10 - 15% low at concentrations of 10 mg/l chromium and nitrite. Sulfide (Na_2S) and silicate do not interfere in concentrations of 1.0 and 10.0 mg/l.

1.3 Minimum detectable concentration: Approximately 30 µg P/l.

Relationship of Light Path Lengths to Phosphate Ranges

Approximate P Range µg/l	Light Path Length cm
0.30 - 2.0	0.5
0.15 - 1.30	1.0
0.03 - 0.25	5.0

2. Apparatus

2.1 Colorimetric equipment: One of the following is required:

2.1.1 Spectrophotometer, with infrared phototube for use at 880 mµ, providing a light path of 0.5 cm or longer.

2.1.2 Filter Photometer, equipped with a red color filter and a light path of 0.5 cm or longer.

2.2 Acid-washed glassware.

3. Reagents

3.1 Alcohol, ethyl (95%) or isopropyl.

3.2 Sulfuric acid solution, 5N: Dilute 70 ml conc. H_2SO_4 with distilled water to 500 ml.

3.3 Antimony potassium tartrate: Dissolve 4.3888 g $K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$ in 200 ml distilled water. Store in a dark bottle at 4°C.

3.4 Ammonium molybdate solution: Dissolve 20 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in 500 ml distilled water. Store in a plastic bottle at 4°C.

3.5 Ascorbic acid, 0.1M: Dissolve 1.76 g ascorbic acid in 100 ml distilled water. The solution is stable for about a week if stored at 4°C.

3.6 Combined reagent: Mix the above reagents in the following proportions for 100 ml combined reagent: 50 ml 5N sulfuric acid, 5 ml antimony potassium tartrate, 15 ml ammonium molybdate solution, and 30 ml ascorbic acid solution. Allow all reagents to reach room temperature before they are mixed, and mix in the order given. If turbidity forms in the combined reagent after the addition of antimony potassium tartrate or ammonium molybdate, shake the combined reagent and let it stand for a few minutes until the turbidity disappears before proceeding. The reagent is stable for at least 1 week if stored at 4°C.

3.7 Stock phosphate solution: (prepared as in reference).

3.8 Standard phosphate solution: Dilute 50.0 ml stock phosphate solution to 1,000 ml with distilled water to form a solution containing 2.00 µg P per 1.00 ml.

4. Procedure

4.1 Treatment of sample: Pipet 20.0 ml clear sample into a clean, dry test tube or a 125 ml erlenmeyer flask. Add 1 ml ethyl or isopropyl alcohol. Mix thoroughly. Because curves prepared with ethyl alcohol are slightly different from those prepared with isopropyl alcohol, use the same alcohol in treating samples and standards. Add 1 ml combined reagents. Mix thoroughly and allow to stand 10 minutes for color development before reading in a spectrophotometer at a wavelength of 880 $m\mu$, or a filter photometer equipped with a red color filter.

4.2 Correction for turbidity or interfering color: Natural color of water generally does not interfere at the high wavelength used. In the case of highly colored or turbid waters, prepare a blank by adding all the reagents except ascorbic acid and antimony potassium tartrate to the sample. Subtract the absorbance of the blank from the absorbance of each of the unknown samples.

4.3 Preparation of calibration curve: Prepare individual calibration graphs from a series of six standards within the phosphate range indicated in table above. Use a distilled water blank with the combined reagent to make the photometric readings for the calibration curve. Plot absorbance vs. phosphate concentration, which should form a straight line passing through the origin.

Test at least one phosphate standard with each set of samples.

5. Calculations

5.1 $$\text{mg/l P} = \frac{\text{mg P} \times 1000}{\text{ml sample}}$$

If phosphate as PO_4 is desired, multiply the result as phosphorus by 3.06.

Total Phosphorus in Bottom Sediments*

1. General Discussion

1.1 Principle: Ammonium molybdate and hydrazine sulfate react in an acid medium with dilute solutions of orthophosphate to form a heteropoly acid (phosphomolybdic acid) which is reduced to the intensely colored molybdenum blue by sodium sulfite.

1.2 Interferences: Arsenic, iron, tungsten, silica, titanium, zirconium and vanadium do not interfere.

1.3 Precautions: All glassware should be washed with hot 1:1 hydrochloric acid and then rinsed thoroughly with distilled water. The glassware is then filled with distilled water and all reagents added and allowed to stand 15 to 20 minutes, followed by a distilled water rinse. Commercial detergents should not be used.

2. Apparatus

Colorimetric equipment: A spectrophotometer for measurement at a wavelength of 880 mμ or a filter photometer equipped with a red color filter.

3. Reagents

3.1 3% H_2O_2.

3.2 50% Mg $(NO_3)_2 \cdot 6H_2O$: Dissolve 500 g Mg $(NO_3)_2 \cdot 6H_2O$ in 1,000 ml of distilled water.

*Adopted from "Chemistry Laboratory Manual, Bottom Sediments", compiled by Great Lakes Region Committee on Analytical Methods, EPA, Dec., 1969, and from "Standard Methods", for the Examination of Water and Wastewater, 13th Edition, 1971, with modification.

3.3 Concentrated hydrochloric acid.

3.4 All other reagents listed in Persulfate Digestion Method and Ascorbic Acid Method, in the Analysis of Total Phosphorus Content in Water and in Standard Elutriate.

4. Procedure

4.1 Weigh 1.00 g of well-blended sample into a 250 ml Vycor dish.

4.2 Add 10 ml of 3% H_2O_2 and heat on hot plate for 10 or 15 minutes with stirring to prevent overflowing from frothing.

4.3 Add 10-15 ml of distilled water and continue to boil until frothing has ceased and almost all of the water has evaporated.

4.4 Add 10 ml of 50% Mg $(NO_3)_2 \cdot 6H_2O$ and place in a cold muffle furnace. (Keep stiring rod in Vycor dishes and make sure dishes are permanently marked.)

4.5 Start at 100°C and increase the heat gradually until the samples are dry (about 350°C). Then increase heat to 500-550°C and ash for one hour.

4.6 Remove samples from furnace and let cool on asbestos pads.

4.7 When cool, add 20 ml of conc. HCl, place on hot plate and heat with stirring until effervescence has stopped.

4.8 Add approximately 50 ml of distilled water and clean the sides of the dish with a rubber policeman.

4.9 Filter through membrane filter 0.45μ into a 250 ml volumetric flask, wash dish and filter paper with distilled water and make up to volume.

4.10 Take a 100 ml aliquot and digest by Persulfate Digestion Method (same as in Water and in Standard Elutriate Test.)

4.11 Determine concentration of total Phosphorus colorimetrically using Ascorbic Acid Method (same as in Water and in Standard Elutriate Test.).

5. Calculations

5.1 Wet Basis

$$mg/kg = \frac{\text{mg in Std.}}{\text{O. D. Std.}} \times \frac{\text{O. D. Sample}}{\text{(grams sample in aliquot)}} \times 1,000$$

5.2 Dry Basis

$$mg/kg = \frac{\text{mg/kg wet basis}}{\text{\% solids (decimal fraction)}}$$

Chemical Oxygen Demand of Water and in Elutriate*

STORET No. 00340

1. Scope and Application

1.1 The Chemical Oxygen Demand (COD) method determines the quantity of oxygen required to oxidize the organic matter in a waste sample, under specific conditions of oxidizing agent, temperature, and time.

1.2 Since the test utilizes a rigorous chemical oxidation rather than a biological process, the result has no defineable relationship to the Biochemical Oxygen Demand (BOD) of the waste. The test result should be considered as an independent measurement of organic matter in the sample, rather than as a substitute for the BOD test.

1.3 The method can be applied to domestic and industrial waste samples having an organic carbon concentration greater than 15 mg/l. For lower concentrations of carbon such as in surface water samples, the Low Level Modification should be used. When the chloride concentration of the sample exceeds 2000 mg/l, the modification for saline waters is required.

2. Summary of Method

2.1 Organic substances in the sample are oxidized by potassium dichromate in 50% sulfuric acid solution at reflux temperature. Silver sulfate is used as a catalyst and mercuric sulfate is

*Adpoted from "Manual of Methods for Chemical Analysis of Water and Wastes", EPA 625-/6-74-003, 1974, Page 20.

added to remove chloride interference. The excess dichromate is titrated with standard ferrous ammonium sulfate, using orthophenanthroline ferrous complex as an indicator.

3. Sampling and Preservation

3.1 Collect the samples in glass bottles, if possible. Use of plastic containers is permissible if it is known that no organic contaminants are present in the containers.

3.2 Biologically active samples should be tested as soon as possible. Samples containing settleable material should be mixed, preferably homogenized, to permit removal of representative aliquots.

3.3 Samples may be preserved with sulfuric acid at a rate of 2 ml of conc. H_2SO_4 per liter of sample.

4. Interferences

4.1 Traces of organic material either from the glassware or atmosphere may cause a gross, positive error.

4.1.1 Extreme care should be exercised to avoid inclusion of organic materials in the distilled water used for reagent preparation or sample dilution.

4.1.2 Glassware used in the test should be conditioned by running blank procedures to eliminate traces of organic material.

4.2 Volatile materials may be lost when the sample temperature rises duri[illegible]he sulfuric acid addition step.

4.3 Chlorides are quantitatively oxidized by dichromate and represent a positive interference. Mercuric sulfate is added to the digestion flask to complex the chlorides, thereby effectively eliminating the interference on all but brine and estuarine samples.

5. Apparatus

5.1 Reflux apparatus: Glassware should consist of a 500 ml Erlenmeyer flask or a 300 ml round bottom flask made of heat-resistant glass connected to a 12 inch Allihn condenser by means of a ground glass joint. Any equivalent reflux apparatus may be substituted provided that a ground-glass connection is used between the flask and the condenser.

6. Reagents (as given in reference)

6.1 Distilled water.

6.2 Standard potassium dichromate solution (0.025 N).

6.3 Sulfuric acid reagent.

6.4 Standard ferrous ammonium sulfate (0.025 N).

6.5 Mercuric sulfate: Powdered $HgSO_4$

6.6 Phenanthroline ferrous sulfate (ferroin) indicator solution.

6.7 Silver sulfate: Powdered Ag_2SO_4.

6.8 Sulfuric acid (sp. gr. 1.84): Concentrated H_2SO_4.

7. Procedure

7.1 Place several boiling stones in the reflux flask, followed by 1 g of $HgSO_4$ (6.5). Add 5.0 ml conc. H_2SO_4 (6.8); swirl

until mercuric sulfate has dissolved. Place reflux flask in an ice bath and slowly add, with swirling, 25.0 ml of 0.025 N $K_2Cr_2O_7$ (6.2). Now add 70 ml of sulfuric acid-silver sulfate solution (6.3) to the cooled reflux flask, again using slow addition with swirling motion.

7.2 With the reflux flask still in the ice bath, place 50.0 ml of sample or an aliquot diluted to 50.0 ml into the reflux flask. Caution: Care must be taken to assure that the contents of the flask are well mixed. If not, superheating may result, and the mixture may be blown out of the open end of the condenser. Attach the flask to the condenser and start the cooling water.

7.3 Apply heat to the flask and reflux for 2 hours. For some waste waters, the 2-hour reflux period is not necessary. The time required to give the maximum oxidation for a wastewater of constant or known composition may be determined and a shorter period of refluxing may be permissable.

7.4 Allow the flask to cool and wash down the condenser with about 25 ml of distilled water. If a round bottom flask has been used, transfer the mixture to a 500 ml Erlenmeyer flask, washing out the reflux flask 3 or 4 times with distilled water. Dilute the acid solution to about 300 ml with distilled water and allow the solution to cool to about room temperature. Add 8 to 10 drops of ferroin indicator (6.6) to the solution and titrate the excess dichromate with 0.025 N ferrous ammonium sulfate

(6.4) solution to the end point. The color change will be sharp, changing from a blue-green to a reddish blue.

7.5 Blank--Simultaneously run a blank determination following the details given in (7.1) and (7.2), but using low COD water in place of sample.

8. Calculation

8.1 Calculate the COD in the sample in mg/l as follows:

$$\text{COD, mg/liter} = \frac{(a-B)N \times 8000}{S}$$

where

A = milliliters of $Fe(NH_4)_2(SO_4)_2$ solution required for titration of the blank,

B = milliliters of $Fe(NH_4)_2(SO_4)_2$ solution required for titration of the sample,

N = normality of the $Fe(NH_4)_2(SO_4)_2$ solution, and

S = milliliters of sample used for the test.

Chemical Oxygen Demand of Bottom Sediments*

1. General Discussion

2. Apparatus

Reflux apparatus consisting of 250 ml Erlenmeyer flasks with ground-glass 24/40 neck** and 300 mm jacket Liebig, West, or equivalent condensers*** with 24/40 ground-glass joint, and a hot plate with sufficient power to produce at least 9 watts/sq. in. of heating surface, or equivalent, to insure an adequate boiling of the contents of the refluxing mixture.

3. Reagents (as given in reference.)

3.1 Sulfuric acid reagent, conc. H_2SO_4.

3.2 Silver sulfate is dissolved in the H_2SO_4 acid.

3.3 Mercuric sulfate, analytical grade crystals.

3.4 Ferroin indicator solution, 0.025 M.

3.5 Standard potassium dichromate solution, 0.500 N.

3.6 Standard ferrous ammonium sulfate, 0.500 N.

3.7 Standardization of ferrous ammonium sulfate: Dilute 25 ml standard potassium dichromate solution to approximately 250 ml. Add 50 ml conc. H_2SO_4 and allow to cool. Titrate with the ferrous ammonium sulfate titrant, using 2 or 3 drops of

*Adopted from "Chemistry Laboratory Manual, Bottom Sediments", Compiled by Great Lakes Region Committee on Analytical Methods, EPA, Dec., 1969.
**Corning 5000 or equal
***Corning 2360, 91548, or equal

ferroin indicator.

$$\text{Normality} = \frac{\text{ml } K_2Cr_2O_7 \times .25}{\text{ml } Fe(NH_4)_2(SO_4)_2}$$

4. Procedure

4.1 Add 25 ml $K_2Cr_2O_7$ (0.2500 N) to a suitable sized sample (0.5 g - 1.0 g) of bottom sediment that will consume one-half of the $K_2Cr_2O_7$.

4.2 Add 1.0 g $HgSO_4$ and 0.75 g Ag_2SO_4.

4.3 Add 50 ml of distilled water.

4.4 Add 75 ml conc. H_2SO_4 (cautiously) and mix thoroughly.

4.5 Add boiling stones and reflux for 2 hours.

4.6 Cool and rinse condenser with distilled H_2O (approximately 50 ml) while condenser is still connected to flask.

4.7 Disconnect and add approximately 150 ml distilled H_2O. Cool to room temperature and then titrate (after adding 3 to 5 drops ferroin indicator) to end point (the color changes sharply from blue-green to reddish-brown).

4.8 For standard, use 25 ml $K_2Cr_2O_7$ + 50 ml conc. H_2SO_4 and dilute to approximately 250-300 ml. Cool and titrate.

For blank, use 25 ml $K_2Cr_2O_7$, 75 ml H_2SO_4, 50 ml distilled H_2O, 1 g $HgSO_4$, 0.75 g Ag_2SO_4; reflux for 2 hours and continue in the same manner as the sample.

5. Calculations

5.1 Wet Basis

$$\text{mg/kg} = \frac{(a-b)c \times 8}{\text{grams sample}} \times 1000$$

5.2 Dry Basis

$$mg/kg = \frac{mg/kg \text{ wet basis}}{\% \text{ solids}}$$

where:

a = mls of $Fe(NH_4)_2(SO_4)_2$ required for blank

b = mls of $Fe(NH_4)_2(SO_4)_2$ required for sample

c = normality of $Fe(NH_4)_2(SO_4)_2$

Total Organic Carbon in Water, Elutriate and Bottom Sediments*

STORET No. 00680

1. Scope and Application

1.1 This method includes the measurement of organic carbon in drinking, surface, and saline waters, domestic and industrial wastes.

1.2 The method is most applicable to measurement of organic carbon above 1 mg/l.

2. Summary of Method

2.1 Organic carbon in a sample is converted to carbon dioxide (CO_2) by catalytic combustion or wet chemical oxidation. The CO_2 formed can be measured directly by an infrared detector or converted to methane (CH_4) and measured by a flame ionization detector. The amount of CO_2 or CH_4 is directly proportional to the concentration of carbonaceous material in the sample.

3. Sample Handling and Preservation

3.1 Sampling and storage of samples in glass bottles is preferable. Sampling and storage in plastic bottles such as conventional polyethylene and cubitainers is permissible if it is established that the containers do not contribute contaminating organics to the samples.

NOTE 1: A brief study performed in theEPA Laboratory indicated that distilled water stored in new, one quart cubitainers did not show any increase in organic carbon after two weeks exposure.

*Adapted from "Manual of Methods for Chemical Analysis of Water and Wastes", EPA-625-/6-74-003, 1974; page 236, with modification.

3.2 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 ($4^{o}C$) and protected from sunlight and atmospheric oxygen.

3.3 In instances where analysis cannot be performed within two hours (2 hours) from time of sampling, it is recommended that the sample is acidified (pH 2) with HCl or H_2SO_4.

4. Interferences

4.1 Carbonate and bicarbonate carbon represent an interference under the terms of this test and must be removed or accounted for in the final calculation.

4.2 This procedure is applicable only to homogeneous samples which can be injected into the apparatus reproducibly by means of a microliter type syringe or pipette. The openings of the syringe or pipette limit the maximum size of particles which may be included in the sample.

5. Apparatus

5.1 Apparatus for blending or homogenizing samples: Generally, a Waring-type blender is satisfactory.

5.2 Apparatus for total and dissolved organic carbon:

5.2.1 A number of companies manufacture systems for measuring carbonaceous material in liquid samples. Considerations should be made as to the types of samples to be analyzed, the expected concentration range, and forms of carbon to be measured.

5.2.2 No specific analyzer is recommended as superior. However, analyzers which have been found to be reliable are the Dow-Beckman Carbonaceous Analyzer Model No. 915, the Dohrmann Envirotech DC-50 Carbon Analyzer and the Oceanography International Total Carbon Analyzer.

6. Reagents: As recommended in the reference source.

7. Procedure

7.1 Follow instrument manufacturer's instruction for calibration, procedure, and calculations.

7.2 For calibration of the instrument, it is recommended that a series of standards encompassing the expected concentration range of the samples to be used.

Hydrometer Grain Size Analysis Test Using A Control Cylinder and Soil Hydrometer

1. Procedure

1. Select a representative sample of sediment material containing approximately 50 grams of solids, which has been washed through a 0.074 mm sieve. Place this sample in a small evaporating dish.
2. Mix the sample thoroughly with enough deflocculating agent (10% sodium hexa-meta-phosphate solution) to ensure dispersion of individual particles.
3. Wash this mixture into a soil dispersion cup and add enough distilled demineralized water to fill the cup 2/3 full. Place the cup with sample on a soil dispersion mixer and mix until all particles are dispersed (about 10 minutes).
4. While the sample is mixing prepare the control cylinder. Into a graduated cylinder place the same amount of deflocculating agent as added to the sample in Step 2, above, and fill it to the 1000 cc mark with distilled demineralized water. Mix this solution thoroughly and place the control cylinder into a constant temperature bath. Keep the control cylinder covered as much as possible to prevent evaporation and accumulation of dust.
5. After mixing, wash the specimen into a graduate cylinder and add enough distilled demineralized water to bring the level to 1000 cc mark.
6. Mix the soil and water suspension in the graduate by placing the palm of the hand over the open end and turning the graduate upside down and back. When the graduate is upside down, be sure no soil is stuck to the base of the graduate.

7. After shaking it for two minutes, always keeping the suspension in motion, place the cylinder in the constant temperature bath. The timer must be started the exact instant when the cylinder comes upright the last time. The hydrometer is inserted in the suspension and readings commence.
8. Take hydrometer readings at the top of meniscus for total elapsed times of 1/4, 1/2, 1 and 2 minutes without removing the hydrometer. The hydrometer must be inserted into and removed from the suspension for each subsequent reading. Before each insertion of the hydrometer, dry the stem. (The hydrometer to be used is an ASTM 152H model which reads grams of solids in suspension per 1000 cc).
9. Continue taking readings at total elapsed times approximately doubling the previous time interval: 4, 8, 15, 30 minutes; 1, 2, 4, 8, 16, 24 hours. Observations must be taken until the hydrometer reading in the suspension equals that in the control cylinder or until 24 hours have elapsed.
10. Take temperature observations in the suspension and control cylinder approximately every 30 minutes at the beginning of the test and whenever taking readings as the test progresses. Take top-of-meniscus readings of the hydrometer in the control cylinder solution approximately every 10 minutes at the beginning of the test and when taking readings in the suspension as the test progresses.
11. Keep the top of the cylinder containing the soil suspension covered to retard evaporation and to prevent collection of dust, etc., from the air.
12. After the final reading, pour the suspension into a large evaporating dish of known weight. Take <u>unusual</u> care to avoid losing any soil.

13. Evaporate the suspension to dryness in the oven at 105° to 110°C, cool the dishes in a dessicator, and weigh to 0.01 g of the weight of dish from step 12 subtracted from the weight obtained here gives the weight of dry solids used.

Analysis

Development of a grain size analysis curve is dependent on two kinds of data. The first of these is the grain size being measured. The suspension hydrometer reading is converted, by the use of a chart, into the effective depth of immersion of the hydrometer. Knowing this depth, elapsed time corresponding to that depth, the specific gravity of solids, and the temperature of the suspension, Casagrande's nomograph of Stoke's Law is utilized in finding the particle diameter measured. The second data input necessary is the percent of solids still in suspension finer in size than that diameter measured. Hydrometer readings in the suspension are corrected, as described below, using control cylinder solution readings and then are divided by the weight of solids to give the percent finer than the measured diameter still in suspension.

Test corrections normally required in hydrometer analysis include the effects of test temperature, addition of dispersing agent to the soil-water suspension, and meniscus rise on the hydrometer stem. These effects may be considered by use of correction factors, but the control cylinder procedure eliminates the need for these corrections. When the hydrometer is read in the suspension cylinder (top of meniscus) it is also read in the control cylinder (top of meniscus). The difference between the two

readings, test minus control, is the actual average increase in the number of grams in 1000 cc suspension caused by the solids in that suspension. Since the test is done using a 1000 cc suspension volume, the corrected reading is the actual number of grams of the sample still in suspension (smaller than measured diameter). This can be converted to "percent finer than" by dividing it by the total weight of solids in the suspension.

Static Bioassay Tests With Elutriate* For Acute Toxicity

Procedure

The experimental procedure for determining the toxicity of the elutriate water consists of adding a known volume of sediment to a known volume of river water. The bioassay test to determine toxicity to Daphnia magna over a 96-hour test period are performed with the elutriate. The total elutriate water-sediment volume is two liters. The sediment to water volume ratios are 1 part sediment and 4 parts water. The sediment-water mixtures are placed in 1 liter Erlenmeyer flasks. These mixtures are aerated for 30 minutes at 5 psi. The sediment water mixtures are then allowed to settle for 60 minutes. After 60 minutes of settling, the elutriate water is carefully decanted from the two liter flask containing the sediment and placed in a separate flask. The following chemical and physical characteristics are measured: temperature, pH, turbidity, dissolved oxygen, ammonia nitrogen, and specific conductance. The dissolved oxygen and ammonia concentrations of the bioassay elutriate waters are also determined at the completion of the 96 hour test period.

Adapted from:

(1) Standard Methods for the Examination of Water and Wastewater, 14th Edition, 1975.

(2) Methods for Acute Toxicity Tests with Fish, Macroinvertibrates, and Amphibians, EPA Corvallis, Origon EPA-660/3-75-0009, April 1975.

(3) Ecological Evaluation of Proposed Discharge of Dredged or Fill Material into Navigable Waters Environmental Effects Laboratory U.S. Army Engineer Waterways Experiment Station, Vicksburg, Miss., May 1976.

Two 200 ml aliquot, elutriate water sample are placed in two separate 250 ml beakers. A desired number of young Daphnia magna are added to each test beaker. Selection of test organisms is based upon a random selection of active specimens. The organisms may be removed from the culture tank using a large-mouth 10 cm serum pipette. Mortalities of Daphnia magna are recorded after two hours and every 12 hours of exposure throughout the 96-hour test period. All test and control tanks are maintained at the same temperature in which the test organisms are cultured. Tests are run on a 14-hour light and 10-hour dark regime. At least two replicates must be run simulatneously for each eultriate test, including the controls. Control mortality exceeding 10 percent invalidates test results.

Bioassay Test Water

The water used in the bioassay should be water taken from the proposed dredging site. The site water should be prepared by sterilizing (15 minutes at 15 psi) and then aerating the cooled water to reach 80 to 100 percent dissolved oxygen saturation at desired temperature. Alternatively, the sterile water should be aerated to the original DO concentration. It is necessary that a healthy culture of Daphnia magna is able to grow and reproduce in the clean site water prior to testing. Once a culture has been maintained in the clean site for a period of two weeks, it may be used in the bioassay test water.

Dissolved Oxygen Concentration

The dissolved oxygen concentration of the bioassay test water should reflect the concentration of the dredged site water prior to dredging. If this information is not available, the dissolved oxygen concentration of the

bioassay test water should be between 80 and 100 percent saturation before the introduction of bottom sediments.

Substrates Used in Bioassay Test Chambers

The test chambers, including the controls, should not contain any sediments or artificial substrates.

Feeding*

The test organisms must not be fed during the 96-hour test period. In addition, the test organisms should not be fed for 48 hours perior to the start of the static bioassay test.

Turbidity

The test water may often remain highly turbid even after one hour of settling. If such condition is encountered, longer settling period may be employed. Alternatively, the elutriate may be centrifuged for a short period to reduce turbidity. Filteration should not be used as an alternate method for reduction of turbidity, unless tests are conducted on filtered river water and elutriate.

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*If necessary, food and toxicant will be added into the test culture as indicated in "Tentative Procedure for Daphnia Magna Chronic Tests in a Standing System", Federal Register, Volume 40, No. 123 - Wednesday, June 25, 1975.

Oxidation - Reduction Potential Measurements*

The oxidation-reduction (redox or E_h) potential is defined as the electromotive force developed by a platinum electrode immersed in the water or bottom sediment, referred to the standard hydrogen electrode.

This is a measure of the oxygen potential of the bottom sediments. When E_h is positive, this indicates the presence of oxygen or the material is in the oxidized state and when it is negative the absence of oxygen is indicated or the material is in the reduced state. An E_h measurement would give a good indication whether the iron was in the ferric state or the ferrous state.

To measure the potential, a Beckman Zeromatic pH Meter or a Beckman Model N is used in conjection with a calomel (saturated KCL solution used) and platinum electrode system. Instructions are followed for the specific meter to obtain MV readings. E_h is measured by inserting the electrodes just into the surface of the undisturbed sediment (about 1/2").

The oxidation-reduction potential of the sample in millivolts referred to the hydrogen scale is calculated as follows:

Oxidation-reduction potential, $Mv = E - C$ where:

E = electromotive force, in millivolts of the cell

C = potential, in millivolts of the saturated calomel electrode referred to the hydrogen scale.

Note: There should not be any electrical interferences in the immediate locale.

*Adapted from "Chemistry Laboratory Manual, Bottom Sediments", Compiled by Great Lakes Region Committee in Analytical Methods, EPA, Dec. 1969.

APPENDIX K

PREPARATION OF BOTTOM SEDIMENTS FOR ANALYSIS OF HEAVY METALS AND HALOGENATED HYDROCARBANS

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APPENDIX K

PREPARATION OF BOTTOM SEDIMENTS FOR ANALYSIS FOR ANALYSIS OF HEAVY METALS AND HALOGENATED HYDROCARBONS*

Atomic Absorption

1. General Discussion

Metal complexes are freed by digestion of bottom sediment samples with concentrated HNO_3 acid H_2O_2 (30%). A wide range of elements can be determined by atomic absorption with the selection of the proper source (hollow cathode lamp).

1.1 Principle: The principle of atomic absorption and its application to the analysis of metals is based upon the element of interest being dissociated from its chemical bonds and placed into an unexcited, un-ionized "ground" state. It is then capable of absorbing at discrete lines of narrow band width radiation provided by a hollow cathode lamp with a cathode made of the element being sought. The absorption of the light by the metal in the ground state is related to the concentration of the metal being sought.

1.2 Interference: The atomic absorption method is relatively free of interferences.

2. Apparatus

2.1 Atomic absorption spectrophotometer.

2.2 Muffle furnace.

2.3 Pipettes.

2.4 250 ml beakers.

2.5 Watch glasses.

2.6 250 ml volumetric flasks.

2.7 Polyethylene bottles (60 ml).

2.8 Centrifuge (20,000 rpm).

*Adapted from "Chemistry Laboratory Manual, Bottom Sediments", Compiled by Great Lakes Region Committee in Analytical Methods, EPA, Dec. 1969, pages 18-20, and 56-58.

3. Reagents

3.1 Nitric acid (conc. metal-free).

3.2 Hydrogen peroxide (30%).

3.3 Hydrochloric acid (conc. metal-free).

3.4 Ammonium chloride.

3.5 Calcium nitrate.

3.6 Redistilled water or double deionized water (metal-free).

3.7 Bottled acetylene gas.

3.8 Bottled nitrous oxide gas.

3.9 Compressed air.

4. Preparation of Standards

4.1 Using a commercial certified atomic absorption standard, containing 1,000 mg/l of the metal, prepare an appropriate dilute stock standard. Standards may be prepared in the laboratory using pure metals.

4.2 Make up working standards to approximate the concentration in the sample using the dilute stock standard.

5. Preparation of Samples

5.1 Place 2.5 g of a well mixed bottom sediment sample in a 250 ml beaker, add 10 ml of conc. HNO_3 acid and 0.5 ml of H_2O_2 (30%) and evaporate to dryness.

5.2 Ash at 400-425°C for one hour in a muffle furnace and cool.

5.3 Add 25 ml of acid mixture (200 ml of conc. HNO_3, 50 ml conc. HCl and 750 ml of redistilled water), 20 ml of 10% NH_4Cl and 1 ml of $Ca(NO_3)_2 \cdot 4H_2O$ (11.8 g/100 ml). Heat gently for 15 minutes and cool for five minutes or longer.

5.4 Transfer sample to centrifuge tube and centrifuge for 10 minutes at 20,000 rpm. Transfer the supernatant to a 250 ml volumetric flask. Rinse the residue in the centrifuge tube twice with redistilled water and add washings to supernatant and dilute to volume. Then transfer sample to a small plastic bottle.

6. Method for Cu, Dd, Ni, Zn, Cr, Pb, Mn, As, Hg and Other Metals

Follow procedures as outlined in Appendix L.

7. Calculations

7.1 Wet Basis

By use of table from manufacturer's manual, convert percent absorption to absorbance.

$$mg/kg = \frac{mg/l \text{ in std.}}{\text{absorbance of std.}} \text{ X dil. factor X absorbance of sample X } \frac{1,000}{g \text{ of sample/L}}$$

7.2 Dry Basis

$$mg/kg = \frac{mg/kg \text{ wet basis}}{\% \text{ solids (decimal fraction}}$$

8. Atomic absorption is the preferred method because it is much faster, more accurate and there are less interferences.

Pesticides in Bottom Sediments

1. General Discussion

1.1 Principle: Pesticides sorbed on particulate matter may be desorbed by the continuous Soxhlet Extraction of a ground and dried bottom sediment sample with suitable organic solvent(s). The extract containing the pesticide(s) is cleaned up and analyzed by gas chromatography, thin layer chromatography, and infrared spectroscopy.

2. Apparatus

2.1 Soxhlet extractor, flask capacity (500 ml), with Allihn condenser.

2.2 Extraction thimbles, Whatman single thickness, 43 x 123 mm or a convenient size.

2.3 Chromatographic tube 20 x 400 mm.

2.4 Thin layer chromatography equipment.

2.5 Gas chromatograph equipped with microcoulometric titration cells.

3. Reagents

3.1 Hexane, redistilled in glass b.p. 68° - 69°C.

3.2 Ethyl ether, redistilled in glass b.p. 34° - 35°C.

3.3 Chloroform, redistilled in glass b.p. 60° - 61°C.

3.4 6 parts ethyl ether and 94 parts hexane.

3.5 15 parts ethyl ether and 85 parts hexane.

3.6 30 parts ethyl ether and 70 parts hexane.

3.7 50 parts ethyl ether and 50 parts hexane.

3.8 Florisil 60-100 mesh commercial products of this grade may be reactivated by heating 5 hours at 130°C.

4. Procedure

4.1 Preparation for Extraction

a. Allow the bottom sediment sample to dry thoroughly at room temperature for about a week or cover samples with open mesh cheesecloth and accelerate moisture removal employing a cooling fan. This is best accomplished by breaking up the large particles and spreading out in a glass dish or aluminum foil.

b. Grind up sample with a mortar and pestle and pass it through a 30 mesh sieve.

c. Select a 100 g aliquot and place in a pre-extracted thimble. Place a small wad of pre-extracted glass wool or cotton on top of the sample.

4.2 Soxhlet Extraction

a. Using 300 ml chloroform, extract bottom sediment sample for 18 hours (at 60°C).

b. Transfer extract to 250 ml beaker and concentrate on a steam bath to about 10 ml; add one drop 0.005% paraffin oil in hexane prior to evaporation.

4.3 Wet Extraction Procedure

Extraction of soils and bottom sediments. Weigh a 100g sample into a liter erlenmeyer flask. Add distilled water to effect a slurry. Add 2 ml of extraction solvent (hexane/IPA, 3:1) per gram of sample and shake vigorously for 20 minutes using a wrist action shaker or equivalent. Decant and collect the hexane phase into a separatory funnel. Repeat extraction of the bottom sediment/aqueous phase two more times quantitatively decanting the hexane portions each time into the separatory funnel. Wash any remaining alcohol from combined hexane extracts with water, dry over sodium sulfate, and concentrate to an appropriate volume.

4.4 Column Chromatography

a. Prepare a five inch column with 3/4" at top and 1/2" at bottom anhydrous sodium sulfate plus 15 gram Florisil which has been activated 5 hours at 130°C and stored in a desiccator to cool; or for samples containing large quantities of waxes and pigments, use a column containing a mixture of Nuchar C-190 (5g) plus Celite (10 grams). Column may be reduced to 3/8" diameter x 12" (made from glass tubing drawn to approximately 1/16"tip) packed with 1/2" x 1/2" glass wool; reagents must be reduced by a factor of 10.

b. Pre-wet the column with 50 ml of hexane.

c. Place the extract on the column and elute into a 200 ml volumetric flask with 200 ml 6%, 15% and 30% or 50% ethyl ether in hexane.

d. Concentrate the sample from step c to approximately 5 ml in a 250 ml beaker; then transfer to a 15 ml centrifuge tube and concentrate to a volume of 0.1 to 1 ml.

e. The following pesticides are eluted by the above mixtures of ethyl ether and hexane.

ETHYL ETHER IN HEXANE

6%	15%	30% or 50%
Lindane	Dieldrin	Generally elute
BHC	Endrin	Thiophosphate Pesticides
Kelthane	Endosulfan II	
Aldrin	Lindane	50% E. Ether elutes
Heptachlor	Kelthane(possible	Guthion
DDE	trace of total)	
TDE (DDD)		
DDT		
Perthane		
Heptachlor or epoxide		
Methoxychlor		
Toxaphene		
Strobane		
Chlordane		
Endosulfan I		

APPENDIX L

APPROVED EPA ANALYTICAL METHODS FOR METALS BY ATOMIC ABSORPTION

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APPENDIX L

APPROVED EPA ANALYTICAL METHODS FOR METALS BY ATOMIC ABSORPTION

Metals*

(Atomic Absorption Methods)

1. Scope and Application

   1.1 Metals in solution may be readily determined by atomic absorption spectroscopy. The method is simple, rapid, and applicable to a large number of metals in drinking, surface, and saline waters, and domestic and industrial wastes. While drinking waters may be analyzed directly, domestic and industrial wastes require processing to solubilize suspended material. Sludges, sediments and other solid type samples may also be analyzed after proper pretreatment.

   1.2 Detection limits, sensitivity and optimum ranges of the metals will vary with the various makes and models of satisfactory atomic absorption spectrophotometers. The data shown in Table 1, however, provide some indication of the actual concentration ranges measurable with conventional atomization. In the majority of instances the concentration range shown in the table may be extended much lower with scale expansion and conversely extended upwards by using a less sensitive wavelength or by rotating the burner 90 degrees. Detection limits may also be extended through concentration of the sample, through solvent extraction techniques and/or the use of the so called furnace techniques. The latter includes the heated graphite atomizer, the carbon rod and the tantalum strip accessories. When using furnace techniques, however, the analyst should be cautibned as to possible chemical reactions occurring at elevated temperatures which may result in either suppression or enhancement of the analysis element. Methods of standard addition are mandatory with these furnace techniques to insure valid data.

   1.3 Where conventional, atomic absorption techniques do not provide adequate sensitivity, reference is made to colorimetric or specialized procedures. Examples of these specialized techniques would be the gaseous hydride method for arsenic and selenium and the cold vapor technique for mercury.

*Adapted from "Manual of Method for Chemical Analysis of Water and Wastes", EPA-6251/6-74003, (1974).

TABLE 1
Atomic Absorption Concentration Ranges With Conventional Atomization***

Metal	Detection Limit mg/l	Sensitivity mg/l	Optimum Concentration Range mg/l
Aluminum	0.1	1	5 – 100
Antimony	0.2	0.5	1 – 40
Arsenic*	0.002	–	0.002 – 0.02
Barium	0.03	0.4	1 – 20
Beryllium	0.005	0.025	0.05 – 2
Cadmium	0.002	0.025	0.05 – 2
Calcium	0.003	0.08	0.2 – 20
Chromium	0.02	0.1	0.2 – 10
Cobalt	0.03	0.2	0.5 – 10
Copper	0.01	0.1	0.2 – 10
Iron	0.02	0.12	0.3 – 10
Lead	0.05	0.5	1 – 20
Magnesium	0.0005	0.007	0.02 – 2
Manganese	0.01	0.05	0.1 – 10
Mercury**	0.0002	–	0.0002 – 0.01
Molybdenum	0.1	0.3	0.5 – 20
Nickel	0.02	0.15	0.3 – 10
Potassium	0.005	0.04	0.1 – 2
Selenium*	0.002	–	0.002 – 0.02
Silver	0.01	0.06	0.1 – 4
Sodium	0.002	0.015	0.03 – 1
Thallium	0.1	0.5	1 – 20
Tin	0.8	4	10 – 200
Titanium	0.3	2	5 – 100
Vanadium	0.2	0.8	1 – 100
Zinc	0.005	0.02	0.05 – 2

*Gaseous hydride method.

**Cold vapor technique.

***The concentrations shown above are not contrived values and should be obtainable with conventional aspiration on any satisfactory atomic absorption spectrophotometer.

2. Summary of Method

2.1 Atomic absorption spectroscopy is similar to flame emission photometry in that a sample is atomized and aspirated into a flame. Flame photometry, however, measures the amount of light emitted, whereas, in atomic absorption spectrophotometry a light beam is directed through the flame into a monochromator, and onto a detector that measures the amount of light absorbed. In many instances absorption is more sensitive because it depends upon the presence of free unexcited atoms and generally the ratio of unexited to excited atoms at a given moment is very high. Since the wavelength of the light beam is characteristic of only the metal being determined, the light energy absorbed by the flame is a measure of the concentration of that metal in the sample. This principle is the basis of atomic absorption spectroscopy.

2.2 Although methods have been reported for the analysis of solids by atomic absorption spectroscopy (Spectrochim Acta, *24B* 53, 1969) the technique generally is limited to metals in solution or solubilized through some form of sample processing.

2.2.1 Preliminary treatment of wastewater and/or industrial effluents is usually necessary because of the complexity and variability of the sample matrix. Suspended material must be solubilized through some form of digestion. This may vary because of the metals to be determined but generally will include a wet digestion with nitric acid.

2.2.2 In those instances where complete characterization of a sample is desired, the suspended material must be analyzed separately. This may be accomplished by filtration and acid digestion of the suspended material. Metallic constituents in this acid digest are subsequently determined and the sum of the dissolved plus suspended concentrations will then provide the total concentrations present. The sample should be filtered as soon as possible after collection and the filtrate acidified immediately.

2.2.3 The total sample may also be treated with acid before filtration to measure what may be termed "extractable" concentrations.

3. Definition of Terms

3.1 Sensitivity: The concentration in milligrams of metal per liter that produces an absorption of 1%.

3.2 Detection Limit: The concentration that produces absorption equivalent to twice the magnitude of the fluctuation in the background (zero absorption).

3.3 Dissolved Metals: Those constituents (metals) which will pass through a 0.45 μ membrane filter.

3.4 Suspended Metals: Those constituents (metals) which are retained by a 0.45 μ membrane filter.

3.5 Total Metals: The concentration of metals determined on an unfiltered sample following vigorous digestion (Section 4.1.3), or the sum of the concentrations of metals in both the dissolved and suspended fractions.

3.6 Extractable Metals: The concentration of metals in an unfiltered sample following treatment with hot dilute mineral acid (Section 4.1.4).

4. Sample Handling and Preservation

4.1 For the determination of trace metals, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. For liquid samples, containers can introduce either positive or negative errors in the measurement of trace metals by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis requires particular attention. The sample bottle should be thoroughly washed with detergent and tap water; rinsed with 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water and finally deionized distilled water in that order.

NOTE 1: Chromic acid may be useful to remove organic deposits from glassware; however, the analyst should be cautioned that the glassware must be thoroughly rinsed with water to remove the last traces of chromium. This is especially important if chromium is to be included in the analytical scheme. Chromic acid should not be used with plastic bottles.

Before collection of the sample a decision must be made as to the type of data desired, i.e., dissolved, suspended, total or extractable.

4.1.1 For the determination of dissolved constituents the sample must be filtered through a 0.45 μ membrane filter as soon as practical after collection. (Glass or plastic filtering apparatus are recommended to avoid possible contamination.) Use the first 50-100 ml to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with 1:1 redistilled HNO_3 to a pH of 2. Normally, 3 ml of (1:1) acid per liter should be sufficient to preserve the sample (See Note

2). Analyses performed on a sample so treated shall be reported as "dissolved" concentrations.

NOTE 2: It has been suggested (International Biological Program, Symposium on Analytical Methods, Amsterdam, Oct. 1966) that additional acid, as much as 25 ml of conc. HCl/liter, may be required to stabilize certain types of highly buffered samples if they are to be stored for any length of time. Therefore, special precautions should be observed for preservation and storage of unusual samples intended for metal analysis.

4.1.2. For the determination of suspended metals a representative volume of unpreserved sample must be filtered through a 0.45 μ membrane filter. When considerable suspended material is present, as little as 100 ml of a well mixed sample is filtered.

Record the volume filtered and transfer the membrane filter containing the insoluble material to a 250 ml Griffin beaker and add 3 ml conc. redistilled HNO_3. Cover the beaker with a watch glass and heat gently. The warm acid will soon dissolve the membrane. Increase the temperature of the hot plate and digest the material. When the acid has evaporated, cool the beaker and watch glass and add another 3 ml of conc. redistilled HNO_3.

Cover and continue heating until the digestion is complete, generally indicated by a light colored residue. Add distilled 1:1 HCl (2 ml) to the dry residue and again warm the beaker gently to dissolve the material. Wash down the watch glass and beaker walls with deionized distilled water and filter the sample to remove silicates and other insoluble material that could clog the atomizer. Adjust the volume to some predetermined value based on the expected concentrations of metals present. This volume will vary depending on the metal to be determined. The sample is now ready for analysis. Concentrations so determined shall be reported as "suspended".

4.1.3 For the determination of total metals the sample is acidified with 1:1 redistilled HNO_3 to a pH of 2 at the time of collection. The sample is not filtered before processing. Choose a volume of sample appropriate for the expected level of metals. If much suspended material is present, as little as 50-100 ml of well mixed sample will most probably be

sufficient. (The sample volume required may also vary proportionally with the number of metals to be determined).

Transfer a representative aliquot of the well mixed sample to a Griffin beaker and add 3 ml of conc. redistilled HNO_3. Place the beaker on a hot plate and evaporate to dryness cautiously, making certain that the sample does not boil. Cool the beaker and add another 3 ml portion of conc. redistilled HNO_3. Cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated by a light colored residue). Add sufficient distilled 1:1 HCl and again warm the beaker to dissolve the residue. Wash down the beaker walls and watch glass with distilled water and filter the sample to remove silicates and other insoluble material that could clog the atomizer. Adjust the volume to some predetermined value based on the expected metal concentrations. The sample is now ready for analysis. Concentrations so determined shall be reported as "total" (See Note 3). STORET parameter numbers for reporting this type of data have been assigned and are given for each metal.

NOTE 3: Certain metals such as titanium, silver, mercury, and arsenic require modification of the digestion procedure and the individual sheets for these metals should be consulted.

4.1.4 To determine metals soluble in hot, dilute, HCl – HNO_3, acidify the entire sample at the time of collection with conc. redistilled HNO_3, 5 ml/l. At the time of analysis a 100 ml aliquot of well mixed sample is transferred to a beaker or flask. Five ml of distilled HCl (1:1) is added and the sample heated for 15 minutes at 95°C on a steam bath or hot plate. After this treatment the sample is filtered and the volume adjusted to 100 ml. The sample is then ready for analysis.

The data so obtained are significant in terms of "total" metals in the sample, with the reservation that something less than "total" is probably measured. Concentrations of metal found, especially in heavily silted samples, will be substantially higher than data obtained on only the soluble fraction. STORET parameter numbers for the storage of this type data are not available at this time.

5. Interferences

5.1 The most troublesome type of interference in atomic absorption spectrophotometry is usually termed "chemical" and is caused by lack of absorption of atoms bound in molecular combination in the flame. This phenomenon can occur when the flame is not sufficiently hot to dissociate the molecule, as in the case of phosphate interference with magnesium, or because the dissociated atom is immediately oxidized to a compound that will not dissociate further at the temperature of the flame. The addition of lanthanum will overcome the phosphate interference in the magnesium, calcium and barium determinations. Similarly, silica interference in the determination of manganese can be eliminated by the addition of calcium.

5.1.1 Chemical interferences may also be eliminated by separating the metal from the interfering material. While complexing agents are primarily employed to increase the sensitivity of the analysis, they may also be used to eliminate or reduce interferences.

5.2 The presence of high dissolved solids in the sample may result in an interference from non-atomic absorbance such as light scattering. If background correction is not available, a non-absorbing wavelength should be checked. Preferably, high solids type samples should be extracted (See 5.1.1 and 9.2).

5.3 Ionization interferences occur where the flame temperature is sufficiently high to generate the removal of an electron from a neutral atom, giving a positively charged ion. This type of interference can generally be controlled by the addition, to both standard and sample solutions, of a large excess of an easily ionized element.

5.4 Spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the width of the absorption line of the element of interest. The results of the determination will then be erroneously high, due to the contribution of the interfering element to the atomic absorption signal. Spectral interference may sometimes be reduced by narrowing the slit width.

6. Apparatus

6.1 Atomic absorption spectrophotometer: Any commercial atomic absorption instrument having an energy source, an atomizer burner system, a monochromator, and a detector is suitable.

6.2 Burner: The burner recommended by the particular instrument manufacturer should be used. For certain elements the nitrous oxide burner is required.

6.3 Separatory flasks: 250 ml, or larger, for extraction with organic solvents.

6.4 Glassware: All glassware, including sample bottles, should be washed with detergent, rinsed with tap water, 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water and deionized distilled water in that order. [See Note 1 under (4.1) concerning the use of chromic acid.]

6.5 Borosilicate glass distillation apparatus.

7. Reagents

7.1 Deionized distilled water: Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized distilled water for the preparation of all reagents, calibration standards, and as dilution water.

7.2 Nitric acid (conc.): If metal impurities are found to be present, distill reagent grade nitric acid in a borosilicate glass distillation apparatus. Prepare a 1:1 dilution with deionized distilled water.

Caution: Distillation should be performed in hood with protective sash in place.

7.3 Hydrochloric acid (1:1): Prepare a 1:1 solution of reagent grade hydrochloric acid and deionized distilled water. If metal impurities are found to be present, distill this mixture from a borosilicate glass distillation apparatus.

7.4 Stock metal solutions: Prepare as directed in (8.1) and under the individual metal procedures. Commercially available stock standard solutions may also be used.

7.5 Standard metal solutions: Prepare a series of standards of the metal by dilution of the appropriate stock metal solution to cover the concentration range desired.

7.6 Fuel and oxidant: Commercial grade acetylene is generally acceptable. Air may be supplied from a compressed air line, a laboratory compressor, or from a cylinder of compressed air. Reagent grade nitrous oxide is also required for certain determinations.

7.7 Special reagents for the extraction procedure.

7.7.1 Pyrrolidine dithiocarbamic acid (PDCA): Prepare by adding 18 ml of analytical reagent grade pyrrolidine to 500 ml of chloroform in a liter flask. Cool and add 15 ml of carbon disulfide in small portions and with swirling. Dilute to 1 liter with chloroform. The solution can be used for several months if stored in a brown bottle in a refrigerator.

7.7.2 Ammonium hydroxide, 2N: Dilute 3 ml conc. NH_4OH to 100 ml with deionized distilled water.

7.7.3 Bromphenol blue indicator.

7.7.4 HCl: Dilute 2 ml redistilled HCl to 40 ml with deionized distilled water.

8. Preparation of Standards and Calibration

8.1 Stock solutions are prepared from high purity metals, oxides or nonhygroscopic reagent grade salts using redistilled nitric or hydrochloric acids. Sulfuric or *phosphoric acids should be avoided as they produce an adverse effect on many* elements. The stock solutions are prepared at concentrations of 1000 mg of the metal per liter.

8.2 Standard solutions are prepared by diluting the stock metal solutions at the time of analysis. For best results, calibration standards should be prepared fresh each time an analysis is to be made and discarded after use. Prepare a blank and calibration standards in graduated amounts in the appropriate range. The *calibration standards* should be prepared using the same type of acid (HCl, HNO_3 or H_2SO_4) and at the same concentration as will result in the samples following processing. As filtered water samples are preserved with 1:1 redistilled HNO_3 (3 ml per liter), calibration standards for these analyses should be similarly prepared with HNO_3. Samples processed for suspended metals (4.1.2) or total metals (4.1.3) should be analyzed using calibration standards prepared in HCl. Beginning with the blank and working toward the highest standard, aspirate the solutions and record the readings. Repeat the operation with both the calibration standards and the samples a sufficient number of times to secure a reliable average reading for each solution.

8.3 Where the sample matrix is so complex that viscosity, surface tension and components cannot be accurately matched with standards, the method of standard addition must be used. This technique relies on the addition of small, known amounts of the analysis element to portions of the sample – the absorbance difference between those and the original solution giving the slope of the calibration curve. The method of standard addition is described in greater detail in (8.5).

8.4 For those instruments which do not read out directly in concentration, a calibration curve is prepared to cover the appropriate concentration range. Usually, this means the preparation of standards which produce an absorption of 0 to 80 percent. The correct method is to convert the percent absorption readings to absorbance and plot that value against concentration. The following relationship is used to convert absorption values to absorbance:

$$\text{absorbance} = \log(100/\%T) = 2 - \log \%T$$

where $\%T = 100 - \%$ absorption

As the curves are frequently nonlinear, especially at high absorption values, the number of standards should be increased in that portion of the curve.

8.5 Standard Addition Method: In this method, equal volumes of sample are added to a deionized distilled water blank and to three standards containing different known amounts of the test element. The volume of the blank and the standards must be the same. The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An example of a plot so obtained is shown in Fig. 1.

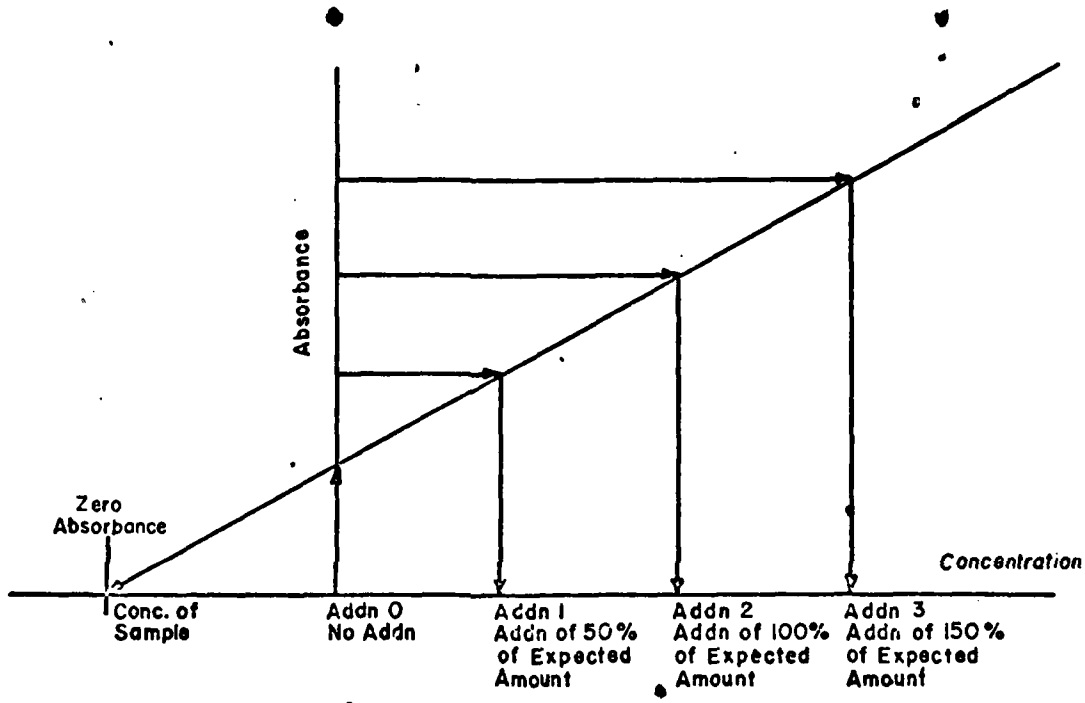

FIGURE 1. STANDARD ADDITION PLOT

9. General Procedure for Analysis by Atomic Absorption

9.1 Differences between the various makes and models of satisfactory atomic absorption spectrophotometers prevent the formulation of detailed instructions applicable to every instrument. The analyst should follow the manufacturer's operating instructions for his particular instrument. In general, after choosing the proper hollow cathode lamp for the analysis, the lamp should be allowed to warm up for a minimum of 15 minutes. During this period, align the instrument, position the monochromator at the correct wavelength, select the proper monochromator slit width, and adjust the hollow cathode current according to the manufacturer's recommendation. Subsequently, light the flame and regulate the flow of fuel and oxidant, adjust the burner and nebulizer flow rate for maximum percent absorption and stability, and balance the photometer. Run a series of standards of the element under analysis and construct working curves by plotting the concentrations of the standards against the absorbance. For those instruments which read directly in concentration set the curve corrector to read out the proper concentration. Aspirate the samples and determine the concentrations either directly or from the calibration curve. For best results run standards each time a sample or series of samples are run.

9.2 Special Extraction Procedure: When the concentration of the metal is not sufficiently high to determine directly, or when considerable dissolved solids are present in the sample, certain of the metals may be chelated and extracted with organic solvents. Ammonium pyrrolidine dithiocarbamate (APDC) in methyl isobutyl ketone (MIBK) is widely used for this purpose and is particularly useful for zinc, cadmium, iron, manganese, copper, silver, lead and chromium[1,6]. Tri-valent chromium does not react with APDC unless it has first been converted to the hexavalent form [Atomic Absorption Newsletter *6*, p 128 (1967)]. Aluminum, beryllium, barium and strontium also do not react with APDC. While the APDC-MIBK chelating-solvent system can be used satisfactorily, it is possible to experience difficulties. Also, when multiple metals are to be determined either larger sample volumes must be extracted or individual extractions made for each metal being determined. The acid form of APDC-pyrrolidine dithiocarbamic acid prepared directly in chloroform as described by Lakanen, [Atomic Absorption Newsletter 5, p 17 (1966)], has been found to be most advantageous. It is very stable and may be stored in a brown bottle in the refrigerator for months. Because chloroform is used as the solvent, it may not be aspirated into the flame. The following procedure is suggested.

9.2.1 Extraction Procedure with pyrrolidine dithiocarbamic acid (PDCA) in chloroform.

a. Transfer 200 ml of sample into a 250 ml separatory funnel, add 2 drops bromphenol blue indicator solution (7.7.3) and mix.

b. Prepare a blank and sufficient standards in the same manner and adjust the volume of each to approximately 200 ml with deionized distilled water. All of the metals to be determined may be combined into single solutions at the appropriate concentration levels.

c. Adjust the pH by addition of 2N NH_4OH solution (7.7.2) until a blue color persists. Add HCl (7.7.4) dropwise until the blue color just disappears; then add 2.0 ml HCl (7.7.4) in excess. The pH at this point should be 2.3. (The pH adjustment may be made with a pH meter instead of using indicator).

d. Add 5 ml of PDCA-chloroform reagent (7.7.1) and shake vigorously for 2 minutes. Allow the phases to separate and drain the chloroform layer into a 100 ml beaker.

e. Add a second portion of 5 ml PDCA-chloroform reagent (7.7.1) and shake vigorously for 2 minutes. Allow the phases to separate and combine the chloroform phase with that obtained in step (d).

f. Determine the pH of the aqueous phase and adjust to 4.5.

g. Repeat step (d) again combining the solvent extracts.

h. Readjust the pH to 5.5, extract, readjust to 6.5 and extract a fifth time. Combine all extracts and evaporate to dryness on a steam bath.

i. Hold the beaker at a 45 degree angle, and slowly add 2 ml of conc. distilled nitric acid, rotating the beaker to effect thorough contact of the acid with the residue.

j. Place the beaker on a low temperature hotplate and evaporate just to dryness.

k. Add 2 ml of nitric acid (1:1) to the beaker and heat for 1 minute. Cool, quantitatively transfer the solution to a 10 ml volumetric flask and bring to volume with distilled water. The sample is now ready for analysis.

9.3 Special Techniques

9.3.1 General-purpose electrically heated devices (flameless atomization) have recently been introduced as a means of extending detection limits. These techniques are generally acceptable but the analyst should be cautioned as to possible suppression or enhancement effects. With flameless atomization, background correction becomes of high importance. This is because certain samples, when atomized, may absorb or scatter light from the hollow cathode lamp. It can be caused by the presence of gaseous molecular species, salt particles, or smoke in the sample beam. If no correction is made, sample absorbance will be greater than it should be, and the analytical result will be erroneously high.

9.3.2 Analytical Methods for Atomic Absorption Spectroscopy using the HGA Graphite Furnace

9.3.2.1
The technique of flameless atomic absorption enables one to determine metals in amounts as low as 10^{-12} g. The HGA is a supplement to conventional flame techniques and may prove to be an advantage over the flame in many circumstances. One may choose to use the HGA rather than the flame for one of the following reasons:

The HGA offers sensitivities and detection limits 100 to 1000 times better than the flame for most metals. This allows, for example, the determination of many elements in natural or waste waters at less than 10 µg/l without sample pre-concentration.

Liquid samples do not necessarily have to be completely in solution. The HGA has been used to analyze homogeneous suspensions and emulsions that would clog a conventional flame burner system.

Solid samples can often be analyzed with no sample preparation. Such solids as plastics, papers, fingernails and plant tissue have been analyzed directly in the HGA without prior dissolution.

9.3.2.2
There are circumstances where one would not choose to use the HGA in place of the flame. If the sample is in the form of a solution and contains high enough concentrations of the elements to be determined accurately by conventional flame techniques, then the HGA would offer little advantage.

9.3.2.3

The Graphite Furnace can be installed in the burner compartment of any atomic absorption spectrophotometer. The HGA- uses a graphite tube, about 28 mm long and 8 mm in diameter, placed so that the sample beam of the spectrophotometer passes through it. Samples in solution are pipetted through a sample introduction hole in the center of the tube. Solid samples are introduced through the end of the tube. The tube is heated in three stages by passing an electrical current through its walls. First, a low current is used to dry the sample. Then, an intermediate current is applied that chars or ashes the sample. Finally, a high current is applied, heating the tube to incandescence and atomizing the sample.

9.3.2.4

With the HGA- , most metallic elements can be determined with sensitivities and detection limits 50 to 1000 times better than obtainable with conventional burner-nebulizer systems. A given amount of element in the Graphite Furnace gives a much higher absorption signal than it would in a burner for two reasons. In a burner, a large proportion of the sample flows down the drain, while the Graphite Furnace is much more efficient. Also, residence time of the sample atoms in the Graphite Furnace is on the order of seconds while in the flame, sample atoms leave the optical path in a small fraction of a second. The HGA- provides fast, peak-shaped signals, which can be read with a peak reader or on a strip chart recorder.

9.3.2.5

With the HGA- Energy Control Unit (Power Supply) temperature programming is automated. Separate, continuously adjustable controls are provided to set the desired temperature for the Drying, Charring, and Atomization stages. Separate, continuously adjustable timers are also provided for controlling the duration of each step. Once the appropriate temperatures and times have been selected, it is necessary only to insert the sample and push the PROGRAM button. The HGA- Energy Control Unit automatically proceeds through the three temperature steps, stopping after completion of the Atomization stage.

10. Calculation

10.1 Direct determination of liquid samples: Read the metal value in mg/l from the calibration curve or directly from the readout system of the instrument.

10.1.1 If dilution of sample was required:

mg/l metal in sample = (mg/l of metal in the diluted aliquot) X D

$$\text{where } D = \frac{\left(\begin{array}{c}\text{ml of}\\ \text{aliquot}\end{array}\right) + \left(\begin{array}{c}\text{ml of deionized}\\ \text{distilled water}\end{array}\right)}{\text{ml of aliquot}}$$

10.2 For samples containing particulates:

$$\text{mg/l metal in sample} = \frac{A \times B}{C}$$

where:

A = mg/l of metal in processed sample

B = final volume of processed sample in ml

C = volume of sample aliquot processed in ml

10.3 For solid samples: Report all concentrations as mg/kg dry weight.

10.3.1 Dry sample

$$\text{mg/kg} = \frac{\left(\begin{array}{c}\text{mg/l of constituent}\\ \text{in prepared sample}\end{array}\right) \times \left(\begin{array}{c}\text{volume of prepared}\\ \text{sample in ml}\end{array}\right)}{\text{weight of dry sample in g}}$$

10.3.2 Wet sample

$$\text{mg/kg} = \frac{\left(\begin{array}{c}\text{mg/l of constituent}\\ \text{in prepared sample}\end{array}\right) \times \left(\begin{array}{c}\text{volume of prepared}\\ \text{sample in ml}\end{array}\right)}{(\text{weight of wet sample in g}) \times (\% \text{ solids})}$$

11. Specific Procedures

11.1 Arsenic (Gaseous Hydride Method)

STORET NO. Total 01002

1. Scope and Application

   1.1 The gaseous hydride method determines inorganic arsenic when present in concentrations at or above 2 µg/l. The method is applicable to most fresh and saline waters in the absence of high concentrations of chromium, cobalt, copper, mercury, molybdenum, nickel and silver.

2. Summary of Method

   2.1 Arsenic in the sample is first reduced to the trivalent form using $SnCl_2$ and converted to arsine, AsH_3, using zinc metal. The gaseous hydride is swept into an argon-hydrogen flame of an atomic absorption spectrophotometer. The working range of the method is 2-20 µg/l. The 193.7 nm wavelength line is used.

3. Comments

   3.1 In analyzing most surface and ground waters, interferences are rarely encountered. Industrial waste samples should be spiked with a known amount of arsenic to establish adequate recovery.

   3.2 Organic forms of arsenic must be converted to inorganic compounds and organic matter must be oxidized before beginning the analysis. The oxidation procedure given in Standard Methods, 13th Edition, Method 104B, p 65, Procedure 4.a has been found suitable.

   3.3 Data to be entered into STORET must be reported as µg/l.

11.2 Cadmium (Standard Conditions)

STORET NO. Total 01027

Optimum Concentration Range: 0.05-2 mg/l using a wavelength of 228.8 nm

Sensitivity: 0.025 mg/l

Detection Limit: 0.002 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 2.282 g of cadmium sulfate ($CdSO_4 \cdot 8H_2O$, analytical reagent grade) and dissolve in deionized distilled water. 1 ml = 1 mg Cd (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid (HCl or HNO_3) and at the same concentration as the samples for analysis.

Sample Preparation

1. The procedure for the determination of total metals as given in part 4.1.3 of the Atomic Absorption Methods section of this manual has been found to be satisfactory.

Instrumental Parameters (General)

1. Cadmium hollow cathode lamp
2. Wavelength: 228.8 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. For levels of cadmium below 20 µg/l, the extraction procedure is recommended.
2. Data to be entered into STORET must be reported as µg/l.

11.3 Chromium (Standard Conditions)

STORET NO. Total 01034

Optimum Concentration Range: 0.2-10 mg/l using a wavelength of 357.9 nm

Sensitivity: 0.1 mg/l

Detection Limit: 0.02 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.923 g of chromium trioxide (CrO_3, reagent grade) in deionized distilled water. When solution is complete, acidify with redistilled HNO_3 and dilute to 1 liter with deionized distilled water. 1 ml = 1 mg Cr (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid (HCl or HNO_3) and at the same concentration as the samples for analysis.

Sample Preparation

1. The procedure for the determination of total metals as given in part 4.1.3 of the Atomic Absorption Methods section of this manual has been found to be satisfactory.

Instrumental Parameters (General)

1. Chromium hollow cathode lamp
2. Wavelength: 357.9 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Slightly fuel rich

Notes

1. **For levels of chromium below 50 µg/l the extraction procedure is recommended.**
2. **Data to be entered into Storet must be reported as µg/l.**

11.4 Copper (Standard Conditions)

STORET NO. Total 01042

Optimum Concentration Range: 0.2-10 mg/l using a wavelength of 324.7 nm

Sensitivity: 0.1 mg/l

Detection Limit: 0.01 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.00 g of electrolyte copper (analytical reagent grade). Dissolve in 5 ml redistilled HNO_3 and make up to 1 liter with deionized distilled water. Final concentration is 1 mg Cu per ml (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid (HCl or HNO_3) and at the same concentration as the samples for analysis.

Sample Preparation

1. The procedure for the determination of total metals as given in part 4.1.3 of the Atomic Absorption Methods section of this manual has been found to be satisfactory.

Instrumental Parameters (General)

1. Copper hollow cathode lamp
2. Wavelength: 324.7 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. For levels of copper below 20 μg/l, the extraction procedure is recommended.

11.5 Lead (Standard Conditions)

STORET NO. Total 01051

Optimum Concentration Range: 1-20 mg/l using a wavelength of 283.3 nm

Sensitivity: 0.5 mg/l

Detection Limit: 0.05 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.599 g of lead nitrate, $Pb(NO_3)_2$ (analytical reagent grade), and dissolve in deionized distilled water. When solution is complete acidify with 10 ml redistilled HNO_3 and dilute to 1 liter with deionized distilled water. 1 ml = 1 mg Pb (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid (HCl or HNO_3) and at the same concentration as the samples for analysis.

Sample Preparation

1. The procedure for the determination of total metals as given in part 4.1.3 of the Atomic Absorption Methods section of this manual has been found to be satisfactory.

Instrumental Parameters (General)

1. Lead hollow cathode lamp
2. Wavelength: 283.3 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Slightly oxidizing

Notes

1. For levels of lead below 100 µg/l, the extraction procedure is recommended. The optimum pH for the extraction of lead is 2.8.
2. Data to be entered into STORET must be reported as µg/l.

11.6 Manganese (Standard Condition)

STORET NO. Total 01055

Optimum Concentration Range: 0.1-10 mg/l using a wavelength of 279.5 nm

Sensitivity: 0.05 mg/l

Detection Limit: 0.01 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.000 g of manganese metal (analytical reagent grade) and dissolve in 10 ml of redistilled HNO_3. When solution is complete dilute to 1 liter with 1% (V/V) HCl. 1 ml = 1 mg Mn (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid (HCl or HNO_3) and at the same concentration as the samples for analysis.

Sample Preparation

1. The procedure for the determination of total metals as given in part 4.1.3 of the Atomic Absorption Methods section of this manual has been found to be satisfactory.

Instrumental Parameters (General)

1. Manganese hollow cathode lamp
2. Wavelength: 279.5 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. For levels of manganese below 25 µg/l, the extraction procedure is recommended.
2. Data to be entered into STORET must be reported as µg/l.

11.7 Mercury in Water (Manual Cold Vapor Technique)

STORET NO. Total 71900

1. Scope and Application

   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

   1.2 In addition to inorganic forms of mercury, organic mercurials may also be present. These organo-mercury compounds will not respond to the flameless atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, a persulfate oxidation step following the addition of the permanganate has been included to insure that organomercury compounds, if present, will be oxidized to the mercuric ion before measurement. A heat step is required for methyl mercuric chloride when present in or spiked to a natural system. For distilled water the heat step is not necessary.

   1.3 The range of the method may be varied through instrument and/or recorder expansion. Using a 100 ml sample, a detection limit of 0.2 μg Hg/l can be achieved; concentrations below this level should be reported as <0.2

2. Summary of Method

   2.1 The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration and recorded in the usual manner.

3. Sample Handling and Preservation

   3.1 Until more conclusive data are obtained, samples should be preserved by acidification with nitric acid to a pH of 2 or lower immediately at the time of collection. If only dissolved mercury is to be determined, the sample should be

filtered through an all glass apparatus before the acid is added. For total mercury the filtration is omitted.

4. Interference

4.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/l of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from distilled water.

4.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/l had no effect on recovery of mercury from spiked samples.

4.3 Sea waters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 ml). During the oxidation step, chlorides are converted to free chlorine which will also absorb radiation at 253 nm. Care must be taken to assure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 ml). In addition, the dead air space in the BOD bottle must be purged before the addition of stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from sea water using this technique.

4.4 Interference from certain volatile organic materials which will absorb at this wavelength is also possible. A preliminary run without reagents should determine if this type of interference is present

5. Apparatus

5.1 Atomic Absorption Spectrophotometer: (See Note 1) Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Note 1: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

5.2 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.

5.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

5.4 Absorption Cell: Standard spectrophotometer cells 10 cm long, having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1" O.D. X 4-1/2". The ends are ground perpendicular to the longitudinal axis and quartz windows (1" diameter X 1/16" thickness) are cemented in place. Gas inlet and outlet ports (also of plexiglass but 1/4" O.D.) are attached approximately

1/2" from each end. The cell is strapped to a burner for support and aligned in the light beam by use of two 2" by 2" cards. One inch diameter holes are cut in the middle of each card; the cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

5.5 Air Pump: Any peristaltic pump capable of delivering 1 liter of air per minute may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

5.6 Flowmeter: Capable of measuring an air flow of 1 liter per minute.

5.7 Aeration Tubing: A straight glass frit having a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

5.8 Drying Tube: 6" X 3/4" diameter tube containing 20 g of magnesium perchlorate (see Note 2). The apparatus is assembled as shown in Figure 1.

NOTE 2: In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

6. Reagents

6.1 Sulfuric Acid, Conc: Reagent grade.

6.1.1 Sulfuric acid, 0.5 N: Dilute 14.0 ml of conc. sulfuric acid to 1.0 liter.

6.2 Nitric Acid, Conc: Reagent grade of low mercury content (See Note 3).

NOTE 3: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

6.3 Stannous Sulfate: Add 25 g stannous sulfate to 250 ml of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

6.4 Sodium Chloride-Hydroxylamine Sulfate Solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100.0 ml. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

6.5 Potassium Permanganate: 5% solution, w/v. Dissolve 5 g of potassium permanganate in 100 ml of distilled water.

6.6 Potassium Persulfate: 5% solution, w/v. Dissolve 5 g of potassium persulfate in 100 ml of distilled water.

6.7 Stock Mercury Solution: Dissolve 0.1354 g of mercuric chloride in 75 ml of distilled water. Add 10 ml of conc. nitric acid and adjust the volume to 100.0 ml. 1 ml = 1 mg Hg.

6.8 Working Mercury Solution: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 μg per ml. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

7. Calibration

7.1 Transfer 0, 0.5, 1.0, 2.0, 5.0 and 10.0 ml aliquots of the working mercury solution containing 0 to 1.0 μg of mercury to a series of 300 ml BOD bottles. Add enough distilled water to each bottle to make a total volume of 100 ml. Mix thoroughly and add 5 ml of conc. sulfuric acid (6.1) and 2.5 ml of conc. nitric acid (6.2) to each bottle. Add 15 ml of $KMnO_4$ (6.5) solution to each bottle and allow to stand at least 15 minutes. Add 8 ml of potassium persulfate (6.6) to each bottle and heat for 2 hours in a water bath maintained at 95°C. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. When the solution has been decolorized wait 30 seconds, add 5 ml of the stannous sulfate solution (6.3) and immediately attach the bottle to the aeration apparatus forming a closed system. At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter per minute, is allowed to run continuously (See Note 4). The absorbance will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass valve and continue the aeration until the absorbance returns to its minimum value (see Note 5). Close the bypass valve, remove the stopper and frit from the BOD bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury.

NOTE 4: An open system where the mercury vapor is passed through the absorption cell only once may be used instead of the closed system.

NOTE 5: Because of the toxic nature of mercury vapor precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as:

a) equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4

b) 0.25% iodine in a 3% KI solution

A specially treated charcoal that will adsorb mercury vapor is also available from Barnebey and Cheney, E. 8th Ave. and N. Cassidy St., Columbus, Ohio 43219, Cat. #580-13 or #580-22.

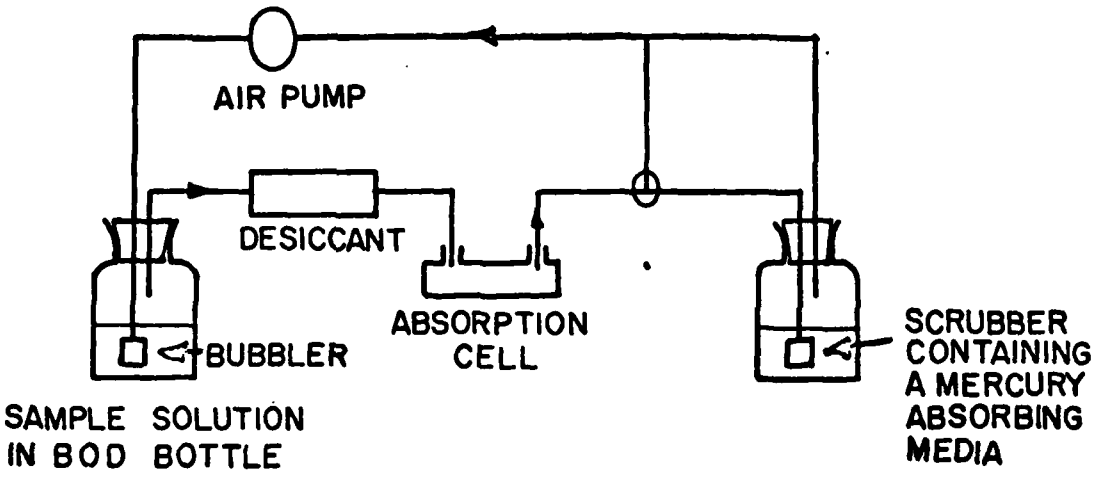

FIGURE 1. APPARATUS FOR FLAMELESS MERCURY DETERMINATION

8. Procedure

8.1 Transfer 100 ml or an aliquot diluted to 100 ml, containing not more than 1.0μg of mercury, to a 300 ml BOD bottle. Add 5 ml of sulfuric acid (6.1) and 2.5 ml of conc. nitric acid (6.2) mixing after each addition. Add 15 ml of potassium permanganate solution (6.5) to each sample bottle. For sewage samples additional permanganate may be required. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 minutes. Add 8 ml of potassium persulfate (6.6) to each bottle and heat for 2 hours in a water bath at 95°C. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate (6.4) to reduce the excess permanganate. After a delay of at least 30 seconds add 5 ml of stannous sulfate (6.3) and immediately attach the bottle to the aeration apparatus. Continue as described under Calibration.

9. Calculation

9.1 Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.

9.2 Calculate the mercury concentration in the sample by the formula:

$$\mu gHg/l = \left(\begin{matrix}\mu g\ Hg\ in \\ aliquot\end{matrix}\right)\left(\frac{1000}{\text{vol. of aliquot in ml.}}\right)$$

9.3 Report mercury concentrations as follows: Below 0.2 μg/l, <0.2; between 1 and 10 μg/l, one decimal; above 10 μg/l, whole numbers.

11.8 Mercury in Sediment (Manual Cold Vapor Technique)

1. Scope and Application
   1.1 This procedure measures total mercury (organic + inorganic) in soils, sediments, bottom deposits and sludge type materials.
   1.2 The range of the method is 0.2 to 5 μg/g. The range may be extended above or below the normal range by increasing or decreasing sample size or through instrument and recorder control.
2. Summary of Method
   2.1 A weighed portion of the sample is digested in aqua regia for 2 minutes at 95°C, followed by oxidation with potassium permanganate. Mercury in the digested sample is then measured by the conventional cold vapor technique.
3. Sample Handling and Preservation
   3.1 Because of the extreme sensitivity of the analytical procedure and the omnipresence of mercury, care must be taken to avoid extraneous contamination. Sampling devices and sample containers should be ascertained to be free of mercury; the sample should not be exposed to any condition in the laboratory that may result in contact or air-borne mercury contamination.
   3.2 While the sample may be analyzed without drying, it has been found to be more convenient to analyze a dry sample. Moisture may be driven off in a drying oven at a temperature of 60°C. No mercury losses have been observed by using this drying step. The dry sample should be pulverized and thoroughly mixed before the aliquot is weighed.
4. Interferences
   4.1 The same types of interferences that may occur in water samples are also possible with sediments, ie., sulfides, high copper, high chlorides, etc.
   4.2 Volatile materials which absorb at 253.7 nm will cause a positive interference. In order to remove any interfering volatile materials, the dead air space in the BOD bottle should be purged before the addition of stannous sulfate.
5. Apparatus
   5.1 Atomic Absorption Spectrophotometer (See Note 1): Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

NOTE 1: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

5.2 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.

5.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

5.4 Absorption Cell: Standard spectrophotometer cells 10 cm long, having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1" O.D. X 4-1/2". The ends are ground perpendicular to the longitudinal axis and quartz windows (1" diameter X 1/16" thickness) are cemented in place. Gas inlet and outlet ports (also of plexiglass but 1/4" O.D.) are attached approximately 1/2" from each end. The cell is strapped to a burner for support and aligned in the light beam to give the maximum transmittance.

NOTE 2: Two 2" X 2" cards with one inch diameter holes may be placed over each end of the cell to assist in positioning the cell for maximum transmittance.

5.5 Air Pump: Any peristaltic pump capable of delivering 1 liter of air per minute may be used. A Masterflex pump with electronic speed control has been found to be satisfactory. (Regulated compressed air can be used in an open one-pass system.)

5.6 Flowmeter: Capable of measuring an air flow of 1 liter per minute.

5.7 Aeration Tubing: Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return. Straight glass tubing terminating in a coarse porous frit is used for sparging air into the sample.

5.8 Drying Tube: 6" X 3/4" diameter tube containing 20 g of magnesium perchlorate (See Note 3). The apparatus is assembled as shown in the accompanying diagram.

NOTE 3: In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

6. Reagents

6.1 Aqua Regia: Prepare immediately before use by carefully adding three volumes of conc. HCl to one volume of conc. HNO_3.

6.2 Sulfuric Acid, 0.5 N: Dilute 14.0 ml of conc. sulfuric acid to 1 liter.

6.3 Stannous Sulfate: Add 25 g stannous sulfate to 250 ml of 0.5 N sulfuric acid (6.2). This mixture is a suspension and should be stirred continuously during use.

6.4 Sodium Chloride-Hydroxylamine Sulfate Solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100 ml.

NOTE 4: A 10% solution of stannous chloride may be substituted for (6.3) and hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate in (6.4).

6.5 Potassium Permanganate: 5% solution, w/v. Dissolve 5 g of potassium permanganate in 100 ml of distilled water.

6.6 Stock Mercury Solution: Dissolve 0.1354 g of mercuric chloride in 75 ml of distilled water. Add 10 ml of conc. nitric acid and adjust the volume to 100.0 ml. 1.0 ml = 1.0 mg Hg.

6.7 Working Mercury Solution: Make successive dilutions of the stock mercury solution (6.6) to obtain a working standard containing 0.1 μg/ml. This working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

7. Calibration

7.1 *Transfer 0, 0.5, 1.0, 2.0, 5.0 and 10 ml aliquots of the working mercury solution* (6.7) containing 0 to 1.0 μg of mercury to a series of 300 ml BOD bottles. Add enough distilled water to each bottle to make a total volume of 10 ml. Add 5 ml of aqua regia (6.1) and heat 2 minutes in a water bath at 95°C. Allow the sample to cool and add 50 ml distilled water and 15 ml of $KMnO_4$ solution (6.5) to each bottle and return to the water bath for 30 minutes. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. Add 50 ml of distilled water. Treating each bottle individually, add 5 ml of stannous sulfate solution (6.3) and immediately attach the bottle to the aeration apparatus. At this point, the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter per minute, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass valve and continue the aeration until the absorbance returns to its minimum value (See Note 5). Close the bypass valve, remove the fritted tubing from the BOD bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury.

NOTE 5: Because of the toxic nature of mercury vapor precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as:

a) equal volumes of 0.1 N $KMnO_4$ and 10% H_2SO_4

b) 0.25% iodine in a 3% KI solution.

A specially treated charcoal that will absorb mercury vapor is also available from Barnebey and Cheney, E. 8th Ave. and North Cassidy St., Columbus, Ohio 43219, Cat. #580-13 or #580-22.

8. Procedure

8.1 Weigh triplicate 0.2 g portions of dry sample and place in bottom of a BOD bottle. Add 5 ml of distilled water and 5 ml of aqua regia (6.1). Heat 2 minutes in a water bath at 95°C. Cool, add 50 ml distilled water and 15 ml potassium permanganate solution (6.5) to each sample bottle. Mix thoroughly and place in the water bath for 30 minutes at 95°C. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate (6.4) to reduce the excess permanganate. Add 55 ml of distilled water. Treating each bottle individually, add 5 ml of stannous sulfate (6.3) and immediately attach the bottle to the aeration apparatus. Continue as described under (7.1).

9. Calculation

9.1 Measure the peak height of the unknown from the chart and read the mercury value from the standard curve.

9.2 Calculate the mercury concentration in the sample by the formula:

$$\mu g\ Hg/g = \frac{\mu g\ Hg \text{ in the aliquot}}{\text{wt of the aliquot in gms.}}$$

9.3 Report mercury concentrations as follows: Below 0.1 μg/gm, <0.1; between 0.1 and 1 μg/gm, to the nearest 0.01 μg; between 1 and 10 μg/gm, to nearest 0.1 μg; above 10 μg/gm, to nearest μg.

11.9 Nickel (Standard Conditions)

STORET NO. Total 01067

Optimum Concentration Range: 0.3-10 mg/l using a wavelength of 232.0 nm

Sensitivity: 0.15 mg/l

Detection List: 0.02 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 4.953 g of nickel nitrate, $Ni(NO_3)_2 \cdot 6H_2O$ (analytical reagent grade) in deionized distilled water. Add 10 ml of conc. nitric acid and dilute to 1 liter with deionized distilled water. 1 ml = 1 mg Ni (1000 mg/l).
2. Prepare dilutions of the stock nickel solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid (HCl or HNO_3) and at the same concentration as the samples for analysis.

Sample Preparation

1. The procedure for the determination of total metals as given in part 4.1.3 of the Atomic Absorption Methods section of this manual has been found to be satisfactory.

Instrumental Parameters (General)

1. Nickel hollow cathode lamp
2. Wavelength: 232.0 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of Flame: Oxidizing

Interferences

1. The 352.4 nm wavelength is less susceptible to nonatomic absorbance and may be used. The calibration curve is more linear at this wavelength; however, there is some loss of sensitivity.

Notes

1. For levels of nickel below 50 µg/l, the extraction procedure is recommended.
2. Data to be entered into STORET must be reported as µg/l.

11.10 Zinc (Standard Conditions)

STORET NO. Total 01092

Optimum Concentration Range: 0.05-2 mg/l using a wavelength of 213.9 nm

Sensitivity: 0.02 mg/l

Detection Limit: 0.005 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.00 g of zinc metal (analytical reagent grade) and dissolve cautiously in 10 ml HNO_3. When solution is complete make up to 1 liter with deionized distilled water. 1 ml = 1 mg Zn (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid (HCl or HNO_3) and at the same concentration as the samples for analysis.

Sample Preparation

1. The procedure for the determination of total metals as given in part 4.1.3 of the Atomic Absorption Methods section of this manual has been found to be satisfactory.

Instrumental Parameters

1. Zinc hollow cathode lamp
2. Wavelength: 213.9 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. High levels of silicon may interfere.
2. The air-acetylene flame absorbs about 25% of the energy at the 213.9 nm line.
3. The sensitivity may be increased by the use of low-temperature flames.
4. Data to be entered into STORET must be reported as µg/l.

APPENDIX M

APPROVED EPA ANALYTICAL METHODS FOR ORGANOCHLORINE, PESTICIDES AND POLYCHORINATED BI-PHENYLS IN INDUSTRIAL EFFLUENTS

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APPENDIX M

APPROVED EPA ANALYTICAL METHODS FOR ORGANOCHLORINE PESTICIDES AND POLYCHLORINATED BI-PHENYLS IN INDUSTRIAL EFFLUENTS

Method for Organochlorine Pesticides in Industrial Effluents*

1. Scope and Application

1.1 This method covers the determination of various organochlorine pesticides, including some pesticidal degradation products and related compounds in industrial effluents. Such compounds are composed of carbon, hydrogen, and chlorine, but may also contain oxygen, sulfur, phosphorus, nitrogen or other halogens.

1.2 The following compounds may be determined individually by this method with a sensitivity of 1 µg/liter: **lindane, heptachlor, dieldrin, endrin, and DDT. Under favorable circumtances chlordane can also be determined.**

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

***Adapted from "National Discharge Elimination System, Appendix A; Federal Regulation 38, No. 75, Part II, with modification.**

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 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 Part 1, Sections 1.4 and 1.5, (1).

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 (PCB's) - Special attention is called to industrial plasticizers and hydraulic fluids such as the PCB's which are a potential source of interference in pesticide analysis. The presence of PCB's 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 (2,3).

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, eg, 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 (4).

4. Apparatus and Materials

4.1 Gas Chromatograph - Equipped with glass lined injection port.

4.2 Detector

4.2.1 Electron Capture - Radioactive (tritium or nickel 63)

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-17, 1.5% plus QF-1, 1.95%

4.5 Kuderna-Danish (K-D) Glassware (Kontes)

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 I).

5. Reagents, Solvents, and Standards

5.1 Ferrous Sulfate - (ACS) 30% solution in distilled water.

5.2 Potassium Iodide - (ACS) 10% solution in distilled water.

5.3 Sodium Chloride - (ACS) Saturated solution in distilled water (pre-rinse NaCl with hexane).

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

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

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

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

5.7.1 Must contain 2% alcohol and be free of peroxides by following test: To 10 ml of ether in glass-stoppered cylinder previously rinsed with ether, add one ml of freshly prepared 10% KI solution. Shake and let stand one minute. No yellow color should be observed in either layer.

5.7.2 Decompose ether peroxides by adding 40 g of 30% ferrous sulfate solution to each liter of solvent. CAUTION: Reaction may be vigorous if the solvent contains a high concentration of peroxides.

5.7.3 Distill deperoxidized ether in glass and add 2% ethanol.

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

5.9 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 $\leq$ 0.06 ng is injected for electron capture detection and $\leq$ 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.

7. Quality Control

7.1 Duplicate and spiked sample analyses are recommended as quality control checks.

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 Blend the sample if suspended matter is present and adjust pH to near neutral (pH 6.5-7.5) with 50% sulfuric acid or 10 N sodium hydroxide.

8.2 Quantitatively transfer the proper aliquot into a two-liter separatory funnel and dilute to one liter.

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.

9.3 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

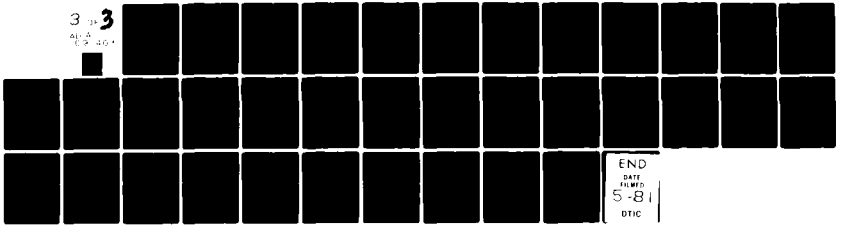
10.1 Interferences in the form of distinct peaks and/or high background in the initial gas chromatographic analysis, as well as the physical characteristics of the extract (color, cloudiness, viscosity) and background knowledge of the sample will indicate whether clean-up is required. When these interfere 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. Of the pesticides listed in Scope (1.2) only mirex is not 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

AD-A097 403 TEXAS UNIV AT ARLINGTON F/G 8/8
TRINITY RIVER BOTTOM SEDIMENT RECONNAISSANCE STUDY, PHASE I, PL--ETC(U)
NOV 76 S R QASIM, V H SORGEE, A T ARMSTRONG DACW63-76-C-0140
UNCLASSIFIED NL



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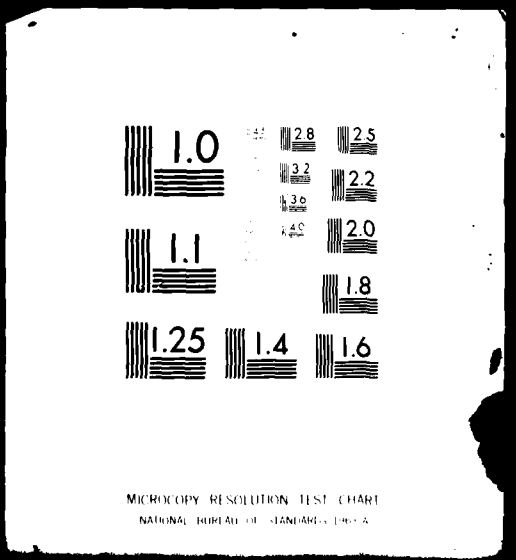

hexane by vigorously shaking about 15 seconds.

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 I) 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 washings. 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	Pentachloro-nitrobenzene
BHC	Heptachlor	
Chlordane	Heptachlor Epoxide	Strobane
DDD	Lindane	Toxaphene
DDE	Methoxychlor	Trifluralin
	Mirex	PCB's

15% Eluate

Endosulfan I
Endrin
Dieldrin
Dichloran
Phthalate esters

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 (6).

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 Part I, Section 3.4.2. (1).

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

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

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.

References

1. "Method for Organic Pesticides in Water and Wastewater," Environmental Protection Agency, National Environmental Research Center, Cincinnati, Ohio 45268, 1971.

2. Monsanto Methodology for Aroclors - Analysis of Environmental Materials for Biphenyls, Analytical Chemistry Method 71-35, Monsanto Company, St. Louis, Missouri 63166, 1970.

3. "Method for Polychlorinated Biphenyls in Industrial Effluents," Environmental Protection Agency, National Environmental Research Center, Cincinnati, Ohio 45268, 1973.

4. "Method for Organophosphorus Pesticides in Industrial Effluents," Environmental Protection Agency, National Environmental Research Center, Cincinnati Ohio 45268, 1973.

5. "Handbook for Analytical Quality Control in Water and Wastewater Laboratories," Chapter 6, Section 6.4, U.S. Environmental Protection Agency, National Environmental Research Center, Analytical Quality Control Laboratory, Cincinnati, Ohio 45268, 1973.

6. "Pesticide Analytical Manual," U.S. Dept. of Health, Education and Welfare, Food and Drug Administration, Washington, D.C.

7. "Analysis of Pesticide Residues in Human and Environmental Samples," U.S. Environmental Protection Agency, Perrine Primate Research Laboratories, Perrine, Florida 33157, 1971.

8. Mills, P.A., "Variation of Florisil Activity: Simple Method for Measuring Adsorbent Capacity and its Use in Standardizing Florisil Columns," Journal of the Association of Official Analytical Chemists, 51, 29 (1968).

9. Goerlitz, D.F. and Brown, E., "Methods for Analysis of Organic Substances in Water," Techniques of Water Resources Investigations of the United States Geological Survey, Book 5, Chapter A3, U.S. Department of the Interior, Geological Survey, Washington, D.C. 20402, 1972, pp. 24-40.

10. Steere, N.V., editor, "Handbook of Laboratory Safety," Chemical Rubber Company, 18901 Cranwood Parkway, Cleveland, Ohio 44128, 1971, pp. 250-254.

Appendix 1

13. Standardization of Florisil Column by Weight Adjustment Based on Adsorption of Lauric Acid.

13.1 A rapid method for determining adsorptive capacity of Florisil is based on adsorption of lauric acid from hexane solution (6) (8). An excess of lauric acid is used and amount not adsorbed is measured by alkali titration. Weight of lauric acid adsorbed is used to calculate, by simple proportion, equivalent quantities of Florisil for batches having different adsorptive capacities.

13.2 Apparatus

13.2.1 Buret. -- 25 ml with 1/10 ml graduations.

13.2.2 Erlenmeyer flasks. -- 125 ml narrow mouth and 25 ml, glass stoppered.

13.2.3 Pipet. -- 10 and 20 ml transfer.

13.2.4 Volumetric flasks. -- 500 ml.

13.3 Reagents and Solvents

13.3.1 Alcohol, ethyl. -- USP or absolute, neutralized to phenolphthalein.

13.3.2 Hexane. -- Distilled from all glass apparatus.

13.3.3 Lauric acid. --Purified, CP.

13.3.4 Lauric acid solution. -- Transfer 10.000 g lauric acid to 500 ml volumetric flask, dissolve in hexane, and dilute to 500 ml (1 ml = 20 mg).

13.3.5 Phenolphthalein Indicator. -- Dissolve 1 g in alcohol and dilute to 100 ml.

13.3.6 Sodium hydroxide. -- Dissolve 20 g NaOH (pellets, reagent grade) in water and dilute to 500 ml (1N). Dilute 25 ml 1N NaOH to 500 ml with water (0.05N). Standardize as follows: Weigh 100-200 mg lauric acid into 125 ml Erlenmeyer flask. Add 50 ml neutralized ethyl alcohol and 3 drops phenolphthalein indicator; titrate to permanent end point. Calculate mg lauric acid/ml 0.05 N NaOH (about 10 mg/ml).

13.4 Procedure

13.4.1 Transfer 2.000 g Florisil to 25 ml glass stoppered Erlenmeyer flasks. Cover loosely with aluminum foil and heat overnight at 130°C. Stopper, co l to room temperature, add 20.0 ml lauric acid solution (400 mg), stopper, and shake occasionally for 15 min. Let adsorbent settle and pipet 10.0 ml of supernatant into 125 ml Erlenmeyer flask. Avoid inclusion of any Florisil.

13.4.2 Add 50 ml neutral alcohol and 3 drops indicator solution; titrate with 0.05N to a permanent end point.

13.5 Calculation of Lauric Acid Value and Adjustment of Column Weight

13.5.1 Calculate amount of lauric acid adsorbed on Florisil as follows:

Lauric Acid value = mg lauric acid/g Florisil = 200 - (ml required for titration X mg lauric acid/ml 0.05N NaOH).

13.5.2 To obtain an equivalent quantity of any batch of Florisil, divide 110 by lauric acid value for that batch and multiply by 20 g. Verify proper elution of pesticides by 13.6.

Method for Polychlorinated Biphenyls (PCB's) in Industrial Effluents*

1. Scope and Application

   1.1 This method covers the determination of certain polychlorinated biphenyl (PCB) mixtures including: Aroclors 1221, 1232, 1242, 1248, 1254, 1260 and 1016.

   1.2 The method is an extension of the method for organochlorine pesticides in industrial effluents (1). It is designed so that determination of both the PCB's and the organochlorine pesticides may be made on the same sample.

   1.3 The limit of detection is approximately 1 µg/l for each Aroclor mixture.

2. Summary

   2.1 The PCB's and the organochlorine pesticides are co-extracted by liquid-liquid extraction and, insofar as possible, the two classes of compounds separated from one another prior to gas chromatographic determination. A combination of the standard Florisil column cleanup procedure and a silica gel microcolumn separation procedure (2)(3) are employed. Identification is made from gas chromatographic patterns obtained through the use of two or more unlike columns. Detection and measurement is accomplished using an electron capture, microcoulometric, or electrolytic conductivity detector. Techniques for confirming qualitative identification are suggested.

*Adapted from "National Discharge Elimination System, Appendix A, Federal Regulation, 38, No. 75, Part III, with modification.

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 (4), Part I, Sections 1.4 and 1.5.

3.2 The interferences in industrial effluents are high and varied and pose great difficulty in obtaining accurate and precise measurement of PCB's and organochlorine pesticides. Separation and cleanup procedures are generally required to eliminate these interferences; however, such techniques may result in the loss of certain organochlorine compounds. For this reason 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 wastes.

3.3 Phthalate esters, certain organophosphorus pesticides, and elemental sulfur will interfere when using electron capture for detection. These materials do not interfere when the microcoulometric or electrolytic conductivity detectors are used in the halogen mode.

3.4 Organochlorine pesticides and other halogenated compounds constitute interferences in the determination of PCB's. Most of these are separated by the method described below. However, certain compounds, if present in the sample, will occur with the PCB's. Included are: Sulfur, Heptachlor, aldrin, DDE, technical chlordane, mirex, and to some extent o,p'-DDT and p,p'-DDT.

4. Apparatus and Materials

4.1 Gas Chromatograph - Equipped with glass lined injection part.

4.2 Detector

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

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

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 SE-30 or OV-1, 3%

4.4.4.2 OV-17, 1.5% + QF-1, 1.95%

4.5 Kuderna-Danish (K-D) Glassware (Kontes)

4.5.1 Snyder Columns - three ball (macro)

4.5.2 Evaporate 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 a coarse fritted plate on bottom.

4.8 Micro Column Pyrex - constructed according to Figure 1.

4.9 Capillary pipets disposable (5-3/4 in.) with rubber bulb. (Scientific Products P5205-1).

4.10 Low pressure regulator - 0 to 5 PSIG - with low-flow needle valve (See Figure 1, Matheson Model 70).

4.11 Beaker - 100 ml

4.12 Micro syringes - 10, 25, 50 and 100 µl.

4.13 Separatory Funnels - 125 ml, 1000 ml, and 2000 ml with Teflon stopcocks

4.14 Graduated Cylinders - 100 ml, 250 ml.

4.15 Blender - High speed, glass or stainless cup.

4.16 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 in foil-covered glass container. Determine lauric-acid value (See Appendix I).

4.17 Silica gel - Davison code 950-08-08-226 (60/200 mesh).

4.18 Glass Wool - Hexane extracted.

4.19 Centrifuge Tubes - Pyrex calibrated (15 ml).

5. Reagents, Solvents and Standards

5.1 Ferrous Sulfate - (ACS) 30% solution in distilled water.

5.2 Potassium Iodide - (ACS) 10% solution in distilled water.

5.3 Sodium Chloride - (ACS) Saturated solution (pre-rinse NaCl with hexane) in distilled water.

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

5.5 Sodium Sulfate - (ACS) Granular, anhydrous, conditioned for 4 hours @ 400 C.

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

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

5.7.1 Must contain 2% alcohol and be free of peroxides by following test: to 10 ml of ether in glass-stoppered cylinder previously rinsed with ether, add one ml of freshly prepared 10% KI solution. Shake and let stand one minute. No yellow color should be observed in either layer.

5.7.2 Decompose ether peroxides by adding 40 g of 30% ferrous sulfate solution to each liter of solvent. CAUTION: Reaction may be vigorous if the solvent contains a high concentration of peroxides.

5.7.3 Distill deperoxidized ether in glass and add 2% ethanol.

5.8 n-Hexane - Pesticide quality (NOT MIXED HEXANES).

5.9 Acetonitrile, Hexane, Methanol, Methylene Chloride, Petroleum Ether (Boiling range 30-60 C) - pesticide quality, redistill in glass if necessary.

5.10 Standards - Aroclors 1221, 1232, 1242, 1248, 1254, 1260, and 1016.

5.11 Anti-static Solution - STATNUL, Daystrom, Inc., Weston Instrument Division, Newark, N.J. 95212.

6. Calibration

6.1 Gas chromatographic operating conditions are considered acceptable when the response to dicapthon is at least 50% of full scale when $\leq$ .06 ng is injected for electron capture detection and $\leq$ 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.

7. Quality Control

7.1 Duplicate and spiked sample analyses are recommended as a quality control check. When the routine occurrence of a pollution parameter is observed, quality control charts are also recommended (5).

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

8. Sample Preparation

8.1 Blend the sample if suspended matter is present and adjust pH to near neutral (pH 6.5-7.5) with 50% sulfuric acid or 10 N sodium hydroxide.

8.2 For sensitivity requirement of 1 µg/1, when using microcoulometric or electrolytic conductivity methods for detection take 1000 ml of sample for analysis. If interferences pose no problem, the sensitivity of the electron capture detector should permit as little as 100 ml of sample to be used. Background information on the extent and nature of interferences will assist the analyst in choosing the required sample size and preferred detector.

8.3 Quantitatively transfer the proper aliquot into a two-liter separatory funnel and dilute to one liter.

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.

9.3 Concentrate the extract to 6-10 ml in the K-D evaporator on a hot water bath.

9.4 Qualitatively analyze the sample by gas chromatography with an electron capture detector. From the response obtained decide:

a. If there are any organochlorine pesticides present,

b. If there are any PCB's present,

c. If there is a combination of a and b,

d. If elemental sulfur is present,

e. If the response is too complex to determine a, b, or c.

9.5 If condition a exists, quantitatively determine the organochlorine pesticides according to (1).

9.6 If condition b exists, PCB's only are present, no further separation or cleanup is necessary. Quantitatively determine the PCB's according to 11. below.

9.7 If condition c exists, compare peaks obtained from the sample to those of standard Aroclors and make a judgment as to which Aroclors may be present. To separate the PCB's from the organochlorine pesticides, continue as outlined in 10.4.

9.8 If condition d exists separate the sulfur from the sample using the method outlined in (10.3) followed by the method in (10.5).

9.9 If condition e exists then the following macro cleanup and separation procedures (10.2 and 10.3) should be employed and, if necessary, followed by the micro separation procedures (10.4 and 10.5).

10. Cleanup 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 cleanup 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 remove 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 the compounds of interest.

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 30-35 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 I) 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 washings. 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 below). 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.

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	Pentachloro-nitrobenzene
BHC	Heptachlor	
Chlordane	Heptachlor Epoxide	Strobane
DDD	Lindane	Toxaphene
DDE	Methoxychlor	Trifluralin
	Mirex	PCB's

15% Eluate	50% Eluate
Endosulfan I	Endosulfan II
Endrin	Captan
Dieldrin	
Dichloran	
Phthalate esters	

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 (6).

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 Silica Gel Micro-Column Separation Procedure (7)

10.4.1 Activation for Silica Gel

10.4.1.1 Place about 20 gm of silica gel in a 100 ml beaker. Activate at 180 C for approximately 16 hours. Transfer the silica gel to a 100 ml glass stoppered bottle. When cool, cover with about 35 ml of 0.50% diethyl ether in benzene (volume:volume). Keep bottle well sealed. If silica gel collects on the ground glass surfaces, wash off with the above solvent before resealing. Always maintain an excess of the mixed solvent in bottle (approximately 1/2 in. above silica gel). Silica gel can be effectively stored in this manner for several days.

10.4.2 Preparation of the Chromatographic Column

10.4.2.1 Pack the lower 2 mm ID Section of the microcolumn with glass wool. Permanently mark the column 120 mm above the glass wool. Using a clean rubber bulb from a disposable pipet seal the lower end of the microcolumn. Fill the microcolumn with 0.50% ether in benzene (v:v) to the bottom of the 10/30 joint (Figure 1). Using a disposable capillary pipet, transfer several aliquots of the silica gel slurry into the microcolumn. After approximately 1 cm of silica gel collects in the bottom of the microcolumn, remove the rubber

bulb seal, tap the column to insure that the silica gel settles uniformly. Carefully pack column until the silica gel reaches the 120 ± 2 mm mark. Be sure that there are no air bubbles in the column. Add about 10 mm of sodium sulfate to the top of the silica gel. Under low humidity conditions, the silica gel may coat the sides of the column and not settle properly. This can be minimized by wiping the outside of the column with an anti-static solution.

10.4.2.2 Deactivation of the Silica Gel

a. Fill the microcolumn to the base of the 10/30 joint with the 0.50% ether-benzene mixture, assemble reservoir (using spring clamps) and fill with approximately 15 ml of the 0.50% ether-benzene mixture. Attach the air pressure device (using spring clamps) and adjust the elution rate to approximately 1 ml/min. with the air pressure control. Release the air pressure and detach reservoir just as the last of the solvent enters the sodium sulfate. Fill the column with *n*-hexane (not mixed hexanes) to the base of the 10/30 fitting. Evaporate all residual benzene from the

reservoir, assemble the reservoir section and fill with 5 ml of n-hexane. Apply air pressure and adjust the flow to 1 ml/min. (The n-hexane flows slightly faster than the benzene). Release the air pressure and remove the reservoir just as the n-hexane enters the sodium sulfate. The column is now ready for use.

b. Pipet a 1.0 ml aliquot of the concentrated sample extract (previously reduced to a total volume of 2.0 ml) on to the column.

As the last of the sample passes into the sodium sulfate layer, rinse down the internal wall of the column twice with 0.25 ml of n-hexane. Then assemble the upper section of the column. As the last of the n-hexane rinse reaches the surface of the sodium sulfate, add enough n-hexane (volume predetermined, see 10.4.3 below) to just elute all of the PCB's present in the sample. Apply air pressure and adjust until the flow is 1 ml/min. Collect the desired volume of eluate (predetermined, see 10.4.3 below) in an accurately calibrated ampul. As the last of the n-hexane reaches the surface

of the sodium sulfate, release the air pressure and change the collection ampul.

c. Fill the column with 0.50% diethyl ether in benzene, again apply air pressure and adjust flow to 1 ml/min. Collect the eluate until all of the organochlorine pesticides of interest have been eluted (volume predetermined, see 10.4.3 below).

d. Analyze the eluates by gas chromatography.

10.4.3 Determination of Elution Volumes

10.4.3.1 The elution volumes for the PCB's and the pesticides depend upon a number of factors which are difficult to control. These include variation in:

a. Mesh size of the silica gel

b. Adsorption properties of the silica gel

c. Polar contaminants present in the eluting solvent

d. Polar materials present in the sample and sample solvent

e. The dimensions of the microcolumns

Therefore, the optimum elution volume must be experimentally determined each time a factor is changed. To determine the elution volumes, add standard mixtures of Aroclors and pesticides to the column and serially collect 1 ml elution

volumes. Analyze the individual eluates by gas chromatography and determine the cut-off volume for n-hexane and for ether-benzene. Figure 2 shows the retention order of the various PCB components and of the pesticides. Using this information, prepare the mixtures required for calibration of the microcolumn.

10.4.3.2 In determining the volume of hexane required to elute the PCB's the sample volume (1 ml) and the volume of n-hexane used to rinse the column wall must be considered. Thus, if it is determined that a 10.0 ml elution volume is required to elute the PCB's, the volume of hexane to be added in addition to the sample volume but including the rinse volume should be 9.5 ml.

10.4.3.3 Figure 2 shows that as the average chlorine content of a PCB mixture decreases the solvent volume for complete elution increases. Qualitative determination (9.4) indicates which Aroclors are present and provides the basis for selection of the ideal elution volume. This helps to minimize the quantity of organochlorine pesticides which will elute along with the low percent chlorine PCB's and insures the most efficient separations possible for accurate analysis.

10.4.3.4 For critical analysis where the PCB's and pesticides are not separated completely, the column should be accurately calibrated according to (10.4.3.1) to determine the percent of material of interest that elutes in each fraction. Then flush the column with an additional 15 ml of 0.50% ether in benzene followed by 5 ml of n-hexane and use this reconditioned column for the sample separation. Using this technique one can accurately predict the amount (%) of materials in each micro column fraction.

10.5 Micro Column Separation of Sulfur, PCB's, and Pesticides

10.5.1 See procedure for preparation and packing micro column in PCB analysis section (10.4.1 and 10.4.2).

10.5.2 Microcolumn Calibration

10.5.2.1 Calibrate the microcolumn for sulfur and PCB separation by collecting 1.0 ml fractions and analyzing them by gas chromatography to determine the following:

1) The fraction with the first eluting PCB's (those present in 1260),
2) The fraction with the last eluting PCB's (those present in 1221),
3) The elution volume for sulfur,
4) The elution volume for the pesticides of interest in the 0.50% ether-benzene fraction.

From these data determine the following:

1) The eluting volume containing only sulfur (Fraction I),
2) The eluting volume containing the last of the sulfur and the early eluting PCB's (Fraction II),
3) The eluting volume containing the remaining PCB's (Fraction III),
4) The ether-benzene eluting volume containing the pesticides of interest (Fraction IV).

10.5.3 Separation Procedure

10.5.3.1 Carefully concentrate the 6% eluate from the florisil column to 2.0 ml in the graduated ampul on a warm water bath.

10.5.3.2 Place 1.0 ml (50%) of the concentrate into the microcolumn with a 1 ml pipet. Be careful not to get any sulfur crystals into the pipet.

10.5.3.3 Collect Fractions I and II in calibrated centrifuge tubes.

Collect Fractions III and IV in calibrated ground glass stoppered ampules.

10.5.3.4 Sulfur Removal (9) - Add 1 to 2 drops of mercury to Fraction II stopper and place on a wrist-action shaker. A black precipitate indicates the presence of sulfur. After approxiately 20 minutes the mercury may become entirely reacted or deactivated

by the precipitate. The sample should be quantitatively transferred to a clean centrifuge tube and additional mercury added. When crystals are present in the sample, three treatments may be necessary to remove all the sulfur. After all the sulfur has been removed from Fraction II (check using gas chromatography) combine Fractions II and III. Adjust the volume to 10 ml and analyze gas chromatography. Be sure no mercury is transferred to the combined Fractions II and III, since it can react with certain pesticides.

By combining Fractions II and III, if PCB's are present, it is possible to identify the Aroclor(s) present and a quantitative analysis can be performed accordingly. Fraction I can be discarded since it only contains the bulk of the sulfur. Analyze Fractions III and IV for the PCB's and pesticides. If DDT and its homologs, aldrin, heptachlor, or technical chlordane are present along with the PCB's, an additional micro-column separation can be performed which may help to further separate the PCB's from the pesticides (See 10.4).

11. Quantitative Determination

11.1 Measure the volum n-hexane eluate, containing the PCB's and inject 1 to 5 µl into the gas chromatograph. If necessary, adjust

the volume of the eluate to give linear response to the electron capture detector. The microcoulometric or the electrolytic detector may be employed to improve specificity for samples having higher concentrations of PCB's.

11.2 Calculations

11.2.1 When a single Aroclor is present, compare quantitative Aroclor reference standards (e.g., 1242, 1260) to the unknown. Measure and sum the areas of the unknown and the reference Aroclor and calculate the result as follows:

$$\text{Microgram/liter} = \frac{[A]\ [B]\ [V_t]}{[(V_i)\ (V_s)]} \times [N]$$

$$A = \frac{\text{ng of Standard Injected}}{\Sigma \text{ of Standard Peak Areas}} = \frac{ng}{mm^2}$$

$B = \Sigma$ of Sample Peak Areas = (mm^2)

V_i = Volume of sample injected (µl)

V_t = Volume of Extract (µl) from which sample is injected into gas chromatograph

V_s = Volume of water sample extracted (ml)

N = 2 when micro column used
1 when micro column not used

Peak Area = Peak height (mm x Peak Width at 1/2 height

11.2.2 For complex situations, use the calibration method described below. Small variations in components between different Aroclor batches make it necessary to obtain samples of several specific Aroclors. These reference Aroclors can be obtained from Dr. Ronald Webb, Southest Environmental Research Laboratory, EPA, Athens, Georgia

30601. The procedure is as follows:

11.2.2.1 Using the OV-1 column, chromatograph a known quantity of each Aroclor reference standard. Also chromatograph a sample of p,p'-DDE. Suggested concentration of each standard is 0.1 ng/µl for the Aroclors and 0.02 ng/µl for the p,p'-DDE.

11.2.2.2 Determine the relative retention time (RRT) of each PCB peak in the resulting chromatograms using p,p'-DDE as 100.

$$RRT = \frac{RT \times 100}{RT_{DDE}}$$

RRT = Relative Retention Time

RT = Retention time of peak of interest

RT_{DDE} = Retention time of p,p'-DDE

Retention time is measured as that distance in mm between the first appearance of the solvent peak and the maximum for the compound.

11.2.2.3 To calibrate the instrument for each PCB measure the area of each peak.

Area = Peak height (mm) x Peak width at 1/2 height. Obtain the proper mean weight factor, then determine the response factor ng/mm^2.

$$ng/mm^2 = \frac{(ng_i)\ \frac{(\text{mean weight percent})}{100}}{(\text{Area})}$$

ng_i = ng of Aroclor Standard Injected

Mean weight percent = obtained from Tables 1 through 6.

11.2.2.4 Calculate the RRT value and the area for each PCB peak in the sample chromatogram. Compare the sample chromatogram to those obtained for each reference Aroclor standard. If it is apparent that the PCB peaks present are due to only one Aroclor then calculate the concentration of each PCB using the following formula:

ng PCB = ng/mm^2 x Area

Where Area = Area (mm^2) of sample peak

ng/mm^2 = Response factor for that peak measured.

Then add the nanograms of PCB's present in the injection to get the total number of nanograms of PCB's present. Use the following formula to calculate the concentration of PCB's in the sample:

$$\text{Micrograms/Liter} = \frac{[ng]\ [V_t]}{[V_s]\ [V_i]} \times [N]$$

V_s = volume of water extracted (ml)

V_t = volume of extract (µl)

V_i = volume of sample injected (µl)

Σng = sum of all the PCB's in nanograms for that Aroclor identified

N = 2 when microcolumn used

N = 1 when microcolumn not used

The value can then be reported as Micrograms/ Liter PCB's reported as the Aroclor. For samples containing more than one Aroclor, use Figure 9 chromatogram divisional flow chart to assign a proper response factor to each peak and also identify the "most likely" Aroclors present. Calculate the ng of each PCB isomer present and sum them according to the divisional flow chart. Using the formula above, calculate the concentration of the various Aroclors present in the sample.

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.

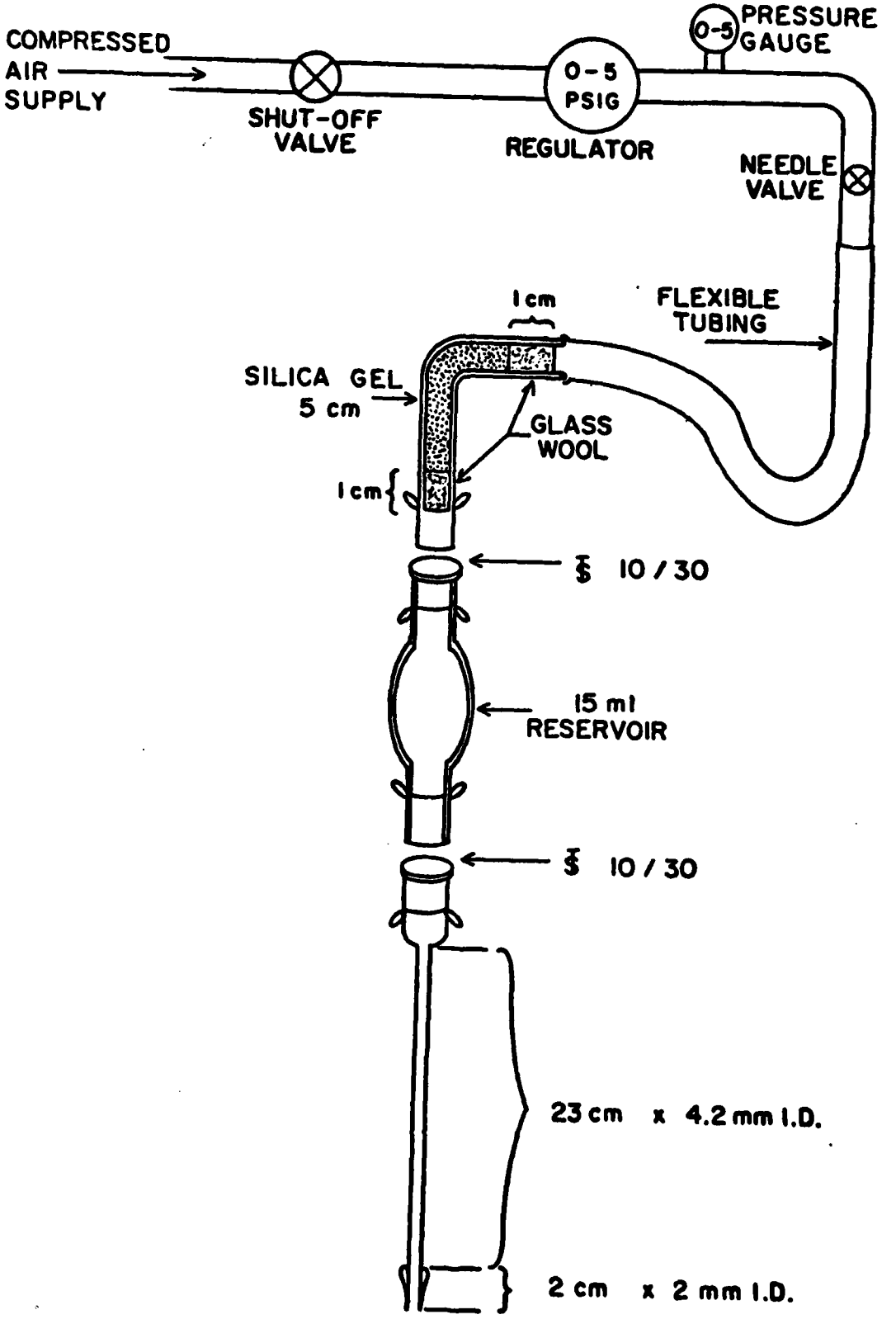

FIGURE 1. MICROCOLUMN SYSTEM

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Appendix 2

13. Standardization of Florisil Column by Weight Adjustment Based on Adsorption of Lauric Acid.

13.1 A rapid method for determining adsorptive capacity of Florisil is based on adsorption of lauric acid from hexane solution (6) (8). An excess of lauric acid is used and amount not adsorbed is measured by alkali titration. Weight of lauric acid adsorbed is used to calculate, by simple proportion, equivalent quantities of Florisil for batches having different adsorptive capacities.

13.2 Apparatus

13.2.1 Buret. -- 25 ml with 1/10 ml graduations.

13.2.2 Erlenmeyer flasks. -- 125 ml narrow mouth and 25 ml, glass stoppered.

13.2.3 Pipet. -- 10 and 20 ml transfer.

13.2.4 Volumetric flasks. -- 500 ml.

13.3 Reagents and Solvents

13.3.1 Alcohol, ethyl. -- USP or absolute, neutralized to phenolphthalein.

13.3.2 Hexane. -- Distilled from all glass apparatus.

13.3.3 Lauric acid. --Purified, CP.

13.3.4 Lauric acid solution. -- Transfer 10.000 g lauric acid to 500 ml volumetric flask, dissolve in hexane, and dilute to 500-ml (1 ml = 20 mg).

13.3.5 Phenolphthalein Indicator. -- Dissolve 1 g in alcohol and dilute to 100 ml.

13.3.6 Sodium hydroxide. -- Dissolve 20 g NaOH (pellets, reagent grade) in water and dilute to 500 ml (1N). Dilute 25 ml 1N NaOH to 500 ml with water (0.05N). Standardize as follows: Weigh 100-200 mg lauric acid into 125 ml Erlenmeyer flask. Add 50 ml neutralized ethyl alcohol and 3 drops phenolphthalein indicator; titrate to permanent end point. Calculate mg lauric acid/ml 0.05 N NaOH (about 10 mg/ml).

13.4 Procedure

13.4.1 Transfer 2.000 g Florisil to 25 ml glass stoppered Erlenmeyer flasks. Cover loosely with aluminum foil and heat overnight at 130°C. Stopper, cool to room temperature, add 20.0 ml lauric acid solution (400 mg), stopper, and shake occasionally for 15 min. Let adsorbent settle and pipet 10.0 ml of supernatant into 125 ml Erlenmeyer flask. Avoid inclusion of any Florisil.

13.4.2 Add 50 ml neutral alcohol and 3 drops indicator solution; titrate with 0.05N to a permanent end point.

13.5 Calculation of Lauric Acid Value and Adjustment of Column Weight

13.5.1 Calculate amount of lauric acid adsorbed on Florisil as follows:

Lauric Acid value = mg lauric acid/g Florisil = 200 - (ml required for titration X mg lauric acid/ml 0.05N NaOH).

13.5.2 To obtain an equivalent quantity of any batch of Florisil, divide 110 by lauric acid value for that batch and multiply by 20 g. Verify proper elution of pesticides by 13.6.

13.6 Test for Proper Elution Pattern and Recovery of Pesticides: Prepare a test mixture containing aldrin, heptachlor epoxide, p,p'-DDE, dieldrin, Parathion and malathion. Dieldrin and Parathion should elute in the 15% eluate; all but a trace of malathion in the 50% eluate and the others in the 6% eluate.

APPENDIX N

OIL AND GREASE

IN BOTTOM SEDIMENTS

APPENDIX N

OIL AND GREASE IN BOTTOM SEDIMENTS

1. General Discussion

1.1 Definition: Grease is defined as that material extracted by hexane from an acidified sample which would not be voltatilized during the procedure; it includes soaps, fats, waxes, and oils.

1.2 Principle: Drying of acidified sludges by heating leads to low results. Magnesium sulfate monohydrate is capable of combining 75 per cent of its own weight in water in forming the heptahydrate. Magnesium sulfate monohydrate can be used to dry sludge. After drying, the grease can be extracted with hexane.

1.3 Interference: Elemental sulfur; certain organic dyes; oxidation of extract and loss in weight of residue due to volatilization of low boiling components.

1.4 Sampling and Storage: Every possible precaution must be taken to obtain a representative sample. When analyses can not be made immediately, samples may be preserved with 1 ml conc H_2SO_4 for each 80 g of sample, or by freezing.

2. Apparatus

2.1 Extraction apparatus, soxhlet or A.S.T.M. apparatus.

3. Reagents

3.1 Hydrochloric acid conc.

3.2 Magnesium sulfate monohydrate: Prepare $MgSO_4 \cdot H_2O$ by drying overnight a thin layer of $MgSO_4 \cdot 7H_2O$ in an oven at 103°C.

3.3 N-Hexane, boiling point 69°C.

3.4 Grease free cotton: Nonabsorbent cotton after extraction with N-hexane.

4. Procedure

4.1 In a 150 ml beaker weigh a 20 g sample of wet sludge, of which the dry-solids content is known.

4.2 Acidify to a pH 2.0 (generally 0.3 ml conc HCl is sufficient.

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*Adapted from "Chemistry Laboratory Manual, Bottom Sediments" compiled by Great Lakes Region Committee on Analytical Methods, EPA, Dec., 1969, pages 42 & 43.

4.3 Add 25 g magnesium sulfate monohydrate. Stir to a smooth paste and spread on the sides of the beaker to facilitate subsequent moisture removal. Allow to stand until solidified 15 to 30 minutes.

4.4 Remove the solids and grind in a porcelain mortar.

4.5 Add the powder to a paper extraction thimble. Wipe the beaker and mortar with small pieces of filter paper moistened with hexane and add to the thimble. Fill the thimble with small glass beads.

4.6 Extract in a soxhlet apparatus using hexane at a rate of 20 cycles per hour for 4 hours.

4.7 If any turbidity or suspended matter is present in the extraction flask, remove by filtering through grease-free cotton into another weighed flask. Rinse flask and cotton with hexane.

4.8 Distill hexane from the extraction flask in water at 85°C. Dry by placing on a steam bath and drawing air through the flask with a vacuum for 15 minutes.

4.9 Cool in a desiccator for 30 minutes and weigh.

5. Calculation

5.1 Wet basis

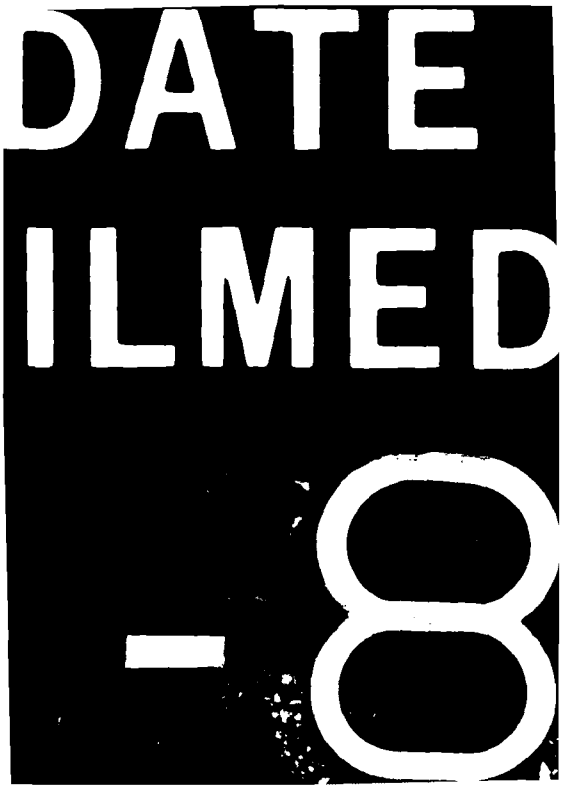
$$mg/kg = \frac{\text{mg of residue}}{\text{grams of sample}} \times 1000$$

5.2 Dry basis

$$mg/kg = \frac{\text{mg/kg wet basis}}{\text{\% solids (decimal fraction)}}$$

6. Reference

Standard Methods for the Examination of Water and Wastewater, 12th Ed., APHA, Inc., N.Y., 1965, 531-532.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