

WORK PLAN FOR BASELINE ENVIRONMENTAL
MONITORING STUDY
U.S. ARMY/GAF CHEMICALS CORPORATION
HUNTSVILLE, ALABAMA PLANT

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1

WORK PLAN FOR BASELINE ENVIRONMENTAL MONITORING STUDY
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INTRODUCTION

GAF Chemicals Corporation operates a carbonyl iron powder manufacturing facility at Redstone Arsenal (RSA) near Huntsville, Alabama. GAF has been leasing this facility from the Department of the Army since 1949. The chemical process equipment was originally installed in 1943 by Army contractors.

GAF retained AWARE Incorporated of Nashville, Tennessee to develop a Work Plan for a baseline environmental monitoring study at the Huntsville Plant. The objective of the study is to define the present condition of soils, ground water, and surface water at and immediately adjacent to the leased property to determine if these three environmental media may have been impacted by operations at the site. AWARE has previously acquired knowledge of certain facets of operations at the Huntsville Plant. This knowledge was supplemented by a detailed site reconnaissance on September 1, 1987, including discussion with plant personnel and Mr. William Schroder of the Environmental Office, Directorate of Engineering and Housing, RASA. Mr. Schroder also provided useful background literature about the environmental setting at RSA and environmental studies of areas near the GAF operation.

SITE DESCRIPTION

Location

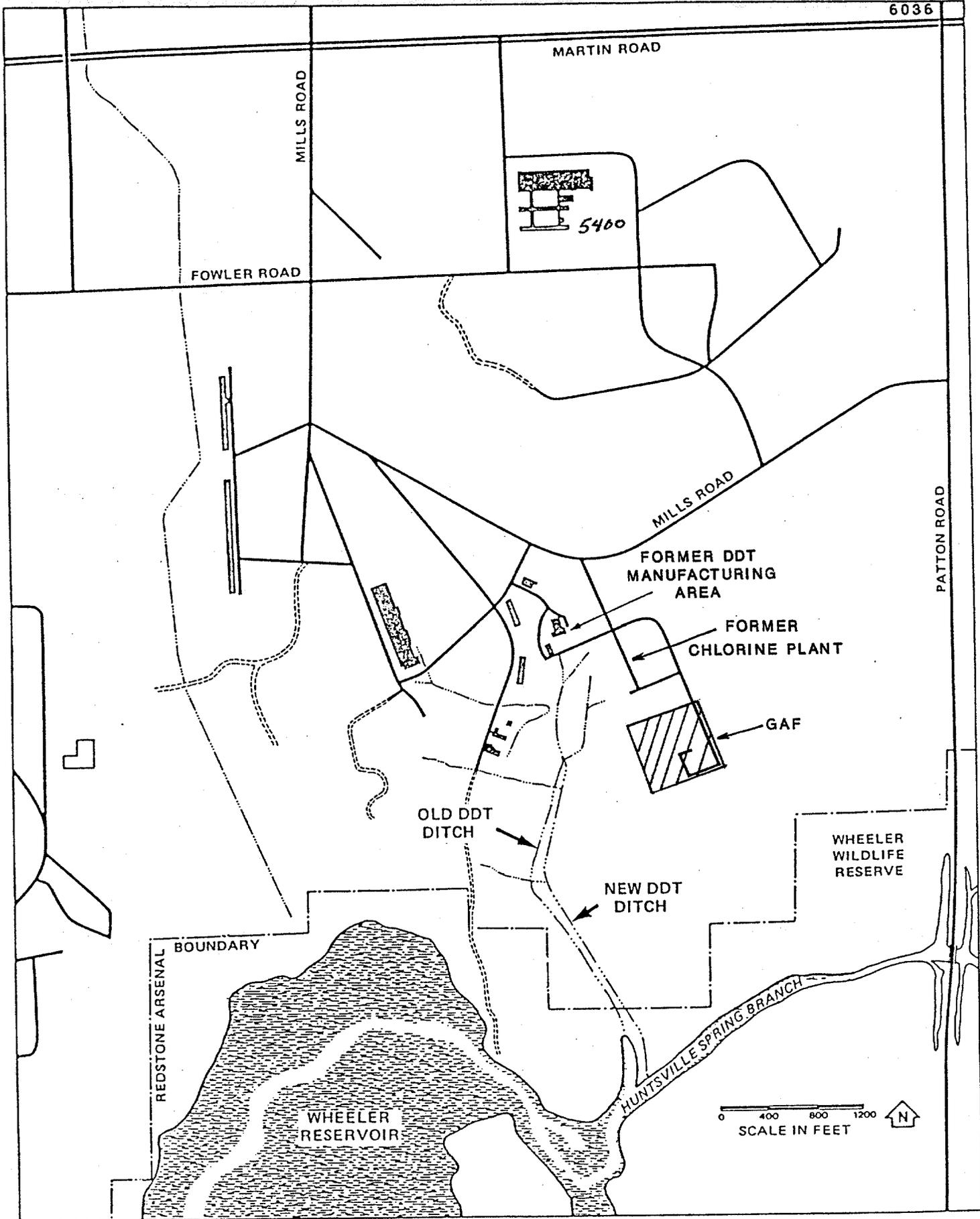
RSA is located in the southwestern portion of Madison County, Alabama, just to the west and southwest of the City of Huntsville. Madison County is

located in north-central Alabama; the northern border of the County traverses the Alabama-Tennessee border. RSA encompasses an area of just under 39,000 acres.

The GAF facility is located on an approximately 10 acre leased parcel in the central interior of RSA (see Figure 1). This parcel is bounded to the west and north by the sites of former chemical process plants and to the east and south by forest and wetlands. Wheeler National Wildlife Refuge is located roughly 1,300 ft to the south of GAF's leased property.

Layout and Topography

The chemical storage and processing facilities utilized by GAF are located in the southeast quadrant of the leasehold. The site is accessed by an asphaltic concrete road which traverses a route parallel to the eastern boundary of the parcel. There are eight (8) brick buildings used to house the chemical process vessels and for raw material and product storage, and a variety of sites of outdoor storage vessels for raw materials and intermediate storage of gaseous and liquid chemicals. Figure 2 is a recent topographic map provided by RSA. Please note that RSA identification numbers have been assigned to each room in several of the buildings. Topographic relief at the site ranges from approximately 570 to 584 ft msl. However, the manufacturing area is relatively flat, with drainage ditches and topography which route surface water drainage predominantly to the southwest and south, with a smaller area draining to the east.



**FIGURE 1 LOCATION GAF FACILITY AT RSA
HUNTSVILLE, ALABAMA**

Manufacturing

In the first step of carbonyl iron powder production, reduced sponge iron (Fe), which is a very pure powder, is reacted with carbon monoxide (CO) to produce iron pentacarbonyl (IPC) or $\text{Fe}(\text{CO})_5$. The IPC is condensed and decomposed to form the product carbonyl iron powder, which may be subsequently milled. Compressors are used to assist in the condensation of IPC. IPC is unstable under ambient conditions and readily decomposes to iron and carbon monoxide. Several other chemicals are used at the GAF Huntsville plant; Table 1 provides an inventory.

Until February 1977, carbon monoxide was produced at the plant using coke and carbon dioxide as raw materials. During a 4 to 5 month period ending in 1959, liquid carbonyl nickel was distilled at the plant site in a process area identified as No. 5562 in Figure 2. This involved the same basic manufacturing scheme as carbonyl iron, except that the nickel had to be purified in the still prior to use in the process. GAF reports that residuals were purged from the nickel system after shutdown.

Environmental Control Facilities and Potential Areas of Concern

GAF discharges non-contact cooling water and pretreated wastewater from the site in accordance with two NPDES discharge permits issued by the Alabama Department of Environmental Management (ADEM). The non-contact cooling water discharges to the east of the property into a tributary of Huntsville Spring Branch. Pretreated process wastewater and sewage are discharged by permit into the RSA sanitary sewer system. The pretreated process wastewater

TABLE 1
 CHEMICAL INVENTORY FOR THE
 GAF HUNTSVILLE PLANT
 SEPTEMBER 1987

| Storage | Material | Formula | Physical State | Comment |
|-------------|---------------------|-----------------------------------|----------------|---|
| Tanks | Hydrogen | H ₂ | Gas | |
| Tank | Ammonia | NH ₃ | Gas | |
| Tanks | Carbon Dioxide | CO ₂ | Gas | |
| Tanks | Carbon Monoxide | CO | Gas | Principal raw material |
| Fiber Drums | Sponge Iron | Fe | Solid | Principal raw material |
| Drums | Surfactants | -- | Liquid | Used in process |
| Drums | Compressor Oil | -- | Liquid | Used in IPC compressors |
| Bags | Silicon Dioxide | SiO ₂ | Solid | Used as a binder for milling product powder |
| Drums | Carbonyl Iron | Fe | Solid | Finished product |
| Tank | Iron Pentacarbonyl | Fe (CO) ₅ | Liquid | Finished product |
| Drums | Hydrochloric Acid | HCl | Liquid | Used for equipment cleaning |
| Drums | Sulfamic Acid | NH ₂ SO ₃ H | Solid | Used for equipment cleaning |
| Drums | Sulfuric Acid | H ₂ SO ₄ | Liquid | Used in process water treatment |
| Drums | Sodium Hydroxide | NaOH | Liquid | Used in process water treatment |
| Drums | Sodium Hypochlorite | NaOCl | Liquid | Used in process water treatment |
| Drum | Mineral Spirits | -- | Liquid | Degreaser used for maintenance |
| Bottles | Acetone | CH ₃ COCH ₃ | Liquid | Laboratory reagent ^a |
| Bottles | Phosphoric Acid | H ₃ PO ₄ | Liquid | Laboratory reagent ^a |
| Tank | Fuel Oil No. 2 | -- | Liquid | Used as fuel in process heaters |

^aSmall quantities of other materials are used for maintenance, quality control laboratory, and research and development activities.

discharge includes the effluent from an ammonia stripper unit which was installed around 1979. Prior to installation of the ammonia stripper, the ammonia-bearing wastewater was discharged directly to the marshy area southwest of the plant.

Until the mid-1970's, most of GAF's process wastewater was discharged into an industrial sewer system which flowed to the northwest and joined other industrial plant discharges which ultimately were released to a north-south trending drainage ditch adjacent to GAF's western leasehold boundary. Once this discharge route was no longer available because of the DDT abatement work at the old Olin facility, GAF installed a concrete sewer pipe which conveyed their wastewater to the southwest into a low-lying marshy area (see Figure 2). This low area also receives the waters from the previously described north-south trending ditch. Waters in the marshy area eventually flow to the south into Huntsville Spring Branch.

During the past 10 years, environmental investigations and major remedial activities have been completed as a consequence of previous releases of DDT to the surface water, soil/sediments, and ground water at and downgradient from the old Olin facility (see Figure 1 for location). Low concentrations of DDT/metabolites are present in ground water upgradient of the GAF property. Similarly, parts per billion (ppb) concentrations of mercury and PCBs have been detected in ground waters near the site of the Stauffer chlorine facility, which was also upgradient of the GAF leasehold. However, RSA has informed GAF that the electrical transformers on the western side of building No. 5562 do not contain PCBs.

There are two underground storage tanks (USTs) at the leased facility. RSA is going to remove the inactive propane tank in the near future. The other underground tank, which is in use and contains fuel oil, is to be assessed under RSA's ongoing program for UST evaluation. GAF will assess the integrity of this tank and piping system in accordance with EPA regulations when promulgated.

Drums of used compressor oil are temporarily stored on a covered concrete pad, which is located in the western half of building No. 5577, prior to off-site incineration. At the time of the site reconnaissance, there were two (2) drums on the pad. Since there was no visual evidence of spillage, further evaluation is not warranted.

In the past, by-product iron sludges from the process were used as roadway aggregate for the plant's interior roadways. The presence of the resultant iron oxide is evident on the surface in several areas. By-product iron sludges have also been placed into an above ground pile measuring 30,000 to 40,000 sq ft in area and 8 to 10 ft in depth. This pile is located at the southwest corner of the process area boundary limits (see Figure 2).

For a period of time, an earthen refuse pit for trash burning was located to the west of building No. 5567 (see Figure 2). The pit was backfilled and has not been in use for at least 10 years.

Waste coke chunks have been observed on the ground to the west of the process area (see Figure 2). Waste drums from the nickel carbonyl unit purging were also temporarily stored in this area.

Other than the coke chunks described above, there is no evidence of waste burial at the site and plant personnel have no knowledge of any disposal. There have been no chemical spills reported at this facility.

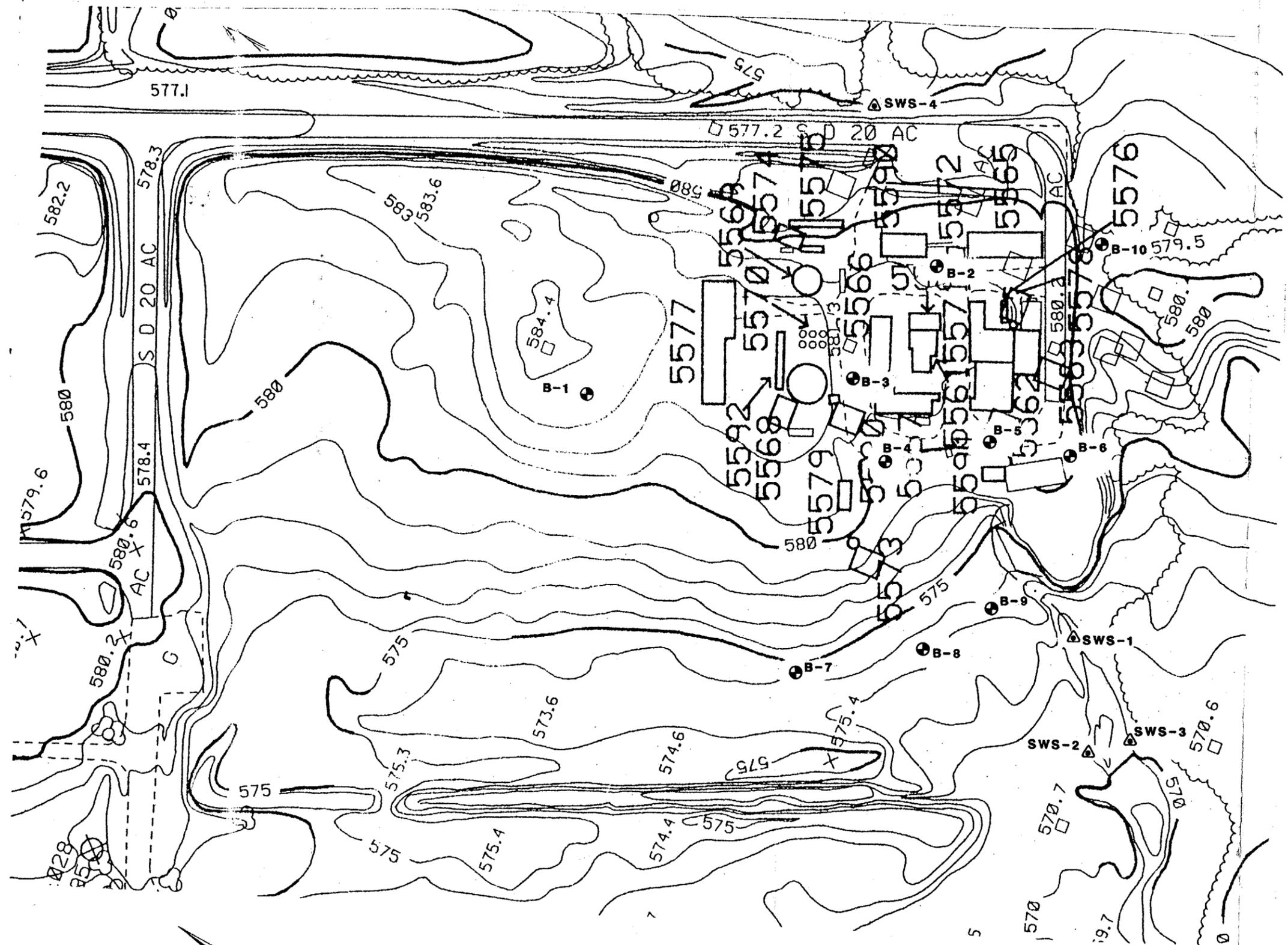
SOIL SAMPLING

Ten (10) exploratory borings will be completed at the site to define the condition of subsurface soils. Boring locations are depicted in Figure 3.

The rationale for selection of these locations is summarized below:

| | |
|---------------|----------------------------------|
| B-1 | Upgradient/background |
| B-2, B-3, B-5 | Plant process area |
| B-4 | Previous "Refuse Pit" |
| B-6 | Inactive nickel carbonyl unit |
| B-7, B-8, B-9 | Previous waste coke storage area |
| B-10 | Southern boundary |

Continuous split-spoon samples will be obtained from each of the borings, to a depth of 10 to 11 ft. Soil samples from the top two (2) interval spoons (sample depths ending at 18 to 24 in. and 36 to 48 in.) from each hole will be subjected to chemical analysis, as defined in Table 2. The deeper samples will be held pending GAF's evaluation of the analytical results from the shallow samples. (Boring B-4, at the site of the previous "Refuse Pit," will be advanced to a depth just below the level of disturbance; therefore, for this particular boring it may be necessary to drill to a depth greater than 10 or 11 ft. In addition, a sample at the level of disturbance in this boring will be subjected to chemical analysis per Table 2.) The split-spoon sampler will be thoroughly cleaned between the collection of each sample. In addition, the soil samples will be carefully trimmed to remove any portion that may have been in contact with the sampler or fluids within the borehole. Drilling equipment that contacts the subsurface, including augers, rods, and bits, will be steam-cleaned between borings.



LEGEND

- B-1 ● SOIL BORING
- SWS-1 ▲ SURFACE WATER/SEDIMENT SAMPLE STATION

SCALE: 1" = 200'

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FIGURE 3

LOCATION OF SOIL BORINGS AND SURFACE WATER/SEDIMENT SAMPLE STATIONS

SOURCE: RSA

TABLE 2

ANALYTICAL PARAMETERS FOR SOIL AND SURFACE
WATER/SEDIMENT SAMPLES

| Parameter | Soil Samples | Method No. ^a | Waste Coke | Method No. ^b | Sediments | Method No. ^a | Surface Water | Method No. ^c |
|--------------------------------------|--------------|-------------------------|------------|---|-----------|-------------------------|---------------|-------------------------|
| pH | x | 9045 | | | x | 9045 | x | 150.1 |
| Oil and Grease | x | 9071 | | | x | 9071 | x | 413.1 |
| Iron (Fe) | x | 7380 | x | D-3682, D-3683 ^d D-2795 ^d | x | 7380 | x | 236.1 |
| Nickel (Ni) | x | 7520 | | | x | 7520 | x | 249.2 |
| Additional Heavy Metals ^e | x | ^e | | | | | | |
| PCBs | x | 8080 | | | | | | |
| DDT, DDD, DDE | x | 8080 | | | | | | |
| Fixed Carbon | | | x | D-3172 | | | | |
| Total Organic Carbon (TOC) | | | | | | | x | 415.2 |

^aU.S. EPA, SW-846, Test Methods for Evaluating Solid Waste, November 1986.

^bAmerican Society for Testing Materials, 1975.

^cU.S. EPA, 600/4-79-020, Methods for Chemical Analysis of Water and Wastes, March 1984.

^dMethod selection dependent on iron concentration of sample.

^eAs, Ba, Cd, Cr, Pb, Hg, Se, Ag; SW-846 Method No.'s 7060, 7080, 7130, 7190, 7420, 7141, 7740, 7760, respectively.

At least three (3) pieces of suspected waste coke from the land surface to the west of the plant will be subjected to fixed carbon and iron assays to confirm their origin.

SURFACE WATER AND SEDIMENT SAMPLING

Surface water and sediment samples will be collected at four locations as shown in Figure 3. Sample stations SWS-1, SWS-2, and SWS-3 are in the headwaters of the low-lying area to the southwest of the leasehold, which was the discharge route for GAF's process wastewaters in the past. Station SWS-4 is immediately downstream of the current non-contact cooling water discharge. Water samples will be collected by immersion of the sample container; sediment samples will be obtained with a clean spoon or trowel. The analytical parameters for these samples are also listed in Table 2.

GROUND WATER MONITORING

Documents provided by RSA containing information on the geology and hydrogeology of RSA were reviewed prior to the selection of monitoring well locations and drilling methods. Water table and potentiometric contour maps reviewed indicate that the regional ground water flow is from north to south, towards the Tennessee River. In the vicinity of the GAF facility, ground water appears to flow from northwest to southeast, towards the Huntsville Spring Branch. Bedrock is expected to be encountered at 20 to 30 ft below the land surface and is identified as the Tuscumbia Limestone according to the boring logs and geologic maps reviewed.

Installation of Monitoring Wells

A total of eight wells will be sited, constructed, and developed at four locations (see Figure 4). At all locations, a monitoring well couplet or nest will be installed, consisting of one well screened above the soil-bedrock interface (a shallow well) and one well completed in the bedrock below the surficial soils (a deep well). The locations of the wells are based on existing hydrogeologic data such that Well Nest 1 will serve as an upgradient well nest and Well Nests 2, 3, and 4 will serve as downgradient well nests. An approximate schematic of a monitoring well nest is shown in Figure 5.

The deep monitoring wells will be installed to provide information on the potentiometric surface and water quality of the bedrock aquifer, while the shallow wells will provide information about the configuration and quality of the water table aquifer. In addition, the piezometric head differences and degree of interconnection between the shallow and deep water bearing zones will be investigated.

The deep monitoring wells will be constructed first, to provide additional information on the stratigraphy and to allow for finalization of the design of the shallow monitoring wells. The deep wells will be drilled by means of truck-mounted rotary drilling equipment. An initial 10-in. diameter borehole will be advanced as far as possible into the soil-bedrock surface (estimated to be 20 to 30 ft deep), by means of hollow-stem auger drilling technology. Upon reaching auger refusal, a single length of 6-in. diameter steel casing will be placed in the hole and driven beyond auger refusal depth. The annulus between the outside of the 6-in. steel casing and the borehole



LEGEND

1S ● SHALLOW WELL

1D ⊕ DEEP WELL

SCALE: 1" = 200'

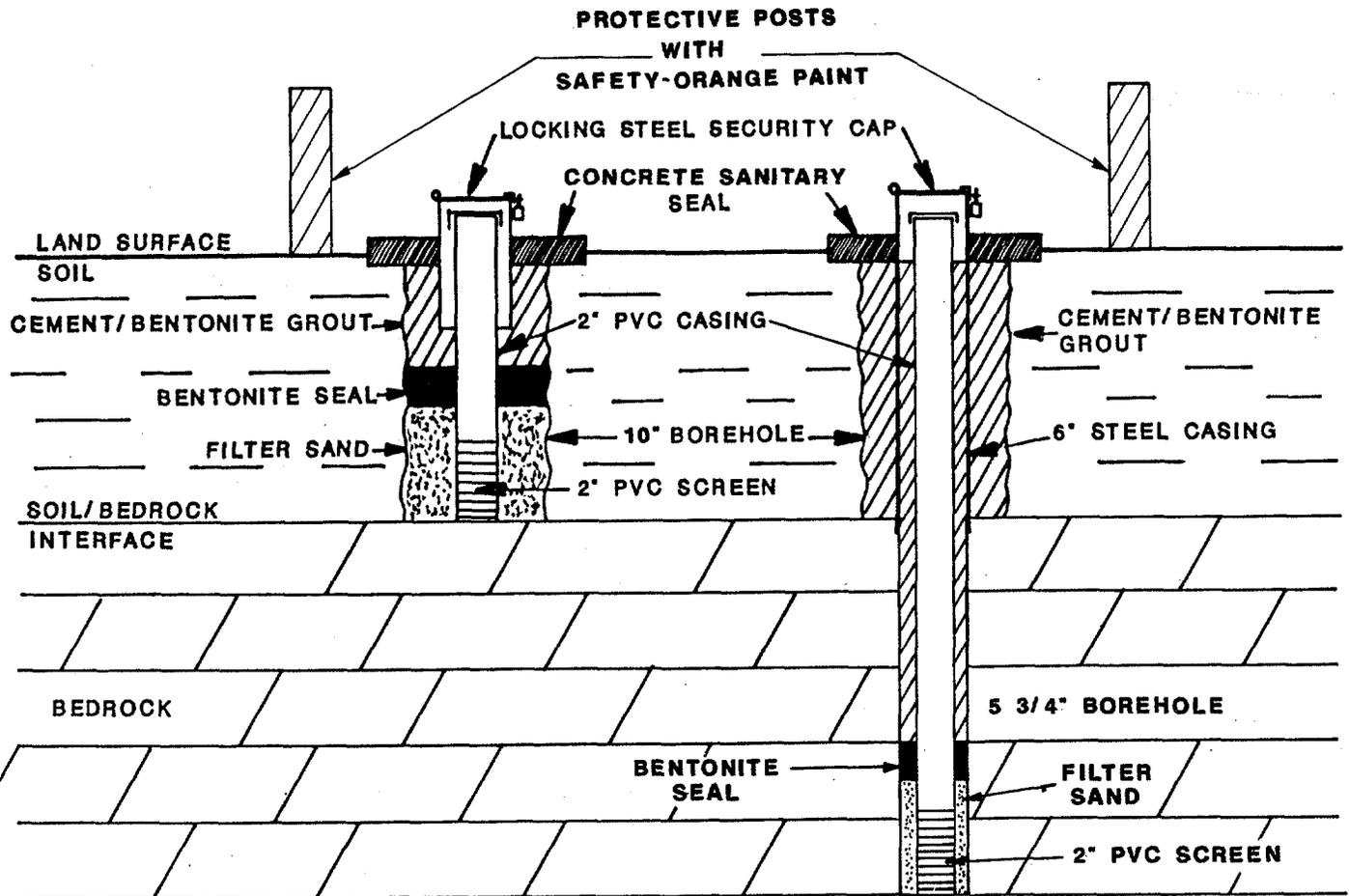
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FIGURE 4

LOCATION OF GROUND-WATER
 MONITORING WELLS

SOURCE: RSA



NOT TO SCALE

NOTE: Minimum acceptable dimensions are as follows:

1. Length of filter sand above top of screen = 5 ft.
2. Thickness of bentonite seal = 5 ft.
3. Distance between top of bentonite seal and bedrock surface (deep wells) = 3 ft.

FIGURE 5

**SCHEMATIC OF MONITOR WELL
NEST CONSTRUCTION**

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wall will be filled with a grout consisting of approximately 95 percent neat cement and 5 percent bentonite using the tremie method, to assure that the borehole does not serve as a pathway for vertical contamination.

After allowing the grout to set overnight, drilling will be advanced through the bottom of the 6-in. steel casing by means of a 5 3/4 in. drill bit, utilizing diamond core barrel drilling techniques for cutting return. This 5 3/4 in. borehole will be advanced to an estimated depth of approximately 43 ft to 53 ft, or 23 ft below the soil-bedrock interface. Upon reaching the target depth, a string of 2-in. diameter Schedule 80 PVC casing will be installed. This casing will utilize flush-joint threaded couplings with no glue used to join the sections. Ten ft of the casing will consist of factory-cut screen with the remainder of the casing consisting of blank PVC riser pipe. The annulus between the screened section and the bore wall will be filled with sized filter sand, placed by means of a tremie line temporarily placed down the annulus. The sand pack will extend 5 ft above the perforated section. The sand pack will, in turn, be capped by a 5 ft bentonite seal, with the remaining annulus filled with a grout consisting of 95 percent neat cement and 5 percent bentonite. A concrete surface sanitary seal approximately 3 ft in radius will be placed around the 6-in. steel casing, and a locking well cap will be welded on top of the steel casing. The concrete seal will prevent infiltration of surface water along the exterior of the well casing and will provide additional mechanical strength to the well installation. A brass plate, to be supplied by the U.S. Army, will be immersed into the surface of the concrete seal. The unique well number and location coordinate can be etched or stamped onto the plate by the Army.

Upon completion the well will be developed by means of a combination of surging and air eduction, to clear the fine material from the well bore and produce relatively sediment-free water. Water level elevations will be measured prior to well development. At a minimum, five standing water volumes will be removed from the well during initial development. The standing water volume is defined as the volume of the well screen and casing plus saturated annulus, assuming 30 percent porosity.

The shallow borings will be advanced by means of a truck-mounted hollow-stem auger rig, utilizing split spoons for sampling. Samples will be collected every five feet, logged for lithology by a qualified hydrogeologist, and placed in glass jars. The jar will be covered with aluminum foil, allowed to warm and the head space "sniffed" with an HNU photoionizer for gross volatile organic content.

Upon reaching the total depth for each of the holes (estimated at this time to be 20 to 30 ft), the borehole will be converted to a shallow monitoring well by means of installation of 2-in. diameter Schedule 80 PVC flush-joint casing down the inside of the hollow stem. The annulus between the borehole and the casing will be filled with sized filter sand, placed down the inside of the hollow stem auger as the auger is removed. The filter sand will extend to a point 5 ft above the screened interval, capped by a 5 ft bentonite seal, and the remaining annulus will be filled with a cement/bentonite grout. A locking steel security cap will be placed around the PVC casing, and cemented in place as a part of the sanitary seal. The concrete seal will prevent infiltration of surface water along the exterior of the well casing and will provide additional mechanical strength to the well

installation. A brass plate, to be supplied by the U.S. Army, will be immersed into the surface of the concrete seal. The unique well number and location coordinate can be etched or stamped onto the plate by the Army.

Water production of the surficial soil wells is not expected to be very large. Therefore, it is anticipated that development and sampling can best be achieved by means of dedicated bottom-entry bailers, placed in each of the shallow monitoring wells. Such bailers will be utilized to remove silt-laden water resulting from drilling activities, as well as collection of subsequent water quality samples. The wells will be developed by means of surging with the bailers, and water quality samples will be recovered by means of the same bailer. Water level elevations will be measured prior to well development. At a minimum, five standing water volumes will be removed from the well during initial development. The standing water volume is defined as the volume of the well screen and casing plus saturated annulus, assuming 30 percent porosity.

The topographic elevation of the top of casing of each monitoring well will be surveyed to within ± 0.05 ft.

Ground-Water Quality Sampling

To ensure chemical equilibrium, the newly installed monitoring wells will be allowed to stabilize for at least two weeks prior to sampling. Water level elevations will be measured to provide a data base for developing piezometric contours. Water quality samples will be collected from each of the wells and assayed for the parameters contained in Table 3. Each well will be purged until dry or until field pH, temperature, and conductivity measurements are stable for at least two consecutive purgings of the standing water volume. A

TABLE 3
PARAMETERS FOR GROUND-WATER QUALITY SAMPLING

| Parameter | Well Nest Number | | | | Method No. ^b |
|----------------------|------------------|------------------|----------------|----------------|-------------------------|
| | 1 ^a | 2 | 3 | 4 | |
| Priority Pollutants | X ^c | X ^{c,d} | X ^c | X ^c | e |
| Metals ^f | X | X | X | X | f |
| DDT, DDD, DDE | X | X | X | X | 8080 |
| PCBs | X | X | X | X | 8080 |
| Oil and Grease | X | X | X | X | 9070 |
| pH | X | X | X | X | 9040 |
| Specific Conductance | X | X | X | X | 9050 |
| TOC | X | X | X | X | 9060 |

^aUpgradient well nest.

^bU.S. EPA, SW-846, Test Methods for Evaluating Solid Waste, November 1986.

^cPriority pollutant analyses will be performed on all of the shallow well samples.

^dPriority pollutant analyses will be performed on only one of the deep well samples (Well 2D).

^eSW-846 Method Nos.: 8240, 8270, 8080, 8010, 8020, 8030, 8040, 9065, 9010, 7040, 7060, 7090, 7131, 7191, 7210, 7421, 7470, 7520, 7740, 7760, 7841, 7950.

^fAs, Ba, Cd, Cr, Fe, Pb, Pg, Ni, Se, Ag; SW-846 Method Nos. 7060, 7080, 7131, 7191, 7380, 7421, 7470, 7520, 7740, 7760, respectively.

minimum of five well volumes will be removed prior to sampling. All samples will be collected into clean sample containers, preserved as appropriate, and transported under chain-of-custody procedures to the AWARE laboratory for analysis. Samples requiring filtration (e.g., dissolved metals) will be field filtered through a 0.45 micron filter, prior to acid preservation.

The results from this sample set will be evaluated to determine if additional baseline and/or future routine ground-water quality monitoring are warranted.

QUALITY ASSURANCE

A summary of AWARE's laboratory quality assurance program is attached to this Work Plan. In addition to these measures, a superimposed quality assurance (QA) sample set will be sent to Wilson Laboratories, Salina, Kansas, for analysis. These samples, which will be duplicates of those analyzed by AWARE, will consist of four (4) of the soil samples, one (1) of the waste coke samples, one (1) of the surface water/sediment samples, one (1) of the ground water priority pollutant samples, and two (2) of the ground water general parameter samples. This will provide a duplicate QA load of at least 20 percent for each media for each analytical parameter. AWARE's laboratory holds certifications/approvals from the states of Tennessee, Alabama, and New Jersey and routinely participates in U.S. EPA Performance Evaluation (PE) analyses. Wilson Laboratories participates in EPA's contract laboratory program (COP) and is certified in several states.

REPORT PREPARATION

A report will be prepared upon completion of the final field work. This report would serve to bring all existing hydrogeologic and geotechnical work into perspective with that obtained during the subject investigation. The report may recommend that supplemental hydrogeologic work would be necessary or desirable as an additional phase.

The report would include the following sections:

- Objectives of the investigation
- Field methods, laboratory methods, and quality assurance
- Subsurface soil conditions
- Surface water and sediment quality
- Ground water occurrence, flow, and quality
- Conclusions and recommendations
- References

REFERENCES

- "Aerial Photo of GAF Site, Redstone Arsenal, Alabama." Provided by General Analine and Film Corp. (GAF) and U.S. Army, Redstone Arsenal, Alabama.
- "GAF Plant Area Location Map, Redstone Arsenal, Alabama," 1943. Provided by General Analine and Film Corp. (GAF), Huntsville, Alabama.
- "Redstone Arsenal, Alabama: Master Plan, Basic Information Maps," 1987. U.S. Army Corps of Engineers, Mobile District, Mobile, Alabama.
- "Topographic Map of GAF Site," 1987. Provided by U.S. Army, Redstone Arsenal, Alabama.
- U.S. Army. 1981. Groundwater Monitoring Plan. U.S. Army Missile Command, Redstone Arsenal, Alabama.
- U.S. Army Corps of Engineers, Nashville District, et al. 1986. Final Environmental Impact Statement for Regulatory Actions Associated with the Olin Corporation Remedial Action Plan to Isolate DDT from the People and Environment in the Huntsville Spring Branch-Indian Creek System, Wheeler Reservoir, Alabama (Madison County). Nashville, Tennessee.
- U.S. Army Toxic and Hazardous Materials Agency. 1977. Installation Assessment of Redstone Arsenal, Report No. 118. Aberdeen Proving Ground, Maryland.
- Water and Air Research, Inc. (WAR). 1983. Redstone Arsenal (RSA) Installation Restoration Summary, Final Report. Contract DAAG29-81-D-0100 (three volumes). Gainesville, Florida.

B

QUALITY ASSURANCE MANUAL ANALYTICAL
AND TESTING SERVICES DIVISION

AWARE Incorporated
Nashville, Tennessee

September 1987

TABLE OF CONTENTS

| <u>Section No.</u> | <u>Title</u> | <u>Page No.</u> |
|--------------------|--|-----------------|
| 1 | TITLE PAGE | 1-1 |
| 2 | MANUAL ORGANIZATION | |
| | Table of Contents | 2-1 |
| | List of Tables | 2-3 |
| | List of Figures | 2-5 |
| 3 | AS A MATTER OF POLICY | 3-1 |
| 4 | ORGANIZATION AND RESPONSIBILITY | 4-1 |
| 4.1 | ATSD Quality-Related Responsibilities | 4-1 |
| 5 | QUALITY ASSURANCE OBJECTIVES | 5-1 |
| 6 | SAMPLING PROCEDURES | 6-1 |
| 6.1 | Sampling Procedures for Groundwater and Surface Water | 6-1 |
| 6.2 | Sampling Procedures for Soils and Sediments | 6-4 |
| 7 | SAMPLE CUSTODY | 7-1 |
| 7.1 | Field Collection and Shipment | 7-1 |
| 7.2 | Document Control | 7-3 |
| 7.3 | Sample Control | 7-3 |
| 7.4 | Shipping and Packaging | 7-5 |
| 7.5 | Sample Receipt | 7-5 |
| 7.6 | Custody During Testing Program | 7-7 |
| 8 | CALIBRATION PROCEDURES | 8-1 |
| 8.1 | Field Instruments | 8-1 |
| 8.2 | Laboratory Instruments | 8-3 |
| 9 | ANALYTICAL PROCEDURES | 9-1 |
| 9.1 | Variance from Stated Analytical Methods | 9-1 |
| 10 | DATA REDUCTION, VALIDATION, AND REPORTING | 10-1 |
| 10.1 | Data Reduction and Reporting | 10-1 |
| 10.2 | Data Verification | 10-4 |

TABLE OF CONTENTS (Cont'd)

| <u>Section No.</u> | <u>Title</u> | <u>Page No.</u> |
|--------------------|---|-----------------|
| 11 | INTERNAL QUALITY CONTROL CHECKS | 11-1 |
| 12 | PERFORMANCE AND SYSTEMS AUDITS | 12-1 |
| 13 | PREVENTIVE MAINTENANCE AND BACKUP | 13-1 |
| 14 | PROCEDURES USED TO ASSESS PRECISION, ACCURACY, AND COMPLETENESS | 14-1 |
| 15 | ANALYTICAL CORRECTIVE ACTIONS | 15-1 |
| 16 | QUALITY ASSURANCE REPORTS TO MANAGEMENT | 16-1 |

LIST OF TABLES

| <u>Table No.</u> | <u>Title</u> | <u>Page No.</u> |
|------------------|--|-----------------|
| 5-1 | Quality Assurance Objectives Wet Chemistry and Gas Chromatography | 5-2 |
| 5-2 | Quality Assurance Objectives Priority Pollutant Scans (Metals, Cyanide, Phenol) | 5-3 |
| 5-3 | Quality Assurance Objectives Organic Priority Pollutants | 5-4 |
| 6-1 | Required Containers, Preservation Techniques and Holding Times- Groundwater and Surface Water | 6-3 |
| 6-2 | Required Containers, Sample Storage Techniques and Recommended Holding Times-Soil and Sediment | 6-6 |
| 7-1 | Sample Information | 7-4 |
| 8-1 | YSI D.O. Meter Operating Instructions | 8-2 |
| 8-2 | DFTPP Key Ions and Ion Abundance Criteria | 8-8 |
| 8-3 | BFB Key Ions and Abundance Criteria | 8-9 |
| 8-4 | Volatile Internal Standards with Corresponding HSL Analytes Assigned for Quantification | 8-11 |
| 8-5 | Semivolatile Internal Standards with Corresponding HSL Analytes Assigned for Quantification | 8-12 |
| 8-6 | Calibration Check Compounds | 8-14 |
| 9-1 | List of Approved Inorganic Test Procedures | 9-2 |
| 9-2 | List of Approved Test Procedures for Non-Pesticide Organic Compounds | 9-8 |
| 9-3 | List of Approved Test Procedures for Soil and Solid Wastes | 9-10 |
| 10-1 | Summary of Equations Used in Calculations | 10-2 |

LIST OF TABLES (Cont'd)

| <u>Table No.</u> | <u>Title</u> | <u>Page No.</u> |
|------------------|---|-----------------|
| 11-1 | Quality Assurance Program Outline Inorganic Analysis | 11-2 |
| 11-2 | Quality Assurance Program Outline Organic Analysis | 11-3 |
| 14-1 | Precision Formulas for Duplicate Determinations | 14-2 |
| 14-2 | Statistics for Accuracy | 14-3 |

LIST OF FIGURES

| <u>Figure No.</u> | <u>Title</u> | <u>Page No.</u> |
|-------------------|--|-----------------|
| 4-1 | Project Organization Chart | 4-4 |
| 7-1 | Sample Chain of Custody Record | 7-2 |
| 10-1 | Data Reduction and Validation Flow Schematic | 10-4 |

SECTION 3
AS A MATTER OF POLICY

It is the formal policy of AWARE's Analytical and Testing Services Division to maintain QA/QC procedures and practices which exceed the overall goals and guidelines currently recommended by the U.S. EPA. State and Federal legislation has placed increased emphasis upon the accuracy of environmental analytical data. These programs require very stringent quality assurance and quality control procedures and documentation. Because of an increasing tendency to resolve discrepancies with litigation, most laboratories must be prepared to defend the accuracy of their reported data in court. This document outlines the elements of a good laboratory quality assurance program. More importantly, however, it emphasizes a systematic approach to both the acquisition and reporting of accurate data from all field and laboratory testing.

The Analytical Testing Services Division (ATSD) of AWARE Incorporated intends to follow all of the procedures referenced within this manual and further, to be fully cognizant of U.S. EPA's guidelines for every project submitted. Any deviations from these established procedures will be submitted to the appropriate regulatory agency prior to project mobilization.

SECTION 4

ORGANIZATION AND RESPONSIBILITY

This section presents specific laboratory personnel positions and the responsibilities which each provides in the implementation of the Quality Assurance Program and the execution of Quality Control activities.

4.1 ASTD QUALITY-RELATED RESPONSIBILITIES

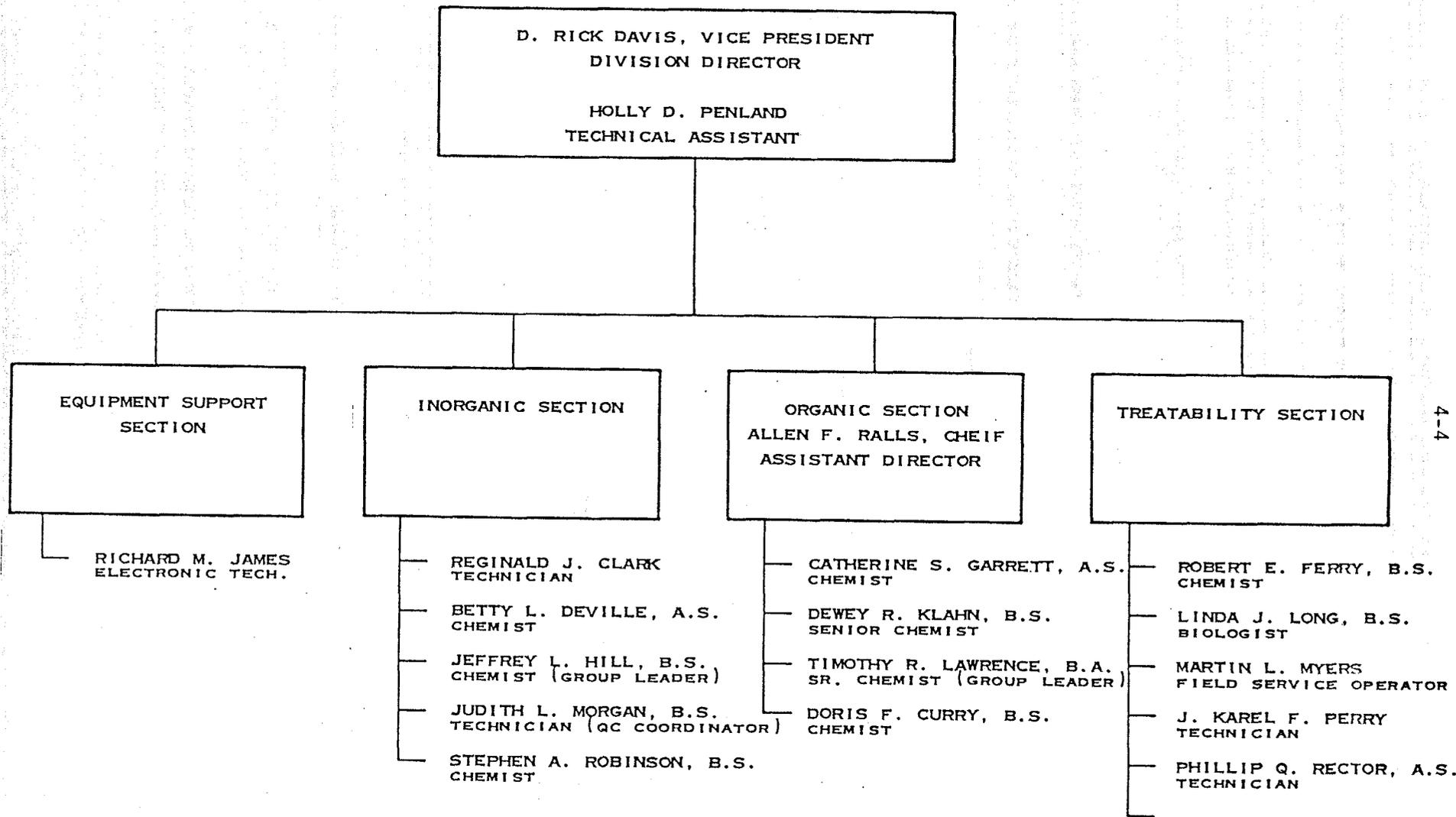
The staff positions outlined subsequently are fully implemented in the ATSD organization. The QA/QC responsibilities of each position are provided in the following.

- ATSD Director
 - Implement the Quality Assurance Program within the ATSD
 - Periodically determine effectiveness of the Quality Assurance Program
 - Supervise Quality Control activities
 - Approve ATSD-specific attachments to the Quality Assurance Manual and project-specific manuals and revisions
 - Make recommendations to the appropriate laboratory section regarding necessary changes in the Quality Assurance Program
 - Maintain current distribution lists for ATSD-specific attachments and project-specific manuals
 - Approve all reports issued by the ATSD
 - Serve as the "focal point" for the reporting and disposition of all nonconformances
 - Maintain current ATSD organization chart

- Section Chief
 - Report to ATSD Director
 - Provide technical overview of section activities
 - Serve as an "in-house" consultant for the applicability of general QC practices to specific needs
 - Review all statistical data to verify that stated QA/QC goals are attained
 - Evaluate new analytical techniques, procedures, instrumentation and QC methods, and provide recommendations to the Director
 - Recommend procedural guidelines for purchasing instrumentation, equipment, reagents, gases, and chemicals
 - Supervise ATSD participation in inter-laboratory accreditation and proficiency programs
 - Define and monitor the instrument calibration program within the ATSD
- Quality Control Coordinator
 - Prepare QC standards, insert QC samples into the sample inventory, and evaluate results
 - Perform statistical evaluation of QC sample analytical results
 - Report all nonconformance to the Director if the situation is not corrected within the ATSD
 - Assist in the performance of in-house Quality Assurance audits and perform Quality Control audits
 - Train analysts in QC procedures
- Group Leaders
 - Serve as the lead analyst within the group (individual Groups include organic analysis, inorganic analysis, special projects, etc.)

- Organize and schedule the analytical testing program with consideration for sample-holding times
 - Implement data verification procedures
 - Assign analysts for data processing and validation activities
 - Prepare data summaries for review by the Section Chief
 - Evaluate instrument performance and supervise instrument calibration and preventive maintenance programs
 - Report out-of-control (beyond control limits) or nonconforming situations to Section Chief and Quality Control Coordinator, as appropriate.
- Analysts
 - Perform analytical procedures and record all data in accordance with accepted methods
 - Perform and document all instrument calibration and preventive maintenance procedures, as appropriate
 - Perform data processing and validation
 - Immediately report out-of-control situations, instrument malfunction, calibration failure, or other nonconformances to the appropriate Group Leader.

The organizational structure of the Analytical Testing Services Division of AWARE Incorporated is presented in Figure 4-1.



4-4

ORGANIZATION CHART
ANALYTICAL AND TESTING SERVICES DIVISION
AWARE INCORPORATED

FIGURE 4-1

SECTION 5

QUALITY ASSURANCE OBJECTIVES

Objectives for precision, accuracy and completeness have been developed for all field and laboratory measurements. These objectives are based upon the intended use of the data to be generated, AWARE's prior experience, and published U.S. EPA information. Examples of the objectives are summarized according to matrix type in Tables 5-1, 5-2, and 5-3.

The precision of analytical data relates to the repeatability of replicate observations. In a quality assurance program, precision normally is determined by duplicate analysis of samples that cover a range of concentrations and a variety of interfering materials, commonly encountered by the analyst. Precision will be expressed in terms of Percent Relative Standard Deviation (%RSD)¹ or sometimes referred to as Coefficient of Variation (CV)¹.

Accuracy refers to the degree of difference between observed values and known or actual values. The accuracy of a method may be determined by replicate analyses of samples to which known amounts (spikes) of standard solutions have been added. Accuracy is expressed in terms of Percent Recovery (%R).²

Completeness is a measure of the information necessary for a valid scientific study. The total number of valid sample results will be divided by the total number of samples collected and reported as a measure of completeness.

Procedures used to assess precision, accuracy, and completeness are described in Section 14.

¹See Table 14-1, page 14-2, for definitions.

²See Table 14-2, page 14-2, for definitions.

TABLE 5-1
 QUALITY ASSURANCE OBJECTIVES^a
 WET CHEMISTRY AND GAS CHROMATOGRAPHY

| | Sample Matrix | Precision ^{b,c} Percent | Accuracy Percent |
|---|---------------|-------------------------------------|---------------------|
| FIELD PARAMETERS | | | |
| pH | Water | +0.20 (units) | NA |
| Specific Conductance | Water | +20 | 70-130 |
| Dissolved Oxygen | Water | +20 | NA ^d |
| Temperature | Water | +10 | NA |
| LABORATORY PARAMETERS | | | |
| pH | Water | +0.20 (units) | NA |
| Calcium | Water | +15 | 75-125 |
| Magnesium | Water | +15 | 75-125 |
| Sodium | Water | +15 | 75-125 |
| Potassium | Water | +15 | 75-125 |
| Iron | Water | +15 | 75-125 |
| Sulfate | Water | +15 | 75-125 |
| Chloride | Water | +15 | 75-125 |
| HCO ₃ ⁻ /CO ₃ ⁻ | Water | +20 | 75-125 |
| Total Suspended Solids | Water | +15 | 75-125 |
| Specific Conductance | Water | +15 | 75-125 |
| Benzene | Water | +20 | 76-127 |
| Dichlorobenzenes | Water | +20 | 43-146 |
| Chlorobenzene | Water | +20 | 75-130 |
| BHC - Alpha | Water | +20 | 37-134 |
| BHC - Beta | Water | +20 | 17-147 |
| BHC - Delta | Water | +20 | 32-127 |
| BHC - Gamma | Water | +20 | 56-123 |

^aCompleteness Objective will be 90% for all parameters listed

^b% RSD unless otherwise stated

^cSample concentration must be at least 5X the detection limit for the data to be subjected to the specified limits.

^dNA = Not Applicable

TABLE 5-2

QUALITY ASSURANCE OBJECTIVES
 PRIORITY POLLUTANT SCANS
 (Metals, Cyanide, Phenol)

| Parameter | Accuracy, Percent | | Precision, Percent | |
|-----------|-------------------|---------------|--------------------|---------------|
| | Water | Soil/Sediment | Water | Soil/Sediment |
| Cyanide | 70-130 | 50-150 | +20 | +40 |
| Phenol | 70-130 | 50-150 | +20 | +40 |
| Antimony | 75-125 | 60-140 | +15 | +30 |
| Arsenic | 70-130 | 60-140 | +25 | +40 |
| Beryllium | 75-125 | 65-135 | +15 | +25 |
| Cadmium | 75-125 | 65-135 | +15 | +25 |
| Chromium | 75-125 | 65-135 | +15 | +25 |
| Copper | 75-125 | 65-135 | +15 | +25 |
| Lead | 75-125 | 65-135 | +15 | +25 |
| Mercury | 60-140 | 50-150 | +35 | +50 |
| Nickel | 75-125 | 65-135 | +15 | +25 |
| Selenium | 70-130 | 60-140 | +25 | +40 |
| Silver | 75-125 | 65-135 | +15 | +25 |
| Thallium | 75-125 | 65-135 | +15 | +30 |

TABLE 5-3
 QUALITY ASSURANCE OBJECTIVES
 ORGANIC PRIORITY POLLUTANTS
 RECOMMENDED QUALITY CONTROL LIMITS^a

| Fraction | Matrix Spike Compound | Water | | Soil/Sediment | |
|-----------|----------------------------|----------|---------|---------------|---------|
| | | (% Rec.) | (% RSD) | (% Rec.) | (% RSD) |
| VOA | 1,1-Dichloroethene | 61-145 | +10 | 59-172 | +15 |
| VOA | Trichloroethene | 71-120 | +10 | 62-137 | +15 |
| VOA | Chlorobenzene | 75-130 | +10 | 60-133 | +15 |
| VOA | Toluene | 76-125 | +10 | 59-139 | +15 |
| VOA | Benzene | 76-127 | +10 | 66-142 | +15 |
| BN | 1,2,4-Trichlorobenzene | 39-98 | +20 | 38-107 | +20 |
| BN | Acenaphthene | 46-118 | +22 | 31-137 | +22 |
| BN | 2,4-Dinitrotoluene | 24-96 | +27 | 28-89 | +27 |
| BN | Di-n-butyl Phthalate | 11-117 | +28 | 29-135 | +28 |
| BN | Pyrene | 26-127 | +22 | 35-142 | +22 |
| BN | N-Nitroso-Di-n-Propylamine | 41-116 | +27 | 41-126 | +27 |
| BN | 1,4-Dichlorobenzene | 36-97 | +20 | 28-104 | +20 |
| Acid | Pentachlorophenol | 9-103 | +35 | 17-109 | +35 |
| Acid | Phenol | 12-89 | +30 | 26-90 | +30 |
| Acid | 2-Chlorophenol | 27-123 | +28 | 25-102 | +28 |
| Acid | 4-Chloro-3-Methylphenol | 23-97 | +30 | 26-103 | +30 |
| Acid | 4-Nitrophenol | 10-80 | +35 | 11-114 | +35 |
| Pesticide | Lindane | 56-123 | +15 | 46-127 | +50 |
| Pesticide | Heptachlor | 40-131 | +20 | 35-130 | +31 |
| Pesticide | Aldrin | 40-120 | +22 | 34-132 | +43 |
| Pesticide | Dieldrin | 52-126 | +18 | 31-134 | +38 |
| Pesticide | Endrin | 56-121 | +21 | 42-139 | +45 |
| Pesticide | 4,4'-DDT | 38-127 | +27 | 23-134 | +50 |

RECOMMENDED SURROGATE SPIKE RECOVERY LIMITS^a

| Fraction | Surrogate Compound | Low/Medium Water | | Low/Medium Soil/Sediment | |
|-----------|-----------------------------------|-----------------------|---------|--------------------------|---------|
| | | (% Rec.) | (% RSD) | (% Rec.) | (% RSD) |
| VOA | Toluene-d ₈ | 86-119 | +10 | 50-160 | +20 |
| VOA | 4-Bromofluorobenzene | 85-121 | +10 | 50-160 | +20 |
| VOA | 1,2-Dichloroethane-d ₄ | 77-120 | +15 | 50-160 | +20 |
| BNA | Nitrobenzene-d ₅ | 41-120 | +26 | 20-140 | +33 |
| BNA | 2-Fluorobiphenyl | 44-119 | +23 | 20-140 | +30 |
| BNA | p-Terphenyl-d ₁₄ | 33-128 | +30 | 20-150 | +36 |
| BNA | Phenol-d ₅ | 15-96 | +44 | 20-140 | +32 |
| BNA | 2-Fluorophenol | 23-107 | +34 | 20-140 | +33 |
| BNA | 2,4,6-Tribromophenol | 20-105 | +34 | 10-140 | +36 |
| Pesticide | Dibutylchloroendate | (48-136) ^a | +37 | (20-150) | +37 |

^aThese limits are for advisory purposes only. They are not to be used to determine if a sample should be reanalyzed.

SECTION 6

SAMPLING PROCEDURES

When AWARE is commissioned to conduct field sampling, a trained field sampling crew is sent to the site for sample collection and delivery of samples to the laboratory. Each crew is supervised by a qualified crew chief, trained in accordance with U.S. EPA protocol for groundwater sampling and other types of environmental sampling.

6.1 SAMPLING PROCEDURES FOR GROUNDWATER AND SURFACE WATER

Samples from groundwater monitoring wells are collected with pre-cleaned teflon bailers except in cases where the client supplies a dedicated bailer. PVC bailers may be used in cases where only inorganic or metal analyses are required. Bailers are pre-cleaned by first rinsing with detergent (acetone may also be used) then with tap water, followed by isopropanol (if organics are present), and a final rinse with distilled water. Prior to sampling, the water level in the well is determined with an electronic water level meter or a fiberglass tape and recorded on the Custody Form. Date, time, location, client name and field notes are also recorded on the Custody Form. The volume of water in the casing is calculated and three to five times that volume is purged from the well. In some cases, the well is purged until the conductivity has stabilized. This is accomplished by checking the conductivity of every fifth bailer volume removed from the well. The conductivity is considered representative if two consecutive readings are constant.

For surface water sampling, the actual sample bottle can be used to collect a grab sample. Care is taken to avoid hand contact with the bottle lip. A clean dipper may be used to collect samples from shallow streams.

Table 6-1 lists the containers used for samples, preservatives, holding times and conditions for groundwater and surface water sampling. Bottles are cleaned prior to delivery to the field. Bottles and caps for phosphate and ammonia are washed with phosphate and ammonia-free detergent and rinsed with tap water and deionized water. Bottles for metal analyses are first rinsed with 10 percent nitric acid followed by three rinses with deionized water. Bottles for non-volatile organics are rinsed in the following sequence: hot soapy water, three times with tap water, 10 mls of pesticide grade acetone, and three times with deionized water (low organic quality). Bottles for volatiles are rinsed in the same sequence as non-volatile organic bottles, dried in a 150 °C oven for 30 minutes and immediately capped.

Volatile bottles (and samples) are stored in an area isolated from the solvent extraction laboratory. Storage time is kept to a minimum. Field blanks for volatiles are prepared in a solvent-free area of the laboratory and kept at all times with the sampling bottles or samples.

For safety reasons and in order to minimize contamination, preservatives are, in general, added to the sample bottles prior to transporting to the field. When bottles or samples are to be transported by common carrier, nitric acid cannot be used as a preservative (U.S. DOT regulations). Where preservation prior to shipping is not allowed, U.S. EPA permits the preservation of such samples with nitric acid immediately following receipt at the laboratory.

6.2 SAMPLING PROCEDURES FOR SOILS AND SEDIMENTS

Soil and sediments are collected according to procedures in Test Methods for Evaluating Solid Waste U.S. EPA-SW-846.

Metal sampling devices are used for collection of samples requiring organics analyses. Plastic or stainless steel sampling devices are used when metals are to be

TABLE 6-1

REQUIRED CONTAINERS, PRESERVATION TECHNIQUES
AND HOLDING TIMES
GROUNDWATER AND SURFACE WATER

| Name | Container ^a | Preservation | Maximum Holding Time |
|---|------------------------|--|----------------------|
| Bacterial Tests: | | | |
| Coliform, fecal and total | P,G | Cool, 4°C, 0.008% Na ₂ S ₂ O ₃ | 6 hr |
| Fecal streptococci | P,G | Cool, 4°C, 0.008% Na ₂ S ₂ O ₃ | 6 hr |
| Inorganic Tests: | | | |
| Acidity | P,G | Cool 4°C | 14 days |
| Alkalinity | P,G | Cool 4°C | 14 days |
| Ammonia | P,G | Cool, 4°C, H ₂ SO ₄ to pH<2 | 28 days |
| Biochemical oxygen demand, carbonaceous | P,G | Cool, 4°C | 48 hr |
| Chemical oxygen demand | P,G | Cool, 4°C, H ₂ SO ₄ to pH<2 | 28 days |
| Chloride | P,G | None required | 28 days |
| Cyanide, total and amenable to chlorination | P,G | Cool, 4°C, NaOH to pH>12, 0.6 g ascorbic acid | 14 days |
| Fluoride | P | None required | 28 days |
| Hardness | P,G | HNO ₃ to pH<2, H ₂ SO ₄ to pH<2 | 6 months |
| Hydrogen ion (pH) | P,G | None required | Analyze immediately |
| Kjeldahl and organic nitrogen | P,G | Cool, 4°C, H ₂ SO ₄ to pH<2 | 28 days |
| Metals | | | |
| Chromium VI | P,G | Cool, 4°C | 24 hr |
| Mercury | P,G | HNO ₃ to pH<2 | 28 days |
| Metals, except chromium VI and mercury | P,G | HNO ₃ to pH<2 | 6 months |
| Nitrate | P,G | Cool, 4°C | 48 hr |
| Nitrate-nitrite | P,G | Cool, 4°C, H ₂ SO ₄ to pH<2 | 28 days |
| Nitrite | P,G | Cool, 4°C | 48 hr |
| Oil and grease | G | Cool, 4°C, H ₂ SO ₄ to pH<2 | 28 days |
| Organic carbon | P,G | Cool, 4°C, HCl or H ₂ SO ₄ to pH<2 | 28 days |
| Orthophosphate | P,G | Filter immediately, cool, 4°C | 48 hr |
| Oxygen, dissolved probe | G bottle and top do | None required | Analyze immediately |
| Winkler | G only | Fix on site and store in dark | 8 hr |
| Phenols | G only | Cool, 4°C, H ₂ SO ₄ to pH<2 | 28 days |
| Phosphorus (elemental) | G | Cool, 4°C | 48 hr |
| Phosphorus, total | P,G | Cool, 4°C, H ₂ SO ₄ to pH<2 | 28 days |
| Residue, total | P,G | Cool, 4°C | 7 days |
| Residue, Filterable | P,G | Cool, 4°C | 7 days |
| Residue, Nonfilterable (TSS) | P,G | Cool, 4°C | 7 days |
| Residue, Settleable | P,G | Cool, 4°C | 48 hr |
| Residue, Volatile | P,G | Cool, 4°C | 7 days |
| Silica | P | Cool, 4°C | 28 days |
| Specific conductance | P,G | Cool, 4°C | 28 days |
| Sulfate | P,G | Cool, 4°C | 28 days |
| Sulfide | P,G | Cool, 4°C, add zinc acetate plus sodium hydroxide to pH>9 | 7 days |
| Sulfite | P,G | None required | Analyze immediately |
| Surfactants | P,G | Cool, 4°C | 48 hr |

TABLE 6-1 (Cont'd)
 REQUIRED CONTAINERS, PRESERVATION TECHNIQUES
 AND HOLDING TIMES
 GROUNDWATER AND SURFACE WATER

| Name | Container ^a | Preservation | Maximum Holding Time |
|-----------------------------------|------------------------|--|---|
| Temperature | P,G | None required | Analyze |
| Turbidity | P,G | Cool, 4°C | 48 hr |
| <u>Organic Tests:</u> | | | |
| Purgeable Halocarbons | G, Teflon-lined septum | Cool, 4°C, 0.008 percent Na ₂ S ₂ O ₃ | 14 days |
| Purgeable aromatic hydrocarbons | G, Teflon-lined septum | Cool, 4°C, 0.008 percent Na ₂ S ₂ O ₃ , HCl to pH < 2 | 14 days |
| Acrolein and acrylonitrile | G, Teflon-lined septum | Cool, 4°C, 0.008 percent Na ₂ S ₂ O ₃ , Adjust pH to 4 to 5 | 14 days |
| Phenols | G, Teflon-lined cap | Cool, 4°C, 0.008 percent Na ₂ S ₂ O ₃ | 7 days until extraction |
| Benzidines | G, Teflon-lined cap | Cool, 4°C, 0.008 percent Na ₂ S ₂ O ₃ | 7 days until extraction |
| Phthalate esters | G, Teflon-lined cap | Cool, 4°C | 7 days until extraction 40 days until extraction |
| Nitrosamines | G, Teflon-lined cap | Cool, 4°C, store in dark, 0.008 percent, Na ₂ S ₂ O ₃ | 40 days after extraction |
| PCBs, acrylonitrile | G, Teflon-lined cap | Cool, 4°C | 40 days after extraction |
| Nitroaromatics and isophorone | G, Teflon-lined cap | Cool, 4°C, 0.008 percent Na ₂ S ₂ O ₃ , store in dark | 40 days after extraction |
| Polynuclear aromatic hydrocarbons | G, Teflon-lined cap | Cool, 4°C, 0.008 percent Na ₂ S ₂ O ₃ , store in dark | 40 days after extraction |
| Haloethers | G, Teflon-lined cap | Cool, 4°C, 0.008 percent Na ₂ S ₂ O ₃ | 40 days after extraction |
| Chlorinated Hydrocarbons | G, Teflon-lined cap | Cool, 4°C, 0.008 percent Na ₂ S ₂ O ₃ | 40 days after extraction |
| TCDD | G, Teflon-lined cap | Cool, 4°C | 40 days after extraction |
| Total organic halogens | G, Teflon-lined | Cool, 4°C, H ₂ SO ₄ to pH < 2 | 7 days |
| <u>Pesticides Tests:</u> | | | |
| Pesticides | G, Teflon-lined | Cool, 4°C, pH 5 to 9 | 40 days after extraction |
| <u>Radiological Tests:</u> | | | |
| Alpha, beta, and radium | P,G | HNO ₃ to pH < 2 | 6 months |

^aPolyethylene (P) or Glass (G).

analyzed. Prior to use, corers and other sampling tools are washed with soapy water and rinsed with deionized water. Nanograde isopropanol or acetone may be used to remove organic contamination. For near surface samples (three feet or less), disposable lengths of pipe can be used for taking cores.

Table 6-2 lists the containers for collection of soil and sediment samples and holding times. Containers for solid samples are cleaned by the same procedures described for water samples.

Soil and sediment samples for volatiles analysis should be quickly added to the sampling vials. Special precautions are taken to minimize head or void space.

Soil and sediment samples for organics and nutrients analyses are stored at 4°C prior to testing.

TABLE 6-2

REQUIRED CONTAINERS, SAMPLE STORAGE TECHNIQUES
AND RECOMMENDED HOLDING TIMES
SOIL AND SEDIMENTS

| Parameter | Sample Container | Sample Storage | Recommended Maximum Holding Times |
|----------------------|---|----------------|--|
| Nutrients/TOC | 0.5 to 1 liter, plastic | 4°C | 7 days |
| Metals | 0.5 to 1 liter, plastic | None required | 6 months |
| Nonvolatile Organics | 0.5 to 1 liter, glass with teflon lined lid | Dark, 4°C | 10 days before extraction and 40 days after extraction |
| Volatile Organics | 2 - 40 ml glass vials with teflon spetum. | Dark, 4°C | 7 days |

SECTION 7
SAMPLE CUSTODY

7.1 FIELD COLLECTION AND SHIPMENT

When transferring and/or shipping from the field, samples are accompanied by chain-of-custody records. The records include the signatures of the relinquisher and the receiver, the date and time of the exchange, and any pertinent remarks. Figure 7-1 illustrates a sample chain-of-custody form.

During sample collection, the following procedures are observed:

1. To maintain the validity of the sample, on-site procedures are reviewed prior to arrival in the field and confirmed for accuracy.
2. Sample handling is minimized in order to reduce the chance of error, confusion, and damage.
3. Only the number of samples necessary to the study are collected to reduce possible confusion and shipping problems.
4. Sample tags are marked in the field, with water proof ink to prevent misidentification due to label illegibility.
5. Samples are provided a tamper proof seal so that sample integrity can be documented upon receipt.
6. The shipping container is either padlocked or provided a tamper proof seal.

Samples are shipped in one of the following ways so that safeguards in chain-of-custody can be observed.

- Registered mail, so that a return receipt is requested and available for documentation,
- Common carrier, so that a bill of lading can serve this purpose,

- Air freight collect, for complete documentation.

7.2 DOCUMENT CONTROL

A log book is maintained as a permanent record of all activities relating to the collection of a sample. Information included in the log book are: signatures of those responsible for a sample, date received, location, and the testing objective. The log book also includes data on the weather at the sampling time and location and other related field conditions. If the log book is lost or damaged, it is promptly reported. This procedure is also used for field data records and in-house records. Table 7-1 presents a list of specific information which should be recorded at the time a sample is collected.

Identification of samples is serialized in an alpha-numeric system consistent with the procedures of the study. If the sample is contaminated, it is to be disposed of properly and noted in the log book. Similarly, if the sample is lost, it is documented and the Project Manager promptly notified.

If photographs are taken, pertinent information is written on the back of each photo as a permanent record. This information is written in permanent ink and includes the location, date, time, scale, photographer, and any other pertinent information.

7.3 SAMPLE CONTROL

Sample control is maintained at the sample site by entering information in the log-book. This information includes the project code or name, station numbers, station location, sample depth increment, date, time, and the sampler(s) observations. Observations may include weather conditions, problems encountered, and general remarks (see Table 7-1). Tags or labels affixed to the sample will include all of the information listed above and the sample number, analyses to be performed, any special information

TABLE 7-1

SAMPLE INFORMATION

IN-SITU SAMPLES (e.g., temperature, pH)Data in Logbook:

project name or code
station number
station location
date
time
sampler(s)
field observations - weather, problems, etc.
remarks
value of parameter measured

TRANSPORTED SAMPLESData on Tags or Labels:

all above information
laboratory sample number
analysis required
split sample/duplicate
sample/blank
grab or composite

relating to the nature of the sample (e.g., split, duplicate, blanks) and the mode of collection, e.g. as grab or composite.

7.4 SHIPPING AND PACKAGING

Sample packaging for shipment is done such that under normal handling, there is no significant release of materials and the effectiveness of the packing is not reduced; and there is no internal mixing of substances. The procedures which are followed to achieve these objectives are as follows:

1. The volume of the sample will be limited to the quantity needed for analysis.
2. Plastic containers will be used whenever possible. The plastic container will be protected from puncture. If glass containers are used, the glass will be well cushioned.
3. Screw lids will be used whenever possible. If corks and stoppers are used, they will be taped to help assure that they remain in place during shipment.
4. Leakage will be minimized by the use of internal bagging.

All samples determined to be hazardous, according to the U.S. Department of Transportation (U.S. DOT) (49 CFR Section 172.101 or 49 CFR 173.3), will be shipped in strict accordance with U.S. DOT regulations.

7.5 SAMPLE RECEIPT

The first step in the receipt of samples is obtaining the necessary sample information. In general, this information is organized by the ATSD Technical Assistant and passed on immediately to the Sample Custodian. The Section Chief, who is expectant of the shipment, notifies the appropriate Group Leaders of the incoming samples.

Upon sample receipt, the Sample Custodian follows this subsequent procedure.

- Examine samples and determine if proper temperature has been maintained during shipment. If samples have been damaged during shipment, the remaining samples are carefully examined to determine whether they were affected. Any affected samples are also considered damaged. It is noted on the chain-of-custody record that specific samples were damaged and that the samples were removed from the analytical schedule. Field personnel are notified as soon as possible that samples were damaged and instructed as to what course of action to take.
- Compare samples received against those listed on the chain-of-custody.
- Verify that sample holding times have not been exceeded.
- Sign and date the chain of custody form and attach the waybill to the chain of custody.
- Enter the samples in the sample log book which contains the following information:
 - Project identification number
 - Sample numbers
 - Type of samples
 - Date received
- Place the samples in adequate storage.
- Notify the appropriate Section Chiefs of sample arrival.
- Place the completed chain-of-custody records in the project file.

If samples collected by AWARE personnel arrive either without a chain-of-custody record or an incorrect chain-of-custody record, the following procedure is undertaken by the Section Chief.

- If the chain-of-custody is incorrect or incomplete, a memorandum to the Project Manager and field personnel is prepared stating the inaccuracy and necessary correction. The memorandum is signed and dated by the person originating the chain-of-custody and the Section Chief. The memorandum serves as an amendment to the chain-of-custody. If the information on the chain-of-custody form cannot be corrected by the Section Chief or the field personnel, the samples affected are removed from the analytical schedule.
- If the chain-of-custody record is not shipped with the samples, the field personnel are contacted and a memorandum prepared which lists the persons involved in collection, shipment, receipt and the times, dates, and events of such. Each person involved must sign and date this memorandum. The completed memorandum is maintained in lieu of the chain-of-custody record.

7.6 CUSTODY DURING TESTING PROGRAM

When chain-of-custody samples are present in the ATSD, the facility is secured by locking all entrances and exits 24 hrs a day. No unauthorized personnel are permitted within the facility without a proper escort.

When chain-of-custody samples are being analyzed or processed, they are signed out by the appropriate analyst. The individual performing the tests becomes responsible for the samples at that point. The samples are maintained within sight or in the secure possession of the individual performing the test. When the work is completed, the samples are returned and logged in to secure them in the proper storage location. During processing, the sample may be split into several fractions, depending upon the analysis required. The chain-of-custody record remains intact, however, for all samples fractions with the corresponding sample number.

After the analytical results have been reported, the chain-of-custody samples remain secured in storage. Restricted access to these samples is maintained.

SECTION 8
CALIBRATION PROCEDURES

8.1 FIELD INSTRUMENTS

1. Dissolved Oxygen Meter

- See Table 8-1 (Manufacturers Specifications)

2. Conductivity Meter (Fisher Scientific Standards)

- Allow meter to equilibrate for 5-10 minutes
- Calibrate meter with a standard in the same concentration range as the samples being analyzed.
- Analyze an EPA Performance Evaluation (PE) sample to check accuracy; if within acceptable limits, proceed with samples.
- EPA PE sample analyzed every fifth sample to insure calibration.
- Recalibrate every hour of continuous operation.
- Recalibrate if there is more than 30 minutes between readings.
- Be sure to rinse probe between readings.

3. pH Meter (Fisher Scientific Standards)

- Calibrate with buffers 10.0 and 4.0
- Check buffer 7.0 for accuracy and record
- Accuracy must be within 0.20 units
- Check buffer 7.0 every fifth sample for QC purposes and record data.
- Recalibrate every hour or as deemed necessary.
- Rinse probe between readings.

TABLE 8-1

YSI D.O. METER OPERATING INSTRUCTIONS

I. CALIBRATION

- A. Switch instrument to Off and adjust meter mechanical zero.
- B. Switch to RED LINE and adjust.
- C. Prepare probe for operation, connect to instrument, wait up to 15 minutes for probe to stabilize. Probe can be in calibration chamber or ambient air.
- D. Switch to ZERO and adjust to "0" on mg/l scale.
- E. Switch to TEMP and read on °C scale.
- F. Use probe temperature and true local atmospheric pressure (or feet above sea level) to determine calibration values from Tables I and II. (See pages 14 and 15).

EXAMPLE: Probe temperature = 21°C; Altitude = 1000 feet. From Table I the calibration value for 21°C is 8.9 mg/l. From Table II the altitude factor for 1000 feet is approximately .96. The correct calibration value, then, is:

$$8.9 \text{ mg/l} \times .96 \text{ factor} = 8.54 \text{ mg/l}$$

- G. Switch to 0.10 or 0.20 mg/l range and adjust meter with CAL control to calibration value determined in Step F.

NOTE: It is desirable to calibrate probe in a high humidity environment. (See calibration section for more detail).

2. MEASUREMENT

- A. Place probe in sample and stir.
- B. Allow sufficient time for probe to stabilize to sample temperature and dissolved oxygen.
- C. Read dissolved oxygen on appropriate range (1-10 or 0-20 mg/l)
- D. We recommend the instrument be left on between measurements to avoid the necessity to repolarize the probe.

3. GENERAL CARE

- A. Recharge batteries in the YSI Model 54ASRC when the instrument can no longer be red lined. Recharge 16-20 hours. Replace with Burgess CD-6 or equivalent. Replace batteries in the YSI Model 54ABP when red line cannot be set with Panasonic UM-2N or equivalent.
 - B. Membranes will last indefinitely, depending on usage. Average replacement is 2-4 weeks. Probe should be stored in humid environment to prevent drying out.
 - C. Calibrate daily.
-
-

8.2 LABORATORY INSTRUMENTS

1. pH Meter (Fisher Scientific Standards)

- Turn meter on and allow it to equilibrate for several minutes.
- Calibrate with buffers 4 and 10; then read buffer 7.0 for accuracy. The reading must be within 0.20 units.
- Check buffer 7.0 after each tenth sample and record value.
- Rinse the probe between samples.

2. Conductivity Meter (Fisher Scientific Standards)

- Turn meter on and allow it to equilibrate for several minutes
- Calibrate meter with 0.0100N KCl (1413 umhos/cm @ 25°C). This standard must be checked after every tenth measurement and at the end of every sample sequence. A limit of within 10% is recommended.
- Analyze EPA Performance Evaluation Sample; measurement must be within EPA established limits. (Normally 10 to 15 percent depending on concentration).
- All samples must be analyzed at 25°C or temperature difference must be taken into account.
- A thorough rinse between samples is mandatory.

3. Atomic Absorption Spectrophotometer (AAS) (Fisher Scientific Standards)

The AAS is standardized for the parameter of interest by the analysis of calibration standards prepared by diluting a stock solution of known concentration. Three to five working standards are prepared from the stock solution. The concentration of the calibration standards is chosen so as to cover the working range of the instrument. Subsequently, all measurements are made within this range. After the working standards are prepared, instrument response is calibrated to provide a

direct readout in absorbance units. The calibration curve is completed by plotting instrument response versus concentration (in ppm) of the parameter being analyzed. Daily verification of the calibration curve is accomplished by analyzing a midpoint standard and reagent blank. The accuracy must conform to within 10 percent before actual processing of samples can begin. If the midpoint standard is outside the specified control limit, a new calibration curve must be prepared.

Once the AAS has been initially calibrated, the analysis of the midpoint standard is checked daily to confirm the initial calibration curve. A typical analysis sequence is presented below:

- Working standards are prepared by dilution of a stock standard solution of the parameter of interest.
- A calibration curve is established within the working range of the instrument by the analysis of three to five calibration standards.
- Midpoint calibration standard is checked daily to confirm the initial calibration curve. A control limit of within 10 percent is used to verify instrument calibration. If this limit is exceeded, a completely new calibration curve is constructed.
- Samples are analyzed for the parameter of interest.
- During the sample analysis, the midpoint standard is analyzed to monitor instrument stability. If the analysis indicates that instrument calibration has changed (not within 10 percent), the instrument is recalibrated and the analysis is repeated.
- Following the completion of the sample analysis, the midpoint standard is reanalyzed to confirm instrument calibration.

If calibration is confirmed (within 10 percent), the analysis is complete. However if calibration is not confirmed, the instrument must be recalibrated and the analysis repeated.

4. Gas Chromatograph/Extractables (Chem-Service-U.S. EPA Standards)

Calibration of the gas chromatograph (GC) for pesticide and polychlorinated biphenyl (PCB) or other organic compound analyses is performed simultaneously with the standardization of the instrument. A four-point standard curve, using a 5ul aliquot, consisting of a method blank and three standards, should be analyzed to calibrate instrument response by the external standard procedure and to define the working range of the GC for the compounds of interest.

The calibration standards are tabulated according to peak height or area responses against mass injected. The results can be used to prepare a calibration curve. Alternatively, if the ratio of response to amount injected (calibration factor) is a constant over the working range (10 percent Relative Standard Deviation, RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

The working calibration curve, calibration factor, or response factor (RF) are verified on each working day by the measurement of one or more calibration standards. If the response varies from the predicted response by more than 15 percent, the test must be repeated using a new calibration standard. If the control limit is still not in compliance, a new calibration curve is prepared.

During the actual processing of samples a continuing calibration check (CCC) sample is analyzed after every tenth sample run to insure instrument calibration. If at any time the response varies more than 15 percent from the predicted value, a new calibration curve is prepared and all affected samples reanalyzed. When sample responses exceed the range of the standard curve, the sample is diluted so as to fall within the range of the standard curve and reanalyzed.

5. Gas Chromatograph/Volatiles (Chem-Service Standards)

Calibration standards are prepared at a minimum of three concentration levels for each parameter by carefully adding 20.0 μ l of one or more secondary dilution standards to 100, 500 or 1000ml of reagent water. A 25 μ l syringe with a 0.006 in. ID needle is used for this operation. One of the external standards should be at a concentration slightly above the Method Detection Limit (MDL). The other concentrations should either correspond to the expected range of concentrations found in real samples or define the working range of the detector. These aqueous standards must be prepared fresh on a daily basis.

Analyze each calibration standard and tabulate peak height or area responses versus the concentration in the standard. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (10 percent Relative Standard Deviation, RSD), linearity through the origin can be assumed and the average ratio or calibration factor used in place of a calibration curve.

The working calibration curve and calibration factor (or response factor (RF)) are verified on each working day by the measurement of a QC check sample. The control limit for this sample is 25 percent RSD. If this criterion is not satisfied, a new calibration curve is prepared.

6. Gas Chromatograph/Mass Spectrometer (GC/MS)

This section outlines the minimum operations necessary to satisfy analytical requirements associated with the determination of organic Hazardous Substance List (HSL) compounds in water and soil/sediment samples. The following operations should be performed routinely in the laboratory:

- Documentation of GC/MS mass calibration and abundance pattern

- Documentation of GC/MS response factor stability
- Internal standard response and retention time monitoring

Tuning and GC/MS Mass Calibration

Prior to initiating data collection, it is necessary to establish that a given GC/MS system meets the standard mass spectral abundance criteria. This is accomplished through the analysis of decafluorotriphenylphosphine (DFTPP) for base/neutral and acid (BNA) compounds or p-bromofluorobenzene (BFB) for volatile compounds. The ion abundance criteria for each calibration compound should be satisfied before any samples, blanks, or standards are analyzed.

DFTPP (decafluorotriphenylphosphine)

Each GC/MS system used for the analysis of semivolatile or pesticide HSL compounds is tuned to meet the abundance criteria as listed in Table 8-2 for a 50 ng injection of DFTPP. DFTPP can be analyzed separately or as part of the calibration standard, but the criteria is demonstrated daily. Documentation of the calibration is provided in the form of a bar graph plot and as a mass listing.

BFB (p-bromofluorobenzene)

Each GC/MS system used for the analysis of volatile HSL compounds is tuned to meet the abundance criteria listed in Table 8-3 for a 50 ng injection of BFB. The criteria is demonstrated daily. Documentation of the calibration is provided in the form of a bar graph plot and as a mass listing.

Analysts complete a GC/MS Tuning and Mass Calibration Form or a copy of the instrument printout each time an analytical system is tuned.

TABLE 8-2
DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

| Mass | Ion Abundance Criteria |
|------|---|
| 51 | 30.0 to 60.0 percent of mass 198 |
| 68 | Less than 2.0 percent of mass 69 |
| 70 | Less than 2.0 percent of mass 69 |
| 127 | 40.0 to 60.0 percent of mass 198 |
| 197 | Less than 1.0 percent of mass 198 |
| 198 | Base peak, 100 percent relative abundance |
| 199 | 5.0 to 9.0 percent of mass 198 |
| 275 | 10.0 to 30.0 percent of mass 198 |
| 365 | Greater than 1.0 percent of mass 198 |
| 441 | Present, but less than mass 443 |
| 442 | Greater than 40 percent of mass 198 |
| 443 | 17.0 to 23.0 percent of mass 442 |

TABLE 8-3
BFB KEY IONS AND ABUNDANCE CRITERIA

| Mass | Ion Abundance Criteria |
|------|--|
| 50 | 15.0 to 40.0 percent of the base peak |
| 75 | 30.0 to 60.0 percent of the base peak |
| 95 | Base peak, 100 percent relative abundance |
| 96 | 5.0 to 9.0 percent of the base peak |
| 173 | Less than 1.0 percent of the base peak |
| 174 | Greater than 50.0 percent of the base peak |
| 175 | 5.0 to 9.0 percent of mass 174 |
| 176 | Greater than 95.0 percent, but less than 101.0 percent of mass 174 |
| 177 | 5.0 to 9.0 percent of mass 176 |

CALIBRATION OF THE GC/MS SYSTEM

Internal Standard Calibration

Prior to the analysis of samples and after tuning criteria are satisfied, the GC/MS system is initially calibrated at a minimum of three concentrations to determine the linearity of response utilizing HSL compound standards. For GC/MS analysis, typical linear ranges are 0 to 400 ng for base neutrals, 0 to 1,000 ng for phenols and 0 to 1,000 ng for volatiles.

Calibration standards are prepared to yield the following specific concentrations.

Volatile HSL Compounds

Initial calibration of volatile HSL compounds is recommended at 20, 50, 100, 150 and 200 µg/l. Volatile internal standards with corresponding HSL analytes are listed in Table 8-4.

Semivolatile and Pesticide HSL Compounds

Initial calibration of semivolatile compounds is recommended at 20, 50, 80, 120 and 160 total nanograms. Ten compounds including: benzoic acid, 2,4-dinitrophenol, 2,4,5-trichlorophenol, 2-nitroaniline, 3-nitroaniline, 4-nitroaniline, 4-nitrophenol, 4,6-dinitro-2-methylphenol, pentachlorophenol and benzidine use a four-point initial calibration at 50, 80, 120 and 160 total nanograms. Detection at less than 50 ng per injection is difficult. Semivolatile internal standards with corresponding HSL analytes are listed in Table 8-5.

U.S. EPA criteria specify both the concentration levels for initial calibration and the specific internal standard to be used on a compound-by-compound basis for quantification. The response factor (RF) for each compound at each concentration level is calculated using the following equation:

TABLE 8-4

VOLATILE INTERNAL STANDARDS WITH CORRESPONDING
HSL ANALYTES ASSIGNED FOR QUANTIFICATION

| Bromochloromethane | 1,4-Difluorobenzene | Chlorobenzene-d ₅ |
|--|---------------------------|-------------------------------|
| Chloromethane | 2-Butanone | 2-Hexanone |
| Bromomethane | 1,1,1-Trichloroethane | 4-Methyl-2-Pentanone |
| Vinyl Chloride | Carbon Tetrachloride | Tetrachloroethene |
| Chloroethane | Vinyl Acetate | 1,1,2,2-Tetrachloroethane |
| Methylene Chloride | Bromodichloromethane | Toluene |
| Acetone | 1,2-Dichloropropane | Chlorobenzene |
| Carbon Disulfide | trans-1,3-Dichloropropene | Ethylbenzene |
| 1,1-Dichloroethene | Trichloroethene | Styrene |
| 1,1-Dichloroethane | Dibromochloromethane | Total Xylenes |
| trans-1,2-Dichloroethene | 1,1,2-Trichloroethane | Bromofluorobenzene (surr) |
| Chloroform | Benzene | Toluene-d ₈ (surr) |
| 1,2-Dichloroethane | cis-1,3-Dichloropropene | |
| 1,2-Dichloroethane-d ₄ (surr) | Bromoform | |

TABLE 8-5

SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING
HSL ANALYTES ASSIGNED FOR QUANTIFICATION

| 1,4-Dichlorobenzene-d ₄ | Naphthalene-d ₈ | Acenaphthene-d ₁₀ | Phenanthrene-d ₁₀ | Chrysene-d ₁₂ | Perylene-d ₁₂ |
|------------------------------------|------------------------------------|------------------------------|------------------------------|----------------------------------|--------------------------|
| N-Nitrosodimethylamine | Nitrobenzene | Hexachlorocyclopentadiene | 4,6-Dinitro-2-methylphenol | Benzidine | Di-n-octyl Phthalate |
| Phenol | Isophrone | 2,4,6-Trichlorophenol | N-nitrosodiphenylamine | Pyrene | Benzo(b)fluoranthene |
| Aniline | 2-Nitrophenol | 2,4,5-Trichlorophenol | 1,2-Diphenylhydrazine | Butylbenzyl Phthalate | Benzo(k)fluoranthene |
| bis(2-chloroethyl) ether | 2,4-Dimethylphenol | 2-Chloronaphthalene | 4-Bromophenyl Phenyl Ether | 3,3'-Dichlorobenzidine | Benzo(a)pyrene |
| 2-Chlorophenol | Benzoic acid | 2-Nitroaniline | Hexachlorobenzene | Benzo(a)-anthracene | Indeno(1,2,3-cd) pyrene |
| 1,1-Dichlorobenzene | bis(2-Chloro-ethoxy)methane | Dimethyl Phthalate | Pentachlorophenol | bis(2-ethylhexyl) Phthalate | Dibenzo(a,h)anthracene |
| 1,4-Dichlorobenzene | 2,4-Dichlorophenol | Acenaphthylene | Phenanthrene | Chrysene | Benzo(g,h,i)perylene |
| Benzyl Alcohol | 1,2,4-Trichlorobenzene | 3-Nitroaniline | Anthracene | Terphenyl-d ₁₄ (surr) | |
| 1,2-Dichlorobenzene | Naphthalene | Acenaphthene | Di-n-butyl Phthalate | | |
| 2-Methylphenol | 4-Chloroaniline | 2,4-Dinitrophenol | Fluoranthene | | |
| bis(2-Chloroisopropyl) ether | Hexachlorobutadiene | 4-Nitrophenol | | | |
| 4-Methylphenol | 4-Chloro-1-methylphenol | Dibenzofuran | | | |
| N-nitroso-Di-n-propylamine | 2-Methylnaphthalene | 2,4-Dinitrotoluene | | | |
| Hexachloroethane | Nitrobenzene-d ₅ (surr) | 2,6-Dinitrotoluene | | | |
| 2-Fluorophenol (surr) | | Diethyl Phthalate | | | |
| Phenol-d ₆ (surr) | | 4-Chlorophenylphenyl ether | | | |
| | | Fluorene | | | |
| | | 4-Nitroaniline | | | |
| | | 2-Fluorobiphenyl (surr) | | | |
| | | 2,4,6-Tribromo Phenol (surr) | | | |

$$RF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

where:

- A_x = area of the characteristic ion for the compound to be measured
- A_{is} = area of the characteristic ion for the specific internal standards
- C_{is} = concentration of the internal standard (ng/ μ l)
- C_x = concentration of the compound to be measured (ng/ μ l).

Calibration Check Compound Response

Using the RF from the initial calibration, calculate the percent relative standard deviation (percent RSD) for compounds identified as Calibration Check Compounds using the equation presented below.

$$\% \text{ RSD} = \frac{\alpha}{x} \times 100$$

where:

- RSD = relative standard deviation
- α = standard deviation of initial five response factors (per compound)
- x = mean of initial five response factors (per compound).

The percent RSD for each individual Calibration Check Compound should be less than 30 percent. This criteria must be satisfied for the initial calibration to be valid.

Calibration check compounds are listed in Table 8-6.

System Performance Check Compound Response

A system performance check should be performed so that minimum average response factors are met before the calibration curve is used.

For volatiles, the five System Performance Check Compounds (SPCCs) are: chloromethane, 1,1-dichloroethane, bromoform, 1,1,2,2-tetrachloroethane, and chlorobenzene. The minimum acceptable average response factor (RF) for these compounds is 0.3. These compounds typically have RFs of 0.4 to 0.6.

TABLE 8-6
CALIBRATION CHECK COMPOUNDS

| Base/Neutral Fraction | Acid Fraction | Volatile Fraction |
|----------------------------|-------------------------|---------------------|
| Acenaphthene | 4-Chloro-3-Methylphenol | 1,1-Dichloroethene |
| 1,4-Dichlorobenzene | 2,4-Dichlorophenol | Chloroform |
| Hexachlorobutadiene | 2-Nitrophenol | 1,2-Dichloropropane |
| N-Nitroso-di-n-phenylamine | Phenol | Toluene |
| Di-n-octyl phthalate | Pentachlorophenol | Ethylbenzene |
| Fluoranthene | 2,4,6-Trichlorophenol | Vinyl Chloride |
| Benzo(a)pyrene | | |

For semivolatiles, the SPCCs are: n-nitroso-di-n-propylamine, hexachlorocyclopentadiene, 2,4-dinitrophenol, 4-nitrophenol and benzidine. The minimum acceptable average RF for these compounds is 0.05. These compounds (SPCCs) typically have very low RFs (0.1 to 0.2).

Continuing Calibration (GC/MS)

A calibration standard containing all volatile or semivolatile HSL compounds and all required surrogates, should be performed each 12 hr during analysis. The RF data from the standards each 12 hr are compared with the average RF from the initial calibration for a specific instrument. A system performance check must be made each 12 hr. If the SPCC criteria are satisfied, a comparison of RFs is made for all compounds. This is the same check that is applied during the initial calibration. If the minimum response factors are not satisfied, the system is evaluated and corrective action taken before sample analysis begins.

SECTION 9

ANALYTICAL PROCEDURES

Whenever possible, the ATSD will utilize industry recognized analytical methods from source documents published by the following agencies.

- U.S. Environmental Protection Agency (U.S. EPA),
- American Public Health Association (APHA),
- American Society for Testing and Materials (ASTM),
- National Institute for Occupational Safety and Health (NIOSH).

The format presented in Tables 9-1 through 9-2 has been adopted from the referenced U.S. EPA document. Tables 9-3 provides analytical procedures for analyses not cited in Tables 9-1, 9-2 and procedures for different matrices.

9.1 VARIANCE FROM STATED ANALYTICAL METHODS

Analyses will be performed in accordance with the methods cited herein unless specific project requirements or needs dictate adoption of an alternate method or modification of the cited methods.

TABLE 9-1

LIST OF APPROVED INORGANIC TEST PROCEDURES

| PARAMETER, UNITS, AND METHOD | REFERENCE (METHOD NO. OR PAGE) | | | | |
|--|---|-----------------------------------|---|--|---|
| | EPA 1979 | STANDARD METHODS 15th Ed. | ASTM | USGS ⁽¹⁾ | OTHER |
| 1. Acidity, as CaCO ₃ , mg/L: Electrometric end point or phenolphthalein end point. | 305.1 | 402(4.d) | D1067-70(E) | - | - |
| 2. Alkalinity, as CaCO ₃ , mg/L: Electrometric or colorimetric: Titration to pH 4.5, manual Or automated | 310.1 310.2 | 403 - | D1067-70(B) - | 1-1030-78 1-2030-78 | P. 548 ⁽²⁾ - |
| 3. Aluminum--Total, (3) mg/L: Digestion ⁽³⁾ followed by: AA direct aspiration AA furnace Inductively coupled plasma Or colorimetric (Eriochrome cyanine R) | 202.1 202.2 - - | 303C 304 - 306B | - - - - | 1-3051-78 - - - | - - Method 200.7 ⁽⁴⁾ - |
| 4. Ammonia (as N), mg/L: Manual distillation ⁽⁵⁾ . (at pH 9.5): Followed by Nesslerization Titration Electrode Automated phenate, or Automated electrode | 350.2 350.2 350.2 350.3 350.1 | 417A 417B 417D - 417F | - D1426-79(A) - D1426-79(D) D1426-79(C) | - 1-3520-78 - - 1-4523-78 | - P. 553 ⁽²⁾ - - (6) |
| 5. Antimony--Total, (3) mg/L: Digestion ⁽³⁾ followed by: AA direct aspiration AA furnace, or Inductively coupled plasma | 204.1 204.2 - | 303A 304 - | - - - | - - - | - - Method 200.7 ⁽⁴⁾ |
| 6. Arsenic--Total, (3) mg/L: Digestion ⁽³⁾ followed by Hydride AA furnace Inductively coupled plasma Or, colorimetric (SDDC) | 206.5 206.3 206.2 206.4 | - 303E 304 307B | - D2972-78(B) - D2972-78(A) | - 1-3062-78 - 1-3060-78 | - - Method 200.7 ⁽⁴⁾ - |
| Barium--Total, (3) mg/L: Digestion ⁽³⁾ followed by: AA direct aspiration AA furnace, or Inductively coupled plasma | 208.1 208.2 - | 303C 304 - | - - - | 1-3084-78 - - | - - Method 200.7 ⁽⁴⁾ |
| 8. Beryllium--Total, (3) mg/L: Digestion ⁽³⁾ followed by: AA direct aspiration AA furnace Inductively coupled plasma Or colorimetric (aluminon) | 210.1 210.2 - | 303C 304 309B | - D3645-78 - - | 1-3095-78 - - | - - Method 200.7 ⁽⁴⁾ |
| 9. Biochemical oxygen demand (BOD ₅), mg/L: Winkler (Azide modification) Or electrode method | 405.1 - | 507 - | - - | 1-1578-78 - | P. 17 ⁽⁸⁾ P. 548 ⁽²⁾ |
| 10. Boron--Total, mg/L: Colorimetric (curcumin) or Inductively coupled plasma | 212.3 - | 404A - | - - | 1-3112-78 - | - Method 200.7 ⁽⁴⁾ |
| 11. Bromide, mg/L: Titrimetric | 320.1 | - | D1246-77(C) | 1-1125-78 | P. 544 ⁽²⁵⁾ |
| 12. Cadmium--Total, (3) mg/L: Digestion ⁽³⁾ followed by: AA direct aspiration AA furnace Inductively coupled plasma Voltammetry ⁽⁹⁾ or Colorimetric (Dithizone) | 213.1 213.2 - - | 303A or 303B 304 - 310B | D3557-78(A or B) - - D3557-78(C) | 1-3135-78 or 1-3136-78 - - - | Pg. 557 ⁽²⁾ Pg. 37 ⁽⁸⁾ Method 200.7 ⁽⁴⁾ - |
| 13. Calcium--Total, (3) mg/L: Digestion ⁽³⁾ followed by: Atomic absorption Inductively coupled plasma Or EDTA titration | 215.1 - 215.2 | 303A - 311C | D511-77(C) - D511-77(B) | 1-3152-78 - - | - Method 200.7 ⁽⁴⁾ - |
| 14. Carbonaceous Biochemical oxygen demand ⁽⁷⁾ (CBOD ₅), mg/L: Winkler (Azide modification) or electrode method with nitrification inhibitor | - | 507(5.e.6) | - | - | - |
| 15. Chemical oxygen demand (COD), mg/L: Titrimetric colorimetric Manual or Automated Spectrophotometric | 410.1 410.2 410.3 410.4 - | 506A - - - - | D1252-78 - - - - | 1-3560-78 1-3562-78 1-3561-78 - - | P. 550 ⁽²⁾ P. 17 ⁽⁸⁾ (10) - (11) |
| 16. Chloride, mg/L: Titrimetric (silver nitrate) or Mercuric nitrate Colorimetric (ferricyanide) manual or Automated | - 325.3 - 325.1 or 325.2 | 407A 407B - 407D | D512-67(B) D512-67(A) D512-67(C) - | 1-1183-78 1-1184-78 1-1187-78 1-2187-78 | - P. 554 ⁽²⁾ - - |

TABLE 9-1 (Cont'd)

LIST OF APPROVED INORGANIC TEST PROCEDURES

| PARAMETER, UNITS, AND METHOD | REFERENCE (METHOD NO. OR PAGE) | | | | |
|---|---|--------------------------------------|--|---|---|
| | EPA 1979 | STANDARD METHODS 15th Ed. | ASTM | USCS ⁽¹⁾ | OTHER |
| 7. Chlorine--Total residual (12) mg/L: Titrimetric-mercurimetric Starch end point Iodometric or DPD-FAS Spectrophotometric, DPD, or Electrode | 330.1 330.2 330.3 330.4 330.5 | 408C 408B 408A 408D 408E | D1253-76(A) - D1253-76(B) - - | - - - - - | - - - - (27) |
| Chromium VI dissolved, mg/L: 0.45 micron filtration with: Extraction and atomic absorption, or Colorimetric (Diphenylcarbazide) | 218.4 | 303B | - - | 1-1232-78 1-1230-78 | - - |
| 8. Chromium--Total, (3) mg/L: Digestion ⁽³⁾ (optional extraction) followed by: AA direct aspiration AA furnace Inductively coupled plasma Or colorimetric (Diphenylcarbazide) | 218.3 218.1 218.2 - | - 303A or 303B 304 312A | - D1687-77(D) - D1687-77(A) | - 1-3236-78 - - | - P. 557(2) Method 200.7(4) - |
| Cobalt--Total, (3) mg/L: Digestion ⁽³⁾ followed by: AA direct aspiration AA furnace, or Inductively coupled plasma | 219.1 219.2 | 303A or 303B 304 | D3558-77(A or B) - | 1-3240-78 or 1-3239-78 - | P. 37(8) Method 200.7(4) |
| Color, platinum Cobalt units or dominant wavelength hue, luminance, purity: Colorimetric, ADMI Platinum cobalt; or Spectrophotometric | 110.1 110.2 110.3 | 204D 204A 204B | - - - | - 1-1250-78 - | (13) - |
| Copper--Total, (3) mg/L: Digestion ⁽³⁾ followed by: AA direct aspiration AA furnace Inductively coupled plasma Colorimetric (Neocuproine) Choninate | 220.1 220.2 - - | 303A or 303B 304 313B | D1688-77(D or E) - D1688-77(A) | 1-3271-78 or 1-3270-78 - - | P. 557(2) and P. 37(8) Method 200.7(4) (14) |
| -Total, mg/L: Manual distillation with MgCl ₂ followed by titrimetric Manual or Automated ⁽¹⁵⁾ spectrophotometric | 335.2 335.2 335.2 335.3 | 412D 412B 412C 412D | - - D2036-75(A) D2036-75(A) | - - 1-3300-78 - | P. 22(8) - |
| Cyanide amenable to chlorination, mg/L: Manual distillation with MgCl ₂ ; followed by titrimetric, manual or automated ⁽¹⁵⁾ spectrophotometric | 335.1 | 412F | D2036-75(B) | - | - |
| 26. Fluoride--Total, mg/L ⁽³⁾ Manual distillation Followed by manual or Automated electrode SPADNS Or automated complexone | - 340.2 340.1 340.3 | 413A 413B 413C 413E | - D1179-72(B) - D1179-72(A) | - - 1-4327-78 - | - - - - |
| Gold--Total, (3) mg/L: Digestion ⁽³⁾ followed by: AA direct aspiration Or AA furnace | 231.1 231.2 | 303A 304 | - - | - - | - - |
| 27. Hardness--Total as CaCO ₃ , mg/L: Automated colorimetric EDTA titration Inductively coupled plasma Or atomic absorption (sum of Ca and Mg as their respective carbonates) | 130.1 130.2 215.1+ 242.1 | - 314B 303A | - D1126-67(B) - | 1-1338-78 - 1-3153-78+ 1-3446-78 | - Method 200.7(4) - |
| 28. Hydrogen ion (pH), pH units: Electrometric measurements Or automated electrode | 150.1 | 423 | D1293-78(A) or D1293-78(B) | 1-1586-78 - | - (16) |
| 29. Iridium--Total, (3) mg/L: Digestion ⁽³⁾ followed by: AA direct aspiration Or AA furnace | 235.1 235.2 | 303A 304 | - - | - - | - - |
| Iron--Total, (3) mg/L: Digestion ⁽³⁾ followed by AA direct aspiration AA furnace Inductively coupled plasma Or colorimetric (Phenanthroline) | - 236.1 236.2 - | 303A or 303B 303B 304 315B | D1068-77 (C or D) - - D1068-77(A) | - 1-3381-78 - - | - P. 557(2) Method 200.7(4) (17) |

TABLE 9-1 (Cont'd)

LIST OF APPROVED INORGANIC TEST PROCEDURES

| PARAMETER, UNITS, AND METHOD | REFERENCE (METHOD NO. OR PAGE) | | | | |
|--|---|--|--|---|--|
| | EPA 1979 | STANDARD METHODS 15th Ed. | ASTM | USGS ⁽¹⁾ | OTHER |
| 31. Kjeldahl nitrogen--Total (as N), mg/L: Digestion and distillation Followed by titration Nesslerization or Electrode Automated phenate Semi-automated block digester Or potentiometric | 351.3 351.3 351.3 351.3 351.1 351.2 351.4 | 420A or B 417D 417B 417E - - - | - D3590-77 - - - - - | - - - 1-4551-78 1-4552-78 - - | P. 552 ⁽²⁾ - - - - - - |
| 32. Lead--Total, ⁽³⁾ mg/L: Digestion ⁽³⁾ followed by: AA direct aspiration AA furnace Inductively coupled plasma Voltametry ⁽⁹⁾ or Colorimetric (Dithizone) | 239.1 239.2 - - - | 303A or 303B 304 - - 316B | D3559-78(A or B) - - D3559-78(C) - | 1-3399-78 - - - - | P. 557 ⁽²⁾ - Method 200.7 ⁽⁴⁾ - - |
| 33. Magnesium--Total, ⁽³⁾ mg/L: Digestion ⁽³⁾ followed by: Atomic absorption Inductively coupled plasma Or gravimetric | 242.1 - - | 303A - 318B | D511-77(B) - D511-77(A) | 1-3447-78 - - | P. 557 ⁽²⁾ Method 200.7 ⁽⁴⁾ - |
| 34. Manganese--Total, ⁽³⁾ mg/L: Digestion ⁽³⁾ followed by: AA direct aspiration AA furnace Inductively coupled plasma Or colorimetric (persulfate) Periodate | 243.1 243.2 - - - | 303A or 303B 304 - 319B - | D858-77(B or C) - - D858-77(A) - | 1-3454-78 - - - - | P. 557 ⁽²⁾ - Method 200.7 ⁽⁴⁾ P. 564 ⁽²⁾ (18) |
| 35. Mercury--Total, ⁽³⁾ mg/L: Cold vapor, manual or Automated | 245.1 245.2 | 303F - | D3223-79 - | 1-3462-78 - | P. 559 ⁽²⁾ - |
| 36. Molybdenum--Total, ⁽³⁾ mg/L: Digestion ⁽³⁾ followed by: AA direct aspiration AA furnace, or Inductively coupled plasma | 246.1 246.2 - | 303C 304 - | - - - | 1-3490-78 - - | - - Method 200.7 ⁽⁴⁾ |
| 37. Nickel--Total, ⁽³⁾ mg/L: Digestion ⁽³⁾ followed by: AA direct aspiration AA furnace Inductively coupled plasma Or colorimetric (Heptoxime) | 249.1 249.2 - - | 303A or 303B 304 - 321B | D1886-77(C or D) - - - | 1-3499-78 - - - | - - Method 200.7 ⁽⁴⁾ - |
| 38. Nitrate (as N), mg/L: Brucine sulfate, or Nitrate-nitrite N minus Nitrite N | 352.1 See parameters 39 and 40 | - See parameters 39 and 40 | D092-71 See parameters 39 and 40 | - See parameters 39 and 40 | P. 554 ⁽²⁾ P. 28 ⁽⁸⁾ |
| 39. Nitrate-nitrite (as N), mg/L: Cadmium reduction, manual Or automated; or Automated hydrazine | 353.3 353.2 353.1 | 418C 418F - | D3867-79(B) D3867-79(A) - | - 1-4545-78 - | - - - |
| 40. Nitrite (as N), mg/L: Spectrophotometric, manual or Automated (Diazotization) | 354.1 - | 419 - | D1254-67 - | - 1-4540-78 | (19) - |
| 41. Oil and grease--Total recoverable, mg/L: Gravimetric (extraction) | 413.1 | 503A | - | - | - |
| 42. Organic carbon--Total (TOC), mg/L: Combustion or oxidation | 415.1 | 505 | D2579-78(A) or D2579-78(B) | - | P. 551 ⁽²⁾ and P. 4 ⁽²⁰⁾ |
| 43. Organic nitrogen (as N), mg/L: Total Kjeldahl N minus ammonia N | See parameters 31 and 4 | 420A | D3590-77 minus D1426-79(A) | See parameters 31 and 4 | PP. 552-53 ⁽²⁾ |
| 44. Orthophosphate (as P), mg/L: Ascorbic acid method automated Or manual single reagent or Manual two reagents | 365.1 365.2 365.3 | 424G 424F - | - D515-78(A) - | 1-4601-78 - - | P. 561 ⁽²⁾ - - |
| 45. Osmium--Total, ⁽³⁾ mg/L: Digestion ⁽³⁾ followed by: AA direct aspiration, or AA furnace | 252.1 252.2 | 303C 304 | - - | - - | - - |
| 46. Oxygen, dissolved, mg/L: Winkler (Azide modification) Or electrode | 360.2 360.1 | 421B 421F | D1589-60(A) - | 1-1575-78 1-1576-78 | P. 550 ⁽²⁾ - |
| 47. Palladium--Total, ⁽³⁾ mg/L: Digestion ⁽³⁾ followed by: AA direct aspiration Or AA furnace | 253.1 253.2 | - - | - - | - - | P. 527 ⁽²⁵⁾ P. 528 ⁽²⁵⁾ |

TABLE 9-1 (Cont'd)

LIST OF APPROVED INORGANIC TEST PROCEDURES

| PARAMETER, UNITS, AND METHOD | REFERENCE (METHOD NO. OR PAGE) | | | | OTHER |
|---|---|--------------------------------|---------------------------------|----------------------------------|---|
| | EPA 1979 | STANDARD METHODS 15th Ed. | ASTM | USGS ⁽¹⁾ | |
| 48. Phenols, mg/L: Manual distillation Followed by manual Or automated ⁽¹⁵⁾ colorimetric (4AAP) | 420.1 420.1 420.2 | - - - | D1783-70 (A or B) - - | - - - | (26) (26) - |
| 49. Phosphorus (elemental), mg/L: Gas-liquid chromatography | - | - | - | - | (21) |
| 50. Phosphorus--Total, mg/L: Persulfate digestion Followed by manual or Automated ascorbic acid reduction; or semi-automated block digester | 365.2 365.2 or 365.3 365.1 365.4 | 424C(III) 424F 424G - | - D515-78 (A) - - | - - I-4600-78 I-4603-78 | P. 561 ⁽²⁾ - - - |
| 51. Platinum--Total, (3) mg/L: Digestion ⁽³⁾ followed by: AA direct aspiration Or AA furnace | 255.1 255.2 | 303A 304 | - - | - - | - - |
| 52. Potassium--Total, (3) mg/L: Digestion ⁽³⁾ followed by: Atomic absorption Inductively coupled plasma Or flame photometric | 258.1 - - | 303A - 322B | - - D1428-64 (A) | I-3630-78 - - | P. 560 ⁽²⁾ Method 200.7 ⁽⁴⁾ - |
| 53. Residue--total, mg/L: Gravimetric, 103-105°C | 160.3 | 209A | - | I-3750-78 | - |
| 54. Residue--filterable, mg/L: Gravimetric, 180°C | 160.1 | 209B | - | I-1750-78 | - |
| 55. Residue--nonfilterable, (TSS), mg/L: Gravimetric, 103-105°C post washing of residue | 160.2 | 209D | - | I-3765-78 | - |
| 56. Residue--settleable, mg/L: Volumetric (Imhoff cone) or gravimetric | 160.5 | 209F | - | - | - |
| 57. Residue--volatile, mg/L: Gravimetric, 550°C | 160.4 | 209E | - | I-3753-78 | - |
| 58. Rhodium--Total, (3) mg/L: Digestion ⁽³⁾ followed by: AA direct aspiration Or AA furnace | 265.1 265.2 | 303A 304 | - - | - - | - - |
| 59. Rhenium--Total, (3) mg/L: Digestion ⁽³⁾ followed by: AA direct aspiration Or AA furnace | 267.1 267.2 | 303A 304 | - - | - - | - - |
| 60. Selenium--Total, (3) mg/L: Digestion ⁽³⁾ followed by: AA furnace Inductively coupled plasma Or hydride | 270.2 - 270.3 | 304 - 303E | - - D3859-79 | - - I-3667-78 | - Method 200.7 ⁽⁴⁾ - |
| 61. Silica--Dissolved, mg/L: 0.45 micron filtration: Followed by manual or Automated colorimetric (Molybdisilicate), or Inductively coupled plasma | 370.1 - - | 425C - - | D859-68 (B) - - | I-1700-78 I-2700-78 - | - - Method 200.7 ⁽⁴⁾ |
| 62. Silver--Total, (22) mg/L: Digestion ⁽³⁾ followed by: AA direct aspiration AA furnace, or Inductively coupled plasma | 272.1 272.2 - | 303A or 303B 304 - | - - - | I-3720-78 - - | P. 557 ⁽²⁾ and 37 ⁽⁸⁾ - Method 200.7 ⁽⁴⁾ |
| 63. Sodium--Total, (3) mg/L: Digestion ⁽³⁾ followed by: Atomic absorption Inductively coupled plasma Or flame photometric | 273.1 - - | 303A - - | - - D1428-64 (A) | I-3735-78 - - | P. 561 ⁽²⁾ Method 200.7 ⁽⁴⁾ - |
| 64. Specific conductance, mhos/cm: Wheatstone bridge | 120.1 | 205 | D1125-77 (A) | I-1780-78 | P. 547 ⁽²⁾ |
| 65. Sulfate (as SO ₄), mg/L: Automated methylthymol blue Gravimetric, or Turbidimetric | 375.2 375.3 375.4 | - 426A or 426B 426C | - D516-68 (A) D516-68 (B) | I-2822-78 - - | - PP. 562-63 ⁽²⁾ - |
| 66. Sulfide (as S), mg/L: Titrimetric (iodine) or Colorimetric (methylene blue) | 376.1 376.2 | 427D 427C | - - | I-3840-78 - | - - |
| 67. Sulfitc (as SO ₃), mg/L: Titrimetric (iodine iodate) | 377.1 | 428F | D1339-78 (C) | - | - |
| 68. Surfactants, mg/L: Colorimetric (methylene blue) | 425.1 | 512A | D2330-68 (A) | - | - |
| 69. Temperature, °C: Thermometric | 170.1 | 212 | - | - | (23) |
| 70. Thallium--Total, (3) mg/L: Digestion ⁽³⁾ followed by: AA direct aspiration AA furnace, or Inductively coupled plasma | 279.1 279.2 - | 303A 304 - | - - - | - - - | - - Method 200.7 ⁽⁴⁾ |

TABLE 9-1 (Cont'd)

LIST OF APPROVED INORGANIC TEST PROCEDURES

| PARAMETER, UNITS, AND METHOD | EPA 1979 | REFERENCE (METHOD NO. OR PAGE) | | | OTHER |
|---|--------------------------|--------------------------------|--------------------------------------|--------------------------|---|
| | | STANDARD METHODS 15th Ed. | ASTM | USGS(1) | |
| 71. Tin--Total, (3) mg/L: Digestion(3) followed by: AA direct aspiration or AA furnace | 282.1 282.2 | 303A 304 | - - | 1-3850-78 - | - - |
| 72. Titanium--Total, (3) mg/L: Digestion(3) followed by: AA direct aspiration or AA furnace | 283.1 283.2 | 303C 304 | - - | - - | - - |
| 73. Turbidity, NTU: Nephelometric | 180.1 | 214A | D1889-71 | 1-3860-78 | - |
| 74. Vanadium--Total, (3) mg/L: Digestion(3) followed by: AA direct aspiration AA furnace Inductively coupled plasma Or colorimetric (Gallic acid) | 286.1 286.2 - - | 303C 304 - - | - - - D3373-75 | - - - - | - - - Method 200.7(4) |
| 75. Zinc--Total, (3) mg/L: Digestion(3) followed by: AA direct aspiration AA furnace Inductively coupled plasma Or colorimetric (Zincon) | 289.1 289.2 - - | 303A or 303B 304 - - | D1691-77(D) D1691-77(C) - - | 1-3900-78 - - - | - - - P.557(2) P.37(8) Method 200.7(4) (24) |

(1) "Methods for Analysis of Inorganic Substances in Water and Fluvial Sediments," U.S. Department of the Interior, U.S. Geological Survey, Open-File Report 78-679, or "Methods for Determination of Inorganic Substances in Water and Fluvial Sediments," N.W. Skougstad, et al., U.S. Geological Survey, Techniques of Water-Resources Investigation, Book 5, Chapter A1, 1979.

(2) "Official Methods of Analysis of the Association of Official Analytical Chemists" methods manual, 13th ed. (1980).

(3) For the determination of total metals the sample is not filtered before processing. A digestion procedure is required to solubilize suspended material and to destroy possible organic-metal complexes. Two digestion procedures are given in "Methods for Chemical Analysis of Water and Wastes," 1979. One (§4.1.3), is a vigorous digestion using nitric acid. A less vigorous digestion using nitric and hydrochloric acids (§4.1.4) is preferred; however, the analyst should be cautioned that this mild digestion may not suffice for all samples types. Particularly, if a colorimetric procedure is to be employed, it is necessary to ensure that all organo-metallic bonds be broken so that the metal is in a reactive state. In those situations, the vigorous digestion is to be preferred making certain that at no time does the sample go to dryness. Samples containing large amounts of organic materials would also benefit by this vigorous digestion. Use of the graphite furnace technique, inductively coupled plasma, as well as determinations for certain elements such as arsenic, the noble metals, mercury, selenium, and titanium require a modified digestion and in all cases the method write-up should be consulted for specific instructions and/or cautions.

If the digestion procedure for direct aspiration or graphite furnace atomic absorption analysis included in one of the other approved references is different than the above, the EPA procedure must be used.

Dissolved metals are defined as those constituents which will pass through a 0.45 micron membrane filter. Following filtration of the sample, the referenced procedure for total metals must be followed. Sample digestion of the filtrate for dissolved metals, or digestion of the original sample solution for total metals, may be omitted for AA (direct aspiration or graphite furnace) and ICP analyses provided the sample has a low COD and the filtrate meets the following criteria:

- Is visibility transparent
- Has no perceptible odor, and
- Is free of particulate or suspended matter following acidification.

(4) The full text of Method 200.7, "Inductively Coupled Plasma Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes," is given at Appendix C of 40 CFR Part 136 as published in the October 26, 1984, Federal Register.

(5) Manual distillation is not required if comparability data on representative effluent samples are on company file to show that this preliminary distillation step is not necessary; however, manual distillation will be required to resolve any controversies.

(6) Ammonia, Automated Electrode Method, Industrial Method Number 379-75WE, dated February 19, 1976, Technicon AutoAnalyzer II, Technicon Industrial Systems, Tarrytown, New York 10591.

(7) Carbonaceous biochemical oxygen demand (CBOD₅) must not be confused with the traditional BOD₅ test which measures "total BOD". The addition of the nitrification inhibitor is not a procedural option, but must be included to report the CBOD₅ parameter. A discharger whose permit requires reporting the traditional BOD₅ may not use a nitrification inhibitor in the procedure for reporting the results. Only when a discharger's permit specifically states CBOD₅ is required can the permittee report data obtained using the nitrification inhibitor.

(8) American National Standard on Photographic Processing Effluents, Apr. 2, 1975. Available from ANSI, 1430 Broadway, New York, NY 10018.

(9) The use of normal and differential pulse voltage ramps to increase sensitivity and resolution is acceptable.

(10) Chemical Oxygen Demand, Method 8000, Hach Handbook of Water Analysis, 1979, Hach Chemical Company, P.O. Box 389, Loveland, Colorado 80537.

(11) COD Method, Oceanography International Corporation, 512 West Loop, P.O. Box 2980, College Station, Texas 77840.

(12) The back titration method will be used to resolve controversy.

(13) National Council of the Paper Industry for Air and Stream Improvement, Inc., Technical Bulletin 253, December 1971.

(14) Copper, Bicinchoninate Method, Method 8506, Hach Handbook of Water Analysis, 1979, Hach Chemical Company, P.O. Box 389, Loveland, Colorado 80537.

(15) After the manual distillation is completed, the auto-analyzer manifolds in EPA Methods 335.3 (Cyanide) or 420.2 (phenols) are simplified by connecting the re-sample line directly to the sampler. When using the manifold setup shown in Method 335, the buffer 6.2 should be replaced with the buffer 7.6 found in Method 335.2.

(16) Hydrogen Ion (pH) Automated Electrode Method, Industrial Method Number 378-75WA, October 1976, Technicon Auto-Analyzer II, Technicon Industrial Systems, Tarrytown, New York 10591.

(17) Iron, 1,10-Phenanthroline Method, Method 8008, 1980, Hach Chemical Company, P.O. Box 389, Loveland, Colorado 80537.

(18) Manganese, Periodate Oxidation Method, Method 8034, Hach Handbook of Wastewater Analysis, 1979, pages 2-113 and 2-117, Hach Chemical Company, Loveland, Colorado 80537.

(19) Nitrogen, Nitrite, Method 8507, Hach Chemical Company, P.O. Box 389, Loveland, Colorado 80537.

(20) Gerlitz, D., Brown, E., "Methods for Analysis of Organic Substances in Water," U.S. Geological Survey, Techniques of Water-Resources Investigations, Book 5, Chapter A3, p.4 (1972).

Addison and R. G. Ackman, "Direct Determination of Elemental Phosphorus by Gas-Liquid Chromatography," Journal of Chromatography, Vol. 47, 3, pp. 421-426, 1970.

TABLE 9-1 (Cont'd)

LIST OF APPROVED INORGANIC TEST PROCEDURES

- Recommended methods for the analysis of silver in industrial wastewaters at concentrations of 1 mg/L and above are inadequate where silver exists as an inorganic halide. Silver halides such as the bromide and chloride are relatively insoluble in reagents such as nitric acid but are readily soluble in an aqueous buffer of sodium thiosulfate and sodium hydroxide to a pH of 12. Therefore, for levels of silver above 1 mg/L, 20 mL of sample should be diluted to 100 mL by adding 40 mL each of 2M $\text{Na}_2\text{S}_2\text{O}_3$ and 2M NaOH. Standards should be prepared in the same manner. For levels of silver below 1 mg/L the recommended method is satisfactory.
- (23) Stevens, R. H., Ficke, J. F., and Smoot, G. F., "Water Temperature-Influential Factors, Field Measurement and Data Presentation," U.S. Geological Survey, Techniques of Water-Resources Investigations, Book 1, Chapter D1, 1975.
- (24) Zinc, Zincon Method, Method 8009, Hach Handbook of Water Analysis, 1979, pages 2-231 and 2-333, Hach Chemical Company, Loveland, Colorado 80537.
- (25) "Selected Analytical Methods Approved and Cited by the United States Environmental Protection Agency," Supplement to the Fifteenth Edition of Standard Methods for the Examination of Water and Wastewater (1981).
- (26) The approved method is that cited in Standard Methods for the Examination of Water and Wastewater, 14th Edition. The colorimetric reaction is conducted at a pH of 10.0± 0.2. The approved methods are given on pp. 576-81 of the 14th Edition: Method 510A for distillation, Method 510B for the manual colorimetric procedure, or Method 510C for the manual spectrophotometric procedure.
- (27) ORION Research Instruction Manual, Residual Chlorine Electrode Model 97-70, 1977, Orion Research Incorporated, 840 Memorial Drive, Cambridge, Massachusetts 02138.

TABLE 9-2

LIST OF APPROVED TEST PROCEDURES FOR NON-PESTICIDE ORGANIC COMPOUNDS

| PARAMETER (1) | EPA METHOD NUMBER (2,7) | | | OTHER |
|---------------------------------|-------------------------|-----------------|------|------------------------------------|
| | GC | GC/MS | HPLC | |
| 1. Acenaphthene | 610 | 625, 1625 | 610 | |
| 2. Acenaphthylene | 610 | 625, 1625 | 610 | |
| 3. Acrolein | 603 | (4) 624, 1624 | - | |
| 4. Acrylonitrile | 603 | (4) 624, 1624 | - | |
| 5. Anthracene | 610 | 625, 1625 | 610 | |
| 6. Benzene | 602 | 624, 1624 | - | |
| 7. Benzidine | - | (5) 625, 1625 | 605 | Note 3, p. 1 |
| 8. Benzo(a)anthracene | 610 | 625, 1625 | 610 | |
| 9. Benzo(a)pyrene | 610 | 625, 1625 | 610 | |
| 10. Benzo(b)fluoranthene | 610 | 625, 1625 | 610 | |
| 11. Benzo(ghi)perylene | 610 | 625, 1625 | 610 | |
| 12. Benzo(k)fluoranthene | 610 | 625, 1625 | 610 | |
| 13. Benzyl Chloride | - | - | - | Note 3, p. 130; Note 6, p. S102 |
| 14. Benzyl Butyl Phthalate | 606 | 625, 1625 | - | |
| 15. Bis(2-chloroethoxy) methane | 611 | 625, 1625 | - | |
| 16. Bis(2-chloroethyl) ether | 611 | 625, 1625 | - | |
| 17. Bis(2-ethylhexyl) phthalate | 606 | 625, 1625 | - | |
| 18. Bromodichloromethane | 601 | 624, 1624 | - | |
| 19. Bromoform | 601 | 624, 1624 | - | |
| 20. Bromomethane | 601 | 624, 1624 | - | |
| 21. 4-Bromophenylphenyl ether | 611 | 625, 1625 | - | |
| 22. Carbon tetrachloride | 601 | 624, 1624 | - | Note 3, p. 130 |
| 23. 4-Chloro-3-methylphenol | 604 | 625, 1625 | - | |
| 24. Chlorobenzene | 601, 602 | 624, 1624 | - | Note 3, p. 130 |
| 25. Chloroethane | 601 | 624, 1624 | - | |
| 26. 2-Chloroethylvinyl ether | 601 | 624, 1624 | - | |
| 27. Chloroform | 601 | 624, 1624 | - | Note 3, p. 130 |
| 28. Chloromethane | 601 | 624, 1624 | - | |
| 29. 2-Chloronaphthalene | 612 | 625, 1625 | - | |
| 30. 2-Chlorophenol | 604 | 625, 1625 | - | |
| 31. 4-Chlorophenylphenyl ether | 611 | 625, 1625 | - | |
| 32. Chrysene | 610 | 625, 1625 | 610 | |
| 33. Dibenzo(a,h)anthracene | 610 | 625, 1625 | 610 | |
| 34. Dibromochloromethane | 601 | 624, 1624 | - | |
| 35. 1,2-Dichlorobenzene | 601, 602, 612 | 624, 625, 1625 | - | |
| 36. 1,3-Dichlorobenzene | 601, 602, 612 | 624, 625, 1625 | - | |
| 37. 1,4-Dichlorobenzene | 601, 602, 612 | 625, 1624, 1625 | - | |
| 38. 3,3'-Dichlorobenzidine | - | 625, 1625 | 605 | |
| 39. Dichlorodifluoromethane | 601 | - | - | |
| 40. 1,1-Dichloroethane | 601 | 624, 1624 | - | |
| 41. 1,2-Dichloroethane | 601 | 624, 1624 | - | |
| 42. 1,1-Dichloroethene | 601 | 624, 1624 | - | |
| 43. trans-1,2-Dichloroethene | 601 | 624, 1624 | - | |
| 44. 2,4-Dichlorophenol | 604 | 625, 1625 | - | |
| 45. 1,2-Dichloropropane | 601 | 624, 1624 | - | |
| 46. cis-1,3-Dichloropropene | 601 | 624, 1624 | - | |
| 47. trans-1,3-Dichloropropene | 601 | 624, 1624 | - | |
| 48. Diethyl phthalate | 606 | 625, 1625 | - | |
| 49. 2,4-Dimethylphenol | 604 | 625, 1625 | - | |
| 50. Dimethyl phthalate | 606 | 625, 1625 | - | |
| 51. Di-n-butyl phthalate | 606 | 625, 1625 | - | |
| 52. Di-n-octyl phthalate | 606 | 625, 1625 | - | |
| 53. 2,4-Dinitrophenol | 604 | 625, 1625 | - | |
| 54. 2,4-Dinitrotoluene | 609 | 625, 1625 | - | |
| 55. 2,6-Dinitrotoluene | 609 | 625, 1625 | - | |
| 56. Epichlorohydrin | - | - | - | Note 3, p. 130; Note 6, p. S102 |
| 57. Ethylbenzene | 602 | 624, 1624 | - | |
| 58. Fluoranthene | 610 | 625, 1625 | 610 | |
| 59. Fluorene | 610 | 625, 1625 | 610 | |
| 60. Hexachlorobenzene | 612 | 625, 1625 | - | |
| 61. Hexachlorobutadiene | 612 | 625, 1625 | - | |
| 62. Hexachlorocyclopentadiene | 612 | (5) 625, 1625 | - | |
| 63. Hexachloroethane | 612 | 625, 1625 | - | |
| 64. Ideno(1,2,3-cd)pyrene | 610 | 625, 1625 | 610 | |
| 65. Isophorone | 609 | 625, 1625 | - | |
| 66. Methylene Chloride | 601 | 624, 1624 | - | Note 3, p. 130 |
| 67. 2-Methyl-4,6-Dinitrophenol | 604 | 625, 1625 | - | |
| 68. Naphthalene | 610 | 625, 1625 | - | |
| 69. Nitrobenzene | 609 | 625, 1625 | - | |
| 70. 2-Nitrophenol | 604 | 625, 1625 | - | |
| 71. 4-Nitrophenol | 604 | 625, 1625 | - | |
| 72. N-Nitrosodimethylamine | 607 | 625, 1625 | - | |
| 73. N-Nitrosodi-n-propylamine | 607 | (5) 625, 1625 | - | |
| 74. N-Nitrosodiphenylamine | 607 | (5) 625, 1625 | - | |
| 75. 2,2-oxybis(1-chloropropane) | 611 | 625, 1625 | - | |
| 76. PCB-1016 | 608 | 625 | - | Note 3, p. 43 |
| 77. PCB-1221 | 608 | 625 | - | Note 3, p. 43 |

TABLE 9-2 (Cont'd)

LIST OF APPROVED TEST PROCEDURES FOR NON-PESTICIDE ORGANIC COMPOUNDS

| PARAMETER ⁽¹⁾ | EPA METHOD NUMBER ^(2,7) | | | OTHER |
|---|------------------------------------|-----------|------|----------------|
| | GC | GC/MS | HPLC | |
| 78. PCB-1232 | 608 | 625 | - | Note 3, p. 43 |
| 79. PCB-1242 | 608 | 625 | - | Note 3, p. 43 |
| 80. PCB-1248 | 608 | 625 | - | Note 3, p. 43 |
| 81. PCB-1254 | 608 | 625 | - | Note 3, p. 43 |
| 82. PCB-1260 | 608 | 625 | - | Note 3, p. 43 |
| 83. Pentachlorophenol | 604 | 625, 1625 | - | Note 3, p. 140 |
| 84. Phenanthrene | 610 | 625, 1625 | 610 | |
| 85. Phenol | 604 | 625, 1625 | - | |
| 86. Pyrene | 610 | 625, 1625 | 610 | |
| 87. 2,3,7,8-Tetrachlorodibenzo-p-dioxin | - | (5a) 613 | - | |
| 88. 1,1,2,2-Tetrachloroethane | 601 | 624, 1624 | - | Note 3, p. 130 |
| 89. Tetrachloroethene | 601 | 624, 1624 | - | Note 3, p. 130 |
| 90. Toluene | 602 | 624, 1624 | - | |
| 91. 1,2,4-Trichlorobenzene | 612 | 625, 1625 | - | Note 3, p. 130 |
| 92. 1,1,1-Trichloroethane | 601 | 624, 1624 | - | |
| 93. 1,1,2-Trichloroethane | 601 | 624, 1624 | - | Note 3, p. 130 |
| 94. Trichloroethene | 601 | 624, 1624 | - | |
| 95. Trichlorofluoromethane | 601 | 624 | - | |
| 96. 2,4,6-Trichlorophenol | 604 | 625, 1625 | - | |
| 97. Vinyl Chloride | 601 | 624, 1624 | - | |

(1) All parameters are expressed in micrograms per liter (ug/L).

(2) The full text of Methods 601-613, 624, 625, 1624, and 1625, are given at Appendix A, "Test Procedures for Analysis of Organic Pollutants," of 40 CFR 136 as published in the October 26, 1984 Federal Register. The standardized test procedure to be used to determine the method detection limit (MDL) for these test procedures is given at Appendix B, "Definition and Procedure for the Determination of the Method Detection Limit," of 40 CFR 136 as published in the October 26, 1984 Federal Register.

(3) "Methods for Benzidine, Chlorinated Organic Compounds, Pentachlorophenol and Pesticides in Water and Wastewater," U.S. Environmental Protection Agency, September, 1978.

(4) Method 624 may be extended to screen samples for Acrolein and Acrylonitrile. However, when they are known to be present, Method 603 or Method 1624 are preferred methods for these compounds.

(5) Method 625 may be extended to include benzidine, hexachlorocyclopentadiene, N-nitrosodimethylamine, and N-nitrosodiphenylamine. However, when they are known to be present, Methods 605, 607, and 612, or Method 1625, are preferred methods for these compounds.

(5a) 625, Screening only.

(6) "Selected Analytical Methods Approved and Cited by the United States Environmental Protection Agency," Supplement to the Fifteenth Edition of Standard Methods for the Examination of Water and Wastewater (1981).

(7) Each analyst must make an initial, one-time, demonstration of their ability to generate acceptable precision and accuracy with Methods 601-613, 624, 625, 1624, and 1625 (See Appendix A of 40 CFR 136 as published in the October 26, 1984 Federal Register) in accordance with procedures in Section 8.2 of each of these Methods. Additionally, each laboratory, on an on-going basis must spike and analyze 10% (5% for Methods 624 and 625 and 100% for Methods 1624, and 1625) of all samples to monitor and evaluate laboratory data quality in accordance with Sections 8.3 and 8.4 of these Methods. When the recovery of any parameter falls outside the warning limits, the analytical results for that parameter in the unspiked sample are suspect and cannot be reported.

TABLE 9-3

LIST OF APPROVED TEST PROCEDURES
FOR SOIL AND SOLID WASTES

| Parameter | U.S. EPA TMSW ^a | |
|--|----------------------------|-------------------|
| | Section No. | Method No. |
| CHARACTERISTICS OF SOLID WASTE | 2.1 | |
| • Ignitability | 2.1.1 | |
| - Pensky-Martens Closed Cup Method | 2.1.1 | 1010 |
| - Setaflash Closed Cup Method | 2.1.1 | 1020 |
| • Corrosivity | 2.1.2 | |
| - Corrosion Towards Steel | 2.1.2 | 1110 _b |
| - Electrochemical Corrosion Method | 2.1.2 | 1120 _b |
| • Reactivity | 2.1.3 | |
| • Extraction Procedure Toxicity | 2.1.4 | |
| - Method and Structural Integrity Test | 2.1.4 | 1310 |
| - Multiple Extraction Procedure | 2.1.4 | 1320 |
| - Extraction Procedure for Oil Wastes | 2.1.4 | 1330 |
| SAMPLE PREPARATION TECHNIQUES | 4.0 | |
| • Inorganic Techniques | 4.1 | |
| - Acid Digestion for Flame AAS | 4.1 | 3010 |
| - Acid Digestion for Furnace AAS | 4.1 | 3020 |
| - Acid Digestion of Oil, Grease, or Wax | 4.1 | 3030 |
| - Dissolution Procedure for Oil, Grease, or Wax | 4.1 | 3040 |
| • Organic Techniques | 4.2 | |
| - Separatory Funnel Liquid-Liquid Extraction | 4.2 | 3510 |
| - Continuous Liquid-Liquid Extraction | 4.2 | 3520 |
| - Acid-Base Cleanup Extraction | 4.2 | 3530 |
| - Soxhlet Extraction | 4.2 | 3540 _b |
| - Reverse Phase Cartridge Extraction | 4.2 | 3560 _b |
| - Column Clean-Up for Oily Wastes | 4.2 | 3570 _b |
| - Sonication Extraction | 4.2 | 3550 |
| - Gas Bulb and Gas Bag Sample Preparation | 4.2 | 3710 |
| - Volatile Organics Sampling Train Purge and Trap Sample Preparation | 4.2 | 3720 _b |

TABLE 9-3 (Cont'd)
 LIST OF APPROVED TEST PROCEDURES
 FOR SOIL AND SOLID WASTES

| Parameter | U.S. EPA TMESW ^a | |
|---|-----------------------------|-------------------|
| | Section No. | Method No. |
| SAMPLE INTRODUCTION TECHNIQUES | 5.0 | |
| • Headspace | 5.0 | 5020 |
| • Purge and Trap | 5.0 | 5030 |
| MULTIELEMENT INORGANIC METHODS | 6.0 | |
| • Inductively Coupled Plasma Method | 6.0 | 6010 ^b |
| INORGANIC ANALYTICAL METHODS | 7.0 | |
| • Antimony, Flame AAS | 7.0 | 7040 |
| • Antimony, Furnace AAS | 7.0 | 7041 |
| • Arsenic, Furnace AAS | 7.0 | 7060 |
| • Arsenic, Gaseous Hydride AAS | 7.0 | 7061 |
| • Barium, Flame AAS | 7.0 | 7080 ^b |
| • Beryllium, Flame AAS | 7.0 | 7090 ^b |
| • Beryllium, Furnace AAS | 7.0 | 7091 ^b |
| • Cadmium, Flame AAS | 7.0 | 7130 |
| • Cadmium, Furnace AAS | 7.0 | 7131 |
| • Chromium, Flame AAS | 7.0 | 7190 |
| • Chromium, Furnace AAS | 7.0 | 7191 |
| • Chromium, Hexavalent, Chelation | 7.0 | 7197 |
| • Chromium, Hexavalent, Colorimetric | 7.0 | 7196 |
| • Chromium, Hexavalent, Coprecipitation | 7.0 | 7195 ^b |
| • Chromium, Hexavalent, Polarographic | 7.0 | 7198 ^b |
| • Copper, Flame AAS | 7.0 | 7210 ^b |
| • Copper, Furnace, AAS | 7.0 | 7211 ^b |
| • Iron, Flame AAS | 7.0 | 7380 ^b |
| • Iron, Flame AAS | 7.0 | 7380 |
| • Iron, Furnace AAS | 7.0 | 7381 |
| • Lead, Flame AAS | 7.0 | 7420 |
| • Lead, Furnace AAS | 7.0 | 7421 ^b |
| • Manganese, Flame AAS | 7.0 | 7460 ^b |
| • Manganese, Furnace AAS | 7.0 | 7461 ^b |
| • Mercury, Cold Vapor Liquid | 7.0 | 7470 |
| • Mercury, Cold Vapor, Solid | 7.0 | 7471 |
| • Nickel, Flame AAS | 7.0 | 7520 |
| • Nickel, Furnace AAS | 7.0 | 7521 ^b |
| • Osmium, Flame AAS | 7.0 | 7550 ^b |
| • Osmium, Furnace AAS | 7.0 | 7551 ^b |
| • Selenium, Furnace AAS | 7.0 | 7740 |
| • Selenium, Gaseous Hydride AAS | 7.0 | 7741 |
| • Silver, Flame AAS | 7.0 | 7760 |

TABLE 9-3 (Cont'd)

LIST OF APPROVED TEST PROCEDURES
FOR SOIL AND SOLID WASTES

| Parameter | U.S. EPA TMESW ^a | |
|--|-----------------------------|-------------------|
| | Section No. | Method No. |
| • Silver, Furnace AAS | 7.0 | 7761 ^b |
| • Sodium, Flame AAS | 7.0 | 7770 ^b |
| • Thallium, Flame AAS | 7.0 | 7840 ^b |
| • Thallium, Furnace AAS | 7.0 | 7841 ^b |
| • Vanadium, Flame AAS | 7.0 | 7910 ^b |
| • Vanadium, Furnace AAS | 7.0 | 7911 ^b |
| • Zinc, Flame AAS | 7.0 | 7950 ^b |
| • Zinc, Furnace AAS | 7.0 | 7951 ^b |
| ORGANIC ANALYTICAL METHODS | 8.0 | |
| • Gas Chromatographic Methods | 8.1 | |
| - Acrolein, Acrylonitrile, Acetonitrile | 8.1 | 8030 |
| - Aromatic Volatile Organics | 8.1 | 8020 |
| - Chlorinated Herbicides | 8.1 | 8150 |
| - Chlorinated Hydrocarbons | 8.1 | 8120 |
| - Halogenated Volatile Organics | 8.1 | 8010 |
| - Nitroaromatics and Cyclic Ketones | 8.1 | 8090 |
| - Nonhalogenated Volatile Organics | 8.1 | 8015 |
| - Organochlorine Pesticides and PCBs | 8.1 | 8080 |
| - Organophosphorus Pesticides | 8.1 | 8140 |
| - Phenols | 8.1 | 8040 |
| - Phthalate Esters | 8.1 | 8060 |
| - Polynuclear Aromatic Hydrocarbons | 8.1 | 8100 |
| • Gas Chromatographic/Mass Spectroscopy Methods (GC/MS) | 8.2 | |
| - GC/MS Volatiles | 8.2 | 8240 |
| - GC/MS Semivolatiles, Packed Column | 8.2 | 8250 |
| - GC/MS Semivolatiles, Capillary | 8.2 | 8270 |
| • High Performance Liquid Chromatographic Methods (HPLC) | 8.3 | |
| - Polynuclear Aromatic Hydrocarbons | 8.3 | 8310 ^b |
| - Phenols and Miscellaneous Compounds | 8.3 | 8320 ^b |
| - Thioureas and Miscellaneous Compounds | 8.3 | 8330 ^b |

TABLE 9-3 (Cont'd)

LIST OF APPROVED TEST PROCEDURES
FOR SOIL AND SOLID WASTES

| Parameter | U.S. EPA TME SW ^a | |
|---|------------------------------|-------------------|
| | Section No. | Method No. |
| • Polarographic Methods | 8.4 | |
| - Formaldehyde | 8.4 | 8410 ^b |
| - Formaldehyde | 8.4 | 8411 ^b |
| • Screening Methods | 8.6 | |
| - Hierarchical Analysis Protocol for Ground Water | 8.6 | 8600 ^b |
| - Dinitrobenzoylchloride Derivatization for Appendix VIII Compounds | 8.6 | 8630 ^b |
| - Total Aromatics by Ultra Violet Absorption | 8.6 | 8610 ^b |
| - Total Nitrogen/Phosphorus Gas Chromatographable Compounds | 8.6 | 8620 ^b |
| MISCELLANEOUS ANALYTICAL METHODS | 9.0 | |
| • Cation Exchange Capacity | 9.0 | 9080 ^b |
| • Cation Exchange Capacity | 9.0 | 9081 ^b |
| • Chloride | 9.0 | 9250 ^b |
| • Chloride | 9.0 | 9251 ^b |
| • Coliform | 9.0 | 9131 ^b |
| • Coliform | 9.0 | 9132 ^b |
| • Cyanide, Photodegradable | 9.0 | 9011 ^b |
| • Cyanide, Total and Amendable to Chlorination | 9.0 | 9010 |
| • Free Liquids Test, Paint Filter | 9.0 | 9095 |
| • Gross Alpha and Beta | 9.0 | 9310 ^b |
| • Nitrate | 9.0 | 9200 ^b |
| • pH Measurement | 9.0 | 9040 |
| • pH Paper Method | 9.0 | 9041 |
| • Phenolics | 9.0 | 9065 ^b |
| • Phenolics | 9.0 | 9066 ^b |
| • Phenolics | 9.0 | 9067 ^b |
| • Radium | 9.0 | 9315 ^b |
| • Radium, 228 | 9.0 | 9320 ^b |
| • Soil pH | 9.0 | 9045 ^b |
| • Specific Conductance | 9.0 | 9050 |
| • Sulfate | 9.0 | 9035 ^b |
| • Sulfate | 9.0 | 9036 ^b |
| • Sulfate | 9.0 | 9037 ^b |
| • Sulfate | 9.0 | 9038 ^b |
| • Sulfides | 9.0 | 9030 |

TABLE 9-3 (Cont'd)

LIST OF APPROVED TEST PROCEDURES
FOR SOIL AND SOLID WASTES

| Parameter | U.S. EPA TME SW ^a | |
|---|------------------------------|-------------------|
| | Section No. | Method No. |
| • Total Oil and Grease | 9.0 | 9070 ^b |
| • Total Oil and Grease | 9.0 | 9071 ^b |
| • Total Organic Carbon | 9.0 | 9060 |
| • Total Organic Halogen (TOX) | 9.0 | 9020 |
| • Total Organic Halogen (TOX) by Neutron Activation | 9.0 | 9022 ^b |

^aTest Methods for Evaluation Solid Waste, Physical/Chemical Methods, Second Edition, SW-846, U.S. Environmental Protection Agency, 1982.

^bProposed Method as Published in the "Federal Register," Vol. 49, No. 191, October 1, 1984.

SECTION 10

DATA REDUCTION, VALIDATION, AND REPORTING

10.1 DATA REDUCTION AND REPORTING

In general, data will be reduced by an analyst in one of the following ways:

- Manual computation of results directly on the laboratory bench sheet or on calculation pages attached to the data sheets. (See Attachments to this Section)
- Input of raw data for computer processing.
- Direct acquisition and processing of raw data by a computer.

If data are manually processed by an analyst, all steps in the computation are provided including the equations used and the source of input parameters such as response factors, dilution factors, and calibration constants. If calculations are not performed directly on the data sheet, calculations are done on standard calculation paper and attached to the data sheets. The analyst signs (full signature) and dates each page of calculations in ink. Table 10-1 summarizes the equations used for calculations of results and reporting units.

For data that are input by an analyst and processed using a computer, a copy of the input is kept and uniquely identified with the project number and other information as needed. The samples analyzed shall be evident and the input signed and dated by the analyst.

If data are directly acquired from instrumentation and processed, the analyst verifies that the following are correct: project and sample numbers, calibration constants and response factors, output parameters such as units, and numerical values used for detection limits (if a value is reported as less than). The analyst signs and dates the resulting output.

The data reduction/validation flow chart is shown as Figure 10-1.

TABLE 10-1

SUMMARY OF EQUATIONS USED IN CALCULATIONS

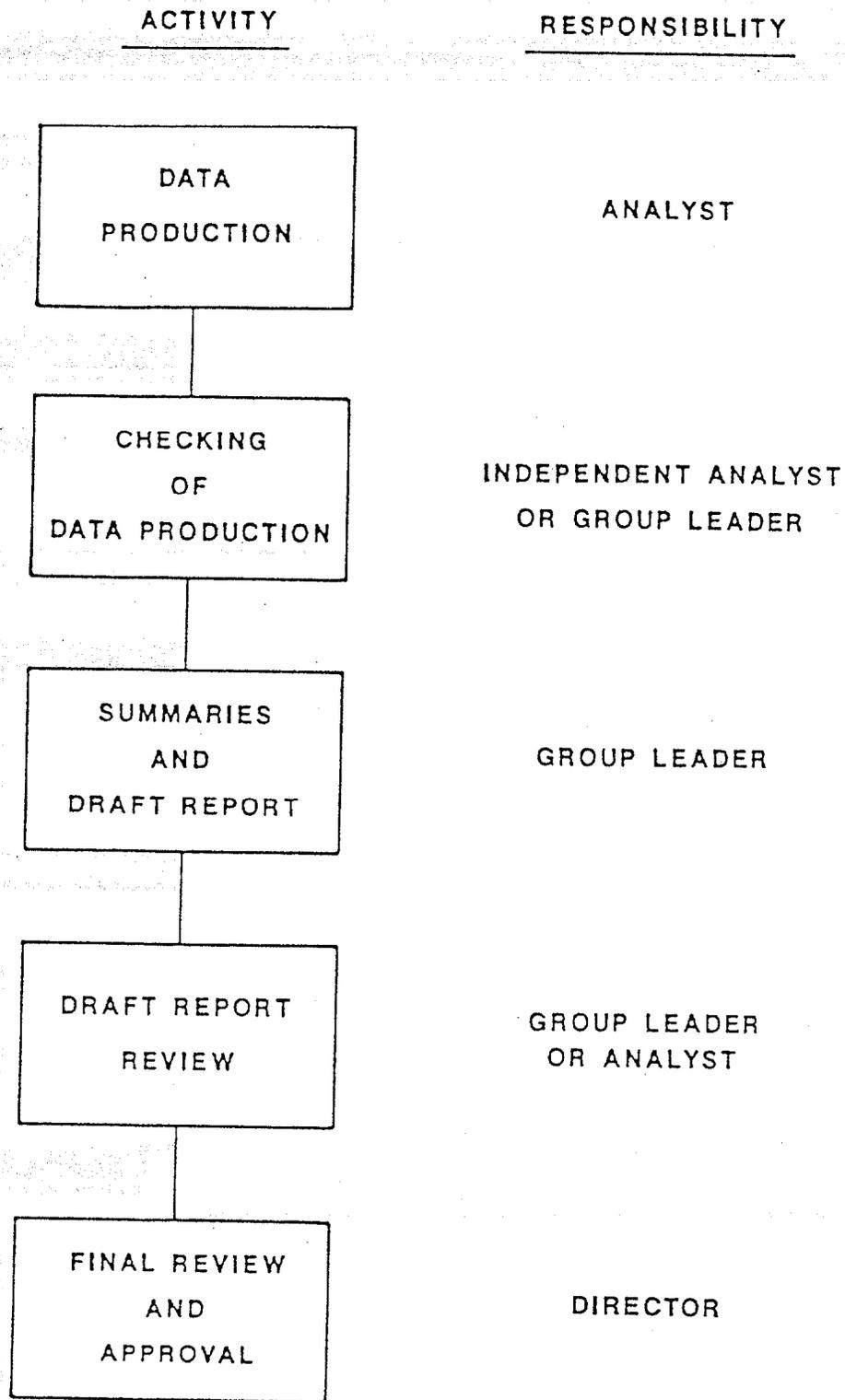
| Parameter | Equations | Reporting Units | |
|---|---|---------------------------|-----------------------------|
| | | Water | Sediment |
| BN/A Extractables | <p>Internal Standard Method (625 and 8270)</p> <p>Response Factor (RF) = $\frac{As \text{ Cis}}{Ais \text{ Cs}}$</p> <p>As = area of the characteristic ion standard Ais = area of the characteristic ion internal standard Cs = concentration of standard ($\mu\text{g/l}$) Cis = concentration of the internal standard ($\mu\text{g/l}$)</p> <p>Water Concentration ($\mu\text{g/l}$) = $\frac{As}{Ais} \times \frac{Cis}{RF}$</p> <p>As = area of the characteristic ion (sample) Ais = area of the characteristic ion (internal standard) Cis = concentration of the internal standard ($\mu\text{g/l}$) RF = response factor</p> <p>Sediment Concentration ($\mu\text{g/kg}$) = $\frac{\mu\text{g of internal standard}}{(\text{kg of sample})(\% \text{ solids} \times 0.01)} \times \frac{As}{Ais} \times \frac{1}{RF}$</p> <p>As = area of characteristic ion (sample) Ais = area of characteristic ion (internal standard) RF = response factor</p> | $\mu\text{g/l}$ (or mg/l) | $\mu\text{g/kg}$ (or mg/kg) |
| Nutrients and other colorimetric procedures | <p>Water Concentration (mg/l) = $\text{mg/l}^a \times \text{dilution factor}$</p> <p>Sediment Concentration (mg/kg) = $\text{mg/l}^a \times \frac{\text{liters of leachate (or digestate)}}{(\text{kg of sample})(\% \text{ solids} \times 0.01)}$</p> | mg/l | mg/kg |
| VOCs (methods 601, 602) | <p>Response factor (RF) = $\frac{\mu\text{g/l of compound to be measured}}{\text{peak height}}$</p> <p>Water Concentration $\mu\text{g/l} = \text{RF} \times \text{peak ht} \times \text{dilution factor (sample)}$</p> <p>Sediment Concentration $\mu\text{g/kg} = \text{RF} \times \text{peak ht} \times \frac{\text{liter equivalent of standard volume}}{(\text{kg of sample})(\% \text{ solids} \times 0.01)}$</p> | $\mu\text{g/l}$ (or mg/l) | $\mu\text{g/kg}$ (or mg/kg) |
| VOC (method 624) | Internal Standard Method - See section on BN/A | | |

TABLE 10-1 (Cont'd)

SUMMARY OF EQUATIONS USED IN CALCULATIONS

| Parameter | Equations | Reporting Units | |
|--|--|---------------------------|-----------------------------|
| | | Water | Sediment |
| Pesticides/PCBs (and other GC parameters) | $\text{Response factor (RF)(Standards)} = \frac{\mu\text{g of analyte}}{\text{peak height}}$ $\text{Water sample concentration } (\mu\text{g/l}) = \text{RF} \times \text{peak height} \times \frac{\text{volume extract in } \mu\text{l}}{\text{injection volume in } \mu\text{l}} \times \frac{\text{liters extracted}}{\text{liters extracted}}$ $\text{Sediment sample concentration } (\mu\text{g/kg}) = \text{RF} \times \frac{\text{peak height} \times \frac{\text{volume extract in } \mu\text{l}}{\text{injection volume in } \mu\text{l}}}{(\text{kg extracted})(\% \text{ solids} \times 0.01)}$ | $\mu\text{g/l (or mg/l)}$ | $\mu\text{g/kg (or mg/kg)}$ |
| Metals | <p>Calibration Curve Construction:</p> $y = mx + b$ $y = \text{absorbance}$ $m = \text{slope} \frac{\text{absorbance}}{\text{concentration}}$ $x = \text{concentration (mg/l)}$ $b = \text{y intercept}$ <p>Calculation of water sample concentration:</p> $x = \frac{y - b}{m} \times \text{dilution factor}$ <p>Sediment = Conversion of mg/l to mg/kg:</p> $\text{mg/l}^a \times \text{dilution factor} \times \frac{\text{final volume (liters) of digestate}}{(\text{kg of sample})(\% \text{ solids} \times 0.01)}$ | $\mu\text{g/l (or mg/l)}$ | mg/kg |

^aConcentration of sample from standard curve.



DATA REDUCTION AND VALIDATION FLOW SCHEMATIC

FIGURE 10-1

10.2 DATA VERIFICATION

Data verification involves a series of steps taken within an analytical laboratory to ensure that reported results correctly represent the analyses performed. There are two basic verification activities:

- The use of quality control sample results to demonstrate that analyses are within prescribed bounds for accuracy, precision, and completeness.
- Data validation to demonstrate that numerical computation of data is correct and that it is correctly reported.

ORGANIC ANALYSIS DATA SHEET

SAMPLE/CALIBRATION/QC

DATE EXTRACTED/PREPARED _____ BY _____

DATE ANALYZED _____ BY _____

METHOD 608 PESTICIDE/PCB

| R. T. | LABORATORY ID | | | | | | | | | | |
|-------|--------------------------------|------|------|------|------|------|------|------|------|------|------|
| | COMPOUND | AREA | CONC |
| | ALPHA-BHC | | | | | | | | | | |
| | BETA-BHC | | | | | | | | | | |
| | DELTA-BHC | | | | | | | | | | |
| | GAMMA-BHC (LINDANE) | | | | | | | | | | |
| | HEPTACHLOR | | | | | | | | | | |
| | ALDRIN | | | | | | | | | | |
| | HEPTACHLOR EPOXIDE | | | | | | | | | | |
| | ENDOSULFAN I | | | | | | | | | | |
| | DIELDRIN | | | | | | | | | | |
| | 4,4'-DDE | | | | | | | | | | |
| | ENDRIN | | | | | | | | | | |
| | ENDOSULFAN II | | | | | | | | | | |
| | 4,4'-DDD | | | | | | | | | | |
| | ENDRIN ALDEHYDE | | | | | | | | | | |
| | ENDOSULFAN SULFATE | | | | | | | | | | |
| | 4,4'-DDT | | | | | | | | | | |
| | METHOXYCHLOR | | | | | | | | | | |
| | ENDRIN KETONE | | | | | | | | | | |
| | CHLORODANE | | | | | | | | | | |
| | TOXAPHENE | | | | | | | | | | |
| | AROCLOR-1016 | | | | | | | | | | |
| | AROCLOR 1221 | | | | | | | | | | |
| | AROCLOR 1232 | | | | | | | | | | |
| | AROCLOR 1242 | | | | | | | | | | |
| | AROCLOR 1248 | | | | | | | | | | |
| | AROCLOR 1254 | | | | | | | | | | |
| | AROCLOR 1260 | | | | | | | | | | |
| | | | | | | | | | | | |
| | VOLUME EXTRACT INJECTED (µL) | | | | | | | | | | |
| | VOLUME EXTRACTED (ML) | | | | | | | | | | |
| | WEIGHT OF SAMPLE EXTRACTED (G) | | | | | | | | | | |
| | VOLUME OF TOTAL EXTRACT (ML) | | | | | | | | | | |
| | DILUTION FACTOR | | | | | | | | | | |

10-7

METAL _____

Job: _____ Date: _____ Analyst: _____

Job No: _____

Flame _____
Method: HGA _____
Other _____

| Flask No. | Waste Description | Sample Volume (ml) | Dilution | Absorbance | Concentration PPM PPB |
|-----------|-------------------|--------------------|----------|------------|-----------------------|
| 1 | | | | | |
| 2 | | | | | |
| 3 | | | | | |
| 4 | | | | | |
| 5 | | | | | |
| 6 | | | | | |
| 7 | | | | | |
| 8 | | | | | |
| 9 | | | | | |
| 10 | | | | | |
| 11 | | | | | |
| 12 | | | | | |
| 13 | | | | | |
| 14 | | | | | |

Notes: Wavelength _____ Flow _____ Div. _____ Sample Volume _____
 Slit _____ Mode _____ Sec. _____
 Time Const _____ Dry _____ C^o _____ Sec. _____
 BG - ON _____ Off _____ Char _____ C^o _____ Sec. _____
 Air - Ac _____ NO - Ac _____ Atom _____ C^o _____ Sec. _____

Job: _____ Date: _____ Analyst: _____

Job No: _____ Type: _____ Method: _____

| Flask No. | Waste Description | Sample Volume (ml) | Dilution | Absorbance | Concentration |
|-----------|-------------------|--------------------|----------|------------|---------------|
| 1. | | | | | |
| 2. | | | | | |
| 3. | | | | | |
| 4. | | | | | |
| 5. | | | | | |
| 6. | | | | | |
| 7. | | | | | |
| 8. | | | | | |
| 9. | | | | | |
| 10. | | | | | |
| 11. | | | | | |
| 12. | | | | | |
| 13. | | | | | |

note:

10-10

SECTION 11

INTERNAL QUALITY CONTROL CHECKS

Internal QC checks are accomplished through standard programs (see Tables 11-1 and 11-2) and through specially-imposed QC samples sent from the field.

TABLE 11-1
QUALITY ASSURANCE PROGRAM OUTLINE
INORGANIC ANALYSIS

-
-
- A) Standard Curves for each analytical parameter
- B) New Curve for each new set of reagents
- 1) At least five concentration levels
 - 2) One reagent-water blank
- C) Control procedures for 20 samples
- 1) One reagent-water blank
 - 2) One midpoint standard
 - a) Average of three consecutive readings
 - b) Must agree with original curves within 10 percent
 - 3) One Duplicate
 - 4) One Matrix Spike
 - 5) One U.S. EPA Performance Evaluation Sample or Internal Standard
- D) Inter-laboratory quality control
- 1) Reference samples provided by U.S. EPA and NBS.
 - 2) Participation in performance evaluation and method studies available for U.S. EPA and ASTM.
 - 3) Split samples between laboratories.

Accuracy determination can be achieved by one of these methods:

- 1) Reference samples
- 2) In-house standards
- 3) Internal matrix spiking with reference samples or in-house standards

NOTE: In choosing the appropriate spike concentration, use the following criteria as a good rule of thumb.

- Sample concentration expected to be less than 10 times MDL; Spike at 20 times MDL
 - Sample concentrations expected to be greater than 10 times MDL; Spike at 2 times expected concentration
-
-

TABLE 11-2

QUALITY ASSURANCE PROGRAM OUTLINE
ORGANIC ANALYSIS

-
-
- A) Standard Curves for each analytical parameter
- 1) Three calibration standards are prepared and analyzed at the concentration of interest.
 - 2) One reagent-water blank
 - 3) A calibration curve is constructed from the above generated data for each compound of interest.
- B) Control procedures for twenty samples
- 1) One reagent-water blank
 - 2) One midpoint calibration verification standard
 - a) Must agree within 15 percent of the original calibration curve
 - b) If greater than 15 percent variance a new calibration curve must be prepared
 - 3) One Duplicate
 - 4) One Matrix Spike
 - 5) One U.S. EPA Performance Evaluation Sample or Internal Standard
- C) Inter-laboratory quality control
- 1) Reference samples provided by U.S. EPA and NBS.
 - 2) Participation in performance evaluation and method studies available for U.S. EPA and ASTM
 - 3) Split samples between laboratories

Accuracy determination can be achieved by one of these methods:

- 1) Reference samples;
- 2) In-house standards;
- 3) Internal matrix spiking with reference samples or in-house standards

NOTE: In choosing the appropriate spike concentration, use the following criteria as a good rule of thumb.

- Sample concentration expected to be less than 10 times MDL; Spike at 20 times MDL increments
 - Sample concentrations expected to be greater than 10 times MDL; Spike at 2 times expected concentration
-
-

SECTION 12

PERFORMANCE AND SYSTEMS AUDITS

Each QA Project Plan describes the performance and system audits which are required to monitor the total analytical system. The project plan specifically lists the schedule and extent of each system and performance audit.

The personnel listed below are responsible for all performance and system audits:

ATSD Director - D. Rick Davis

Assistant Director - Allen F. Ralls

Quality Control Coordinator - Judy Morgan

The ATSD participates in the following certification programs which require performance evaluation samples to be analyzed annually and on-site audits to be performed semi-annually.

- Tennessee Department of Health and Environment
- New Jersey Department of Environmental Protection

SECTION 13

PREVENTIVE MAINTENANCE AND BACKUP

All field equipment and instrumentation is checked-out by the Instrumentation Specialist (IS) before the item is taken to the field. A log book is kept by the IS to verify the working condition of the equipment before it is shipped to the field.

AWARE possesses a large inventory of spare equipment parts such as GC Columns, AA Hollow Cathode Lamps, D.O. probes, pH probes, pumps, controllers, and numerous other items. In addition to the spare parts, AWARE has a number of backup instruments i.e., two-GC's for Volatile Organic Analysis; three-Total Organic Carbon Analyzers; two-Total Organic Halogen Analyzers; two-GC's for extractables; two-Flame Atomic Absorption units; and two-Graphite Furnace Atomic Absorption units. With this magnitude of backup instrumentation, downtime is kept to a minimum.

SECTION 14

PROCEDURES USED TO ASSESS PRECISION, ACCURACY, AND COMPLETENESS

The following procedures are utilized for evaluating the precision and accuracy of data generated within the ATSD.

- Field blanks are analyzed to determine possible sample contamination during collection and shipment.
- Reagent or method blanks are analyzed with each set of samples.
- Calibration curves and verification checks are made.
- Laboratory and field duplicates (percent RSD) or (RPD) are analyzed.
- Matrix spikes (percent Recovered) are performed.
- Blind duplicates submitted by field personnel are analyzed.
- Performance Evaluation Samples are analyzed.
- Proper sample holding times are maintained.

Completeness is assessed by the total number of valid sample results divided by the total number of samples collected. Completeness is reported in terms of a percentage.

Equations and calculations used to express precision and accuracy are presented in Tables 14-1 and 14-2.

TABLE 14-1

PRECISION FORMULAS FOR DUPLICATE DETERMINATIONS

These formulas should be used for duplicate determinations only. They do not apply to replicate sets of data with more than two values.

1. Percent Relative Standard Deviation (% RSD)

$$\text{Range (R)} = x_{\max} - x_{\min}$$

Arithmetic mean (average):

$$\bar{x} = \frac{x_1 + x_2}{2}$$

Shewhart's estimated standard deviation:

$$s_{\text{est}} = \frac{R}{d_2}, \text{ with } d_2 = 1.128$$

or

$$s_{\text{est}} = (R) \frac{1}{1.128} = (R) .89$$

Coefficient of Variation (CV) = $(s_{\text{est}}/\bar{x}) 100$. This is sometimes referred to as percent relative standard deviation (% RSD).

FOR PRECISION CONTROL CHARTS:

Upper Control Limit (UCL) = $\bar{C}\bar{V} + 3S$, and

Upper Warning Limit (UWL) = $\bar{C}\bar{V} + 2S$, where S is the calculated standard deviation.

$$S = \sqrt{\frac{\sum x_i^2 - (\sum x_i)^2/n}{n-1}}$$

2. Relative Percent Difference (RPD)

$$\text{RPD} = \frac{D_2 - D_1}{(D_1 + D_2)/2} \times 100$$

where:

D_1 = first sample result

D_2 = second sample result

TABLE 14-2

STATISTICS FOR ACCURACY

I. Percent Recovery Calculations

A. Percent recovery for a standard:

$$p = \frac{\text{Observed}}{\text{Known}} \times 100$$

B. Percent recovery for a spiked sample:

$$p = \frac{\text{Spiked sample concentration} - \text{unspiked sample concentration}}{\text{spike concentration}} \times 100$$

Control limits set at ± 3 standard deviations from \bar{p}

II. Percent Bias (Percent Relative Error) Calculations

bias = mean - true value

$$\% \text{ bias} = \frac{\text{mean} - \text{true value}}{\text{true value}} \times 100$$

A. Percent bias for a standard:

$$\% \text{ bias} = \frac{\bar{X} \text{ standard} - \text{true value}}{\text{true value}} \times 100$$

B. Percent bias for a spiked sample:

$$\% \text{ bias} = \frac{\text{observed} - (\text{background} + \text{spike amount})}{\text{sum of background} + \text{spike}} \times 100$$

C. Checking percent bias capability using a spiked sample:

$$\% \text{ bias} = \frac{\bar{X} \text{ spiked sample} - (\bar{X} \text{ unspiked sample} + \text{spike amount})}{\text{sum of unspiked} + \text{spike}} \times 100$$

III. Relationship of percent recovery and percent bias (percent relative error):

$$\% \text{ bias} (\% \text{ relative error}) = \% \text{ recovery} - 100$$

SECTION 15

ANALYTICAL CORRECTIVE ACTIONS

Corrective actions are undertaken at any time during the analytical process when deemed necessary based on the judgement of the analyst or when established QC data indicate a need for action. (Specific limits are addressed in Section 5). Generally, corrective action is triggered by the poor analysis replication, poor recovery, instrument calibration problems, blank contamination, etc. (Previous sections outline specifics).

Nonconformances associated with the statistical analysis and review of data are, in general easy to identify. The Quality Control Coordinator is responsible for assessment of QC sample information. If data outlie accepted limits, the Quality Control Coordinator immediately notifies the responsible Group Leader. The Group Leaders are responsible for identifying the source of the nonconformance and initiating corrective action. Completion of corrective action should be evidenced by data returning to prescribed acceptable limits. If the situation is not corrected so that an out-of-control condition occurs, or is expected to, the Section Chief is notified.

Corrective actions may include, but are not necessarily limited to: reanalysis, calculation checks, instrument recalibration, preparation of new standards/blanks, re-extraction/digestion, dilution, application of another analysis method, additional training, etc. Many of these corrective actions are initiated by the analyst at the time of analysis. However, some corrective actions are initiated subsequently based on evaluations performed by management personnel.

Nonconformances which do not readily result in an observed impact on data quality are more difficult to identify. Such events can sometimes be tracked to samples stored at an incorrect temperature or held beyond prescribed holding times, or improper maintenance of records. The entire staff is responsible for reporting "system" nonconformances. Analysts report nonconformances to their Group Leader, the Group Leaders in turn to the Section Chief. Corrective action is again the responsibility of the Group Leaders and the Section Chiefs. They shall review and approve the action(s) taken.

All corrective actions are noted on the appropriate log, chromatogram, strip chart, or data report.

SECTION 16

QUALITY ASSURANCE REPORTS TO MANAGEMENT

Periodic reports on project quality assurance are issued to management during the course of the project. These reports typically include:

1. internal performance and systems audit results;
2. quarterly assessments of accuracy, precision, and completeness;
3. reports on significant QA problems and solutions, if any; and
4. a final project QA report for inclusion in the report appendices, as appropriate.