Black & Decker (U.S.), Inc.

Work Plan for Soil and Groundwater Remediation Design Investigation Hampstead, Maryland Facility

WESTON SM
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WORK PLAN FOR
SOIL AND GROUNDWATER REMEDIATION
DESIGN INVESTIGATION
HAMPSTEAD, MARYLAND FACILITY

Prepared for:

Black & Decker (U.S.), Inc.

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BACKGROUND

An environmental investigation was initiated in 1987 at the request of Black & Decker (U.S.), Inc. (B&D) for its Hampstead, Maryland Facility. The investigation was conducted by Roy F. Weston, Inc. (WESTON) in several phases which culminated in the submission of an Environmental Investigation Report (April, 1989) submitted to the Maryland Department of the Environment. The investigation of the site groundwater quality, hydrogeology, and potential source areas indicated that:

- A PCE plume is present primarily on the western half of the facility, while TCE is present in groundwater primarily in the northeastern part of the facility.
- Groundwater is predominantly migrating along the hydraulic gradient both in the saprolite and bedrock to the south-southwest.
- A minor component of groundwater flow on the northeastern corner of the facility may be directed east toward State Route 30.
- Soils located in the area of the former underground storage Tank Farm 2 contain PCE, TCE and petroleum hydrocarbons. This area may be a continuing, relatively low-level source of groundwater contamination.
- Other potential source areas investigated were found not to be contributing significant contaminants to the environment.

Based on these conclusions, remediation strategies to recover and treat the contaminated groundwater on-site and prevent its off-site migration and to excavate and treat the contaminated soil in the Tank Farm 2 area were proposed in the 1989 Environmental Investigation Report. Details of the proposed remediation strategies are presented in this Work Plan. The groundwater remediation plan, proposed as a pump and treat well system, and its implementation are discussed in Section 2, including plans for field activities to develop design information for the remediation system. The soil remediation plan incorporates the use of low temperature thermal treatment. Plans for its implementation are discussed in Section 3. A schedule is presented in Section 4.

SECTION 2

GROUNDWATER REMEDIATION

2.1 SUMMARY OF PREVIOUS FINDINGS

Previous investigations have confirmed that the volatile organic constituents in groundwater at the Black & Decker Hampstead facility are tetrachloroethene (PCE) and trichloroethene (TCE). Data collected from 24 monitor wells and B&D production wells indicate that largely separate plumes of PCE and TCE exist. They are present in both the shallow water-bearing zone and in the deeper fractured bedrock to a depth of 150 feet along the local hydraulic gradient.

As shown in Figure 2-1, TCE has been detected primarily in the groundwater on the eastern half of the facility. Concentrations of TCE in excess of 1 ppm in monitor wells RFW-12 and RFW-8 delineate a plume possibly originating at the former aboveground TCE storage tank and/or Tank Farm 2 and extending south toward the lagoons. Hydrogeologic data indicate that in addition to flow toward the lagoon, a component of groundwater flow from the northeast corner of the plant, adjacent to RFW-8, may be directed east toward State Route 30.

As shown in Figure 2-2, PCE is the predominant constituent on the western half of the plant site. The highest concentrations, in excess of 1 ppm, appear to be limited to a small area that includes production Well No. 7. Lower concentrations were detected in wells across most of the site. PCE was not detected in the upgradient wells, in wells along the eastern site boundary or in wells on the northwestern side of the stream. However, PCE concentrations between 50 and 100 ppb were detected in wells adjacent to the western site boundary.

2.2 REMEDIATION PLAN OVERVIEW

The groundwater remedial plan involves the development of a pump and treat system designed to restrict potential off-site migration, recover and treat contaminated groundwater from the B&D property. A system of recovery wells, both existing and to be installed are proposed for the eastern and western site boundaries. The new well(s) will be completed in high yielding, water-bearing zones in order to produce a hydraulic barrier to groundwater and avoid contaminant flow off-site.

The concept of developing a hydraulic barrier is based on groundwater hydraulics. A barrier is created during pumping as the water surface surrounding the well forms a "cone of depression", inducing groundwater to flow toward the well. Depending on the pumping rate and the aquifer characteristics at the well

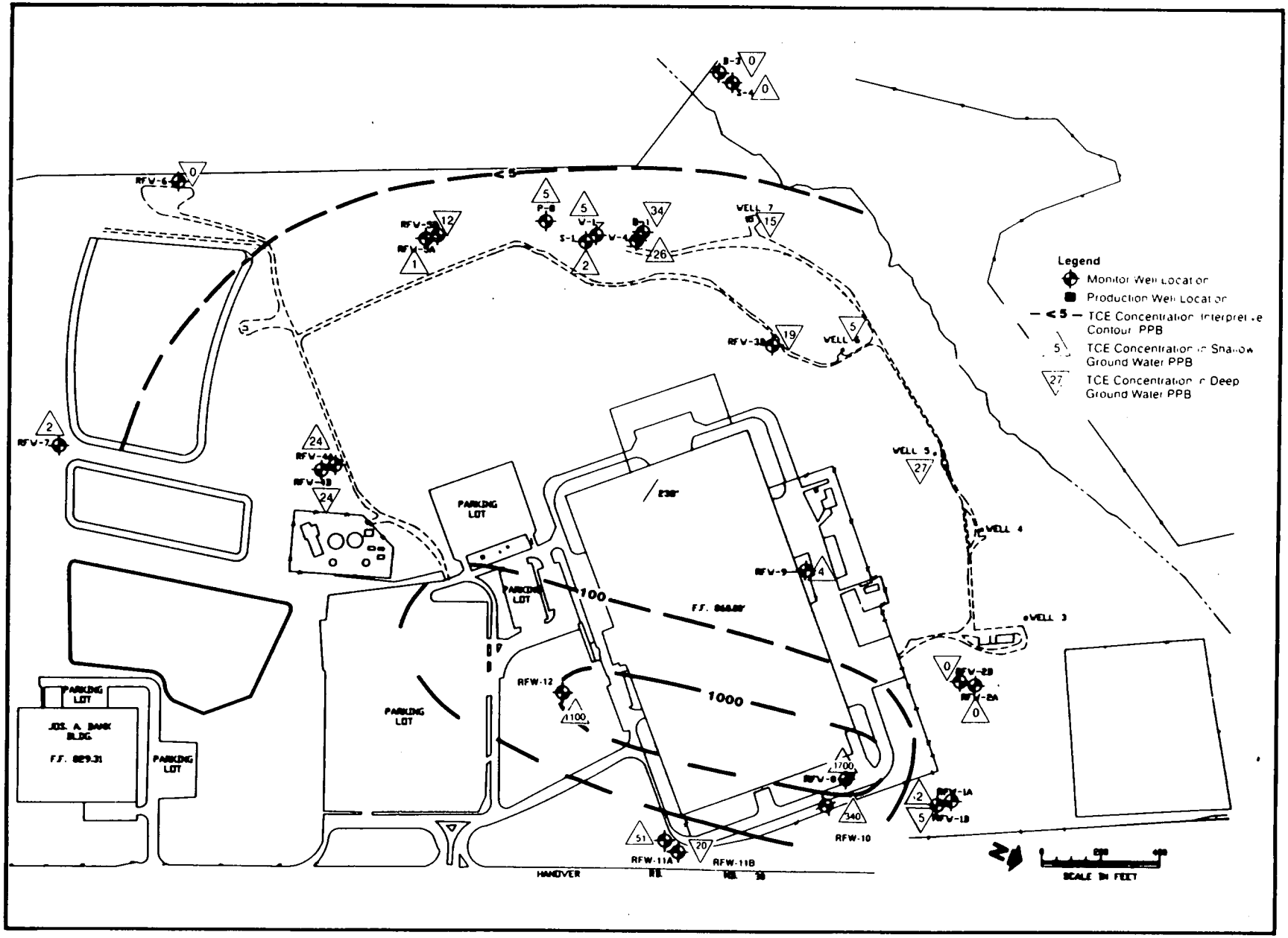


FIGURE 2-1 TCE CONCENTRATION IN GROUNDWATER 7/88 AND 12/88, BLACK & DECKER, HAMPSTEAD, MD

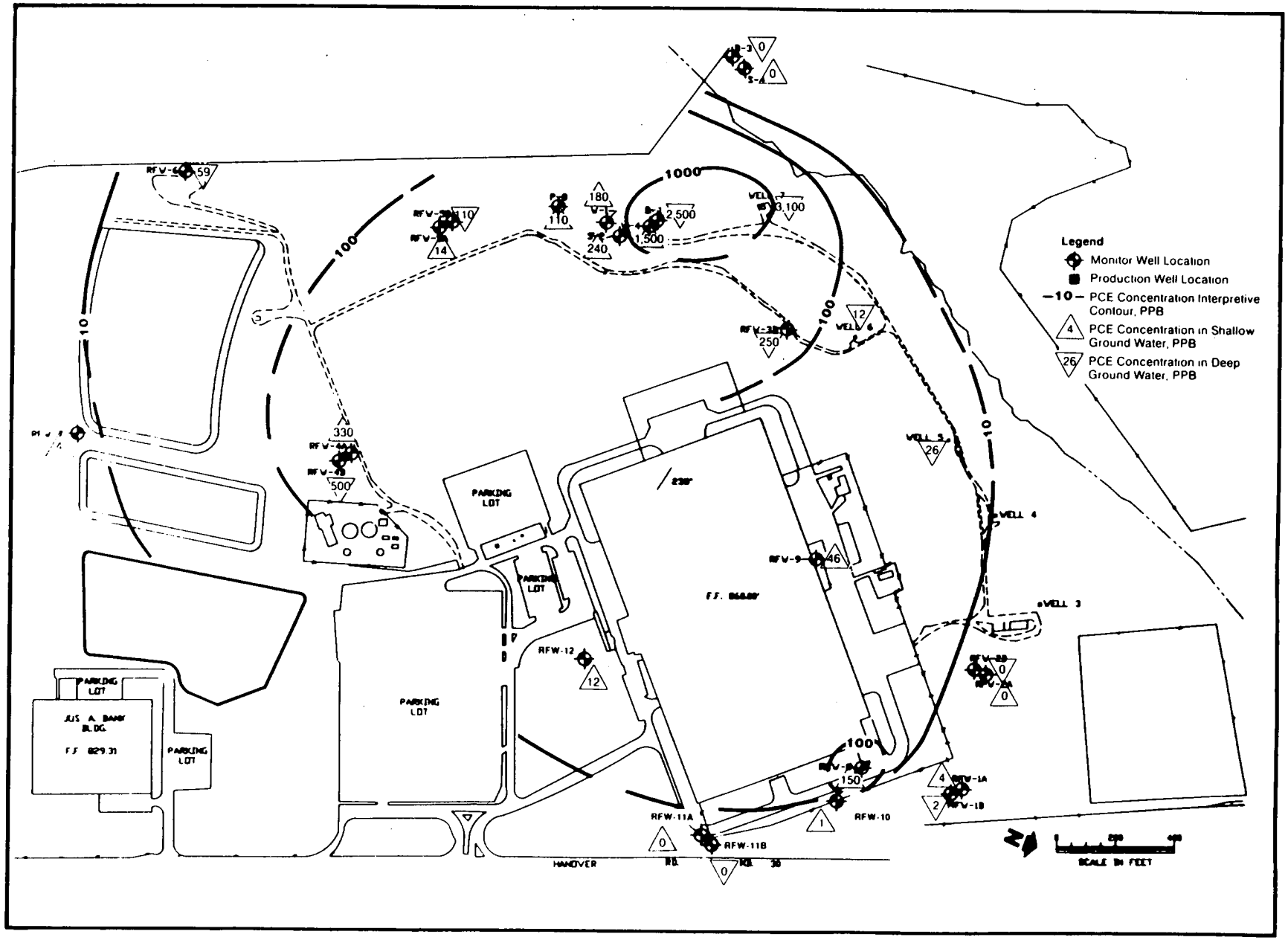


FIGURE 2-2 PCE CONCENTRATION IN GROUNDWATER 7/88 AND 12/88, BLACK & DECKER, HAMPSTEAD, MD

location, the cone of depression will vary in size and shape. When the area of influence of the well or wells is sufficient, the contaminated groundwater directed toward the eastern and western B&D site boundaries will be intercepted by the cone(s) of depression and recovered by the well system.

The remedial plan for the B&D site involves testing the area of influence of existing, relatively high yielding monitor wells and installing and testing additional well(s) in locations proximal to both the site boundaries and the highest areas of contamination. Evaluation of this data will allow design of an "optimal" recovery system, providing adequate hydraulic control while not needlessly depleting groundwater resources. Because it is difficult to predict well yields at a given location in a fractured-bedrock aquifer system such as is present in the area (even along fracture trends, where higher yields can be anticipated, areas of pumping influence can be difficult to predict), the remedial design investigation will be implemented in three stages. Each stage is contingent in detail upon the results of the previous stage in order to efficiently construct the hydraulic barriers. The stages of design investigation are proposed as follows:

2.2.1 Stage 1 Design Investigation

- Evaluate the effectiveness of monitor well RFW-12 as a recovery well for the eastern part of the facility by conducting a pumping test on the well. The critical factor in the evaluation will be identifying the area of hydraulic influence obtained by pumping RFW-12.

- Construct an "ideal" recovery well on the southwestern boundary of the property in an expected high yield fracture zone, south of production well 7. Perform a pumping test to evaluate the extent of pumping influence achieved.

2.2.2 Stage 2 Design Investigation

- If hydraulic influence in the area of Tank Farm 2 cannot be achieved by pumping RFW-12, construct and test an additional bedrock recovery well in the vicinity of Tank Farm 2.

- If hydraulic influence on the west side cannot be achieved by pumping at the western "ideal" recovery well, evaluate the use of an additional pumping well by pump testing existing deep monitor well RFW-5B.

2.2.3 Stage 3 Design Investigation

- If necessary, based on the results of Stage 2, complete the evaluation of the hydraulic influence by

development of an analytical flow model and placement of additional wells as indicated by the results of the model.

Procedures for the Stage 1 effort are described in Subsection 2.3. The Stage 2 effort is outlined in Subsection 2.4. Stage 3, if required, can be designed only with information specifically obtained from the Stage 1 and 2 results and is not discussed in the Work Plan. Implementation of the remedial system, including final design and construction is discussed in Section 2.5.

Following completion of the Stage 1 effort, a summary letter report will be submitted presenting initial findings and any changes necessary in the Stage 2 program based upon the Stage 1 results.

2.3 STAGE 1 DESIGN INVESTIGATION

Stage 1 consists of:

- Pumping test and sampling to evaluate the use of RFW-12 as a recovery well in the eastern part of the facility.
- Installation and testing of an "ideal" recovery well, RFW-14, in the western part of the facility.

2.3.1 RFW-12 Evaluation

Monitor well RFW-12 was selected as a potential recovery well because of:

- Potential high yield as indicated by previous pumping conducted during installation and sampling.
- The relatively high concentration of TCE in groundwater samples from this well, and its favorable location within the indicated TCE impacted area.

The relatively high yield of RFW-12, in excess of 40 gpm (estimated), can be attributed to its partial completion in a fractured quartz vein encountered in weathered schist immediately above competent rock. At the site, quartz veins in general appear to serve as preferred migration pathways within both the saprolite and bedrock. The possibility exists that the residual quartz veins within the saprolite extend into competent rock, serving as conduits between water migrating in the pore spaces within the saprolite and water migrating within the fractured bedrock.

The relatively high concentration of TCE in groundwater sampled from RFW-12 indicates that the water-bearing quartz vein may represent a preferred pathway for groundwater from the former

TCE storage tank and RFW-8 areas. This is supported by results of groundwater analyses from lower-yielding downgradient wells closer to RFW-8 which had lower TCE concentrations then the RFW-12 sample by one to two orders of magnitude.

Evaluation of RFW-12 to determine the area of influence during pumping, its potential as a recovery well, and the hydraulic parameters of the aquifer will be accomplished by two tasks:

- Pumping test.
- Time series sampling.

2.3.1.1 Pumping Test

Evaluation of RFW-12 will consist of a short duration stepdrawdown test followed by an approximately 72 hour constant-rate pumping test. The purpose of the step-drawdown test is to evaluate the performance of RFW-12 at various discharge rates. The measurements of drawdown versus discharge obtained from the test will be used to calculate values of specific capacity. This information can be used to determine if the well performance is sufficient to conduct a constant-rate test and if so, to select an efficient pumping rate for the test.

The constant-rate test will be used to evaluate the hydraulic influence of RFW-12 and to estimate hydraulic parameters of the aquifer. While pumping the well at the preestablished rate, measurements of drawdown versus time in observation wells (monitor wells RFW-8, -11A, -11B and 10) as well as in RFW-12 will be used to calculate the radius of the cone of depression and indicated aquifer transmissivity.

The test will be conducted with a stainless-steel submersible pump with a capacity of at least 50 gal/min. Dedicated tubing will be used to route discharge water to a nearby sewer for eventual treatment in the facility's wastewater treatment plant. An in-line fitting will be used for regulating and measuring discharge rates of the pump and to provide an outlet for sam- pling. Water level and elapsed time data will be collected using an automated data collection system, the In-Situ SE2000 Hermit Data logger.

Prior to use, all down-hole equipment will be decontaminated using a steam cleaner, according to the WESTON Quality Assurance/Quality Control (QA/QC) procedures as described in the September 1987 Work Plan.

After the data is collected and reviewed, the appropriate method(s) for evaluation of the results and calculation of aquifer parameters will be selected and applied. Again, the primary focus will be upon evaluation of the most efficient method to obtain hydraulic influence in the area of concern as discussed above.

2.3.1.2 Time-Series Sampling

During the constant-rate pumping test at RFW-12, the well discharge will be sampled at approximately four sequential time intervals and analyzed for VOCs. The samples will be collected following a logarithmic distribution as the rate of spread of area of pumping influence decreases with time. The analysis will be used as an indication of the proximity of higher concentrations of contaminants to the pumping well, as the area of influence expands during pumping. The results can then be used to evaluate the efficiency of the well in recovering contaminated groundwater and the probable trend in composition. Samples will be collected directly from the pump discharge tubing into laboratory prepared glassware. Time intervals selected for sampling will be determined based on the pumping rate and drawdown in both the RFW-12 and observation wells. Appropriate QA/QC samples will be included in the VOC analysis. The standard WESTON QA/QC procedures will be followed as described in the September 1987 Work Plan.

2.3.2 RFW-14 Location, Installation, Evaluation

Installation of a well to recover contaminated groundwater adjacent to the western site boundary is necessary. Previous pumping tests of nearby Production Well No. 7, which exhibited the highest PCE concentrations and has the highest specific capacity of wells on site, have indicated that the area of influence of this well alone is not sufficient to serve as a hydraulic barrier to flow on the western boundary.

As shown in Figure 2-3, fracture trace analysis has revealed the potential presence of two fractures zones, partially delineated by the stream valley, intersecting several hundred yards southwest of Production Well No. 7. A well is proposed to be installed close to the intersection of these fractures for two reasons.

- A well located in a highly fractured zone may potentially intercept several preferred groundwater migration pathways, resulting not only in a high well yield but also an extensive area of influence.
- The area is ideally located proximal to the observed highest PCE concentration levels and the western site boundary.

Several tasks have been proposed to locate, construct, and evaluate an "ideal" recovery well in this zone.

These tasks include:

- Geophysical survey.
- Well installation using air rotary drilling techniques.
- Pumping test.
- Time-series sampling.

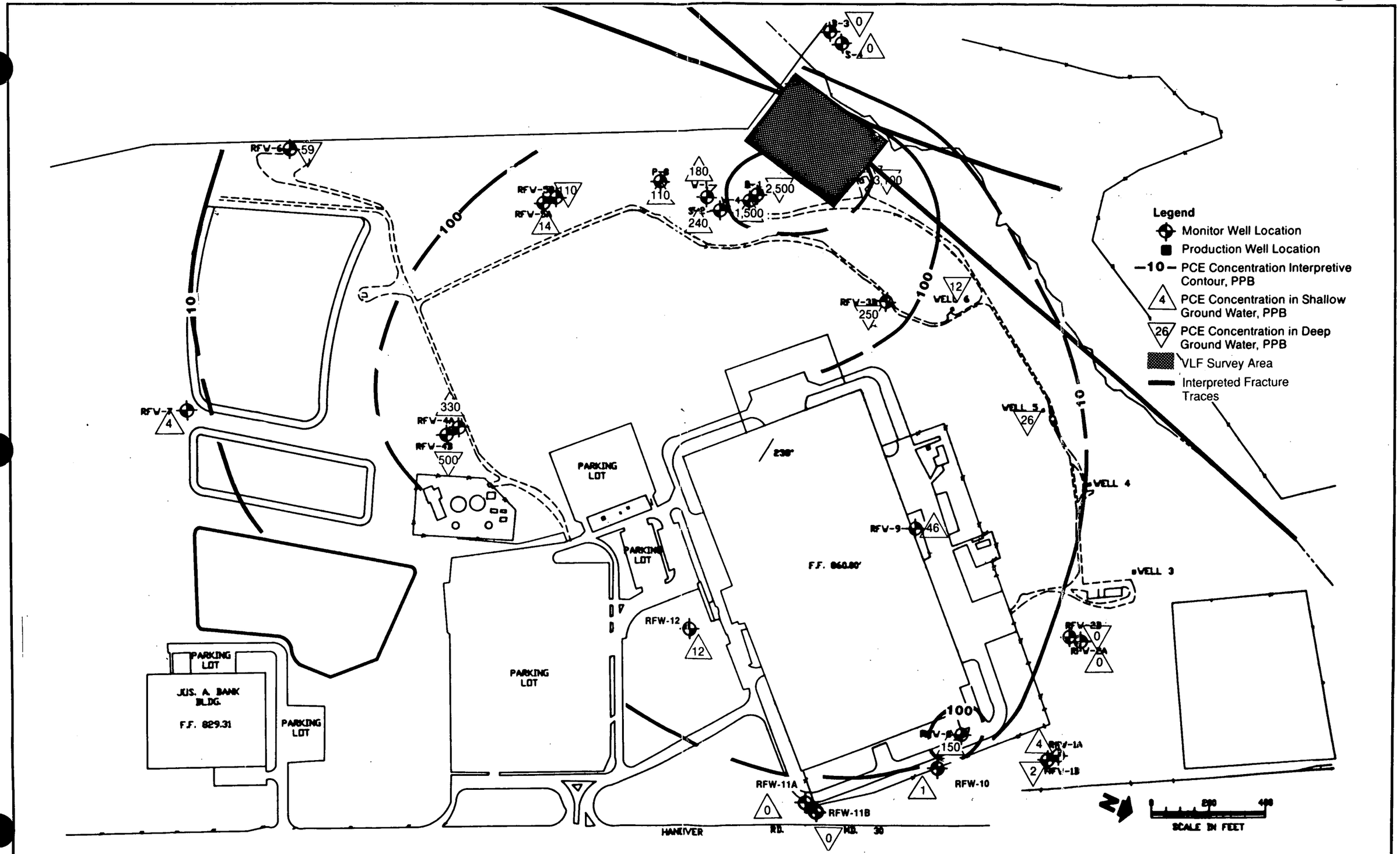


FIGURE 2-3 APPROXIMATE VLF SURVEY

2.3.2.1 Geophysical Survey

The objective of the geophysical survey is to provide information to assist in finding the optimal location for proposed recovery well RFW-14, by locating near-surface, water-bearing fracture zones in an approximate 10 acre area southwest of Production Well No. 7. Fractures will be delineated employing the Very Low Frequency Electromagnetic (VLF) technique. For the survey, an ABEM Wadi instrument will be used to measure fluctuations in the horizontal and vertical components of the magnetic field in the area, compared to the magnetic field transmitted by the VLF station. Although a relatively new technique, the VLF has been proven effective in locating relatively large-scale fractures through mapping trends of contrasting conductivity. A brief summary describing the VLF method is presented in Appendix A.

Using the VLF technique, measurements will be taken at 10 foot intervals along a 100 by 100 foot grid or as allowable by site conditions. The approximate grid area is depicted in Figure 2-3. Data collected in the survey will be used to produce profiles of conductivity contrasts that will be interpreted to predict the potential location of specific water-bearing zones. If results of the VLF survey do not provide adequate resolution for location of pilot holes for the recovery well, the VLF interpretation may be refined by conducting and evaluating an electromagnetic terrain conductivity or electric earth resistivity survey over a specific area of the grid where fractures are suspected to be present.

2.3.2.2 Well Installation

Based on the geophysical survey(s) a pilot hole(s) will be drilled at location(s) identified as being associated with water-bearing fractures. These "temporary wells" will be used to estimate yields of the water-bearing zones prior to installing a permanent recovery well.

The pilot hole(s) will be advanced a minimum of 25 feet into competent schist bedrock with a 6-inch bit using an Ingersol Rand (or equivalent) air rotary rig. Dependent on site conditions, clearing of obstructions from these locations may be required prior to mobilizing the drilling rig. Temporary casing will be set at approximately 70 to 100 feet below ground surface, at the transition between competent and weathered schist to maintain the borehole integrity.

Yields of water-bearing zones encountered during drilling will be estimated by surging the borehole with air and visually approximating the flow rate. If the yield is determined to be sufficient (i.e., 50-100 gpm) the temporary casing will be removed and the borehole will be redrilled to allow for the installation of an 8-inch recovery well (RFW-14). Low-yielding pilot holes will be abandoned by back-filling with a portland cement/bentonite grout.

Construction details for the RFW-14 recovery well are illustrated in Figure 2-4. Steel surface casing will be set above significant water-bearing zones. If the pilot hole testing indicates significant water-bearing zones in the weathered schist, the recovery well will be screened in both upper and lower water-bearing zones. Well development will be accomplished by surging the open borehole with air prior to setting the well screen and by pumping the well once it is complete. A licensed surveyor will establish the elevation and location of the top of casing of RFW-14 based on the permanent benchmark on-site.

During pilot hole and recovery well installation the WESTON QA/QC program established in the September 1987 Work Plan will be followed. This program includes the steam cleaning of all down-hole equipment prior to drilling or the use of dedicated equipment and materials.

2.3.2.3 Pumping Test

Evaluation of the recovery well (RFW-14) will consist of a short duration step-drawdown pumping test followed by a maximum two week constant-rate pumping test. As in the RFW-12 evaluation, the step-drawdown test will be conducted to evaluate the performance of the recovery well at various discharge rates and to select an efficient pumping rate for the constant rate test.

The constant-rate test, used to evaluate the hydraulic influence of RFW-14 and estimate hydraulic parameters of the aquifer, will be conducted in a manner similar to the test of RFW-12. Observation wells to be monitored during the test will include Well No. 7, RFW-5A, RFW-5B, RFW-6, and B-1. All production wells on-site will be idle during the tests.

Procedures for equipment decontamination and for performing the test outlined previously and established by the WESTON QA/QC program will be followed. Discharge from the pump during the test will be routed through the air stripper currently in use at the site and will be used in the plant for meeting regular needs.

2.3.2.4 Time-Series Sampling

As in the RFW-12 evaluation, during the constant-rate pumping test of RFW-14, the well discharge will be sampled at approximately seven sequential time intervals, dependent upon the actual test length, and analyzed for VOCs to characterize the quality of groundwater intercepted by the well's expanding area of influence. The samples will be collected using a logarithmic distribution as the rate of spread of the cone decreases with time.

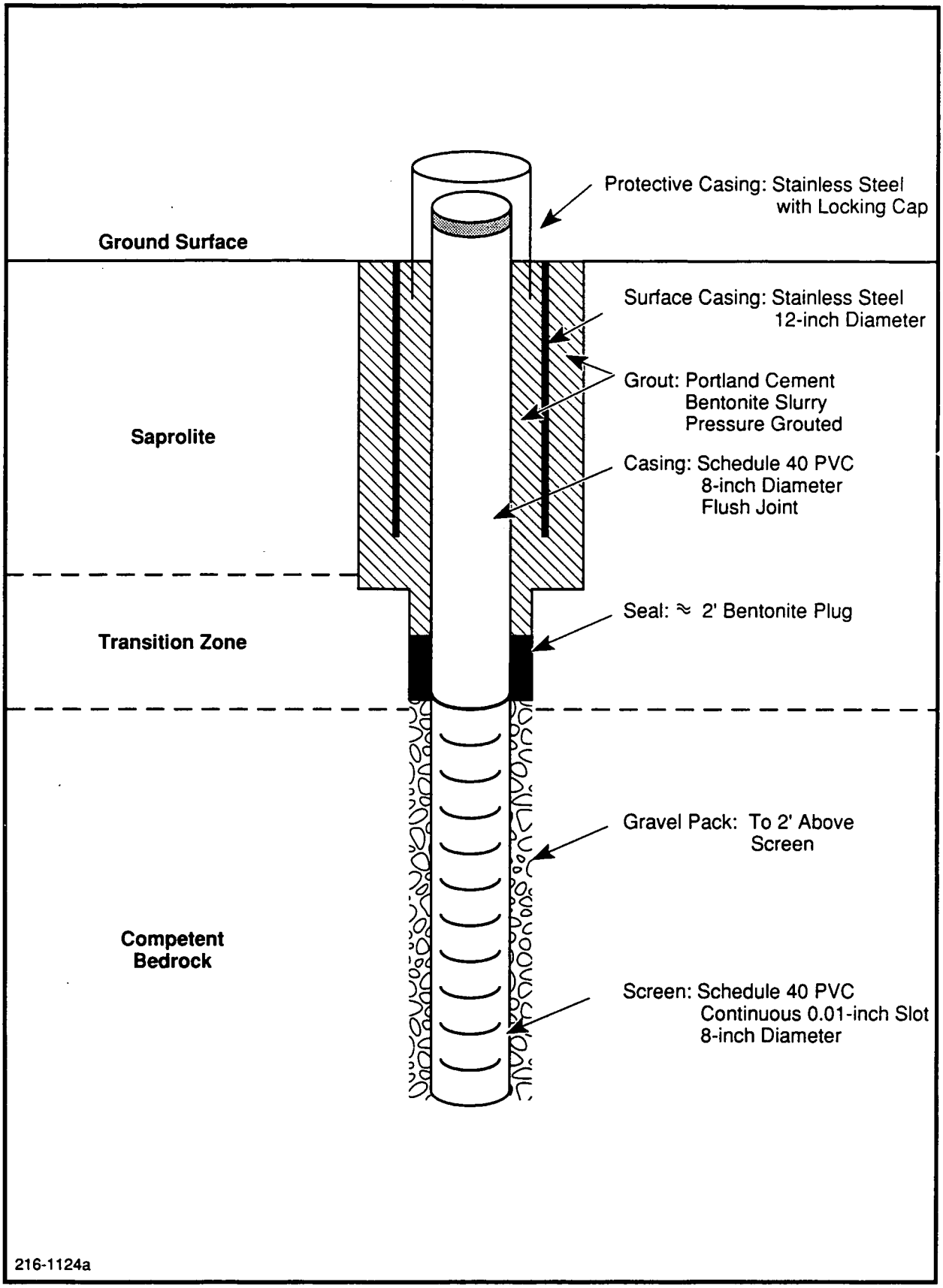


FIGURE 2-4 APPROXIMATE CONSTRUCTION SPECIFICATIONS RFW-14

Samples will be collected from the pump's discharge hose and placed directly into laboratory prepared glassware. Time intervals selected for samples will be included in the VOC analyses. Applicable WESTON QA/QC procedures will be followed as described in the September 1987 Work Plan.

2.4 STAGE 2 DESIGN INVESTIGATION

Following the completion of the Stage 1 effort, a summary letter report will be submitted presenting the initial findings and plans for Stage 2. The Stage 2 tasks will be implemented if evaluation of either RFW-12 or RFW-14 indicates that additional wells are needed to create a hydraulic barrier along the eastern or western site boundaries, respectively.

Stage 2 as preliminarily planned consists of:

- Location, installation, and evaluation of recovery well RFW-15 on the eastern site boundary.
- Pumping test and sampling to evaluate the use of RFW-5B as a recovery well near the western site boundary.

Any changes in Stage 2 tasks will be based on Stage 1 results, and will be included in the letter report.

2.4.1 RFW-15 Location, Installation, Evaluation

If a sufficient area of influence cannot be achieved by the pumping of RFW-12, an additional well will be located, constructed, and evaluated on the eastern property boundary. Information collected in the evaluation of RFW-12 will be used in conjunction with a fracture trace analysis to locate RFW-15. RFW-15 will be located:

- In a potential high yield water-bearing fracture.
- Proximal to the highest TCE concentration levels near the eastern site boundary.

As used in the RFW-14 installation, pilot hole(s) will be drilled at identified locations so that yields of the water-bearing zones encountered can be estimated prior to installing a permanent recovery well. Construction details and procedures will be similar to those presented for the RFW-14 recovery well.

If yields from water-bearing fractures are determined to be sufficient, a 6-inch I.D. recovery well will be installed according to specifications in Figure 2-5. Procedures for the well's installation and development will be similar to procedures used to install RFW-14.

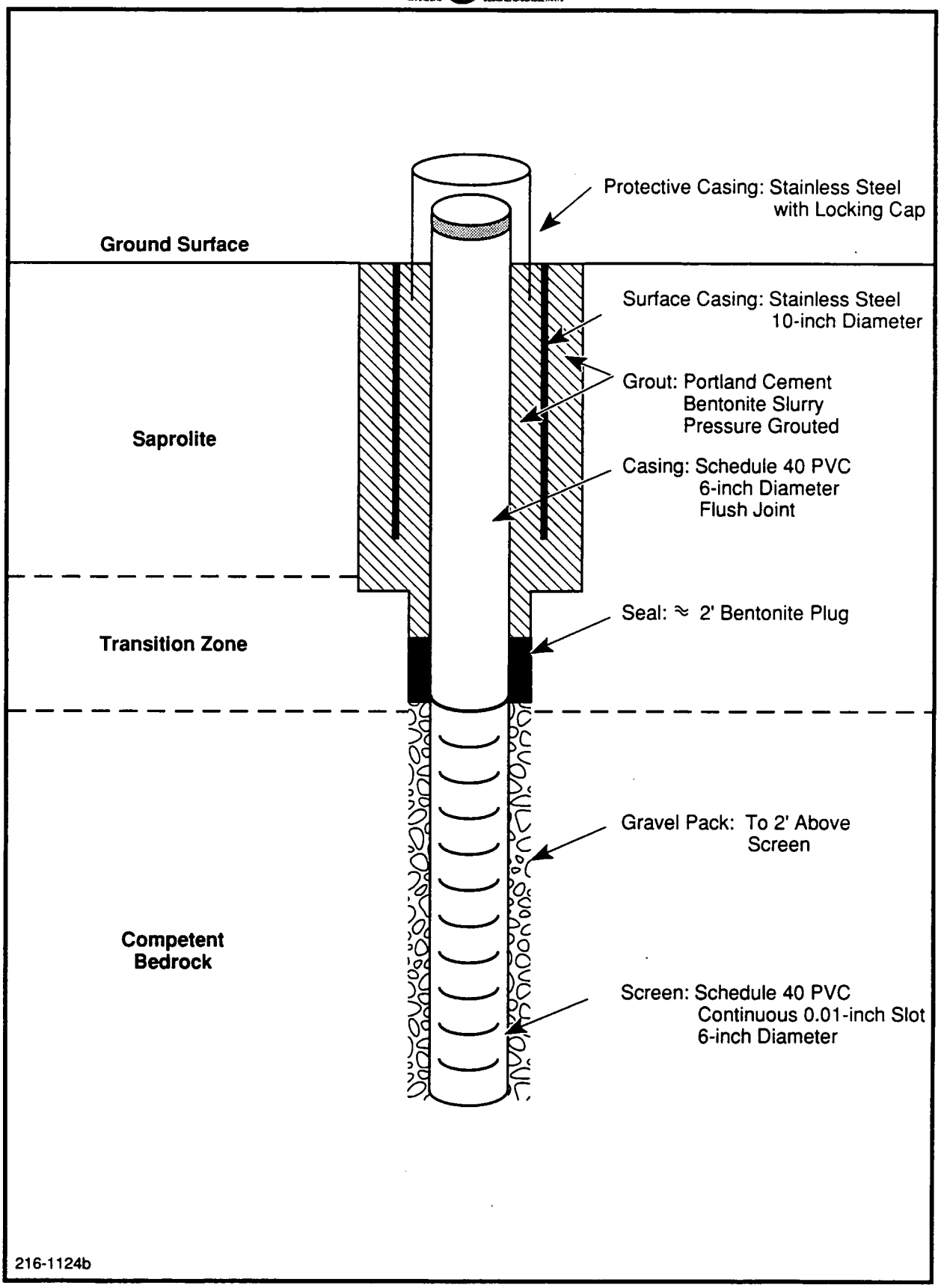


FIGURE 2-5 APPROXIMATE CONSTRUCTION SPECIFICATIONS RFW-15

Evaluation of RFW-15 will include a pumping test and time series sampling. The pumping test will consist of a maximum one-week constant-rate test preceded by a short duration stepdrawdown test to select an efficient pumping rate. The constant-rate test, used to evaluate the hydraulic influence of RFW-15 and to estimate hydraulic parameters of the aquifer, will be conducted similarly to the Stage 1 tests. Observation wells to be monitored during the test will include RFW-12, -10, -11A, -11B, and -8.

Time-series sampling will be conducted during the pumping test over a selected number of time intervals, resulting in a minimum of four samples. The samples will be analyzed for VOCs to characterize the quality of groundwater intercepted by the well's expanding area of influence. Sampling procedures will reflect sampling protocols presented in Subsection 2.3.2.

2.4.2 RFW-5B Evaluation

If a sufficient area of influence cannot be achieved by the pumping of RFW-14, RFW-5B will be evaluated for use as an additional recovery well. Monitor well RFW-5B was selected because of:

- Potential high yield as indicated by previous pumping, conducted during installation and sampling.
- Its location between Production Well No. 7 and the lagoon on the south-western site boundary.

RFW-5B was partially completed in a fractured quartz vein within competent schist. Yield of the well was estimated as greater than 60 gpm when the well was developed, indicating that the well may be intercepting a significant groundwater migration pathway.

Although contaminant concentrations in groundwater sampled from RFW-5B are one order of magnitude less than the highest concentrations detected elsewhere in groundwater (near Well No. 7), RFW-5B is appropriately located between Well No. 7 and the lagoons, southeast of proposed well RFW-14, and along the south-western facility boundary. The focus of the evaluation will be to determine if a sufficient area of influence can be achieved during pumping so that RFW-5B can be coupled with RFW-14 to produce an effective hydraulic barrier.

The evaluation will consist of a pumping test and time-series sampling. The pumping test will include a short duration step-drawdown test to establish an efficient pumping rate for the constant rate test. A maximum two-week constant rate-test will be used to evaluate the hydraulic influence of RFW-5B and to estimate the hydraulic parameters of the aquifer while pumping

the well at the preestablished rate. Measurements of drawdown versus time in observation wells (including wells RFW-5A, -14, -6B, and No. 7) as well as in RFW-5B, will be used to estimate the indicated radius of pumping influence and indicated aquifer transmissivity.

The test will be conducted according to procedures established in previous tests and in accordance with WESTON QA/QC procedures established in the 1987 Work Plan. As during previous constant-rate tests, the well discharge will be sampled at sequential time intervals and analyzed for VOCs, resulting in a minimum of four samples. The analysis will be used as an indication of the proximity of higher concentrations of contaminants to the pumping well, as the area of influence expands during pumping. The results can then be used to evaluate the efficiency of the well in recovering contaminated groundwater. Sampling procedures established during previous testing will be followed as well as WESTON QA/QC procedures.

2.5 REMEDIAL SYSTEM IMPLEMENTATION

If results of Stage 1 and Stage 2 testing indicates adequate hydraulic control cannot be established, Stage 3 design investigations will be planned and presented in a letter report, along with the findings of Stage 1 and Stage 2. At the conclusion of Stage 3 (if necessary), or if results of Stage 1 and/or Stage 2 indicate adequate hydraulic control, the report to be submitted at the completion of these design investigation phases will include plans for a detailed design of a groundwater pump and treat system. Detailed design will include all plans and specifications for well pumps, power, piping, treatment system(s), and permits as necessary. The submission will also include plans for operational monitoring, allowing for system modification based upon the performance of the recovery/ treatment system during the early and later operational stages. A preliminary schedule will be provided indicating estimated lengths of time necessary for completion of design, permitting, and construction.

As the results of Stage 1 and Stage 2 become available, WESTON, along with B&D will evaluate the feasibility of operation of interim recovery systems at the facility. For example, if pumping of RFW-12 indicates significant hydraulic control, construction of piping and power supply to this well to begin groundwater recovery and treatment along the east side of the facility will be considered. Other interim measures may be considered as additional design investigation results are obtained and reviewed.

SECTION 3

SOIL REMEDIATION

3.1 SUMMARY OF PREVIOUS FINDINGS

A source characterization study confirmed that the contaminants of concern in the soils at Tank Farm 2 are petroleum hydrocarbons and the chlorinated hydrocarbons PCE and TCE. Total petroleum hydrocarbons (TPH) concentrations in the soils sampled ranged from below detection (ND) to 93,000 ppm; chlor- inated hydrocarbons concentrations ranged from ND to 7 ppm. Lesser concentrations, below 1 ppb, of benzene and toluene were also detected. Soils with high chlorinated hydrocarbon concentrations were generally also characterized by high TPH concentrations (see Figure 3-1).

Samples from 11 closely spaced borings around Tank Farm 2 were collected at depth and analyzed for VOCs and TPH to define the horizontal and vertical extent of the soil contamination. The data indicated, as depicted in Figure 3-1 that TPH concentrations >100 ppm and VOC concentrations >1 ppm are distributed in the soils:

- Throughout the tank area above 853 feet MSL (top 6 feet of soil), in an approximately 1,800-square foot area.
- In the central part of Tank Farm 2, closest to the building wall from the surface to 839 feet MSL (20 feet below ground surface).

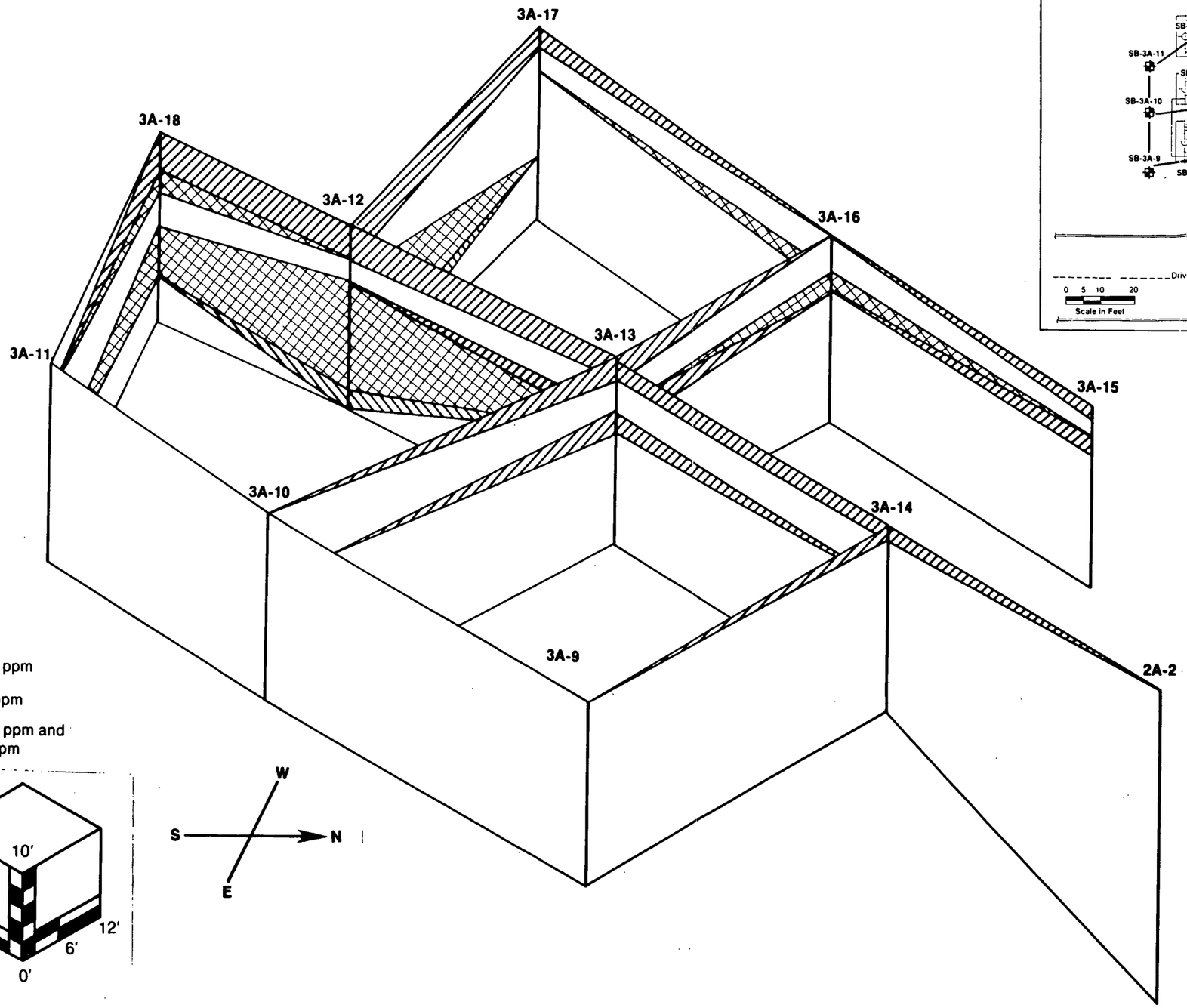
A TCLP leachate analysis of select samples indicated that chlorinated hydrocarbons are mobile in the soils, and therefore represent a potential source of groundwater contaminants. Concern that the Tank Farm 2 soils are a potential contaminant source was further confirmed by the detection of PCE and TCE in groundwater samples from Tank Farm shallow well MW-8.

As part of the environmental investigation findings, it has been recommended that the soils surrounding Tank Farm 2 be removed, treated on-site, and backfilled. A low temperature thermal treatment (LT^3) process was recommended as the most appropriate method of remediation.

3.2. LT^3 PROCESS DESCRIPTION

3.2.1 Introduction

WESTON's U.S. patented Low Temperature Thermal Treatment (LT^3) process is a demonstrated technology that provides



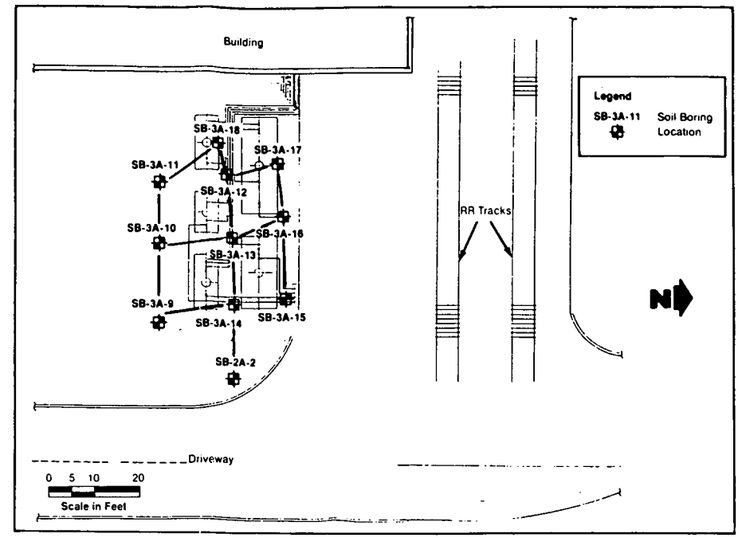


FIGURE 3-1 TANK FARM 2 SOIL PROFILE DEPICTING ZONES OF TPH CONCENTRATION 100 PPM AND

evaporation of volatile organic compounds (VOCs) from contaminated soil without heating the soil matrix to combustion temperatures.

The basis of the LT^3 technology is the thermal processor, an indirect heat exchanger used to dry and heat contaminated soils. Heating the soils to approximately 400°F evaporates or strips the VOCs from the soil. The organic vapors are then processed in an afterburner or fume incinerator independent of the soil.

The LT^3 is divided into three main areas of emphasis: soil treatment, emissions control, and water treatment. A flow diagram diagram of the LT^3 process is shown in Figure 3-2. The LT^3 process equipment is mounted on three tractor trailer beds for transportation and operation. The unit is suitable for highway transport and may be mobilized on a site location within 2 days (plus transportation). The general arrangement of the process equipment and the placement of the trailers during operation is shown in Figure 3-3.

A brief description of the equipment and typical processing steps is contained in the following subsections.

3.2.2 Site Preparation

Site preparation will consist of situating and leveling all LT^3 process equipment on paved areas covered with Visqueen. It is anticipated that all activities will be performed upon paved areas. Should work upon unpaved areas prove necessary, additional discussion will be held with representatives of MDE and B&D to establish acceptable site preparation protocols.

3.2.3 Soil Treatment

3.2.3.1 Soil Feed System

Approximately 510 cubic yards of soil will be excavated from the Tank Farm 2 area (the estimated extent of the contamination) and will be stockpiled adjacent to the LT^3. The staged soil will be stockpiled on visqueen plastic prior to treatment to avoid migration of contaminants. The stockpile will be covered with visqueen plastic and tied down to prevent fugitive emissions. The excavation area will be surrounded by snowfence to prevent wildlife or site personnel from accidentally falling in the open area. The entire facility is guarded from public access by fencing and B&D's 24-hour security staff.

Soil is transported from the stockpile to the system by a backhoe or front-end loader. If required, soil is deposited directly on a power shredding device. The shredder is operated by a 60 horsepower (hp) motor. Classified soil with a topsize of less than 2 inches passes through the shredder into the feed

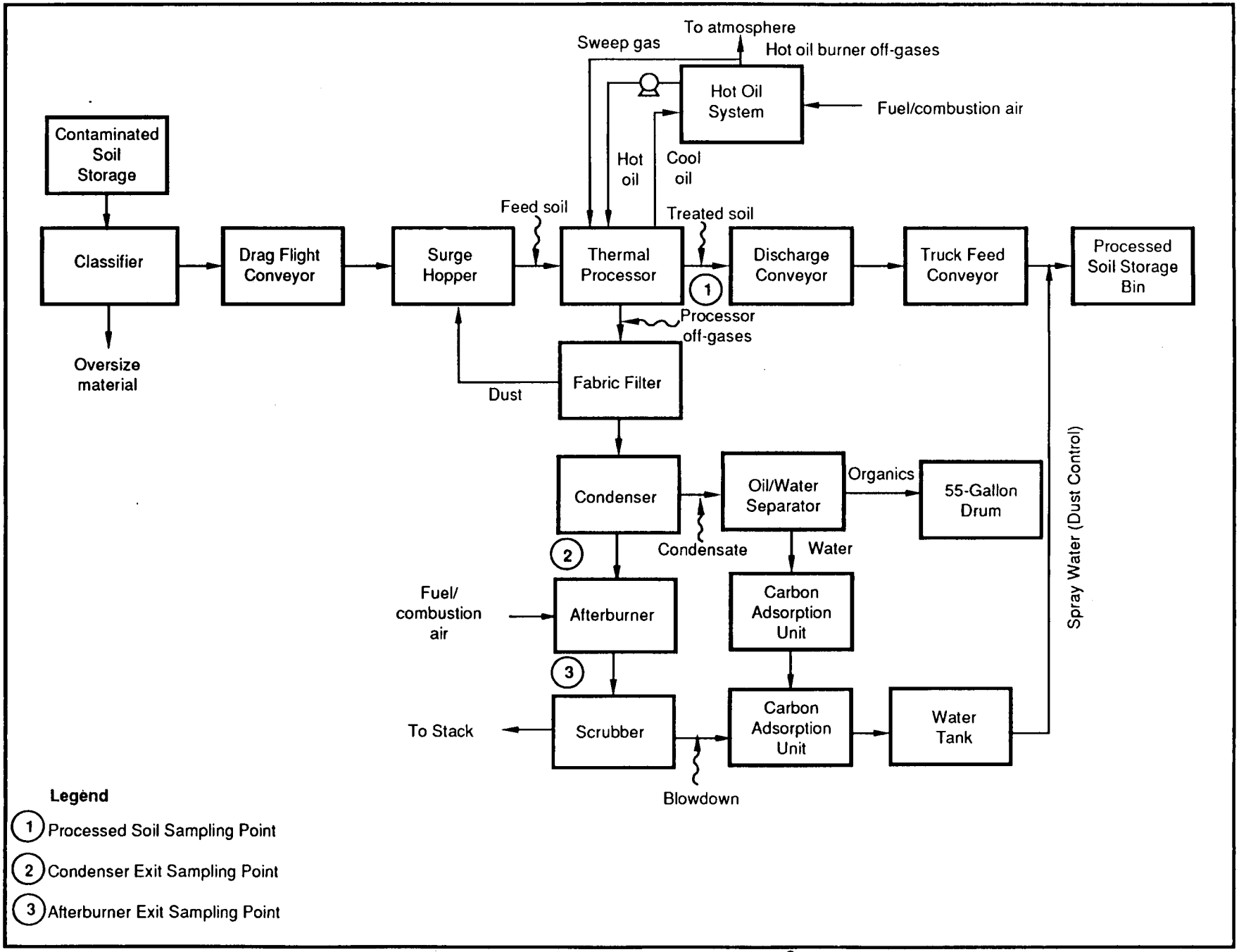


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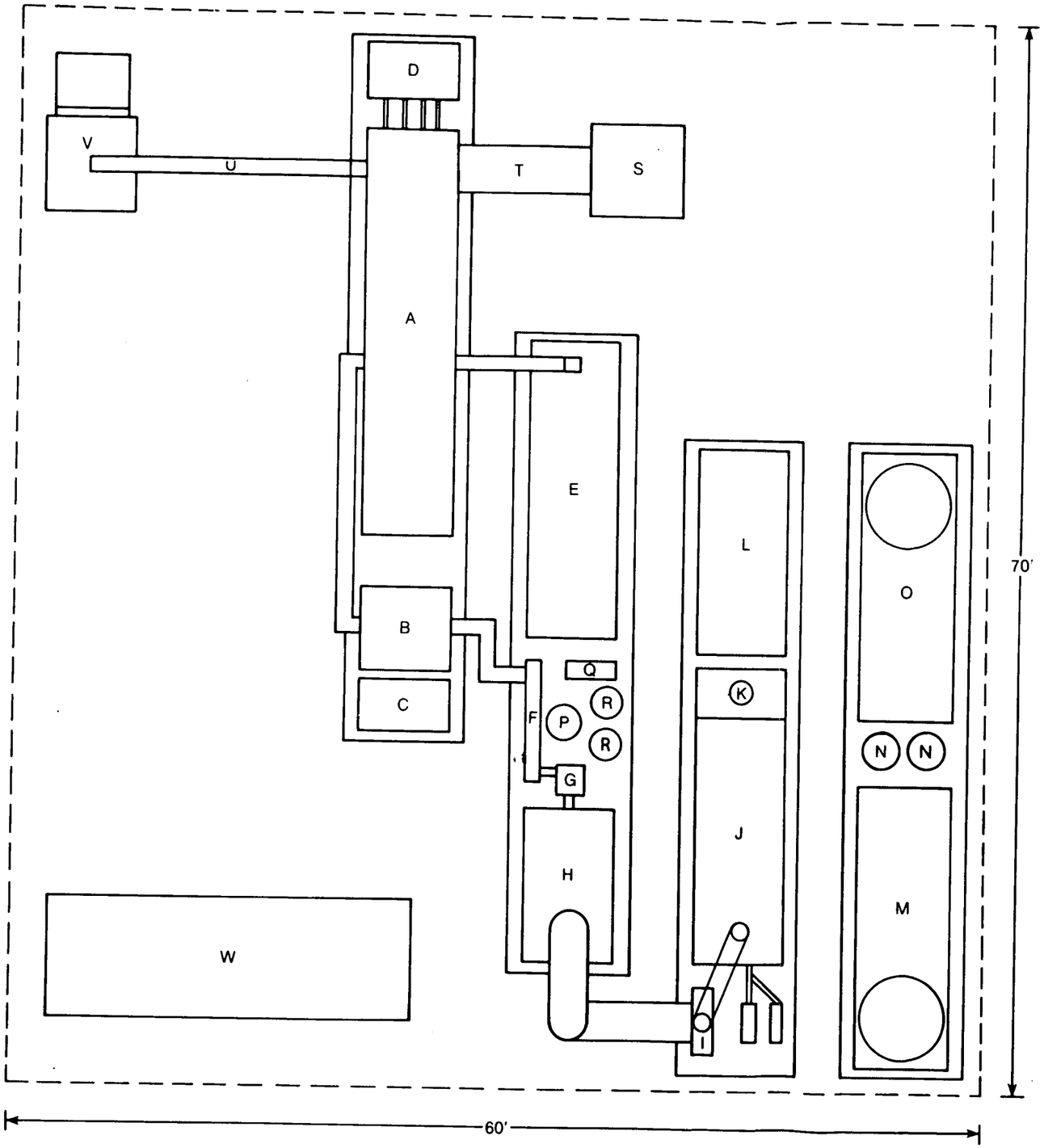
FIGURE 3-2 FLOW DIAGRAM FOR THE LT^3 SYSTEM



Equipment

A. Thermal Processors
B. Baghouse
C. Motor Control Center
D. Thermal Processor Drive Units
E. Hot Oil System
F. Condenser
G. Induced Draft Fan
H. Afterburner
I. Scrubber ID Fan
J. Scrubber System
K. Exhaust Stack
L. Caustic Storage Tank
M. Fresh Water System
N. Blowdown Carbon Adsorption Units
O. Blowdown System
P. Recycle Water Tank & Pump
Q. Oil/Water Separator
R. Water Carbon Adsorption Units
S. Clay Shredder
T. Drag Conveyor
U. Discharge Conveyor
V. Dump Truck
W. Continuous Emissions Monitoring Trailer (CEM)

FIGURE 3-3 MOBLE LOW TEMPERATURE THERMAL TREATMENT

conveyor. Oversized material is removed, washed by steam cleaning in the decontamination area, and backfilled along with the processed soil material. Large volumes of oversize material are not expected based upon the boring logs.

The feed conveyor is an enclosed drag conveyor that is 24 inches wide and 40 feet long. It is mounted at a 60° angle and is driven by a 5 hp motor. The conveyor is designed to convey 15,000 pounds per hour of soil on a wet basis. The conveyor discharges into the surge hopper located above the thermal processor. The soil will be fed into the LT^3 system at regular intervals to maintain the surge hopper seal.

The surge hopper is 5 feet wide by 5 feet long and holds approximately 8,000 pounds of soil, providing feed for approximately 30 minutes of operation. The screws of the thermal processor extend into the bottom of the surge hopper, withdrawing feed material to create a "live bottom hopper" effect. The surge hopper also provides a seal over the thermal processor to minimize air infiltration.

3.2.3.2 Thermal Processor

The thermal processor consists of two jacketed troughs assembled in a piggyback fashion (one above the other). Each houses four intermeshed screw conveyors. Soil is carried across the upper tier of the processor by the screws. When the soil reaches the discharge end of the upper tier, it drops to the second tier via gravity. The soil is moved in the opposite direction, across the second tier and then exits the processor at the same end that it entered.

The shafts and flights of the screw conveyors and the trough jackets are hollow to allow circulation of a heat transfer fluid (i.e., hot oil). The function of each screw conveyor is to move soil forward through the processor and to thoroughly mix the material, providing indirect contact between the heat transfer fluid and the soil (i.e., soil is outside the hollow conveyors and jackets, hot oil is inside the hollow conveyors and jackets).

Each screw conveyor is 18 inches in diameter and runs the entire length of the trough which is 20 feet long. The screw conveyors are intermeshed to break up soil clumps and to improve heat transfer. The four screws of each processor are driven by a 10 hp variable speed drive mechanism. Soil residence time and soil temperature in the thermal processor are adjusted by varying the rotational speed of the screws and the hot oil temperature setting. The heat transfer fluid is pumped through the screw shafts, flights and trough jacket by a 25 hp centrifugal pump.

A draft is maintained in the processor by an induced draft fan. Vapors are driven off the soil and are drawn out of the thermal processor.

3.2.3.3 Processed Soil Handling System

Soil is discharged from the thermal processor into a horizontal screw conveyor driven by a 1.5 hp motor. The conveyor is approximately 5 feet long and is designed to convey 15,000 pounds per hour of material. The horizontal screw conveyor discharges to a second screw conveyor, or conditioner, driven by a 5 hp motor. The conditioner is 5 feet long with a diameter of 9 inches. Water spray nozzles are installed in the conditioner housing to cool the discharge material and to minimize fugitive dust emissions. The conditioner discharges onto an inclined stacker belt conveyor. Soil is carried to the top of the inclined stacker belt and is discharged into a collection dump truck or storage bin. The processed material is transported to a processed soil staging area.

3.2.3.4 Hot Oil System

The hot oil system is a self-contained unit consisting of a 7.2-million British thermal units per hour (Btu/hr) gas-fired burner, flame supervisory system, oil reservoir, hot oil pump, and associated controls.

The hot oil system burner provides the thermal energy to maintain the temperature of the heat transfer oil. The heat transfer fluid used is Dowtherm® HT, produced by Dow Chemical. The maximum recommended oil temperature for continuous operation is 650°F.

A portion of the combustion gases released from the hot oil system is used as sweep gas in the thermal processor. The warm sweep gas (i.e., 700°F) assists in removal of the volatiles from the processor. Sweep gas is introduced to maintain an exhaust gas temperature from the processor above 300°F to avoid contaminant condensation. The sweep gas, which is low in oxygen, also provides an inert atmosphere. The low oxygen is needed to avoid exceeding the lower explosive limit (LEL) of contaminants within the thermal processor and downstream equipment.

3.2.4 Emissions Control System

Emission control equipment is provided to avoid release of particulates, VOC, and acid gases (HCl) during operation. The pollution control equipment consists of a fabric filter, condenser, afterburner, and packed bed scrubber. The operation of the equipment is monitored by a continuous emissions monitor (CEM).

3.2.4.1 Fabric Filter

Sweep air and volatiles from the thermal processor are drawn by an induced-draft fan into a fabric filter for particulate (dust) removal. The fabric filter is designed to handle 1,872 actual cubic feet per minute (acfm) of exhaust gas. The fabric filter is of the jet-pulse design, where high pressure air (80 pounds per square inch gauge (psig)) periodically (every 6 seconds) pulses to remove dust that has accumulated on the bags. Dust drops to the bottom of the fabric filter and is collected in two collection bins. Dust is manually removed on a daily basis and combined with the contaminated soil for reprocessing. The maximum allowable pressure drop across the fabric filter due to accumulated material on the bags is 15 inches of water column (in. w.c.). The temperature of the gases exiting the fabric filter is approximately 300°F.

3.2.4.2 Condenser

The exhaust gas from the baghouse is drawn into a condenser by the I.D. fan. The air-cooled condenser is used to remove condensable water vapor and organics from the exhaust gas. Cooling (ambient) air is forced across the condenser tubes by four 2 hp axial-blade fans. The ambient air cools the exhaust gases to approximately 125°F. Condensed liquid is collected in a trap and is pumped to the water treatment system. Condenser off-gases are directed to the afterburner.

3.2.4.3 Afterburner

The process gas drafted from the condenser passes through the I.D. fan. The gases are directed under a positive pressure into an afterburner. The afterburner is a 3.5 million Btu/hr, gas-fired fume incinerator that operates at approximately 1,800°F. The afterburner will be on-line at all times while the thermal processor is operating. It is used to destroy organics that may remain in the exhaust gases. The afterburner chamber is 10 feet long, 8 feet wide, and 8 feet high, and lined with a fiber-type refractory.

The afterburner is equipped with a combustion air fan that maintains a minimum of 3 percent excess oxygen exiting the afterburner. Also included with the afterburner is a control system for burner management (i.e., flame detector) and system temperature control.

3.2.4.4 Continuous Emissions Monitoring System

An extractive-type continuous emissions monitoring (CEM) system is used to monitor afterburner exhaust gases for oxygen, carbon monoxide, carbon dioxide, and total hydrocarbons. The CEM system also monitors the exhaust gases from the condenser (afterburner inlet) for oxygen and total hydrocarbons.

3.2.4.5 Bleed Air

Gases exit the afterburner at 1,800°F. Bleed air is admitted to the system by a second I.D. fan drawing ambient air. The ambient air mixes with the high temperature afterburner exhaust gases and cools them to approximately 500°F. The gases are then drawn into the scrubbing system by the second I.D. fan.

3.2.4.6 Scrubber

Gases enter the acid gas scrubber at approximately 500°F. In the first stage of the scrubber or quencher, the gases are cooled to saturation temperature, approximately 180°F by a series of four water sprayers. In the second stage or packed bed absorber, acidic gases (HCl) in the saturated exhaust gas, are neutralized to sodium chloride (NaCl) and water using a sodium hydroxide (NaOH) solution. The scrubber is designed for a minimum HCl removal efficiency of 99 percent. Since salts are generated through the neutralization process, a small purge (blowdown) stream is maintained to prevent the buildup of salts. The scrubber blowdown liquor is collected for on-site treatment and reuse as described in Subsection 3.2.5.

3.2.4.7 Caustic Supply System

The caustic supply tank holds approximately 2,000 gallons of 25 percent sodium hydroxide. Caustic solution is supplied to the scrubber by a variable-frequency pump designed to deliver a maximum 1.0 gpm. Proportionate feed of caustic is used to maintain the pH of the recirculating scrubber liquor at a neutral 7.0.

3.2.5 Water Treatment System

Water is generated during the process from the exhaust gas condenser and scrubber blowdown system. This water is treated on the LT^3 system by an oil water separator and an activated carbon adsorption system. The treated water is then reused for soil quenching and dust control.

3.2.5.1 Oil-Water Separator

Liquid exiting the condenser is collected and is pumped to an oil-water separator. The oil-water separator operates by gravity. It consists of a 50-gallon vessel that allows the insoluble, light organic components to separate from the water. The light organic phase is removed by a skimmer. The water phase flows out of the separator and is pumped to carbon adsorption columns. The organic phase removed from the oil-water separator is stored in a 55-gallon drum for off-site disposal.

3.2.5.2 Carbon Adsorption

The water removed from the oil water separator and the scrubber blowdown liquor is directed through two carbon adsorption units for removal of soluble organics. The liquid stream between the two carbon columns is sampled and analyzed by a hydrocarbons analyzer to detect whether breakthrough in the first carbon column has occurred. Should breakthrough occur, the first carbon column will be bypassed while the carbon is replaced and brought back on-line. After leaving the carbon columns, the water from both units is stored in a fresh water tank.

3.2.5.3 Fresh Water System

An 80-gallon fresh water tank is used for intermediate storage of processed water. The water is withdrawn by a 2-gallon per minute (gpm) centrifugal pump and is sprayed on the treated soil for dust control. No water is discharged from the process. If necessary, makeup water for the scrubber and for dust control will be supplied via an existing on-site water source.

3.2.6 Utilities

Operating the LT^3 system requires the following support systems and utilities:

- Electrical power.
- Propane fuel or natural gas.
- Process water.

3.2.6.1 Electrical Power

The electrical power requirements for the systems (oil heater, fans, motors, afterburner, motor control center, control circuits, etc.) is made by a single 460V/3-phase/600-amp power connection. Power will be supplied from the B&D facility.

3.2.6.2 Propane Fuel

Fuel at 15 psig is required for the burners in the oil heater and afterburner. Total consumption for both burners is a maximum of 10.7 million Btu/hr. Propane gas will be stored in a temporary liquid storage container and will be piped to the gas-fired vaporizer.

3.2.6.3 Process Water

Process water is required primarily for makeup water to the acid gas scrubber and dust control. Up to 7.5 gpm may be required due to evaporation losses and blowdown. Additional water is also needed for sampling and decontamination purposes. Water will be obtained from on-site potable supplies.

3.3 BENCH-SCALE LT^3 TEST

A bench-scale LT^3 test will be performed at the WESTON Engineering Technology Laboratory (ETL), prior to the fullscale soil processing operation at the Black and Decker site. The purpose of the bench-scale test is to assure the removal of the contaminants of concern. B&D will provide a representative 15-gallon sample of contaminated soil in a sealed container to WESTON's ETL in Lionville, Pennsylvania.

3.3.1 Bench-Scale LT^3 Process Description

The bench-scale LT^3 system owned by WSI consists of an electrically operated thermal processor. The bench-scale LT^3 is located in WESTON's ETL in Lionville, Pennsylvania. The bench-scale thermal processor is located in a fume hood during processing.

The processor consists of a trough that houses a double screw mechanism. The screws are 3 inches in diameter and 30 inches in length and provide 4.7 square feet of heat transfer surface. A variable speed drive controls the rotational speed of the screws. The range of rotational speeds is from 1 rpm to 20 rpm.

The thermal processor is electrically heated. The unit is designed to simulate the use of hot oil (as in a full-scale field application). The intermeshing screw flights are electrically heated with cartridge-type heaters. The maximum heat input to the screws is 4 kilowatts.

Two Chromalox strip heaters are mounted on the trough to provide additional heat capacity and to simulate the full-scale system. One strip heater is provided on each side of the trough. The strip heaters are 1.5 inches wide with an overall length of 26 3/4 inches. Each strip heater is rated at 1,000 watts at 120 volts and provides 12 watts per square inch.

The area above the twin screws is provided with a vapor dome. The vapor dome is equipped with a vapor discharge stack that is 3 inches in diameter and 12.5 inches high.

3.3.2 Capacity of Bench-Scale Unit

The bench-scale unit used by WSI provides approximately a 15 pounds/hour throughput with a total retention time of 15 minutes per pass. The bench-scale test recycles processed material through the unit three times, providing a total retention

time of 45 minutes. The full-scale LT^3 processor treats material at a rate of 15,000 pounds/hour with a total retention time of 45 minutes. Previous scaleup studies performed by WESTON using the bench-scale unit, a 150-pounds/hour pilot-scale unit, and our full-scale processor have shown that the bench-scale processor test and test procedures are a reliable means of assessing our ability to meet and predict operating capacities and cleanup objectives with the full-scale unit.

3.3.3 Test Procedure

The following procedure will be followed for the bench-scale test.

(1) Screening The representative sample will be manually screened to remove oversized material (> 0.25 inch).

(2) Stabilization Period Prior to the bench-scale test run, feed material will be fed into the unit for 15 minutes to stabilize the temperature and to achieve steady-state conditions.

(3) Test Feed Period Following the stabilization period, the remaining feed material will be fed into the bench-scale LT^3 system. The material will be processed for 15 minutes at a rotational screw speed of 1.8 revolutions per minute. The discharged material will be fed back into the system two more times as follows:

   (a) 1st Pass Processed Soil (approximately 15 minutes of treatment)

   (b) 2nd Pass Processed Soil (approximately 30 minutes of treatment)

   (c) 3rd Pass Processed Soil (approximately 45 minutes of treatment)

(4) Sampling/Analysis Selected samples from the feed soil and from the processed soil will be collected and analyzed for the following parameters:

   (a) Moisture content

   (b) Total Petroleum Hydrocarbons

   (c) PCE/TCE using EPA METHOD 8010/8020.

   (d) Leachate extraction using the TCLP procedure and analysis of the leachate for the volatile organic compounds

The unused treated soil, as well as the treated residuals, will be returned to B&D for future processing.

(5) Reporting A letter report documenting the results of the bench-scale testing will be completed.

3.4 REGULATORY AUTHORIZATION

WESTON expects that the actual time of LT^3 operation will be less than two weeks. Air emissions are expected to be minimal due to the high destruction efficiently in the afterburner. Accordingly, WESTON will seek MDE's assistance in obtaining regulatory authorization to proceed under a state air permit exemption status. We expect to provide an appropriate information package to MDE to obtain such authorization.

3.5 TANK REMOVAL AND SOIL TREATMENT

3.5.1 Site Layout

The LT^3 process equipment will be located adjacent to the staged feed soil to minimize transport and handling of the feed material. The treated soil will be stockpiled next to the excavation area pending results of the sample analysis. When the soil decontamination is verified, the soil will be backfilled in the excavated area.

3.5.2 Site Preparation

B&D will indicate locations of the tanks, associated piping, and utilities with available drawings. The locations of the tanks, piping and other buried lines will be marked at the worksite with stakes and banner guard. WESTON will review the markings with the B&D site representative for approval prior to excavation.

3.5.3 Tank System Removal

The five underground tanks will be removed and disposed during the treatment process.

3.5.3.1 Initial Excavation

Soil above the tanks will be removed. Manways and pipe connections to the top of the tanks will be identified.

3.5.3.2 Overburden

Overburden material will be temporarily stockpiled at the designated feed soil location. Soil in areas previously identified as contaminated will be designated for processing. Any additional soil removed as part of the excavation, overcut to maintain stability, will be examined as it is removed.

3.5.3.3 Line Disconnection/Tank Opening

The fill, gauge, discharge and vent lines will be disconnected from the tank, and the open ends will be capped or plugged. The manways on the top of the tanks will be opened to gain access for removing sand which was previously placed in the cleaned tanks.

3.5.3.4 Tank Contents

Following the removal of the overburden soil and excavation of the tanks, the solid material (sand) in the tanks will be removed while the tanks are in place using a bulk vacuum truck. The sand from the tanks will be placed on a plastic liner, adjacent to the Tank Farm 2 area.

A sample of the sand will be sent to WESTON's Lionville Laboratory for analysis. If the results indicate that the sand is clean, it will be transported to the processed soil area. If not, it will be processed along with the contaminated soil.

3.5.3.5 Tank System Excavation and Removal

Following the removal of the tank and its contents, the soil surrounding the tank will be excavated and stockpiled at the designated feed soil stockpile area. Soil will be excavated to the base of the tanks and around buried lines. Support structures which are encountered will be removed and staged. Buried pipe lines running to the tank will be disconnected and capped at locations specified by B&D. Where necessary, cutting operations will be performed to facilitate tank and piping removal. The ambient air in the tank vicinity will be monitored for volatile organic compounds before and during cutting activities.

3.5.3.6 Tank Decontamination and Disposal

After the sand in the tanks has been vacuumed out and the tanks have been removed from the excavation area by the backhoe and front end loader, the exterior walls of the tank will be decontaminated using either a steam cleaner or water-jet (Butterworth Machine). All liquids and sludges generated during the tank cleaning will be collected for treatment on-site. If the laboratory results indicate contamination of the sand inside the tank, tank interior cleaning will also be necessary. Sufficient holes will be made in the tanks to prevent their reuse. Tanks and disconnected piping will be loaded on to a flat bed truck and transported for disposal or scrap metal reuse.

3.5.4 Final Excavation

WESTON assumes that the soil integrity is sufficient to allow excavation around the tanks and piping without shoring. The soil in the Tank Farm 2 area will be excavated using 1:1 slopes

from the building foundation and the roadway to remove VOC and TPH containing soils as delineated in Figure 3-1. The estimated quantity of excavated soil is 510 cubic yards. The soil will be loaded and transported via trackhoe (or backhoe) and front end loader to the feed soil area. The soil will be placed on a plastic liner to prevent migration of contaminants. The stockpile will also be covered with a plastic liner to prevent contamination from rain water runoff.

3.5.5 Soil Treatment

The material from the designated feed soil stockpile area will be processed by the LT^3 system. The integral part of the system is a heated screw conveyor, which is indirectly heated by hot oil circulating through the shafts and flights. The contaminated soil is heated to 400-450° F in the screw conveyor to vaporize the moisture and VOCs. The vaporized contaminants are treated as follows:

(1) Offgas passes through a fabric filter for particulate removal.

(2) Filtered offgas passes through a condenser to remove condensable moisture and organics.

(3) Noncombustibles are incinerated in an afterburner at 1800° F for approximately one second.

(4) Condensate passes through a two-stage carbon filtration system for final VOC-removal.

(5) Clean filtered water is used for processed soil cooling and/or dust control (i.e., no liquid discharges).

The system includes a feed material screening system and standard dump trucks or storage bins for processed soil collection and transportation.

3.5.6 Sampling and Analytical Procedures

Discrete processed soil samples will be collected from each dumptruck or storage bin during the remediation operation.

The discrete soil samples will be composited into one daily processed soil sample. The samples will be transported to the WESTON Analytics Laboratory in Lionville, Pennsylvania, for analysis. A summary of sampling and analysis procedures, parameters to be analyzed, and frequencies of sampling is presented in Table 3-1.

The afterburner outlet gas will also be monitored and sampled continuously by the continuous emissions monitoring system (CEM). Table 3-2 describes the sampling and analysis methods

Sampling Point Number:*	1		
Description:	Processed Soil		
Sampling Objective:	Determine Final Composition of Processed Soil		
Sample or Monitoring Method:	Grab Samples Collected From Each Bin are Composited Into a Single Sample Every 24 Hours		
Parameters to be Tested:	Total Petroleum Hydrocarbons	Trichloroethene and Tetrachloroethene	Volatile Organic Compounds
Sample Extraction/ Monitoring Method (s):	EPA Methods 3540/ 418.1	EPA Methods 8010 / 8020	TCLP
Sampling of Monitoring Design:			
- Total Number of Samples Collected	One Per Day (125 ml VOA Jar)	One Per Day (250 ml Wide Mouth Jar)	One Per Day (250 ml Wide Mouth Jar)
- Field Blanks	One Per Analytical Batch		
- Trip Blanks	Not Applicable	One Per Analytical Batch	
- Method Blanks	One Per Analytical Batch	One Per Analytical Batch	One Per Analytical Batch
- Blank Spike	One Per Analytical Batch	One Per Analytical Batch	One Per Analytical Batch
- Blank Spike Duplicates	One Per Analytical Batch	One Per Analytical Batch	One Per Analytical Batch
- Replicate	One Per Analytical Batch	One Per Analytical Batch	One Per Analytical Batch

*Refer to Figure 3-2 for Location.

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TABLE 3-1 SAMPLING AND ANALYSIS PLAN FOR THE PROCESSED SOIL

Sampling Point Numbers:*	2, 3			
Description:	System Exhaust Gases			
Sampling Objective:	Determine the Concentration of the System Exhaust Gases			
Sampling or Monitoring Method:	Continuous Emissions Monitoring (CEM)			
Parameters to be Tested:	Total Hydrocarbons	Carbon Dioxide	Carbon Monoxide	Oxygen
Sample Extraction/Analysis Methods:	EPA Method 25A	EPA Method 3A	EPA Method 10	EPA Method 3A
Sample Point 2 Condenser Exit	X			X
Sample Point 3 Afterburner Exit	X	X	X	X

*Refer to Figure 3-2 for Locations.

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TABLE 3-2 SAMPLING AND ANALYSIS PLAN FOR THE SYSTEM EXHAUST GASES

for the CEM sampling procedures. A complete description of the sampling and analytical methods is presented in Appendix B. A description of the CEM system is presented in Appendix C.

3.5.7 Backfill and Restoration

The excavated area will be backfilled in 9-inch lifts with the processed soil staged adjacent to the excavation hole. Processed soil will be placed in separate locations within the designated staging area until the laboratory results are received for each batch. Sample analysis results will be available in 3 days. When the results indicate that is a soil batch is clean, that batch will be back-filled in the excavation hole, making space available for another batch of processed soil. If the laboratory results indicate significant contamination, that batch of soil will be reprocessed. Soil will be compacted to 90 percent of the maximum density. Clean fill will be utilized to match the original slope. Subsequently, the excavated area will be graded and hydroseeded.

3.5.8 Operating Crew

The soil treatment activities will be conducted 24 hours per day. Two operating crews will be working on 12-hour shifts. Typically, each crew will consist of the following personnel:

(a) Site manager/field safety officer (1)
(b) Plant operator (1)
(c) Field technicians/equipment operators (2)
(d) CEM technician/sampling technician (1)

Initially, one crew will be employed for the tank removal activities, while the other crew will be installing the LT^3 equipment, simultaneously. After the startup/shakedown operations are completed and the LT^3 system is in operation, the operating crews will be working on alternate shifts.

3.5.9 Site Restoration and Demobilization Activities

Upon completion of the remediation work, WESTON will demobilize LT^3 process equipment. The disturbed areas will be seeded if necessary, prior to leaving the site.

SECTION 4

SCHEDULE

Field activities for the groundwater remediation design can begin within four to six weeks following notice to proceed, depending upon subcontractor availability. It is anticipated that the Stage 1 and Stage 2 investigation field work will be completed within approximately 16 weeks after start-up. As laboratory turn-around time is normally four to six weeks, assuming analytical samples as part of the Stage 2 investigation are submitted at or near the completion of Stage 2 field activities, approximately eight to 10 weeks will be required for data evaluation and to prepare a letter report summarizing the findings; total project time is estimated to be 32 weeks.

A schedule for the soil clean-up activities is presented in Figure 4-1. Start-up following notice to proceed is difficult to predict at this time; however, B&D and MDE will be given sufficient time to prepare for activity to begin. As only a single LT^3 unit exists, the availability of the unit is dependent upon the status of other projects. We do not anticipate major delays. Please note that total time of operation of the unit at the site is anticipated to be less than three weeks.

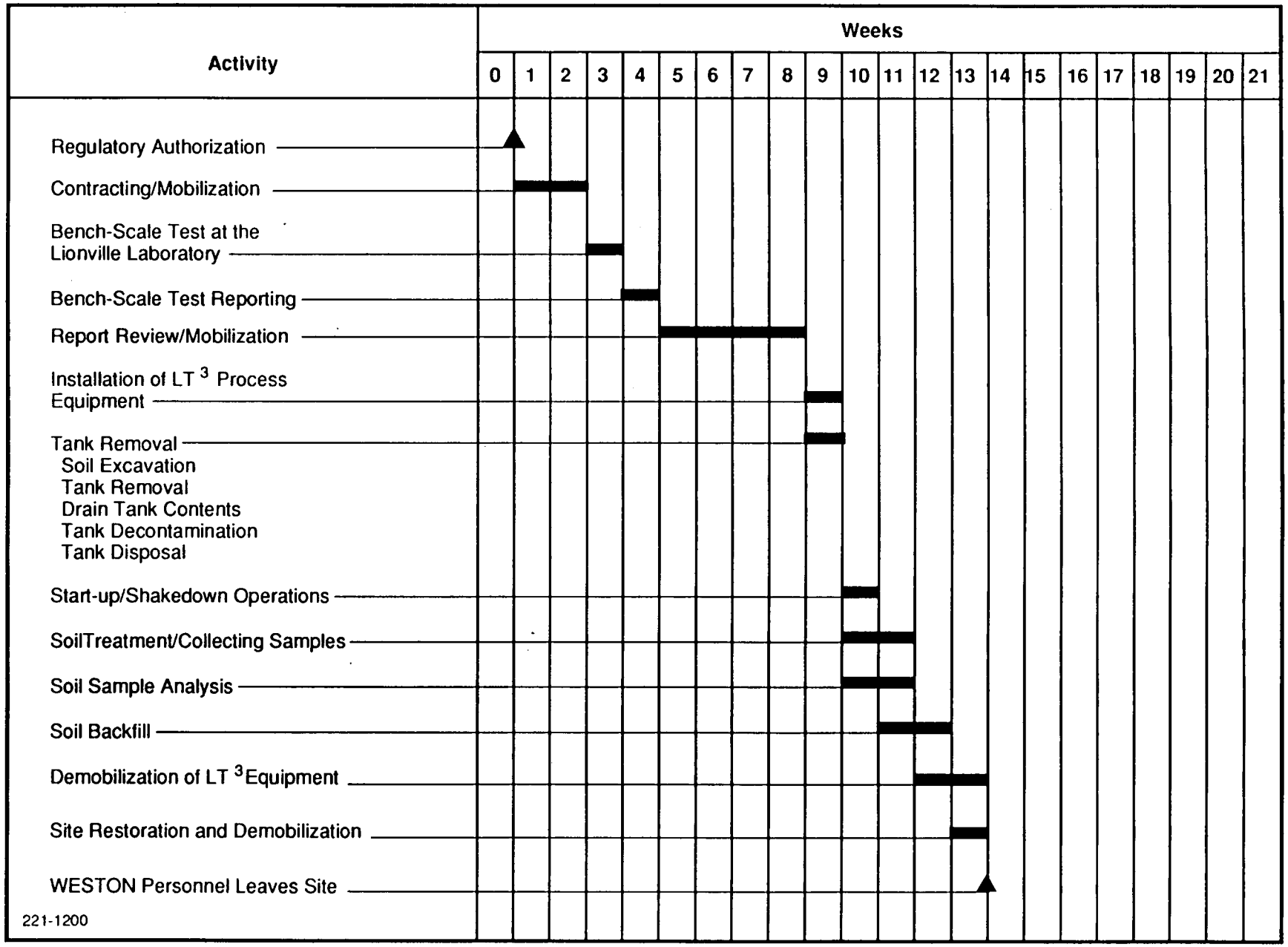

FIGURE 4-1 TENTATIVE OVERALL WORK SCHEDULE FOR SOIL CLEAN-UP

APPENDIX A

VLF METHOD

APPENDIX A

Very Low Frequency (VLF) Electromagnetics: Theory

An electromagnetic field consisting of a magnetic field parallel to the earth's surface (horizontal) and an electrical field oriented perpendicular to the earth's surface (vertical) is generated by a VLF transmitter station. These stations are primarily used by the military to communicate with submarines. The electromagnetic fields generated by these stations are reflected by the ionosphere and/or ground surface and arrive at the observer's location by various routes.

VLF electromagnetic anomalies are produced by two different processes. One type of VLF anomaly is associated with electrical (vortex) currents generated within conductive bodies in the subsurface. As a VLF wave travels over the earth's surface, it is bent or refracted vertically downward. When a conductive body is encountered, the VLF electric field (primary) causes charges to form on the surface of the body, producing secondary electric field within the body. The secondary electric field produces closed loops of electrical current within the body, which create a secondary magnetic field. The secondary magnetic field adds to the primary magnetic field generated by the transmitter, creating localized disturbances or anomalies in the vicinity of the conductive body. A second type of anomaly (galvanic) is created when the primary electric field, flowing as a sheet of current, flows toward conductive bodies and away from resistive bodies. The resulting disturbances in the current flow are reflected anomalies in the electric and magnetic fields. The Wadi measures the vertical and horizontal in-phase (real) and out-of-phase (imaginary) components of the magnetic field.

The VLF method is limited to detecting conducting bodies such as pipelines, mineral deposits, large nests of buried metal debris, and water or clay-filled fractures. In the case of poor conductors like water filled fractures, the fracture must be at least 100 meters long to be detected because the VLF anomaly associated with a water-filled fracture is produced by the galvanic current mechanism. Glavanic anomalies must be long enough to channel sufficient current to produce an anomaly.

Very Low Frequency Electromagnetics (VLF): General Procedure

VLF measurements will be made using the ABE, Wadi (VLF) system. The Wadi consists of a separate control unit, antenna unit, and a measuring unit mounted on a belt worn by the operator. The control unit consists of a keyboard, screen, internal microcomputer, and a memory used to store measured values. When the system is turned off, a lithium battery provides the power necessary to maintain the internal memory. The measuring

unit contains the radio receiver, amplifier, filter, electronic circuitry, computer output port, and is powered by 6 "D" cells. The antenna unit contains the antennas and an inclinometer, which determines if the unit is being carried in a vertical position.

Each day, before beginning the survey, a transmission station will be selected by facing the traverse direction and scanning for a signal which is strongest in the traverse direction and weaker when the antenna is turned perpendicular to the direction of traverse. Transmission stations include Annapolis, MD; Seattle, WA; and Cutler, ME.

VLF measurements will be taken every 10 feet along each surveyed traverse. Cultural features (e.g., powerlines, fences, stone walls, valleys, streams, seeps, and pipes protruding from the surface) will be documented in the field notebook as the survey progresses. At the end of each day, the VLF data will be uploaded to a Zenith lap-top computer and stored on a 3.5 inch floppy disk.

APPENDIX B

SAMPLING AND ANALYTICAL METHODS FOR PROCESSED SOIL AND EXHAUST GAS

EPA METHOD 418.1

PETROLEUM HYDROCARBONS, TOTAL RECOVERABLE

Method 418.1 (Spectrophotometric, Infrared)

STORET NO. 45501

1. Scope and Application
   - 1.1 This method is for the measurement of fluorocarbon-113 extractable petroleum hydrocarbons from surface and saline waters, industrial and domestic wastes.
   - 1.2 The method is applicable to measurement of light fuels, although loss of about half of any gasoline present during the extraction manipulations can be expected.
   - 1.3 The method is sensitive to levels of 1 mg/l and less, and may be extended to ambient monitoring.
2. Summary of Method
   - 2.1 The sample is acidified to a low pH (< 2) and serially extracted with fluorocarbon-113 in a separatory funnel. Interferences are removed with silica gel adsorbant. Infrared analysis of the extract is performed by direct comparison with standards.
3. Definitions
   - 3.1 As in the case of Oil and Grease, the parameter of Petroleum Hydrocarbons is defined by the method. The measurement may be subject to interferences and the results should be evaluated accordingly.
   - 3.2 Oil and Grease is a measure of biodegradable animal greases and vegetable oils along with the relative non-biodegradable mineral oils. Petroleum hydrocarbons is the measure of only the mineral oils. Maximum information may be obtained using both methods to measure and characterize oil and grease of all sources.
4. Sampling and Storage
   - 4.1 A representative sample of 1 liter volume should be collected in a glass bottle. Because losses of grease will occur on sampling equipment, the collection of a composite sample is impractical. The entire sample is consumed by this test; no other analyses may be performed using aliquots of the sample.
   - 4.2 A delay between sampling and analysis of greater than 4 hours requires sample preservation by the addition of 5 ml HCl (6.1). A delay of greater than 48 hours also requires refrigeration for sample preservation.
5. Apparatus
   - 5.1 Separatory funnel, 2000 ml, with Teflon stopcock.
   - 5.2 Filter paper, Whatman No. 40, 11 cm.
   - 5.3 Infrared spectrophotometer, scanning or fixed wavelength, for measurement around 2950 cm^{-1}.
   - 5.4 Cells, 10 mm, 50 mm, and 100 mm pathlength, sodium chloride or infrared grade glass.
   - 5.5 Magnetic stirrer, with Teflon coated stirring bars.
6. Reagents
   - 6.1 Hydrochloric acid, 1:1. Mix equal volumes of conc HCl and distilled water.

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6.2 Fluorocarbon-113,(1,1,2-trichloro-1,2,2-trifluroethane), b.p. 48°C.

6.3 Sodium sulfate, anhydrous crystal.

6.4 Silica gel, 60–200 mesh, Davidson Grade 950 or equivalent. Should contain 1–2% water as defined by residue test at 130°C. Adjust by overnight equilibration if needed.

6.5 Calibration mixtures:

6.5.1 Reference oil: Pipet 15.0 ml n-hexadecane, 15.0 ml isooctane, and 10.0 ml chlorobenzene into a 50 ml glass stoppered bottle. Maintain the integrity of the mixture by keeping stoppered except when withdrawing aliquots.

6.5.2 Stock standard: Pipet 1.0 ml reference oil (6.5.1) into a tared 200 ml volumetric flask and immediately stopper. Weigh and dilute to volume with fluorocarbon-113.

6.5.3 Working standards: Pipet appropriate volumes of stock standard (6.5.2) into 100 ml volumetric flasks according to the cell pathlength to be used. Dilute to volume with fluorocarbon-113. Calculate concentration of standards from the stock standard.

7. Procedure

7.1 Mark the sample bottle at the water meniscus for later determination of sample volume. If the sample was not acidified at time of collection, add 5 ml hydrochloric acid (6.1) to the sample bottle. After mixing the sample, check the pH by touching pH-sensitive paper to the cap to insure that the pH is 2 or lower. Add more acid if necessary.

7.2 Pour the sample into a separatory funnel.

7.3 Add 30 ml fluorocarbon-113 (6.2) to the sample bottle and rotate the bottle to rinse the sides. Transfer the solvent into the separatory funnel. Extract by shaking vigorously for 2 minutes. Allow the layers to separate.

7.4 Filter the solvent layer through a funnel containing solvent-moistened filter paper into a 100 ml volumetric flask.

NOTE 1: An emulsion that fails to dissipate can be broken by pouring about 1 g sodium sulfate (6.3) into the filter paper cone and slowly draining the emulsion through the salt. Additional 1 g portions can be added to the cone as required.

7.5 Repeat (7.3 and 7.4) twice more with 30 ml portions of fresh solvent, combining all solvent into the volumetric flask.

7.6 Rinse the tip of the separatory funnel, filter paper, and the funnel with a total of 5–10 ml solvent and collect the rinsings in the flask. Dilute the extract to 100 ml. If the extract is known to contain greater than 100 mg of non-hydrocarbon organic material, pipet an appropriate portion of the sample to a 100 ml volumetric and dilute to volume.

7.7 Discard about 5–10 ml solution from the volumetric flask. Add 3 g silica gel (6.4) and a stirring bar; stopper the volumetric flask, and stir the solution for a minimum of 5 min on a magnetic stirrer.

7.8 Select appropriate working standards and cell pathlength according to the following table of approximate working ranges:

Pathlength	Range
10 mm	2–40 mg
50 mm	0.5–8 mg
100 mm	0.1–4 mg

Calibrate the instrument for the appropriate cells using a series of working standards (6.5.3). It is not necessary to add silica gel to the standards. Determine absorbance directly for each solution at the absorbance maximum at about 2930 cm^{-1}. Prepare a calibration plot of absorbance vs. mg petroleum hydrocarbons per 100 ml solution.

7.9 After the silica gel has settled in the sample extract, fill a clean cell with solution and determine the absorbance of the extract. If the absorbance exceeds 0.8 prepare an appropriate dilution.

NOTE 2: The possibility that the absorptive capacity of the silica gel has been exceeded can be tested at this point by adding another 3.0 g silica gel to the extract and repeating the treatment and determination.

7.10 Determine the concentration of petroleum hydrocarbons in the extract by comparing the response against the calibration plot.

8. Calculations

8.1 Calculate the petroleum hydrocarbons in the sample using the formula:

$$\text{mg/l Petroleum Hydrocarbons} = \frac{R \times D}{V}$$

where:

R = mg of Petroleum Hydrocarbons as determined from the calibration plot (7.10).
D = extract dilution factor, if used.
V = volume of sample, in liters.

9. Precision and Accuracy

9.1 Precision and accuracy data are not available at this time.

METHOD 3540

SOXHLET EXTRACTION

1.0 Scope and Application

1.1 Method 3540 is a procedure for extracting nonvolatile and semivolatile organic compounds from solids such as soils and sludges. The Soxhlet extraction process ensures intimate contact of the sample matrix with the extraction solvent. Subsequent cleanup and detection are described in the organic analytical method that will be used to analyze the extract.

2.0 Summary of Method

2.1 The solid sample is mixed with anhydrous sodium sulfate, placed in an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in a Soxhlet extractor. Methylene chloride should be employed when a solvent is not specified. The extract is then dried and concentrated, and either cleaned up further or analyzed directly by the appropriate measurement technique.

3.0 Interferences

3.1 A procedural blank should be performed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

3.3 Procedures for the removal of interfering compounds coextracted with target compounds are described in the organic analytical method that will be used to analyze the extract.

4.0 Apparatus and Materials

4.1 Soxhlet extractor: 40-mm I.D., with 500-ml round-bottom flask.

4.2 Kuderna-Danish apparatus with three-ball Snyder column.

4.3 Chromatographic column: Pyrex, 20-mm I.D., approximately 400 mm long, with coarse-fritted plate on bottom and an appropriate packing medium.

4.4 Glass or paper thimble or glass wool to retain sample in Soxhlet extraction device. Should drain freely and may require purification before use.

4.5 Boiling chips: Approximately 10/40 mesh. Heat to 400° C for 30 min or Soxhlet extract with methylene chloride.

4.6 Rheostat controlled heating mantle.

5.0 Reagents

5.1 The specific reagents to be employed in this method may be listed under the organic analytical methods that will be used to analyze the extract. Check analytical method for specific extraction reagent. If a specific extracting reagent is not listed for the compound(s) of interest, methylene chloride shall be used.

5.2 The solvent of choice should be appropriate for the method of measurement to be used and should give an analyte-to-solvent partition coefficient of at least 1 to 1000.

5.3 Sodium sulfate: (ACS) Granular anhydrous (purified by heating at 400° C for 4 hr in a shallow tray).

5.4 Soil samples: Soil samples shall be extracted using either of the following solvent systems.

5.4.1 Toluene/Methanol, 10:1 v/v ACS reagent grade only.

5.4.2 Acetone/Hexane, 1:1 v/v ACS reagent grade only.

5.5 Methylene chloride: Pesticide quality or equivalent.

6.0 Sample Collection, Preservation, and Handling

6.1 Adhere to those procedures specified in the referring analytical methods for collection, preservation, and handling.

7.0 Procedure

7.1 Blend 10 g of the solid sample with an equal weight of anhydrous sodium sulfate and place in either a glass or paper extraction thimble. The extraction thimble must drain freely for the duration of the extraction period. The use of a glass wool plug above and below the sample is also acceptable.

7.2 Place 300 ml of the extraction solvent into a 500-ml round-bottom flask containing a boiling stone. Attach the flask to the extractor, and extract the solids for 16 hr.

7.3 Allow the extract to cool after the extraction is complete. Rinse the condensor with the extraction solvent and drain the Soxhlet apparatus into the collecting round-bottom flask. Filter the extract and dry it by passing it through a 4-in. column of sodium sulfate which has been washed with the extracting solvent. Collect the dried extract in a 500-ml Kuderna-Danish (K-D) flask fitted with a 10-ml graduated concentrator tube. Wash the extractor flask and sodium sulfate column with 100-125 ml of the extracting solvent.

7.4 Add 1 or 2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml solvent to the top. Place the K-D apparatus on a steam or hot water bath so that the concentrator tube and the entire lower rounded surface of the flask are bathed in hot water or vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-20 min. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain for at least 10 min while cooling.

7.5 Rinse the K-D apparatus with a small volume of solvent. Adjust the sample volume to 10.0 ml with the solvent to be used in instrumental analysis. Proceed with analysis and cleanup if necessary.

8.0 Quality Control

8.1 Comprehensive quality control procedures are specified for each target compound in the referring analytical method.

8.2 The analyst should demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples.

EPA METHOD 8010

METHOD 8010

HALOGENATED VOLATILE ORGANICS

1.0 Scope and Application

1.1 Method 8010 is used to determine the concentration of various halogenated volatile organic compounds in groundwater, liquid, and solid matrices. Specifically, Method 8010 may be used to detect the following substances:

Benzyl chloride	1,2-Dichlorobenzene
Bis (2-chloroethoxy)methane	1,3-Dichlorobenzene
Bis (2-chloroisopropyl)ether	1,4-Dichlorobenzene
Bromobenzene	Dichlorodifluoromethane
Bromodichloromethane	1,1-Dichloroethane
Bromoform	1,2-Dichloroethane
Bromomethane	1,1-Dichloroethylene (Vinylidene chloride)
Carbon tetrachloride	trans-1,2-Dichloroethylene
Chloracetaldehyde	Dichloromethane
Chloral	1,2-Dichloropropane
Chlorobenzene	1,3-Dichloropropylene
Chloroethane	1,1,2,2-Tetrachloroethane
Chloroform	1,1,1,2-Tetrachloroethane
1-Chlorohexane	Tetrachloroethylene
2-Chloroethyl vinyl ether	1,1,1-Trichloroethane
Chloromethane	1,1,2-Trichloroethane
Chloromethyl methyl ether	Trichloroethylene
Chlorotoluene	Trichlorofluoromethane
Dibromochloromethane	Trichloropropane
Dibromomethane	Vinyl chloride

1.2 This method is recommended for use by, or under the supervision of, analysts experienced in the operation of gas chromatographs and in the interpretation of chromatograms.

2.0 Summary of Method

2.1 Method 8010 provides chromatographic conditions for the detection of halogenated volatile organic compounds. Waste samples can be analyzed using direct injection, the headspace method (Method 5020) or the purge-and-trap method (Method 5030). Groundwater samples should be determined using Method 5030. A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a halide-specific detector (HSD).

2.2 If interferences are encountered, the method provides an optional gas chromatographic column that may be helpful in resolving the compounds of interest from the interferences.

3.0 Interferences

3.1 Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A field sample blank prepared from reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

3.2 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe or purging device must be rinsed out between samples with reagent water. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high organohalide levels, it may be necessary to wash out the syringe or purging device with a detergent solution, rinse it with distilled water, and then dry it in a 105° C oven between analyses.

3.3 Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water or solvent blank that the entire analytical system is interference-free. Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analyses. Where doubt exists over the identification of a peak on the gas chromatogram, confirmatory techniques such as mass spectroscopy should be used.

3.4 The analyst should maintain constant surveillance of both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix. This is done by spiking each waste sample with known amounts of the compounds that the waste is being analyzed for. Using these spiked waste samples, the sensitivity of the instrument is then readjusted so that 1 µg/g of sample can be readily detected. Detection limits necessary for groundwater monitoring are much lower. The analyst should adjust instrument sensitivity according to Table 1 (below) when analyzing groundwater samples.

4.0 Apparatus and Materials

4.1 Vial with cap: 40-ml capacity screw cap (Pierce #13075 or equivalent). Detergent wash, rinse with tap and distilled deionized water, and dry at 105° C before use.

4.2 Septum: Teflon-faced silicone (Pierce #12722 or equivalent). Detergent wash, rinse with tap and distilled deionized water, and dry at

105° C for 30 min before use. NOTE: Do not heat the TFE seals for extended periods of time (i.e., more than 1 hr) because the silicone layer slowly degrades at 105° C.

4.3 Sample introduction apparatus for Methods 5020 and 5030.

4.4 Gas chromatograph: Analytical system complete with programmable gas chromatograph suitable for on-column injection or purge-and-trap sample introduction and all required accessories, including HSD or FID, column supplies, recorder, and gases. A data system for measuring peak area is recommended.

4.5 GC columns:

Column 1: 8-ft x 0.1-in. I.D. stainless steel or glass column packed with 1% SP-1000 on Carbopac B 60/80 mesh.

Column 2: 6-ft x 0.1-in. I.D. stainless steel or glass column packed with n-octane on Porasil-L 100/120 mesh.

4.6 Detector: Electrolytic conductivity (HSD).

4.7 Syringes: 5-ml glass hypodermic with Luerlok top (2 each).

4.8 Microsyringes: 10, 25, 100 µl.

4.9 Two-way syringe valve with Luer ends (3 each).

4.10 Syringe: 5 ml, gas-tight with shutoff valve.

4.11 Bottle: 15-ml screw-cap, with teflon cap liner.

5.0 Reagents

5.1 Activated carbon: Filtrasorb 200 (Calgon Corp.) or equivalent.

5.2 Organic-free water: Generated by passing tap water through a carbon filter bed containing about 1 lb of activated carbon. A water purification system (Millipore Super-Q or equivalent) may be used to generate organic-free deionized water. Organic-free water may also be prepared by boiling water for 15 min. Subsequently, while maintaining the temperature at 90° C, bubble a contaminant-free inert gas through the water for 1 hr.

5.3 Stock standard solutions: Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methyl alcohol using assayed liquids or gas cylinders as appropriate. Because of the toxicity of many of the compounds

being analyzed, primary dilutions of these materials should be prepared in a hood. A NIOSH/MESA-approved toxic gas respirator should be used when the analyst handles high concentrations of such materials.

5.3.1 Place about 9 ml of methyl alcohol into a 10-ml ground-glass-stoppered volumetric flask. Allow to stand about 10 min or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.3.2 Add the assayed reference material

5.3.2.1 Liquids: Using a 100-µl syringe, immediately add an amount of assayed reference material to the flask, then reweigh. Be sure that the reference material falls directly into the alcohol without contacting the neck of the flask.

5.3.2.2 Gases: To prepare standards from any of the organic compounds that boil below 30° C, fill a 5-ml valved gas-tight syringe with the reference standard to the 5-ml mark. Lower the needle to 5 mm above the methyl alcohol meniscus. Slowly inject the reference standard above the surface of the liquid (the heavy gas will rapidly dissolve into the methyl alcohol).

5.3.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in µg/µl from the net gain in weight. When compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.3.4 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store at 4° C and protect from light.

5.3.5 Prepare fresh standards weekly for those compounds whose boiling point is less than or equal to 30° C and for the 2-chloroethyl-vinyl ether. All other standards must be replaced after 1 month, or sooner if comparison with check standards indicate a problem.

5.4 Secondary dilution standards: Using stock standard solutions, prepare secondary dilution standards in methyl alcohol that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the prepared aqueous calibration standards will completely bracket the working range of the analytical system. Secondary dilution standards must be stored with zero headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Quality control check standards, available from the EPA's Environmental Monitoring and Support Laboratory in Cincinnati, can be used to determine the accuracy of calibration standards.

5.5 Calibration standards: In order to prepare accurate aqueous standard solutions, the following precautions must be observed.

5.5.1 Do not inject more than 20 µl of alcoholic standards into 100 ml of reagent water.

5.5.2 Use a 25-µl Hamilton 702N microsyringe or equivalent. (Variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standards into water.)

5.5.3 Rapidly inject the alcoholic standard into the filled volumetric flask. Remove the needle as fast as possible after injection.

5.5.4 Mix aqueous standards by inverting the flask three times only.

5.5.5 Discard the contents contained in the neck of the flask. Fill the sample syringe from the standard solution contained in the expanded area of the flask.

5.5.6 Never use pipets to dilute or transfer samples or aqueous standards.

5.5.7 Aqueous standards are not stable and should be discarded after 1 hr unless preserved, stored, and sealed according to 6.1 and 6.3.

6.0 Sample Collection, Preservation, and Handling

6.1 Grab samples must be collected in glass containers (see Apparatus, Sections 4.1 and 4.2) having a total volume of at least 25 ml. Fill the sample bottles in such a manner that no air bubbles pass through the sample as the bottle is being filled. Seal the bottle so that no air bubbles are entrapped in it. Solid and semisolid samples are to be taken in the same way. Assure that no solid material interferes with sealing of the glass vial. Maintain the hermetic seal on the sample bottle until time of analysis.

6.2 Sample transfer implements: Implements are required to transfer portions of solid, semisolid, and liquid wastes from sample containers to laboratory glassware. The transfer must be accomplished rapidly to avoid loss of volatile components during the transfer step. Liquids may be transferred using a hypodermic syringe with a wide-bore needle attached or with no needle. Solids may be transferred using a conventional laboratory spatula, spoon, or coring device. A coring device that is suitable for handling some samples can be made by using a glass tubing saw to cut away the enclosed end of the barrel of a glass hypodermic syringe.

6.3 The samples must be iced or refrigerated from the time of collection until extraction. If the sample may contain free or combined chlorine, add sodium thiosulfate preservative (10 mg/40 ml will suffice for up to 5 ppm Cl_2) to the empty sample bottles just prior to shipping to the sampling site, fill with sample just to overflowing, seal the bottle, and shake vigorously for 1 min.

6.4 All samples must be analyzed within 14 days of collection.

7.0 Procedures

7.1 The recommended gas chromatographic columns and operating conditions for the instrument are:

Column 1: Set helium gas flow at 40 ml/min flow rate. Set column temperature at 45° C for 3 min, then program an 8° C/min temperature rise to 220° C and hold for 15 min.

Column 2: Set helium gas flow at 40 ml/min flow rate. Set column temperature at 50° C for 3 min, then program a 6° C/min temperature rise to 170° C and hold for 4 min.

7.2 Calibration

7.2.1 By injecting secondary standards, adjust the sensitivity of the analytical system for each compound being analyzed so as to detect quantities of less than or equal to 1 µg for waste samples. Detection limits to be used for groundwater analysis are given in Table 1. Calibrate the chromatographic system using either the external standard technique (Section 7.2.2) or the internal standard technique (Section 7.2.3).

7.2.2 External standard calibration procedure

7.2.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter by carefully adding 20.0 µl of one or more secondary dilution standards to 100, 500, or 1,000 ml of reagent water or the matrix under study. A 25-µl syringe should be used for this operation. One of the external standards should be at a concentration near, but above, the method detection limit and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector. These aqueous standards must be prepared fresh daily.

7.2.2.2 Analyze each calibration standard according to the procedure being used (direct aqueous injection, headspace, or purge-and-trap) and tabulate peak height or area responses against 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 (less than 10% relative standard deviation), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.2.2.3 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor must be prepared for that compound.

7.2.3 Internal standard calibration procedure. To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standards is not affected by method or matrix interferences. Because of these limitations, no internal standard that would be applicable to all samples can be suggested. The compounds recommended for use as surrogate spikes have been used successfully as internal standards, because of their generally unique retention times.

7.2.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest as described in Section 7.2.2.1.

7.2.3.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Sections 5.3 and 5.4.

7.2.3.3 Analyze each calibration standard according to appropriate methods (direct injection, 5020, 5030), adding the internal standard spiking solution directly to an aliquot of the sample or, in the case of purge-and-trap, to the syringe. Tabulate peak height or area responses against concentration for each compound and internal standard, and calculate response factors (RF) for each compound as follows:

$$RF = (A_s C_{is})/(A_{is} C_s)$$

where:

A_s = Response for the parameter to be measured

A_{is} = Response for the internal standard

C_{is} = Concentration of the internal standard

C_s = Concentration of the parameter to be measured

If the RF value over the working range is a constant (less than 10% relative standard deviation), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} against RF.

7.2.3.4 The working calibration curve or RF must be verified on each working day by measuring one or more calibration standards. If the response for any parameter varies from the predicted response by more than $\pm$10%, either the test must be repeated using a fresh calibration standard, or a new calibration curve must be prepared for that compound.

7.3 Gas chromatographic analysis

7.3.1 Introduce volatile compounds to the gas chromatograph using direct injection, headspace (Method 5020), or purge-and-trap (Method 5030).

7.3.2 Table 1 summarizes the estimated retention times for a number of organic compounds analyzable using this method. An example of the separation achieved by Column 1 is shown in Figure 1.

7.3.3 Calibrate the system immediately prior to conducting any analysis and recheck for each type of waste. Calibration should be done no less frequently than at the beginning and end of each analysis session.

8.0 Quality Control

8.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

TABLE 1. ESTIMATED RETENTION TIMES FOR SOME HALOGENATED VOLATILE ORGANICS

Compound	Retention time (min) Col. 1	Retention time (min) Col. 2	Estimated detection limit[a] (µg/l)
Bis(2-chloroethoxy)methane			
Bis(2-chloroisopropyl)ether			
Bromobenzene			
Bromodichloromethane	13.7	14.6	0.10
Bromoform	19.2	19.2	0.20
Carbon tetrachloride	13.0	14.4	0.12
Chloroacetaldehyde			
Chlorobenzene	24.2	18.8	0.25
Chloroethane	3.33	8.68	0.52
Chloroform	10.7	12.1	0.05
1-Chlorohexane			
2-Chloroethyl vinyl ether	18.0		0.13
Chloromethane	1.50	5.28	0.08
Chlorotoluene			
Dibromochloromethane	16.5	16.6	0.09
Dibromomethane			
1,2-Dichlorobenzene	34.9	23.5	0.15
1,3-Dichlorobenzene	34.0	22.4	0.32
1,4-Dichlorobenzene	35.4	22.3	0.24
Dichlorodifluoromethane			
1,1-Dichloroethane	9.30	12.6	0.07
1,2-Dichloroethane	11.4	15.4	0.03
1,1-Dichloroethylene	8.0	7.72	0.13
trans-1,2-Dichloroethylene	10.1	9.38	0.10
Dichloromethane	6.5		
1,2-Dichloropropane	14.9	16.6	0.04
trans-1,3-Dichloropropylene	15.2	16.6	0.34
1,1,2,2-Tetrachloroethane	21.6		0.03
1,1,1,2-Tetrachloroethane			
Tetrachloroethylene	21.7	15.0	0.03
1,1,1-Trichloroethane	12.6	13.1	0.03
1,1,2-Trichloroethane	16.5	18.1	0.02
Trichloroethylene	15.8	13.1	0.12
Trichlorofluoromethane	7.18		
Trichloropropane			
Vinyl chloride	2.67	5.28	0.18

[a]Using purge-and-trap method (5030). See also Section 8.3.

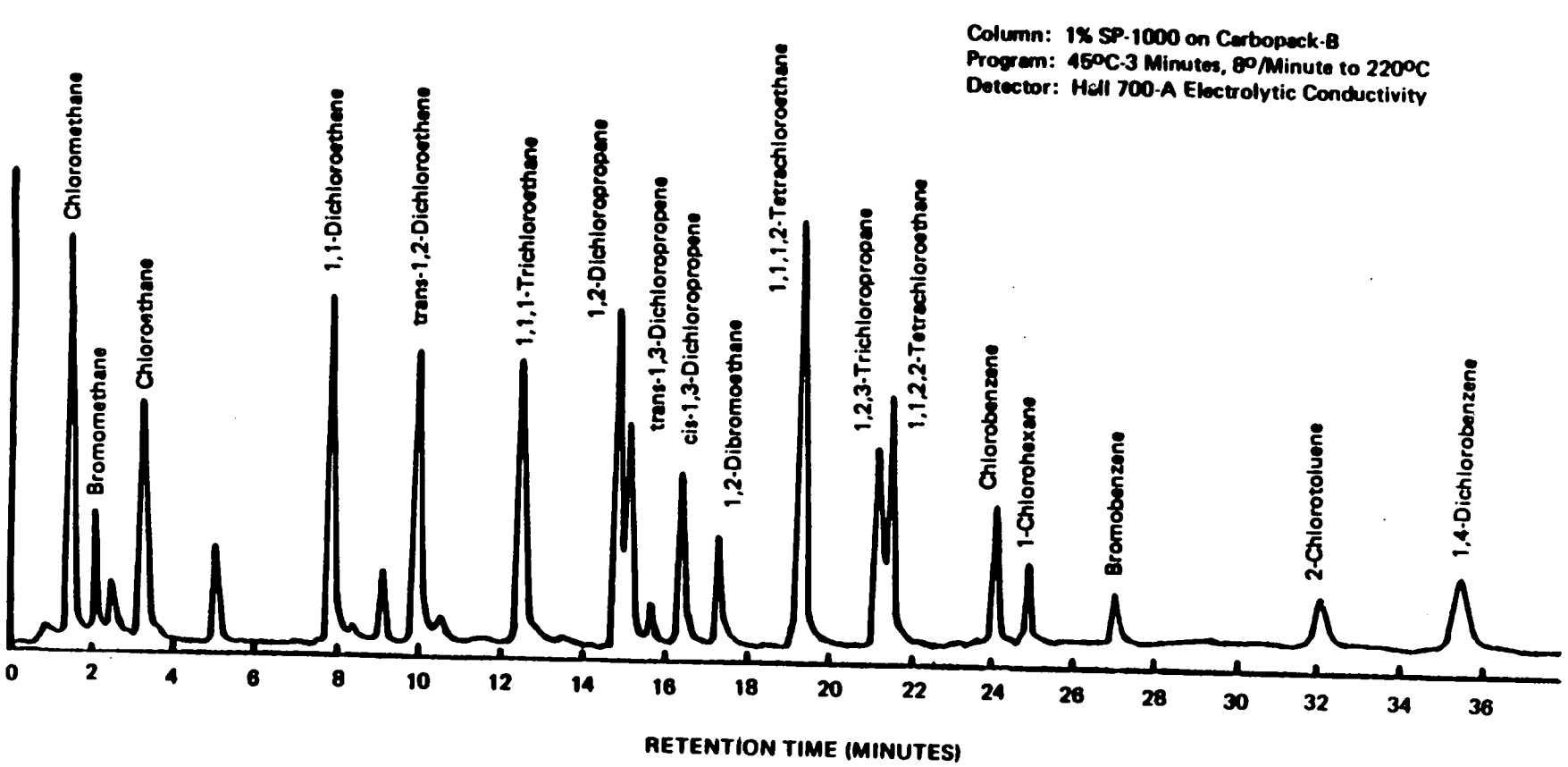


Figure 1. Gas Chromatogram of halogenated volatile organics.

8.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be carried through all stages of sample preparation and measurement; they should be analyzed to validate the sensitivity and accuracy of the analysis. If the fortified waste samples do not indicate sufficient sensitivity to detect less than or equal to 1 µg/g of sample, then the sensitivity of the instrument should be increased or the extract subjected to additional cleanup. Detection limits to be used for groundwater samples are indicated in Table 1. Where doubt exists over the identification of a peak on the chromatograph, confirmatory techniques such as mass spectroscopy should be used.

8.3 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Table 1 were obtained using reagent water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

8.4 In a single laboratory, using reagent water and wastewaters spiked at or near background levels, the average recoveries presented in Table 2 were obtained. The standard deviation of the measurement in percent recovery is also included in Table 2.

9.0 References

1. Bellar, T.A., and J.J. Lichtenberg. 1974. J. Amer. Water Works Assoc. 66(12):739-744.

2. Bellar, T.A., and J.J. Lichtenberg. 1979. Semi-automated headspace analysis of drinking waters and industrial waters for purgeable volatile organic compounds. In: Van Hall (ed.), Measurement of organic pollutants in water and wastewater. ASTM STP 686, pp. 108-129.

3. Development and application of test procedures for specific organic toxic substances in wastewaters. Category 11 - Purgeables and Category 12 - Acrolein, Acrylonitrile, and Dichlorodifluoromethane. Report for EPA Contract 68-03-2635 (in preparation).

TABLE 2. SINGLE OPERATOR ACCURACY AND PRECISION

Parameter	Average percent recovery	Standard deviation (%)	Spike range (µg/l)	Number of analyses	Matrix types
Bromodichloromethane	100.9	5.0	0.43-46.7	21	3
Bromoform	89.5	9.0	1.45-50	20	3
Carbon tetrachloride	82.5	25.6	0.55-50	19	3
Chlorobenzene	93.9	8.9	2.21-50	20	3
Chloroethane	91.5	22.4	3.95-50	21	3
2-Chloroethylvinyl ether	96.3	9.9	4.39-133	20	3
Chloroform	101.7	20.6	0.44-50	20	3
Chloromethane	91.4	13.4	0.55-23.9	21	3
Dibromochloromethane	98.3	6.5	0.75-93.0	21	3
1,2-Dichlorobenzene	102.0	2.0	4.89-154	21	3
1,3-Dichlorobenzene	91.6	4.3	2.94-46.7	21	3
1,4-Dichlorobenzene	97.5	9.3	2.99-51.6	21	3
1,1-Dichloroethane	102.3	5.5	0.44-46.7	21	3
1,2-Dichloroethane	97.8	4.8	0.44-46.7	21	3
1,1-Dichloroethylene	101.1	21.7	0.37-50	19	3
trans-1,2-Dichloroethylene	91.0	19.3	0.44-98.0	20	3
1,2-Dichloropropane	97.7	8.8	0.29-39.0	21	3
trans-1,3-Dichloropropylene	73.5	17.2	0.43-50	20	3
1,1,2,2-Tetrachloroethane	91.9	15.0	0.46-46.7	21	3
Tetrachloroethylene	94.1	18.1	0.50-35.0	21	3
1,1,1-Trichloroethane	75.1	12.5	0.37-29.0	21	3
1,1,2-Trichloroethane	91.0	25.1	0.45-50	21	3
Trichloroethylene	106.1	7.4	0.38-46.7	21	3
Vinyl chloride	101.9	11.4	0.82-32.3	21	3

WESTON

EPA METHODS 8020

METHOD 8020

AROMATIC VOLATILE ORGANICS

1.0 Scope and Application

1.1 Method 8020 is used to determine the concentration of various aromatic volatile organic compounds in groundwater, liquid, and solid matrices. Specifically, Method 8020 may be used to detect the following substances:

Benzene
Chlorobenzene
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
Ethyl benzene
Toluene
Xylenes (Dimethyl benzenes)

1.2 This method is recommended for use by, or under the supervision of, analysts experienced in the operation of gas chromatographs and in the interpretation of chromatograms.

2.0 Summary of Method

2.1 Method 8020 provides chromatographic conditions for the detection of aromatic volatile organic compounds. Waste samples can be analyzed using direct injection, the headspace method (Method 5020) or the purge-and-trap method (Method 5030). Groundwater samples should be determined using Method 5030. A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a photo-ionization detector (PID).

2.2 If interferences are encountered, the method provides an optional gas chromatographic column that may be helpful in resolving the compounds of interest from the interferences.

3.0 Interferences

3.1 Samples can be contaminated by diffusion of volatile organics through the sample container septum during shipment and storage. A field sample blank prepared from reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

3.2 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample

syringe or purging device must be rinsed out between samples with reagent water. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high levels of volatile organics, it may be necessary to wash out the syringe or purging device with a detergent solution, rinse it with distilled water, and then dry it in a 105° C oven between analyses.

3.3 Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water or solvent blank that the entire analytical system is interference-free. Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analyses. Where doubt exists over the identification of a peak on the gas chromatogram, confirmatory techniques such as mass spectroscopy should be used.

3.4 The analyst should maintain constant surveillance of both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix. This is done by spiking each waste sample with known amounts of the compounds that the waste is being analyzed for. Using these spiked waste samples, the sensitivity of the instrument is then readjusted so that 1 µg/g of sample can be readily detected. Detection limits necessary for groundwater monitoring are much lower. The analyst should adjust instrument sensitivity according to Table 1 (below) when analyzing groundwater samples.

4.0 Apparatus and Materials

4.1 Vial with cap: 40-ml capacity screw cap vial (Pierce #13075 or equivalent). Detergent wash, rinse with tap and distilled deionized water, and dry at 105° C before use.

4.2 Septum: Teflon-faced silicone (Pierce #12722 or equivalent). Detergent wash, rinse with tap and distilled deionized water, and dry at 105° C for 30 min before use. NOTE: Do not heat the TFE seals for extended periods of time (i.e., more than 1 hour) because the silicone layer slowly degrades at 105° C.

4.3 Sample introduction apparatus for Methods 5020 and 5030.

4.4 Gas chromatograph: Analytical system complete with programmable gas chromatograph suitable for on-column injection or purge-and-trap sample introduction and all required accessories, including PID, column supplies, recorder, and gases. A data system for measuring peak area is recommended.

4.5 GC columns:

Column 1: 6-ft x 0.082-in. I.D. #304 stainless steel or glass tubing. Packed with 5% SP-1200 + 1.75% Bentone 34 on 100/120 mesh Supelcoport.

Column 2: 6-ft x 0.1-in. I.D. #304 stainless steel or glass tubing packed with 5% 1,2,3-tris(2-cyanoethoxy)propane on 60/80 mesh Chromosorb W-AW.

4.6 Detector: Photoionization (PID).

4.7 Syringes: 5-ml glass hypodermic with Luerlok top (2 each).

4.8 Microsyringes: 10, 25, 100 µl.

4.9 Two-way syringe valve with Luer ends (3 each).

4.10 Syringe: 5-ml, gas-tight with shutoff valve.

4.11 Bottle: 15-ml screw-cap, with teflon cap liner.

5.0 Reagents

5.1 Activated carbon: Filtrasorb 200 (Calgon Corp.) or equivalent.

5.2 Organic-free water: Generated by passing tap water through a carbon filter bed containing about 1 lb of activated carbon. A water purification system (Millipore Super-Q or equivalent) may be used to generate organic-free deionized water. Organic-free water may also be prepared by boiling water for 15 min. Subsequently, while maintaining the temperature at 90° C, bubble a contaminant-free inert gas through the water for 1 hr.

5.3 Stock standard solutions: Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methyl alcohol using assayed liquids. Because of the toxicity of many of the compounds being analyzed, primary dilutions of these materials should be prepared in a hood. A NIOSH/MESA-approved toxic gas respirator should be used when the analyst handles high concentrations of such materials.

5.3.1 Place about 9 ml of methyl alcohol into a 10-ml ground-glass-stoppered volumetric flask. Allow to stand about 10 min or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.3.2 Using a 100-µl syringe, immediately add an amount of assayed reference material to the flask, then reweigh. Be sure that the reference

material falls directly into the alcohol without contacting the neck of the flask.

5.3.3 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store at 4° C and protect from light.

5.3.4 Prepare fresh standards weekly for those compounds whose boiling point is less than or equal to 30° C. All other standards must be replaced after 1 month, or sooner if comparison with check standards indicates a problem.

5.4 Secondary dilution standards: Using stock standard solutions, prepare secondary dilution standards in methyl alcohol that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the prepared aqueous calibration standards will completely bracket the working range of the analytical system. Secondary dilution standards must be stored with zero headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Quality control check standards, available from the EPA's Environmental Monitoring and Support Laboratory in Cincinnati, can be used to determine the accuracy of calibration standards.

5.5 Calibration standards: In order to prepare accurate aqueous standard solutions, the following precautions must be observed.

5.5.1 Do not inject more than 20 µl of alcoholic standards into 100 ml of reagent water.

5.5.2 Use a 25-µl Hamilton 702N microsyringe or equivalent. (Variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standards into water.)

5.5.3 Rapidly inject the alcoholic standard into the filled volumetric flask. Remove the needle as fast as possible after injection.

5.5.4 Mix aqueous standards by inverting the flask three times only.

5.5.5 Discard the contents contained in the neck of the flask. Fill the sample syringe from the standard solution contained in the expanded area of the flask.

5.5.6 Never use pipets to dilute or transfer samples or aqueous standards.

5.5.7 Aqueous standards are not stable and should be discarded after one hour unless preserved, stored, and sealed according to 6.1 and 6.3.

6.0 Sample Collection, Preservation, and Handling

6.1 Grab samples must be collected in glass containers (see Apparatus, Sections 4.1 and 4.2) having a total volume of at least 25 ml. Fill the sample bottles in such a manner that no air bubbles pass through the sample as the bottle is being filled. Seal the bottle so that no air bubbles are entrapped in it. Solid and semisolid samples are to be taken in the same way. Assure that no solid material interferes with sealing of the glass vial. Maintain the hermetic seal on the sample bottle until time of analysis.

6.2 Sample transfer implements: Implements are required to transfer portions of solid, semisolid, and liquid wastes from sample containers to laboratory glassware. The transfer must be accomplished rapidly to avoid loss of volatile components during the transfer step. Liquids may be transferred using a hypodermic syringe with a wide-bore needle attached or with no needle. Solids may be transferred using a conventional laboratory spatula, spoon, or coring device. A coring device that is suitable for handling some samples can be made by using a glass tubing saw to cut away the enclosed end of the barrel of a glass hypodermic syringe.

6.3 The samples must be iced or refrigerated from the time of collection until extraction. If the sample may contain free or combined chlorine, add sodium thiosulfate preservative (10 mg/40 ml will suffice for up to 5 ppm Cl_2) to the empty sample bottles just prior to shipping to the sampling site, fill with sample just to overflowing, seal the bottle, and shake vigorously for 1 min.

6.4 Sample preservation: Non-sterile samples containing aromatic hydrocarbons cannot be stored longer than 4 hr because of biological degradation. Samples can be stabilized by adding free chlorine or by adjusting the pH to less than 2 with 1:1 hydrochloric acid. However, free chlorine will react with styrene and 2,3-benzofuran. Therefore, if styrene or 2,3-benzofuran are to be determined in chlorinated water, the sample must be dechlorinated with sodium thiosulfate at the rate of 1 mg/ppm of free chlorine. Once dechlorinated, the sample pH must be adjusted to less than 2 with 1:1 hydrochloric acid. If chemical preservation is employed, the preservative is also added to the blanks.

6.5 All samples must be analyzed within 14 days of collection.

7.0 Procedures

7.1 The recommended gas chromatographic columns and operating conditions for the instrument are:

Column 1: The carrier gas is helium at a flow rate of 30 ml/min. The temperature program sequences are as follows: for lower boiling compounds, operate at 50° C isothermal for 2 min, then program at 6° C/min to 90° C

and hold until all compounds have eluted. For a higher boiling range of compounds, operate at 50° C isothermal for 2 min, then program at 3°/min to 110° C and hold until all compounds have eluted. Column 1 provides outstanding separations for a wide variety of aromatic hydrocarbons. Column 1 should be used as the primary analytical column because of its unique ability to resolve para, meta, and ortho aromatic isomers.

Column 2: The carrier gas is helium at a flow rate of 30 ml/min. The temperature program sequence is as follows: 40° C isothermal for 2 min, then 2°/min to 100° C and hold until all compounds have eluted. Column 2, an extremely high polarity column, has been used for a number of years to resolve aromatic hydrocarbons from alkanes in complex samples. However, since the resolution between some of the aromatics is not as efficient as with Column 1, Column 2 should be used as a confirmatory column.

7.2 Calibration. Assemble necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Section 7.1.

7.2.1 By injecting secondary standards, adjust the sensitivity of the analytical system for each compound being analyzed so as to detect quantities of less than or equal to 1 µg for waste samples. Detection limits to be used for groundwater analysis are given in Table 1. Calibrate the chromatographic system using either the external standard technique (Section 7.2.2) or the internal standard technique (Section 7.2.3).

7.2.2 External standard calibration procedure

7.2.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter by carefully adding 20.0 µl of one or more secondary dilution standards to 100, 500, or 1,000 ml of reagent water or the matrix under study. A 25-µl syringe should be used for this operation. One of the external standards should be at a concentration near, but above, the method detection limit and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector. These aqueous standards must be prepared fresh daily.

7.2.2.2 Analyze each calibration standard according to the procedure being used (direct aqueous injection, headspace, or purge-and-trap) and tabulate peak height or area responses against 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 (less than 10% relative standard deviation), linearity through the origin can be assumed and the

average ratio or calibration factor can be used in place of a calibration curve.

7.2.2.3 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor must be prepared for that compound.

7.2.3 Internal standard calibration procedure. To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standards is not affected by method or matrix interferences. Because of these limitations, no internal standard that would be applicable to all samples can be suggested. The compounds recommended for use as surrogate spikes have been used successfully as internal standards, because of their generally unique retention times.

7.2.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest as described in Section 7.2.2.1.

7.2.3.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Sections 5.3 and 5.4.

7.2.3.3 Analyze each calibration standard according to appropriate methods (direct injection, 5020, 5030), adding the internal standard spiking solution directly to an aliquot of the sample or, in the case of purge-and-trap, to the syringe. Tabulate peak height or area responses against concentration for each compound and internal standard, and calculate response factors (RF) for each compound as follows:

$$RF = (A_s C_{is})/(A_{is} C_s)$$

where:

A_s = Response for the parameter to be measured

A_{is} = Response for the internal standard

C_{is} = Concentration of the internal standard

C_s = Concentration of the parameter to be measured

If the RF value over the working range is a constant (less than 10% relative standard deviation), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} against RF.

7.2.3.4 The working calibration curve or RF must be verified on each working day by measuring one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±10%, either the test must be repeated using a fresh calibration standard, or a new calibration curve must be prepared for that compound.

7.3 Gas chromatographic analysis

7.3.1 Introduce volatile compounds to the gas chromatograph using direct injection, headspace (Method 5020), or purge-and-trap (Method 5030).

7.3.2 Table 1 summarizes the estimated retention times and detection limits for a number of organic compounds analyzable using this method. An example of the separation achieved by Column 1 is shown in Figure 1. An example of the separation achieved by Column 2 is shown in Figure 2.

7.3.3 Calibrate the system immediately prior to conducting any analysis and recheck for each type of waste. Calibration should be done no less frequently than at the beginning and end of each analysis session.

8.0 Quality Control

8.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

8.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be carried through all stages of sample preparation and measurement; they should be analyzed to validate the sensitivity and accuracy of the analysis. If the fortified waste samples do not indicate sufficient sensitivity to detect less than or equal to 1 µg/g of sample, then the sensitivity of the instrument should be

TABLE 1. RETENTION TIMES FOR SOME AROMATIC VOLATILE ORGANICS

Compound	Retention time (min)	Method detection limit[a] (µg/l)
Benzene	3.33	0.2
Chlorobenzene	9.17	0.2
1,4-Dichlorobenzene	16.8	0.3
1,3-Dichlorobenzene	18.2	0.4
1,2-Dichlorobenzene	25.9	0.4
Toluene	5.75	0.2
Ethyl Benzene	8.25	0.2
Xylenes		

Column: 6-ft x 1/8-in. column packed with 1.75% Bentone 34 and 5% SP-2100 on Supelcoport 100/200.

[a]Using purge-and-trap Method 5030. See also Section 8.3.

TABLE 2. SINGLE OPERATOR ACCURACY AND PRECISION

Parameter	Average percent recovery	Standard deviation (%)	Spike range (µg/l)	Number of analyses	Matrix types
Benzene	91	10.0	0.5-9.7	21	3
Chlorobenzene	97	9.4	0.5-100	21	3
1,2-Dichlorobenzene	104	27.7	0.5-10.0	21	3
1,3-Dichlorobenzene	97	20.0	0.5-4.8	21	3
1,4-Dichlorobenzene	120	20.4	0.5-10.0	21	3
Ethylbenzene	98	12.4	0.5-9.9	21	3
Toluene	77	12.1	0.5-100	21	3

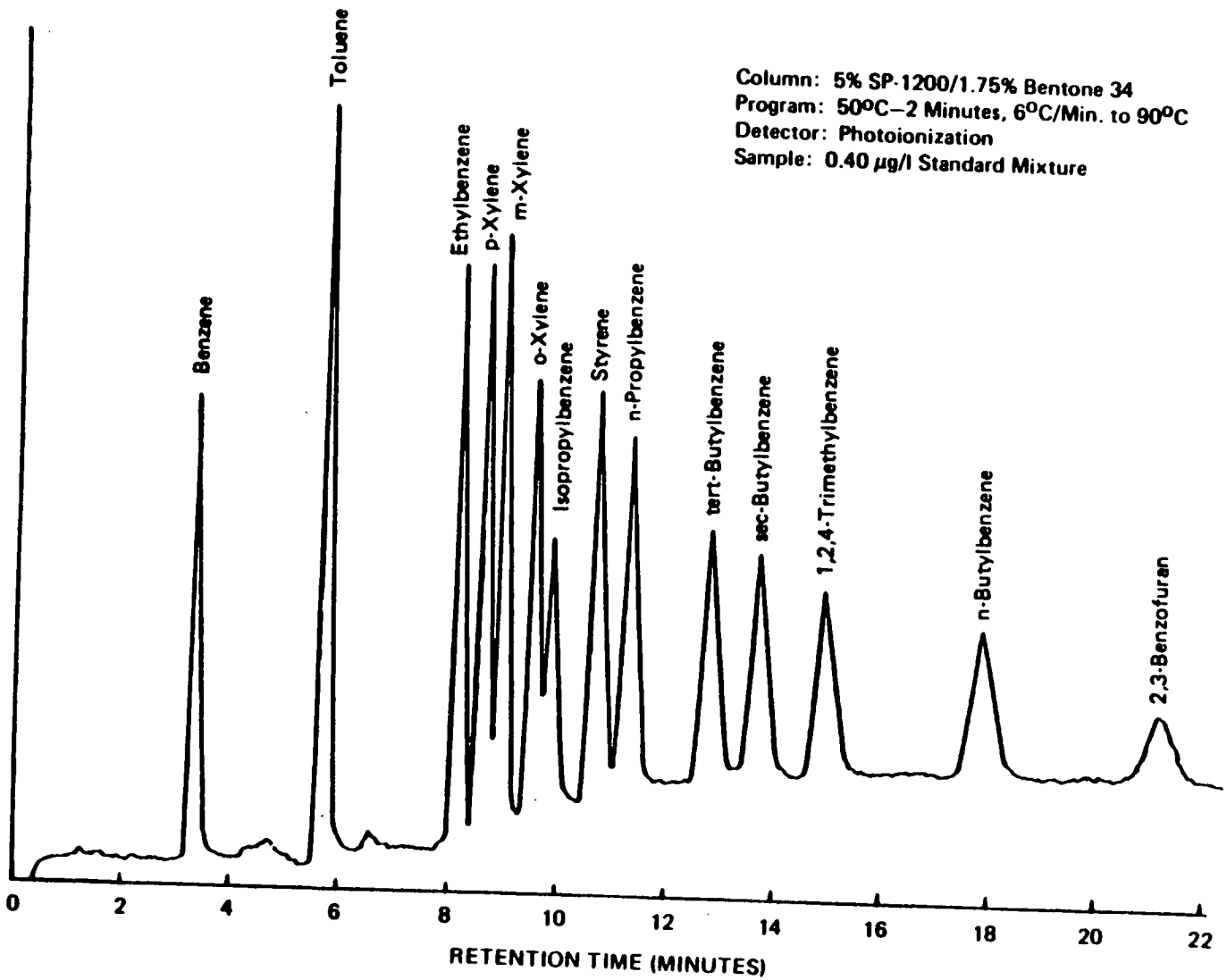


Figure 1. Chromatogram of aromatic volatile organics (column 1 conditions).

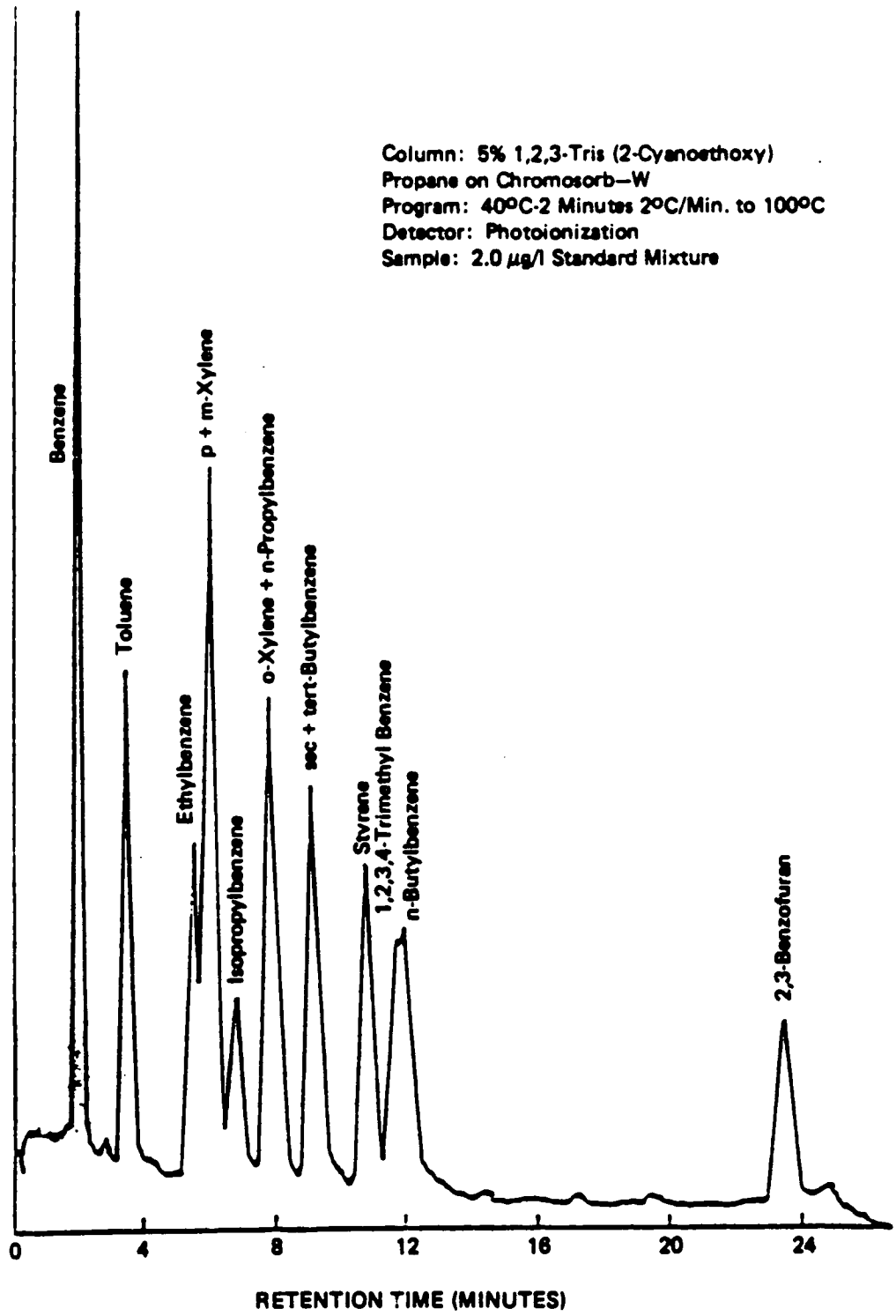


Figure 2. Chromatogram of aromatic volatile organics (column 2 conditions).

increased. Detection limits to be used for groundwater samples are indicated in Table 1. Where doubt exists over the identification of a peak on the chromatograph, confirmatory techniques such as mass spectroscopy should be used.

8.3 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Table 1 were obtained using reagent water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

8.4 In a single laboratory, using reagent water and wastewaters spiked at or near background levels, the average recoveries presented in Table 2 were obtained. The standard deviation of the measurement in percent recovery is also included in Table 2.

9.0 References

1. Bellar, T.A., and J.J. Lichtenberg. 1974. J. Amer. Water Works Assoc. 66(12):739-744.

2. Bellar, T.A., and J.J. Lichtenberg. 1979. Semi-automated headspace analysis of drinking waters and industrial waters for purgeable volatile organic compounds. In: Van Hall (ed.), Measurement of organic pollutants in water and wastewater. ASTM STP 686, pp. 108-129.

3. Dowty, B.J., S.R. Antoine, and J.L. Laseter. 1979. Quantitative and qualitative analysis of purgeable organics by high resolution gas chromatography and flame ionization detection. In: Van Hall (ed.), Measurement of Organic Pollutants in Water and Wastewater. ASTM STP 686, pp. 24-35.

4. Development and application of test procedures for specific organic toxic substances in wastewaters. Category 11 - Purgeables and Category 12 - Acrolein, Acrylonitrile, and Dichlorodifluoromethane. Report for EPA Contract 68-03-2635 (in preparation).

EPA METHOD 3A

Method 3A—Determination of Oxygen and Carbon Dioxide Concentrations in Emissions From Stationary Sources (Instrumental Analyzer Procedure)

1. *Applicability and Principle.*

1.1 Applicability. This method is applicable to the determination of oxygen (O_2) and carbon dioxide (CO_2) concentrations in emissions from stationary sources only when specified within the regulations.

1.2 Principle. A sample is continuously extracted from the effluent stream; a portion of the sample stream is conveyed to an instrumental analyzer(s) for determination of O_2 and CO_2 concentration(s). Performance specifications and test procedures are provided to ensure reliable data.

2. *Range and Sensitivity.*

Same as Method 6C, Sections 2.1 and 2.2, except that the span of the monitoring system shall be selected such that the average O_2 or CO_2 concentration is not less than 20 percent of the span.

3. *Definitions.*

3.1 Measurement System. The total equipment required for the determination of the O_2 or CO_2 concentration. The measurement system consists of the same major subsystems as defined in Method 6C, Sections 3.1.1, 3.1.2, and 3.1.3.

3.2 Span, Calibration Gas, Analyzer Calibration Error, Sampling System Bias, Zero Drift, Calibration Drift, Response Time, and Calibration Curve. Same as Method 6C, Sections 3.2 through 3.8, and 3.10.

3.3 Interference Response. The output response of the measurement system to a component in the sample gas, other than the gas component being measured.

4. *Measurement System Performance Specifications.*

Same as Method 6C, Sections 4.1 through 4.4.

5. *Apparatus and Reagents.*

5.1 Measurement System. Any measurement system for O_2 or CO_2 that meets the specifications of this method. A schematic of an acceptable measurement system is shown in Figure 6C-1 of Method 6C. The essential components of the measurement system are described below:

5.1.1 Sample Probe. A leak-free probe, of sufficient length to traverse the sample points.

5.1.2 Sample Line. Tubing, to transport the sample gas from the probe to the moisture removal system. A heated sample line is not required for systems that measure the O_2 or CO_2 concentration on a dry basis, or transport dry gases.

5.1.3 Sample Transport Line, Calibration Value Assembly, Moisture Removal System, Particulate Filter, Sample Pump, Sample Flow Rate Control, Sample Gas Manifold, and Data Recorder. Same as Method 6C, Sections 5.1.3 through 5.1.9, and 5.1.11, except that the requirements to use stainless steel, Teflon, and nonreactive glass filters do not apply.

5.1.4 Gas Analyzer. An analyzer to determine continuously the O_2 or CO_2 concentration in the sample gas stream. The analyzer shall meet the applicable performance specifications of Section 4. A means of controlling the analyzer flow rate and a device for determining proper sample flow rate (e.g., precision rotameter, pressure gauge downstream of all flow controls, etc.) shall be provided at the analyzer. The requirements for measuring and controlling the analyzer flow rate are not applicable if data are presented that demonstrate the analyzer is insensitive to flow variations over the range encountered during the test.

5.2 Calibration Gases. The calibration gases for CO_2 analyzers shall be CO_2 in N_2 or CO_2 in air. Alternatively, CO_2/SO_2, O_2/SO_2, or $O_2/CO_2/SO_2$ gas mixtures in N_2 may be used. Three calibration gases, as specified Section 5.3.1 through 5.3.3 of Method 6C, shall be used. For O_2 monitors that cannot analyze zero gas, a calibration gas concentration equivalent to less than 10 percent of the span may be used in place of zero gas.

6. *Measurement System Performance Test Procedures.*

Perform the following procedures before measurement of emissions (Section 7).

6.1 Calibration Concentration Verification. Follow Section 6.1 of Method 6C, except if calibration gas analysis is required, use Method 3 and change the acceptance criteria for agreement among Method 3 results to 5 percent (or 0.2 percent by volume, whichever is greater).

6.2 Interference Response. Conduct an interference response test of the analyzer prior to its initial use in the field. Thereafter, recheck the measurement system if changes are made in the instrumentation that could alter the interference response (e.g., changes in the type of gas detector). Conduct the interference response in accordance with Section 5.4 of Method 20.

6.3 Measurement System Preparation, Analyzer Calibration Error, and Sampling System Bias Check. Follow Sections 6.2 through 6.4 of Method 6C.

7. *Emission Test Procedure.*

7.1 Selection of Sampling Site and Sampling Points. Select a measurement site and sampling points using the same criteria that are applicable to tests performed using Method 3.

7.2 Sample Collection. Position the sampling probe at the first measurement point, and begin sampling at the same rate as used during the sampling system bias check. Maintain constant rate sampling (i.e., ±10 percent) during the entire run. The sampling time per run shall be the same as for tests conducted using Method 3 plus twice the system response time. For each run, use only those measurements obtained after twice the response time of the measurement system has elapsed to determine the average effluent concentration.

7.3 Zero and Calibration Drift Test. Follow Section 7.4 of Method 6C.

8. *Quality Control Procedures.*

The following quality control procedures are recommended when the results of this method are used for an emission rate correction factor, or excess air determination. The tester should select one of the following options for validating measurement results:

8.1 If both O_2 and CO_2 are measured using Method 3A, the procedures described in Section 4.4 of Method 3 should be followed to validate the O_2 and CO_2 measurement results.

8.2 If only O_2 is measured using Method 3A, measurements of the sample stream CO_2 concentration should be obtained at the sample by-pass vent discharge using an Orsat or Fyrite analyzer, or equivalent. Duplicate samples should be obtained concurrent with at least one run. Average the duplicate Orsat or Fyrite analyses results for each run. Use the average CO_2 values for comparison with the O_2 measurements in accordance with the procedures described in Section 4.4 of Method 3.

8.3 If only CO_2 is measured using Method 3A, concurrent measurements of the sample stream CO_2 concentration should be obtained using an Orsat or Fyrite analyzer as described in Section 8.2. For each run, differences greater than 0.5 percent between the Method 3A results and the average of the duplicate Fyrite analysis should be investigated.

9. *Emission Calculation.*

For all CO_2 analyzers, and for O_2 analyzers that can be calibrated with zero gas, follow Section 8 of Method 6C, except express all concentrations as percent, rather than ppm.

For O_2 analyzers that use a low-level calibration gas in place of a zero gas, calculate the effluent gas concentration using Equation 3A-1.

$$C_{ma} = \frac{C_{ma} - C_{ma}}{C_{ma} - C_a} (\bar{C} - C_a) + C_{ma} \qquad \text{Eq. 3A-1}$$

where:

C_{ma} = Effluent gas concentration, dry basis, percent.

C_{ma} = Actual concentration of the upscale calibration gas, percent.

C_a = Actual concentration of the low-level calibration gas, percent.

C_{ma} = Average of initial and final system calibration bias check responses for the upscale calibration gas, percent.

C_a = Average of initial and final system calibration bias check responses for the low-level gas, percent.

$\bar{C}$ = Average gas concentration indicated by the gas analyzer, dry basis, percent.

10. *Bibliography.*

Same as bibliography of Method 6C.

EPA METHOD 10

METHOD 10—DETERMINATION OF CARBON MONOXIDE EMISSIONS FROM STATIONARY SOURCES

1. *Principle and Applicability.*

1.1 *Principle.* An integrated or continuous gas sample is extracted from a sampling point and analyzed for carbon monoxide (CO) content using a Luft-type nondispersive infrared analyzer (NDIR) or equivalent.

1.2 *Applicability.* This method is applicable for the determination of carbon monoxide emissions from stationary sources only when specified by the test procedures for determining compliance with new source performance standards. The test procedure will indicate whether a continuous or an integrated sample is to be used.

2. *Range and sensitivity.*

2.1 *Range.* 0 to 1,000 ppm.

2.2 *Sensitivity.* Minimum detectable concentration is 20 ppm for a 0 to 1,000 ppm span.

3. *Interferences.* Any substance having a strong absorption of infrared energy will interfere to some extent. For example, discrimination ratios for water (H_2O) and carbon dioxide (CO_2) are 3.5 percent H_2O per 7 ppm CO and 10 percent CO_2 per 10 ppm CO, respectively, for devices measuring in the 1,500 to 3,000 ppm range. For devices measuring in the 0 to 100 ppm range, interference ratios can be as high as 3.5 percent H_2O per 25 ppm CO and 10 percent CO_2 per 50 ppm CO. The use of silica gel and ascarite traps will alleviate the major interference problems. The measured gas volume must be corrected if these traps are used.

4. *Precision and accuracy.*

4.1 *Precision.* The precision of most NDIR analyzers is approximately ±2 percent of span.

4.2 *Accuracy.* The accuracy of most NDIR analyzers is approximately ±5 percent of span after calibration.

5. *Apparatus.*

5.1 *Continuous sample* (Figure 10-1).

5.1.1 *Probe.* Stainless steel or sheathed Pyrex[1] glass, equipped with a filter to remove particulate matter.

5.1.2 *Air-cooled condenser or equivalent.* To remove any excess moisture.

5.2 *Integrated sample* (Figure 10-2).

5.2.1 *Probe.* Stainless steel or sheathed Pyrex glass, equipped with a filter to remove particulate matter.

5.2.2 *Air-cooled condenser or equivalent.* To remove any excess moisture.

5.2.3 *Valve.* Needle valve, or equivalent, to to adjust flow rate.

5.2.4 *Pump.* Leak-free diaphragm type, or equivalent, to transport gas.

5.2.5 *Rate meter.* Rotameter, or equivalent, to measure a flow range from 0 to 1.0 liter per min. (0.035 cfm).

5.2.6 *Flexible bag.* Tedlar, or equivalent, with a capacity of 60 to 90 liters (2 to 3 ft³). Leak-test the bag in the laboratory before using by evacuating bag with a pump fol-

[1]Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

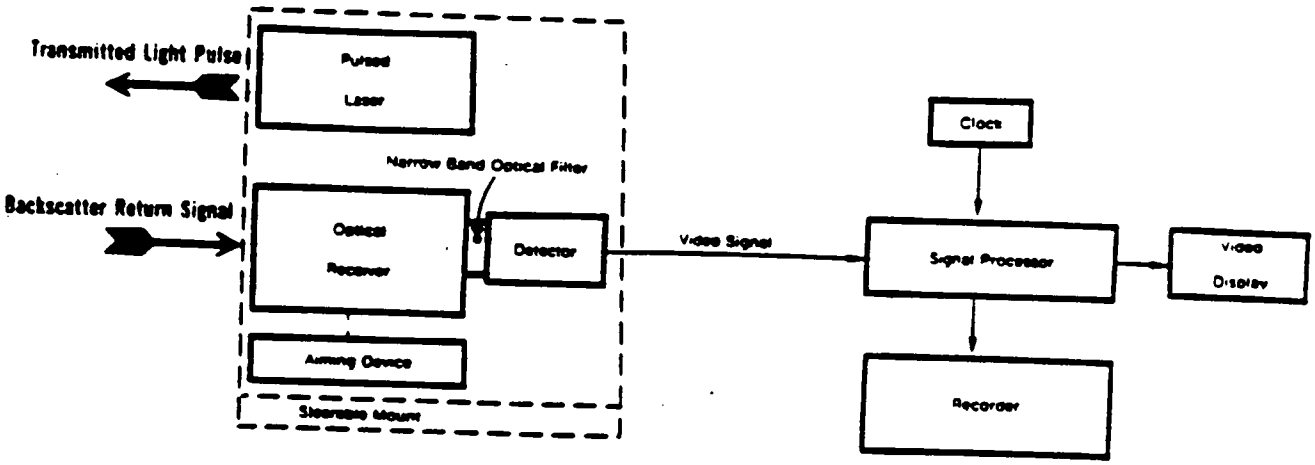


Figure AM1-VII. Functional Block Diagram of a Basic Lidar System

lowed by a dry gas meter. When evacuation is complete, there should be no flow through the meter.

5.2.7 *Pitot tube.* Type S, or equivalent, attached to the probe so that the sampling rate can be regulated proportional to the stack gas velocity when velocity is varying with the time or a sample traverse is conducted.

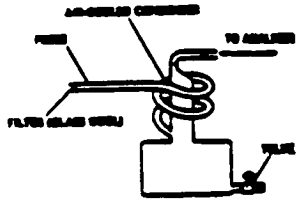
5.3 *Analysis* (Figure 10-3).

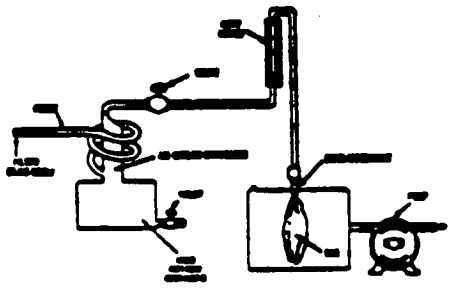
5.3.1 *Carbon monoxide analyzer.* Nondispersive infrared spectrometer, or equivalent. This instrument should be demonstrated, preferably by the manufacturer, to meet or exceed manufacturer's specifications and those described in this method.

5.3.2 *Drying tube.* To contain approximately 200 g of silica gel.

5.3.3 *Calibration gas.* Refer to paragraph 6.1.

5.3.4 *Filter.* As recommended by NDIR manufacturer.





5.3.5 CO_2 removal tube. To contain approximately 500 g of ascarite.

5.3.6 *Ice water bath.* For ascarite and silica gel tubes.

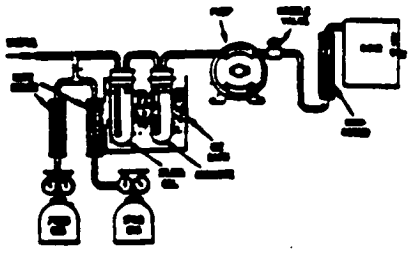
5.3.7 *Valve.* Needle valve, or equivalent, to adjust flow rate

5.3.8 *Rate meter.* Rotameter or equivalent to measure gas flow rate of 0 to 1.0 liter per min. (0.035 cfm) through NDIR.

5.3.9 *Recorder (optional).* To provide permanent record of NDIR readings.

6. *Reagents.*

6.1 *Calibration gases.* Known concentration of CO in nitrogen (N_2) for instrument span, prepurified grade of N_2 for zero, and two additional concentrations corresponding approximately to 60 percent and 30 percent span. The span concentration shall not exceed 1.5 times the applicable source performance standard. The calibration gases shall be certified by the manufacturer to be within ±2 percent of the specified concentration.



6.2 *Silica gel.* Indicating type, 6 to 16 mesh, dried at 175° C (347° F) for 2 hours.

6.3 *Ascarite.* Commercially available.

7. *Procedure.*

7.1 *Sampling.*

7.1.1 *Continuous sampling.* Set up the equipment as shown in Figure 10-1 making sure all connections are leak free. Place the probe in the stack at a sampling point and purge the sampling line. Connect the analyzer and begin drawing sample into the analyzer. Allow 5 minutes for the system to stabilize, then record the analyzer reading as required by the test procedure. (See § 7.2 and 8). CO_2 content of the gas may be determined by using the Method 3 integrated sample procedure (36 FR 24886), or by weighing the ascarite CO_2 removal tube and computing CO_2 concentration from the gas volume sampled and the weight gain of the tube.

7.1.2 *Integrated sampling.* Evacuate the flexible bag. Set up the equipment as shown in Figure 10-2 with the bag disconnected. Place the probe in the stack and purge the sampling line. Connect the bag, making sure that all connections are leak free. Sample at a rate proportional to the stack velocity. CO_2 content of the gas may be determined by using the Method 3 integrated sample procedures (36 FR 24886), or by weighing the ascarite CO_2 removal tube and computing CO_2 concentration from the gas volume sampled and the weight gain of the tube.

7.2 *CO Analysis.* Assemble the apparatus as shown in Figure 10-3, calibrate the instrument, and perform other required operations as described in paragraph 8. Purge analyzer with N_2 prior to introduction of each sample. Direct the sample stream through the instrument for the test period, recording the readings. Check the zero and span again after the test to assure that any drift or malfunction is detected. Record the sample data on Table 10-1.

8. *Calibration.* Assemble the apparatus according to Figure 10-3. Generally an instrument requires a warm-up period before stability is obtained. Follow the manufacturer's instructions for specific procedure. Allow a minimum time of 1 hour for warm-up. During this time check the sample conditioning apparatus, i.e., filter, condenser, drying tube, and CO_2 removal tube, to ensure that each component is in good operating condition. Zero and calibrate the instrument according to the manufacturer's procedures using, respectively, nitrogen and the calibration gases.

TABLE 10-1—FIELD DATA

	Comments
Location	
Test	
Date	
Operator	
Clock time	Reagent setting, flow rate readings, leak check results

9. *Calculation—Concentration of carbon monoxide.* Calculate the concentration of carbon monoxide in the stack using equation 10-1.

$$C_{CO,\,stack} = C_{CO,\,NDIR}(1 - F_{CO_2})$$

where:

$C_{CO,\,stack}$ = concentration of CO in stack, ppm by volume (dry basis).

$C_{CO,\,NDIR}$ = concentration of CO measured by NDIR analyzer, ppm by volume (dry basis).

F_{CO_2} = volume fraction of CO_2 in sample, i.e., percent CO_2 from Orsat analysis divided by 100.

10. *Bibliography.*

10.1 McElroy, Frank. The Intertech NDIR-CO Analyzer. Presented at 11th Methods Conference on Air Pollution. University of California, Berkeley, Calif., April 1, 1970.

10.2 Jacobs, M. B., et al. Continuous Determination of Carbon Monoxide and Hydrocarbons in Air by a Modified Infrared Analyzer. J. Air Pollution Control Association, 8(2): 110-114, August 1958.

10.3 MSA LIRA Infrared Gas and Liquid Analyzer Instruction Book. Mine Safety Appliances Co., Technical Products Division, Pittsburgh, Pa.

10.4 Models 315A, 315A, and 415A Infrared Analyzers. Beckman Instruments, Inc., Beckman Instructions 1635-B, Fullerton, Calif., October 1967.

10.5 Continuous CO Monitoring System, Model A5611, Intertech Corp., Princeton, N.J.

10.6 UNOR Infrared Gas Analyzers, Bendix Corp., Ronceverte, West Virginia.

ADDENDA—A. PERFORMANCE SPECIFICATIONS FOR NDIR CARBON MONOXIDE ANALYZERS.

Range (minimum)	0-1000 ppm.
Output (minimum)	0-10mV.
Minimum detectable sensitivity.	20 ppm.
Rise time, 90 percent (maximum).	30 seconds.
Fall time, 90 percent (maximum).	30 seconds.
Zero drift (maximum)	10% in 8 hours.
Span drift (maximum)	10% in 8 hours.
Precision (minimum)	±2% of full scale.
Noise (maximum)	±1% of full scale.
Linearity (maximum deviation)	2% of full scale.
Interference rejection ratio	CO_2—1000 to 1. H_2O—400 to 1.

WESTON

EPA METHOD 25A

METHOD 25A—DETERMINATION OF TOTAL GASEOUS ORGANIC CONCENTRATION USING A FLAME IONIZATION ANALYZER

1. *Applicability and Principle.*

1.1 Applicability. This method applies to the measurement of total gaseous organic concentration of vapors consisting primarily of alkanes, alkenes, and/or arenes (aromatic hydrocarbons). The concentration is expressed in terms of propane (or other appropriate organic calibration gas) or in terms of carbon.

1.2 Principle. A gas sample is extracted from the source through a heated sample line, if necessary, and glass fiber filter to a flame ionization analyzer (FIA). Results are reported as volume concentration equivalents of the calibration gas or as carbon equivalents.

2. *Definitions.*

2.1 Measurement System. The total equipment required for the determination of the gas concentration. The system consists of the following major subsystems:

2.1.1 Sample Interface. That portion of the system that is used for one or more of the following: sample acquisition, sample transportation, sample conditioning, or protection of the analyzer from the effects of the stack effluent.

2.1.2 Organic Analyzer. That portion of the system that senses organic concentration and generates an output proportional to the gas concentration.

2.2 Span Value. The upper limit of a gas concentration measurement range that is specified for affected source categories in the applicable part of the regulations. The span value is established in the applicable regulation and is usually 1.5 to 2.5 times the applicable emission limit. If no span value is provided, use a span value equivalent to 1.5 to 2.5 times the expected concentration. For convenience, the span value should correspond to 100 percent of the recorder scale.

2.3 Calibration Gas. A known concentration of a gas in an appropriate diluent gas.

2.4 Zero Drift. The difference in the measurement system response to a zero level calibration gas before and after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

2.5 Calibration Drift. The difference in the measurement system response to a mid-level calibration gas before and after a stated period of operation during which no unscheduled maintenance, repair or adjustment took place.

2.6 Response Time. The time interval from a step change in pollutant concentration at the inlet to the emission measurement system to the time at which 95 percent of the corresponding final value is reached as displayed on the recorder.

2.7 Calibration Error. The difference between the gas concentration indicated by the measurement system and the known concentration of the calibration gas.

3. *Apparatus.*

A schematic of an acceptable measurement system is shown in Figure 25A-1. The essential components of the measurement system are described below:

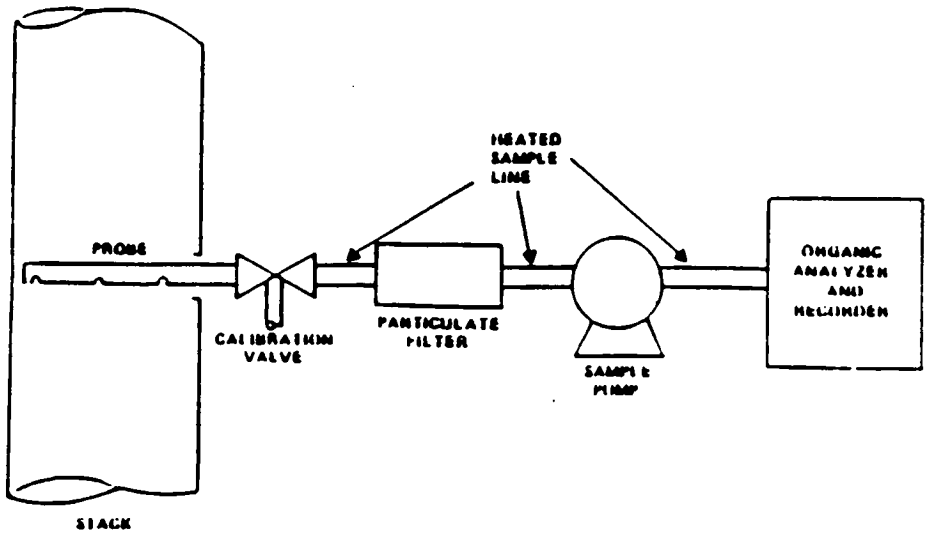


Figure 25A-1. Organic Concentration Measurement System.

3.1 Organic Concentration Analyzer. A flame ionization analyzer (FIA) capable of meeting or exceeding the specifications in this method.

3.2 Sample Probe. Stainless steel, or equivalent, three-hole rake type. Sample holes shall be 4 mm in diameter or smaller and located at 16.7, 50, and 83.3 percent of the equivalent stack diameter. Alternatively, a single opening probe may be used so that a gas sample is collected from the centrally located 10 percent area of the stack cross-section.

3.3 Sample Line. Stainless steel or Teflon® tubing to transport the sample gas to the analyzers. The sample line should be heated, if necessary, to prevent condensation in the line.

3.4 Calibration Valve Assembly. A three-way valve assembly to direct the zero and calibration gases to the analyzers is recommended. Other methods, such as quick-connect lines, to route calibration gas to the analyzers are applicable.

3.5 Particulate Filter. An in-stack or an out-of-stack glass fiber filter is recommended if exhaust gas particulate loading is significant. An out-of-stack filter should be heated to prevent any condensation.

3.6 Recorder. A strip-chart recorder, analog computer, or digital recorder for recording measurement data. The minimum data recording requirement is one measurement value per minute. Note: This method is often applied in highly explosive areas. Caution and care should be exercised in choice of equipment and installation.

4. *Calibration and Other Gases.*

Gases used for calibrations, fuel, and combustion air (if required) are contained in compressed gas cylinders. Preparation of calibration gases shall be done according to the procedure in Protocol No. 1, listed in Reference 9.2. Additionally, the manufacturer of the cylinder should provide a recommended shelf life for each calibration gas cylinder over which the concentration does not change more than ±2 percent from the certified value. For calibration gas values not generally available (i.e., organics between 1 and 10 percent by volume), alternative methods for preparing calibration gas mixtures, such as dilution systems, may be used with prior approval of the Administrator.

Calibration gases usually consist of propane in air or nitrogen and are determined in terms of the span value. Organic compounds other than propane can be used following the above guidelines and making the appropriate corrections for response factor.

4.1 Fuel. A 40 percent H_2/60 percent He or 40 percent H_2/60 percent N_2 gas mixture is recommended to avoid an oxygen synergism effect that reportedly occurs when oxygen concentration varies significantly from a mean value.

4.2 Zero Gas. High purity air with less than 0.1 parts per million by volume (ppmv) of organic material (propane or carbon equivalent) or less than 0.1 percent of the span value, whichever is greater.

4.3 Low-level Calibration Gas. An organic calibration gas with a concentration equivalent to 25 to 35 percent of the applicable span value.

4.4 Mid-level Calibration Gas. An organic calibration gas with a concentration equivalent to 45 to 55 percent of the applicable span value.

4.5 High-level Calibration Gas. An organic calibration gas with a concentration equivalent to 80 to 90 percent of the applicable span value.

5. *Measurement System Performance Specifications.*

5.1 Zero Drift. Less than ±3 percent of the span value.

5.2 Calibration Drift. Less than ±3 percent of span value.

5.3 Calibration Error. Less than ±5 percent of the calibration gas value.

6. Pretest Preparations.

6.1 Selection of Sampling Site. The location of the sampling site is generally specified by the applicable regulation or purpose of the test; i.e., exhaust stack, inlet line, etc. The sample port shall be located at least 1.5 meters or 2 equivalent diameters (whichever is less) upstream of the gas discharge to the atmosphere.

6.2 Location of Sample Probe. Install the sample probe so that the probe is centrally located in the stack, pipe, or duct and is sealed tightly at the stack port connection.

6.3 Measurement System Preparation. Prior to the emission test, assemble the measurement system following the manufacturer's written instructions in preparing the sample interface and the organic analyzer. Make the system operable.

FIA equipment can be calibrated for almost any range of total organics concentrations. For high concentrations of organics (>1.0 percent by volume as propane) modifications to most commonly available analyzers are necessary. One accepted method of equipment modification is to decrease the size of the sample to the analyzer through the use of a smaller diameter sample capillary. Direct and continuous measurement of organic concentration is a necessary consideration when determining any modification design.

6.4 Calibration Error Test. Immediately prior to the test series, (within 2 hours of the start of the test) introduce zero gas and high-level calibration gas at the calibration valve assembly. Adjust the analyzer output to the appropriate levels, if necessary. Calculate the predicted response for the low-level and mid-level gases based on a linear response line between the zero and high-level responses. Then introduce low-level and mid-level calibration gases successively to the measurement system. Record the analyzer responses for low-level and mid-level calibration gases and determine the differences between the measurement system responses and the predicted responses. These differences must be less than 5 percent of the respective calibration gas value. If not, the measurement system is not acceptable and must be replaced or repaired prior to testing. No adjustments to the measurement system shall be conducted after the calibration and before the drift check (Section 7.3). If adjustments are necessary before the completion of the test series, perform the drift checks prior to the required adjustments and repeat the calibration following the adjustments. If multiple electronic ranges are to be used, each additional range must be checked with a mid-level calibration gas to verify the multiplication factor.

6.5 Response Time Test. Introduce zero gas into the measurement system at the calibration valve assembly. When the system output has stabilized, switch quickly to the high-level calibration gas. Record the time from the concentration change to the measurement system response equivalent to 95 percent of the step change. Repeat the test three times and average the results.

7. Emission Measurement Test

7.1 Organic Measurement. Begin sampling at the start of the test period, recording time and any required process information as appropriate. In particular, note on the recording chart periods of process interruption or cyclic operation.

7.2 Drift Determination. Immediately following the completion of the test period and hourly during the test period, reintroduce the zero and mid-level calibration gases, one at a time, to the measurement system at the calibration valve assembly. (Make no adjustments to the measurement system until after both the zero and calibration drift checks are made.) Record the analyzer response. If the drift values exceed the specified limits, invalidate the test results preceding the check and repeat the test following corrections to the measurement system. Alternatively, recalibrate the test measurement system as in Section 6.4 and report the results using both sets of calibration data (i.e., data determined prior to the test period and data determined following the test period).

8. Organic Concentration Calculations.

Determine the average organic concentration in terms of ppmv as propane or other calibration gas. The average shall be determined by the integration of the output recording over the period specified in the applicable regulation.

If results are required in terms of ppmv as carbon, adjust measured concentrations using Equation 25A-1.

$$C_c = K C_{meas}$$

Eq. 25A-1

Where:

C_c = Organic concentration as carbon, ppmv.

C_{meas} = Organic concentration as measured, ppmv.

K = Carbon equivalent correction factor.

K = 2 for ethane.

K = 3 for propane.

K = 4 for butane.

K = Appropriate response factor for other organic calibration gases.

9. Bibliography.

9.1 Measurement of Volatile Organic Compounds—Guideline Series. U.S. Environmental Protection Agency. Research Triangle Park, N.C. Publication No. EPA-450/2-78-041. June 1978. p. 46-54.

9.2 Traceability Protocol for Establishing True Concentrations of Gases Used for Calibration and Audits of Continuous Source Emission Monitors (Protocol No. 1). U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory. Research Triangle Park, N.C. June 1978.

9.3 Gasoline Vapor Emission Laboratory Evaluation—Part 2. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, N.C. EMB Report No. 75-GAS-6. August 1978.

APPENDIX C

DESCRIPTION OF CEM SAMPLING SYSTEM

APPENDIX C

DESCRIPTION OF CEM SAMPLING SYSTEM

The CEM system to be used for gaseous pollutant monitoring by EPA Methods 3A, 7E, 10, and 25A.

C.1 Sampling System. Exhaust gas is drawn from the duct or stack through a heated stainless steel (S.S.) probe that will be inserted into the duct or stack through one of the test ports. A S.S. valve is located at the probe exit to permit introduction of certified zero and calibration span gases. A heated teflon line is used to transport the sample or zero/calibration gases to the Continuous Emission Monitoring (CEM) trailer. Temperatures are monitored at the exit of each section of line to ensure temperatures above the sample dew point. Once inside the CEM trailer, the sample is split into fractions, and each fraction is directed to one of the following:

(a) Exemplar Model PEL-3 Sample Gas Conditioner
(b) Direct Connection to Total Hydrocarbon Analyzers.

The Exemplar Model PEL-3 is an extractive sample conditioner that removes particulates and moisture from the sample gas. The extracted sample gas is passed through a sintered stainless bypass filter, which removes particulates down to 1 micron or less by an intertial filtration technique. The filter is maintained at a temperature above the dew point of the sample gases.

The clean, filtered sample is then introduced to a permeation dryer where moisture is removed without condensation or dilution to achieve a sample dew point well below that of the ambient temperature. The clean, dried sample is then directed to the carbon monoxide (CO), carbon dioxide (CO_2), and oxygen (O_2) analyzers using a teflon-headed sample pump.

In the J.U.M. Engineer VE-7 Total Hydrocarbons Analyzer, a S.S. sample filter and detector are contained in a temperature controlled oven. This permits the direct analysis of total hydrocarbons on a wet basis without condensation or loss of sample.

C.2 CEM System Calibration Procedures. Calibrations will be conducted on a daily basis. The following procedures will also be performed each day of testing:

(a) Analyzer calibration error (pretest).
(b) Sampling system bias check (pretest).
(c) Sampling system bias check (post-test).

Calibrations will use cylinder gas standards prepared according to EPA Protocol 1, where available. All other calibration gases will be traceable to National Bureau of Standards (NBS) standards.

C.3 CEM System Data Collection. Signals from the CEM sampling system are recorded in hard copy from a Molytek strip-chart recorder/data logger.