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October 5, 1989

SUPPLEMENTAL WORK PLAN FOR STAGE II OF THE REMEDIAL INVESTIGATION FOR THE HASSAYAMPA LANDFILL HAZARDOUS WASTE AREA MARICOPA COUNTY, ARIZONA

REGISTERED GEOLOGIST
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October 5, 1989

Daniel D. Opalski (T-4-1), Project Coordinator
U. S. ENVIRONMENTAL PROTECTION AGENCY, REGION 9
215 Fremont Street
San Francisco, California 94105

RE: FINAL SUPPLEMENTAL WORK PLAN FOR STAGE II INVESTIGATION

Dear Mr. Opalski:

In accordance with Subsection VII.B.4 of the Administrative Consent Order (EPA Docket No. 88-08) for the Remedial Investigation / Feasibility Study (RI/FS) for the Hassayampa Landfill hazardous waste area, Maricopa County, Arizona, please find enclosed three copies of the final Supplemental Work Plan, dated October 5, 1989, and entitled:

SUPPLEMENTAL WORK PLAN FOR STAGE II OF
THE REMEDIAL INVESTIGATION FOR
THE HASSAYAMPA LANDFILL HAZARDOUS WASTE AREA
MARICOPA COUNTY, ARIZONA

This final Work Plan was prepared in accordance with comments and responses on the draft Supplemental Work Plan, dated March 13, 1989, and resolutions of the Hassayampa Technical Work Group. If you have questions or require further discussion, please contact us.

Very truly yours,
ERROL L. MONTGOMERY & ASSOCIATES, INC.

William R. Victor

William R. Victor

SENT VIA FEDERAL EXPRESS
Enclosures (3)
cc: A. T. Wilson (3)
Mason Bolitho (3)
James G. Derouin (2)
Robert J. Lloyd (2)
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October 5, 1989

SUPPLEMENTAL WORK PLAN FOR STAGE II OF THE REMEDIAL INVESTIGATION FOR THE HASSAYAMPA LANDFILL HAZARDOUS WASTE AREA
MARICOPA COUNTY, ARIZONA

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October 5, 1989

SUPPLEMENTAL WORK PLAN FOR STAGE II OF THE REMEDIAL INVESTIGATION FOR THE HASSAYAMPA LANDFILL HAZARDOUS WASTE AREA MARICOPA COUNTY, ARIZONA

RECOMMENDATIONS

Results from the Stage I investigation for the hazardous waste area at the Hassayampa Landfill indicate that additional work should be conducted to complete the Remedial Investigation. Recommendations from Errol L. Montgomery & Associates, Inc., and Conestoga-Rovers & Associates (1989) are summarized as follows:

1. TASK F should consist of the following:

   TASK F1: Soil Evaluation
   TASK F2: Groundwater Monitor Wells
   TASK F3: Groundwater Monitoring Program
   TASK F4: Stage III Investigation (if necessary)

2. Four additional soil borings should be drilled under TASK F1 to obtain data for chemical quality of soils beneath the principal disposal pits for hazardous waste. These soil borings should be drilled, at an angle to the vertical, beneath Pits 1, 2, 3, and 4, and should be drilled to auger bit refusal or until the basaltic lava-flow unit is encountered, whichever occurs first.

3. TASK F2 should include construction, developing, testing, equipping, and sampling three to five proposed groundwater monitor wells, which would be completed in Unit A. The proposed monitor well sites are:

Well Site A: Located approximately 10 to 20 feet downgradient from abandoned monitor well (C-1-5)3daa1[HS-1]. The proposed monitor well at Site A will replace abandoned monitor well HS-1 and should provide water level and water quality data representative for Unit A.

Well Site B: Located approximately 280 feet upgradient from monitor well (C-1-5)3dab3[MW-1UA], to define the lateral extent of groundwater contamination at well MW-1UA in an upgradient direction.

Well Site C: Located outside the hazardous waste area, approximately 680 feet downgradient from monitor well MW-1UA and approximately 400 feet northwest, along the fence line for the landfill, from monitor well (C-1-5)3dac[HS-2]. Purpose for Site C is to define, together with existing monitor well HS-2, the lateral extent of groundwater contamination at well MW-1UA in a downgradient direction.

Well Site D: Located on-site approximately 190 feet downgradient from abandoned monitor well HS-1. Site D is optional and will be drilled to define the lateral extent of groundwater contamination in a downgradient direction only if contamination is found in the monitor well constructed at Site A.

Well Site E: Located approximately 200 feet south-southeast from abandoned monitor well HS-1. Site E is optional and will be drilled to define the lateral extent of groundwater contamination in a downgradient direction only if contamination is found in the monitor well constructed at Site A.

4. TASK F3 should be conducted to extend the groundwater monitoring program established under TASK G of the comprehensive Work Plan (Errol L. Montgomery & Associates, Inc., and Conestoga-Rovers & Associates, 1988a) for the Remedial Investigation / Feasibility Study (RI/FS). Results of the monitoring program would be used to document groundwater quality and to detect changes in rate and direction of groundwater movement. The monitoring program would comprise three rounds of collection of groundwater samples and measurement of groundwater levels.

   TASK F3 sampling round no. 1 should be conducted during summer 1989 and would comprise collection of groundwater samples and measurement of water levels at the 11 existing on-site monitor wells. TASK F3 sampling round no. 2 would be conducted approximately 30 days after completion of field operations for TASK F2, and should comprise collection of groundwater samples and measurement of water levels at the new and existing on-site monitor wells. TASK F3 sampling round no. 3 would be conducted 13 weeks after TASK F3 sampling round no. 2. Results from TASKS F2 and F3 sampling rounds would be given in monthly data submittals to EPA, as required in the Consent Order.

5. **Pursuant to the RI/FS Work Plan, the need for Feasibility Study testing has been evaluated. Additional testing for the Feasibility Study outside of the Remedial Investigation is unnecessary given that the nature of the waste is well documented and that the remedial technologies listed for consideration are established remedial technologies, which are not of an experimental nature.**

The chemical quality of air was evaluated under TASK B1 of the Stage I investigation, which included measurement of air quality above the land surface at the hazardous waste area. Results of the TASK B1 air investigation were useful as estimated values; however, EPA qualified the representativeness of the TASK B1 data, based on quality assurance and quality control concerns. Therefore, a Stage II air investigation (TASK B2) is included in the Supplemental Work Plan to augment and verify results from the Stage I air investigation.

October 5, 1989

SUPPLEMENTAL WORK PLAN FOR STAGE II OF THE REMEDIAL INVESTIGATION FOR THE HASSAYAMPA LANDFILL HAZARDOUS WASTE AREA MARICOPA COUNTY, ARIZONA

INTRODUCTION

On authorization by the Hassayampa Steering Committee, Errol L. Montgomery & Associates, Inc. (Montgomery & Associates) and Conestoga-Rovers & Associates (CRA) have prepared this Supplemental Work Plan to give objectives and procedures for conduct of Stage II of the Remedial Investigation for the former hazardous waste disposal area at the Hassayampa Landfill.

The scope of work for TASKS A through J were described in the comprehensive Work Plan (Montgomery & Associates and CRA, 1988a) for the Remedial Investigation / Feasibility Study (RI/FS). The comprehensive RI/FS Work Plan was one of three documents submitted to the U. S. Environmental Protection Agency (EPA), Region 9, in conjunction with an Administrative Consent Order (EPA Docket No. 88-08) for the Hassayampa Landfill. The other two are: the Quality Assurance Project Plan (QAPP) (Montgomery & Associates and CRA, 1988b), which contains the Sampling Plan as an attachment; and the Health and Safety Plan (Montgomery & Associates and CRA, 1988c).

Figure 1 is a regional location map for the Hassayampa Landfill (the landfill). The landfill is located in the southeast quarter of Section 3, Township 1 South, Range 5 West, Maricopa County, Arizona. Locations for the disposal pits are tentative and approximate, and are shown on **Figure 2**.

The northeast part of the Hassayampa Landfill was designated Arizona's interim hazardous waste disposal facility for a period of approximately 18 months, from April 20, 1979, to October 28, 1980. During this period, disposal of hazardous wastes in the hazardous waste area of the landfill was authorized by Arizona Department of Health Services via a manifest program. Compilations of these manifests were reported by Arizona Department of Health Services (1982 and 1985). These manifests indicate that a wide range of hazardous wastes, including about 3.28 million gallons of liquid wastes and about 4,150 tons of solid wastes, were disposed in Pits 1, 2, 3, and 4, and in Special Pits **(Figure 2)**. Types and quantities of wastes reported to have been designated for disposal in these pits are summarized in **Table 1**.

Two additional pits, Pits A and B **(Figure 2)**, in the hazardous waste area were intended for disposal of nonhazardous wastes. Pits A and B were not included in the hazardous waste manifest program. Cesspool waste and septic tank waste are the principal wastes reported to have been disposed in Pit A (Ecology and Environment, Inc., 1981). Although the waste disposed in Pit B has not been fully determined, the waste is reported to have included hydrate waste (Ecology and Environment, Inc., 1981).

The approximate former area of hazardous waste disposal and the approximate location and boundaries of Pits 1, 2, 3, 4, A, and B, and Special Pit areas shown on **Figure 2** were determined from:

- Inspection of aerial photos for the landfill for 1976, 1979, 1981, 1982, 1985, 1986, and 1989;
- Inspection of a hand-drawn sketch of the former hazardous waste disposal area given by Ecology and Environment, Inc. (1981), which was based on results of a site inspection on January 15, 1981; and
- Interviews with Maricopa County Landfill Department personnel.

Results of these investigations indicate that the former area of hazardous waste disposal encompassed an area of approximately 10 acres in the northeast part of the landfill. The entire area used for the landfill operations comprises about 47 acres.

OBJECTIVES

In accordance with the National Contingency Plan, the principal objective of the Remedial Investigation is to characterize site conditions and to evaluate potential existing or future impacts of the former hazardous waste disposal pits on quality of groundwater, surface water, soil, and air, and on public health. Potential impacts of the former hazardous waste disposal pits on the quality of groundwater, surface water, soil, and air were evaluated during the Stage I investigation in accordance with the comprehensive RI/FS Work Plan (Montgomery & Associates and CRA, 1988a) and were reported by Montgomery & Associates and CRA (1989). No additional work is required for the surface water evaluation. Additional work is included in the Supplemental Work Plan for the evaluation of groundwater, soil, and air. The scope of the Supplemental Work Plan is designed to obtain appropriate data to:

1. Augment the existing groundwater monitoring network and evaluate the lateral extent of groundwater contamination in the upper alluvial deposits unit;
2. Characterize the type and depth of potential soil contamination in the vadose zone beneath the four principal manifested disposal pits;
3. Augment and verify existing air quality data for use in the EPA risk assessment; and
4. Provide a sufficient data base for the Feasibility Study.

Groundwater

Potential impacts of the former hazardous waste disposal pits on the chemical quality of groundwater were evaluated under TASK D of the Stage I investigation. The Remedial Investigation for groundwater includes delineation of the extent of groundwater contamination and the establishment of a monitoring network to detect potential future migration of contaminants from former hazardous waste disposal pits. Results of the Stage I groundwater investigation indicate that, although the vertical extent of groundwater contamination was sufficiently defined during Stage I, a Stage II investigation is necessary under TASK F to further define the lateral extent of groundwater contamination in the upper alluvial deposits unit.

Soil

The chemical quality of soil was evaluated under TASKS A and C of the Stage I investigation, which included evaluation of the lateral extent of potential seepage in the vadose zone from waste disposal pits in the hazardous waste area and determination of the chemical quality of surface sediments in potential stormwater drainage pathways from the hazardous waste area. Results of the Stage I soil evaluation suggest that lateral migration of volatile organic compounds in the vadose zone from the disposal pits was not substantial. These results, together with the small amount of groundwater contamination detected during Stage I, indicate that a Stage II soil evaluation would be useful to characterize the type and depth of potential soil contamination in the vadose zone beneath the four principal manifested disposal pits. These data will be used for construction of a model to evaluate the potential effects of evaporation on the volume of wastes available for infiltration into the subsurface. The data will also be used to evaluate remedial alternatives for the vadose zone.

Air

The chemical quality of air was evaluated under TASK B1 of the Stage I investigation, which included measurement of air quality above the land surface at the hazardous waste area. Results of the TASK B1 air investigation were useful as estimated values; however, EPA qualified the representativeness of the TASK B1 data, based on quality assurance and quality control concerns. Therefore, a Stage II air investigation (TASK B2) is included in the Supplemental Work Plan to augment and verify results from the Stage I air investigation.

PROJECT ORGANIZATION AND STUDY TEAM

The scope for the Supplemental Work Plan has been prepared by Errol L. Montgomery & Associates, Inc. (Montgomery & Associates), Tucson, Arizona, and Conestoga-Rovers & Associates (CRA), St. Paul, Minnesota. The association of these two consulting firms will provide a capable team for all potential aspects of work at the Hassayampa Landfill. Although both firms will provide technical support and colleague review for all stages of the RI/FS program, Montgomery & Associates assumes the lead role for the Remedial Investigation and CRA assumes the lead role for the Feasibility Study.

PREVIOUS INVESTIGATIONS

Results of previous investigations for the Hassayampa Landfill and adjacent areas are sources of information for hydrogeologic conditions, historic disposal practices, disposal pit locations, types of substances disposed, and locations of off-site and on-site wells existing prior to the RI/FS. Previous investigations that provide a thorough review of existing data for the landfill or landfill area include, in chronological order:

1. **Hydrogeologic Conditions and Waste Disposal at the Hassayampa, Casa Grande and Somerton Landfills, Arizona.** Report prepared by Kenneth D. Schmidt and Robert C. Scott for Arizona Department of Health Services, dated January 1977.

2. **The Hassayampa Landfill hazardous waste disposal site: disposal analysis (April 20, 1979 - October 28, 1980).** Prepared by Bureau of Waste Control, Arizona Department of Health Services, dated 1980.

3. **Site Inspection Report on Hassayampa Landfill, Hassayampa, Arizona.** Prepared by Ecology and Environment, Inc., for EPA, dated February 10, 1981.

4. Arizona Department of Health Services inter-office memorandum, dated October 27, 1981, from Bob Hollander to Tibaldo Canez. RE: Alternatives and cost estimates for completion of monitoring wells at the Hassayampa Landfill.

5. Letter, dated November 19, 1981, from James Angell, Arizona Department of Health Services, to William Wood, City of Phoenix Engineering Department. RE: Monitoring well specifications.

6. **Geotechnical Evaluation of the Influence of Hassayampa Landfill Hazardous Wastes on the PVNGS Conveyance Pipeline.** Report prepared by Ertec Western, Inc., for Arizona Nuclear Power Project and NUS Corporation, dated March 17, 1982.

7. **Open Dump Inventory of Hassayampa Landfill, Ground Water Criterion.** Report prepared by Arizona Department of Health Services, dated September 1982.

8. **Site Inspection and Sampling Documentation Report, Hassayampa Landfill.** Prepared by Ecology and Environment, Inc., for EPA, dated August 5, 1983.

9. **Analytical Results, Case #1717.** Prepared by Ecology and Environment, Inc., for EPA, dated December 21, 1983.

10. **Hassayampa Landfill Site Inspection Report.** Prepared by Arizona Department of Health Services, dated May 1, 1985.

11. **Study of Waterlogging Problems in the West Salt River and Hassayampa Sub-Basins of the Phoenix Active Management Area: Task 1A - Evaluation of Past Hydrogeologic Conditions.** Report prepared by Montgomery & Associates for Arizona Department of Water Resources, dated August 25, 1986.

12. **Results of Preliminary Hydrogeologic Investigations, Hassayampa Landfill, Maricopa County, Arizona.** Memorandum Report prepared by Montgomery & Associates for the Hassayampa Steering Committee, dated April 22, 1987.

13. **Study of waterlogging problems in the West Salt River and Hassayampa Sub-Basins of the Phoenix Active Management Area: modified overall study evaluation.** Report prepared by Montgomery & Associates and Desert Agricultural and Technology Systems, Inc., for Arizona Department of Water Resources, dated January 14, 1988.

14. **Groundwater monitoring report, Remedial Investigation / Feasibility Study, Hazardous Waste Area, Hassayampa Landfill, Maricopa County, Arizona.** Draft Report prepared by Montgomery & Associates and CRA for the Hassayampa Steering Committee, dated December 23, 1988; draft Report is considered to be final.

15. **Stage I report for Remedial Investigation / Feasibility Study, Hazardous Waste Area, Hassayampa Landfill, Maricopa County, Arizona.** Draft Report prepared by Montgomery & Associates and CRA for the Hassayampa Steering Committee, dated March 13, 1989; finalized October 1989.

TOPOGRAPHY

The topography of the landfill area is characterized by a broad basin floor that slopes gently to the south. Approximately one-half mile south from the landfill, the alluvial plain is broken by Arlington Mesa. The landfill lies on the edge of a flat alluvial plain, adjacent to the Hassayampa River floodplain. Narrow ravines cut the alluvial plain east from the landfill, and form the margin of the Hassayampa River floodplain. From the east boundary of the landfill, slope of the land surface steepens downward approximately four percent to the floodplain.

Topography across the Hassayampa Landfill is undulatory due to the frequent reworking of landfill pits in the active part of the property. However, the closed hazardous waste area is covered by a graded soil cover that is relatively flat to gently sloping. Access for vehicles is generally good in the closed hazardous waste area, where surficial soils are relatively compacted and firm. Surficial soils in parts of the active landfill are loose and are generally passable only to off-road vehicles. Altitude of land surface at the hazardous waste area ranges from about 910 to 915 feet above mean sea level (msl).

HYDROGEOLOGIC CONDITIONS

The Hassayampa Landfill is located in the lower Hassayampa River basin. The lower Hassayampa River basin is bounded on the east by the White Tank Mountains, on the south by the Buckeye Hills, and on the west by the Palo Verde Hills. Hydrogeologic conditions in the basin are typical for the Basin and Range Province in central and southern Arizona, where mountain blocks have been uplifted and basins have been downthrown along high-angle normal faults. However, no structural features have been reported to occur at the landfill. The Hassayampa Landfill lies on an alluvial plain underlain by a thick sequence of basin-fill deposits.

REGIONAL HYDROGEOLOGIC UNITS

Regional hydrogeologic units in the landfill area include, in descending order: the Recent alluvial deposits; the basin-fill deposits; and the bedrock complex.

Recent Alluvial Deposits

The Recent alluvial deposits occur along the floodplain of the Hassayampa River east from the landfill, along Luke Wash west from the landfill, and along large tributary stream channels. These deposits consist chiefly of unconsolidated gravel, sand, and silt of Quaternary age. Groundwater levels in the landfill area generally lie below the base of the Recent alluvial deposits. Because these deposits are commonly coarse-grained and unconsolidated, they have high permeability and provide the principal media for infiltration of ephemeral streamflow.

Basin-fill Deposits

The basin-fill deposits have been classified into the Upper, Middle, and Lower Alluvium units. Analysis of drillers' logs and reports for water wells and exploration boreholes in the Hassayampa Landfill area indicates that a thick sequence of basin-fill deposits underlies most of the landfill area. The basin-fill deposits are underlain by a bedrock complex. Cooley (1973) indicated that thickness of the basin-fill deposits exceeds 1,200 feet at the landfill. Oppenheimer and Sumner (1980) indicated that maximum depth to bedrock at the landfill may be in the range from 3,200 to 4,800 feet. The basin-fill deposits comprise the principal source of groundwater to wells in the landfill area, and are generally referred to as the regional aquifer.

Inspection of drillers' logs for wells in the study area indicates that the Upper Alluvium unit generally consists of a non-lithified to slightly lithified sequence of interbedded, poorly sorted sediments, which range in size from clay to boulders. Zones of caliche are common in the Upper Alluvium unit. Locally, basaltic lava-flow rocks occur within the Upper Alluvium unit. Source for these lava-flow rocks is the Arlington Mesa basalt flow. Data from the drillers' logs and isopach maps given by the U. S. Bureau of Reclamation (1976) suggest that thickness of the Upper Alluvium unit in the landfill area is in the range from 200 to 300 feet.

In general, the Middle Alluvium unit is weakly cemented and consists of interbedded clay, silt, silty sand, sand, and gravel strata. Fugro (1980) reported that the Middle Alluvium unit in areas west from the landfill includes the Palo Verde clay. The Palo Verde clay is reported to be a massive clay layer and is the confining unit for the regional aquifer (Long, 1983). The Palo Verde clay is reported to occur as far north as the Buckeye-Salome Highway and as far east as Arlington.

The Lower Alluvium unit consists of a heterogeneous sequence of interbedded, moderately to firmly lithified conglomerate, gravel, sand, and clay. Based on drillers' logs and structural contour maps given by the U. S. Bureau of Reclamation (1976), depth to the top of the Lower Alluvium unit in the landfill area may be in the range from about 500 to 600 feet.

Bedrock Complex

The bedrock complex crops out in the mountains surrounding the lower Hassayampa River basin and consists chiefly of granitic and metamorphic rocks (Long, 1983). Locally within the bedrock complex, volcanic rocks and sedimentary rocks overlie the granitic and metamorphic rocks. The sedimentary and volcanic rocks may exceed 1,400 feet in thickness and consist of interbedded sequences of fractured basalt, tuff, tuffaceous sandstone, and coarse-grained sandstone (Fugro, 1980).

SITE HYDROGEOLOGIC FEATURES

Hydrogeologic features at the landfill were determined based chiefly on:

- Results of drilling, testing, and lithologic logs for 12 on-site soil borings drilled during the Remedial Investigation (Montgomery & Associates, 1988d, 1988e, and 1989);
- Results of drilling, testing, lithologic logs, and borehole geophysical logs for nine on-site monitor wells and an exploration boring drilled during the Remedial Investigation (Montgomery & Associates, 1988d, 1988e, 1988f, 1988g, 1988h, 1988i, and 1989);
- Lithologic information for pre-existing on-site monitor wells constructed for Arizona Department of Health Services (Arizona Department of Health Services, 1982 and 1985); and
- Lithologic information for two pre-existing on-site vadose zone monitor wells and a soil boring drilled for Ertec Western, Inc. (Ertec Western, Inc., 1982).

The following on-site monitor wells were constructed by Montgomery & Associates during Stage I of the Remedial Investigation:

(C-1-5)3dab3 [MW-1UA]
(C-1-5)3daa2 [MW-2UA]
(C-1-5)3daa4 [MW-3UA]
(C-1-5)3dab5 [MW-4UA]
(C-1-5)3dab7 [MW-5UA]

(C-1-5)3dab1 [MW-1UB]
(C-1-5)3dab4 [MW-2UB]
(C-1-5)3daa3 [MW-3UB]
(C-1-5)3dab6 [MW-4UB]

In addition, Montgomery & Associates drilled on-site exploration boring (C-1-5)3dab2 **[EX-1]**. The following on-site monitor wells were constructed by Arizona Department of Health Services: **(C-1-5)3daa1 [HS-1]**, **(C-1-5)3dac [HS-2]**, and **(C-1-5)3dda1 [HS-3]**. The well numbering system used for the RI/FS is explained in **Appendix A**.

Recent alluvial deposits do not crop out at the landfill. The shallow basin-fill deposits at the landfill were the target of the hydrogeologic investigation. Results of the Stage I drilling program suggest that the Upper Alluvium unit at the landfill occurs from land surface to a depth of about 270 feet. For the purpose of the RI/FS, the Upper Alluvium unit may be subdivided, in order of increasing depth, into the following units: upper alluvial deposits unit; basaltic lava-flow unit; Unit A (UA); and Unit B (UB).

Results indicate that a clay unit, which was encountered at a depth of 268 feet in exploration boring EX-1, may be the top of the Middle Alluvium unit. The landfill is near the outer limit of the area of occurrence reported for the Palo Verde clay. However, lithologic character of the clay unit encountered at a depth of 268 feet in exploration boring EX-1 indicates that the clay unit may be tentatively classified as the Palo Verde clay.

Upper Alluvial Deposits Unit

The upper alluvial deposits unit consists chiefly of interbedded silty sand and gravelly sand, with cobbles and siltstone interbeds, from land surface to an average depth of about 33 feet below land surface. The unit consists chiefly of interbedded clayey silt, silty clay, and sandy silt, with siltstone and claystone interbeds, in the average depth interval from 33 to 57 feet.

Basaltic Lava-flow Unit

The basaltic lava-flow unit consists chiefly of basaltic lava-flow rocks in the average depth interval from 57 to 72 feet below land surface. The lava-flow rocks are generally vesicular, and are generally weathered in the upper part of the unit. The unit is part of the Arlington Mesa basalt flow, which erupted from Arlington Mesa. Results from the Stage I drilling program indicate that the basaltic lava-flow unit dips gently to the northeast.

Unit A

The part of the Upper Alluvium unit from the base of the basaltic lava-flow unit to the top of the Middle Alluvium unit is the uppermost water-bearing part of the regional basin-fill deposits aquifer, and is classified into Units A and B. Unit A comprises the uppermost fine-grained water-bearing strata.

Unit A consists chiefly of interbedded clayey silt and silty clay, with a thin layer of interbedded sandy silt and siltstone. Unit A occurs in the average depth interval from 72 to 107 feet below land surface. On-site monitor wells MW-1UA, MW-2UA, MW-3UA, MW-4UA, and MW-5UA yield groundwater solely from Unit A.

Unit B

Unit B is bounded on the top by Unit A and on the bottom by the Middle Alluvium unit. The uppermost strata of Unit B is defined as the uppermost coarse-grained water-bearing strata of the regional aquifer. Unit B consists chiefly of interbedded coarse-grained and fine-grained strata. The fine-grained strata of Unit B are similar to Unit A, and consist chiefly of interbedded silty clay and clayey silt with some sand. The coarse-grained strata of Unit B consist chiefly of sand and gravel. Top of Unit B occurs at an average depth of 107 feet below land surface. Where penetrated by on-site exploration boring EX-1, Unit B occurs in the depth interval from 116 to 268 feet below land surface.

On-site monitor wells MW-1UB, MW-2UB, MW-3UB, and MW-4UB yield groundwater solely from the uppermost coarse-grained strata of Unit B and from several feet of the underlying fine-grained strata. During the Stage I investigation, the non-pumping water level in the Unit A monitor wells was more than 20 feet higher than the non-pumping water level in the Unit B monitor wells.

Palo Verde Clay

A unit consisting chiefly of silty clay was encountered at exploration boring EX-1, and was tentatively classified as the Palo Verde clay. At this location, top of the unit was penetrated at a depth of 268 feet below land surface. The Palo Verde clay appears to comprise a basal confining unit for Unit B.

Site Stratigraphy

Stratigraphic data for the units penetrated by 12 soil borings, an exploration boring, and 12 monitor wells are summarized as follows:

	DEPTH TO TOP OF UNIT (feet)	THICKNESS (feet)	
		RANGE	AVERAGE
BASIN-FILL DEPOSITS UNIT			
coarse-grained part	0	25 - 45	33
fine-grained part	25 - 45	12 - 35	25
BASALTIC LAVA-FLOW UNIT	39 - 68	12 - 29	17
UNIT A	67 - 82	32 - 44	36
UNIT B	101 - 116	152	152
PALO VERDE CLAY	268	---	---

SUPPLEMENTAL WORK PLAN

The scope of the Supplemental Work Plan for Stage II of the Remedial Investigation is described under TASKS B2, F1, F2, F3, and F4. The Sampling Plan for soil and water for Stage II is given in Appendix B. Table 2 gives quantities, types, and frequency of water, soil, and air samples to be obtained during Stage II, including Quality Assurance/ Quality Control (QA/QC) samples. A schedule graph for estimated project timing is shown on Figure 3.

The Remedial Investigation comprises seven principal TASKS:

TASK A: Source and Soil Evaluation

TASK B: Air Investigation
  B1: Stage I
  B2: Stage II

TASK C: Surface Sediment Investigation

TASK D: Groundwater Investigation - Stage I

TASK E: Groundwater Monitoring Program

TASK F: Stage II Investigation
  F1: Soil Evaluation
  F2: Groundwater Monitor Wells
  F3: Groundwater Monitoring Program
  F4: Stage III Investigation (if necessary)

TASK G: Remedial Investigation Analysis and Report

Within 15 days after the end of each calendar month during conduct of the RI/FS, Monthly Progress Reports will be submitted to EPA. As set forth in the Consent Order, these reports shall include:

- A description of progress made during the reporting period;
- A description of notable findings and events during the reporting period, including problems encountered and project delays;

- **A summary of items submitted to EPA under the Consent Order during the reporting period;**
- **A description of the work schedule during the next reporting period, including sampling and testing; and**
- **A description of deliverables to be submitted to EPA under the Consent Order during the next month.**

Results of Stage II will be given to EPA in monthly Data Submittals, as required by the Consent Order, and will be included in the draft Remedial Investigation Report.

TASK B2: STAGE II AIR INVESTIGATION

Task B of the comprehensive RI/FS Work Plan was developed by CRA to investigate the potential impacts on air quality from the former hazardous waste disposal area. This air investigation was completed during Stage I and is herein referred to as TASK B1. EPA qualified the representativeness of the TASK B1 data, based on quality assurance and quality control concerns. These concerns were based on the fact that the analytical laboratory did not meet the required holding times for analysis and some contamination unrelated to the landfill may have appeared in the samples.

Following discussions with EPA regarding approval of the draft Stage I Report, it was agreed that the air investigation would be repeated. The Stage II air investigation will be conducted by CRA in a manner similar to the Stage I air investigation, except extra precautions are proposed to minimize the potential for contaminants unrelated to the landfill to enter the sample and to ensure that the laboratory will meet the holding time requirements.

Air monitoring will be conducted at:

- **Five stations located on the perimeter of the hazardous waste area;**
- **One station (AMP-B) located over the existing lined excavation pit for cuttings disposal; and**
- **One station (AMP-A) located at or downwind from former waste disposal Pit 1.**

Approximate locations for these air monitoring stations are shown on **Figure 3a**. The final locations will be selected based on wind direction and site conditions at the time of sampling.

Concentrations of volatile organic compounds in air will be measured using Tenax (EPA method TO-1) and charcoal (EPA method TO-2) sorbent tubes. Sampling procedures for EPA methods TO-1 and TO-2 are given in **Appendix C**. Wind speed, wind direction, and temperature will be measured during air sampling operations. Barometric pressure and relative humidity data will be obtained from the National Weather Service at Sky Harbor Municipal Weather Office, Phoenix, Arizona.

One low-volume air sampling pump will be placed at each sampling location. Each pump will be set approximately five to six feet above ground surface. At sampling station AMP A **(Figure 3a)**, an additional sampling station will be used to obtain duplicate air samples. In addition to the collection of investigative and duplicate air samples, a trip blank and a field blank will be collected. The trip blank will consist of one Tenax tube and one charcoal tube, and will be removed from the shipping cooler without opening the tubes. The field blank will be handled in the same manner as the investigative sample tubes, except that no air will be drawn through it. All samples will be prepared for shipment to the laboratory in the same manner.

Before and after each air sample is collected and twice during the sampling period, the sampling pump will be calibrated using a representative sample calibration tube and sorbent media in line to assure that proper flow rates are maintained. A primary standard will be attached to the inlet of the sample calibration tube. The volume of air displaced and elapsed time will be recorded. The pre-sample, post-sample, and two intermediate flow rates will be recorded for each sampling period. Concentration calculations for the sample period will be based on the average of the four flow rates.

At each sampling station, a primary tube and a secondary tube will be connected in series; pumped air will enter the primary tube first. The primary tube will contain 1.6 grams of Tenax resin. The secondary tube will contain one gram of Tenax resin and one gram of charcoal; pumped air will pass through the Tenax resin before passing through the charcoal. Tenax resin adsorbs several of the volatile organic compounds reported to have been disposed in the hazardous waste area. The secondary tubes containing Tenax and charcoal are present to adsorb any volatile organic compounds that are not adsorbed in the primary tube due to break-through or other mechanisms. The sampling pump will be operated for a period of approximately eight hours and will be adjusted to pump a total air volume of approximately 20 liters. The investigation will be conducted during daylight hours, when atmospheric conditions would be most favorable for volatilization of volatile organic compounds.

Additional field sampling protocols are:

1. The culture tubes that contain the sorbent tubes will be marked with sample identification information. No marks will be made on the sorbent tubes. The culture tubes are used to provide a sanitary enclosure for the sorbent tubes and a barrier against artificial contamination.

2. Sorbent tubes will not be touched with bare hands. Disposable gloves will be used to handle the tubes.

3. After starting the sampler, the flow rate will be measured and the starting time, date, and temperature will be recorded.

4. The sorbent tubes will be removed from the culture tubes immediately prior to sampling and will be returned to the respective culture tubes immediately after sampling.

The Tenax-adsorbed samples will be collected in accordance with EPA method TO-1 **(Appendix C)**. The charcoal-adsorbed samples will be collected in accordance with EPA method TO-2 **(Appendix C)**. EPA method 8240 will be used to analyze the materials adsorbed.

Potential impacts on air quality will be addressed in the Remedial Investigation Report by a discussion of waste characteristics, by documentation of the integrity of the soil cover, and by analysis of results from air sampling. The assurance of no future impacts on air quality depends chiefly on the existence and maintenance of a sufficient soil cover. The information gathered during TASK B will be used in the Feasibility Study to evaluate the need for upgrading the soil cover as a remedial alternative. Field work for TASK B2 will be conducted prior to other field activities and, if practicable, during a period when the landfill is closed.

TASK F1: SOIL EVALUATION

Stage I investigations conducted by Montgomery & Associates have included delineation of the general boundaries of the former hazardous waste disposal area and the former disposal pits **(Figure 2)**, and the maximum potential extent of lateral migration of liquid wastes in the vadose zone from the hazardous waste area. The Stage II soil evaluation consists of a soil boring program to:

- **Characterize substances that may have seeped into the vadose zone from the four principal manifested disposal pits; and**
- **Generally characterize the potential extent of downward seepage of liquid wastes from these disposal pits.**

Results of TASK F1 will be used in the Feasibility Study to evaluate remedial alternatives.

To provide data for evaluation of the general extent of contaminant migration in the vadose zone, 12 soil borings were drilled and sampled during conduct of TASK A of the comprehensive Work Plan (Montgomery & Associates and CRA, 1988a). Results of TASK A indicate that volatile organic compounds were not detected and that concentrations of trace metals exceeding Maximum Contaminant Levels were not detected.

Four additional soil borings will be drilled under TASK F1 of the Supplemental Work Plan. One soil boring will be drilled at an angle to vertical beneath each of Pits 1, 2, 3, and 4 **(Figure 2)**. Location and angle of these four soil borings will depend on pit geometry and the capabilities of the drilling equipment. The edges of Pits 1, 2, 3, and 4 will be investigated by digging a shallow trench transverse to the expected north, south, east, and west edges of each pit. Final locations for the four proposed soil borings will be determined based on the trenching operations, and may be modified from the locations shown on **Figure 2**.

The soil borings will be drilled to auger refusal or until the basaltic lava-flow unit is encountered, whichever occurs first. Top of the basaltic lava-flow unit typically occurs at a depth ranging from 50 to 60 feet in the area of Pits 1, 2, 3, and 4. Soil samples for laboratory chemical analyses will be obtained from each of the borings at intervals to be selected by the on-site hydrogeologist based on data obtained during drilling; however, 10-foot sampling intervals, beginning at about five feet below land surface, are expected. A maximum of six to eight soil samples for laboratory chemical analyses will be obtained from each soil boring. For every 10 soil samples analyzed, a duplicate sample will be prepared from the soil samples by the chemical laboratory. Zones of low permeability, where contaminants in the vadose zone may tend to accumulate, will be targeted for sampling.

Because a wide range of substances are reported to have been disposed into Pits 1, 2, 3, and 4, all soil samples obtained for laboratory chemical analyses from soil borings will be analyzed for: volatile organic compounds using EPA method 8240; semi-volatile organic compounds using EPA method 8270;

pesticides and polychlorinated biphenyls (PCBs) using EPA method 8080; and eight metals (arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver) using the EPA EP Toxicity method. Duplicate soil samples will also be analyzed using these methods. Individual organic compounds to be analyzed with these methods are listed in the QAPP (Montgomery & Associates and CRA, 1988b). Soil samples will be obtained in accordance with the Sampling Plan given in **Appendix B**.

At the start of field operations, an excavation will be made in an unused part of the fenced hazardous waste area, near the excavation previously used for the Stage I investigation, and will be lined with a double layer of six-mil thickness plastic liner. This excavation will be used for placement of drill cuttings, drilling fluids, and rinse water. Materials in this lined excavation will remain exposed to the atmosphere for a period of several months, preferably summer months, after which a composite sample of the materials will be obtained and analyzed for: volatile organic compounds using EPA method 8240; semi-volatile organic compounds using EPA method 8270; pesticides and PCBs using EPA method 8080; the characteristic of EP Toxicity; and appropriate tests for determining characteristics of hazardous wastes. If, based on these laboratory chemical analyses, the materials in the lined excavation are not classified as hazardous, the excavation would be covered using soil from the landfill and the burial site would be marked at land surface. If the material is classified as hazardous, the fate of the materials would be decided as part of the Feasibility Study.

The soil borings will be drilled using a hollow-stem flight auger, preferably with the capability for continuous sampling. Prior to drilling the first soil boring and after drilling at each site, the auger drill stem and drilling tools will be cleaned using a hot, high-pressure, tap water rinse. Water solutions used to clean the drilling tools will be placed in the lined excavation in the hazardous waste area. Soil samples for lithologic descriptions will be obtained at five-foot intervals. Lithologic descriptions will also be prepared by the on-site hydrogeologist for soil samples obtained for laboratory chemical analyses. **Figure 4** shows the general format for lithologic descriptions. Soil moisture will be monitored closely by visual inspection. Drill cuttings samples, cores, and split-spoon samples that are not used for laboratory analyses, either will be placed in containers, labeled, and preserved, or will be disposed in the lined excavation. If split-spoon samplers are used, a record will be made of the number of blows required to drive the samplers for each depth interval sampled. After soil sample collection is complete, the soil borings will be back-filled from total depth to land surface with a slurry comprised of cement or Volclay grout. Each soil boring location will be marked at land surface. Excess drill cuttings will be placed in the second lined excavation in the hazardous waste area.

During soil boring operations, air quality in the work space will be monitored using a HNU portable gas analyzer. Procedures for air monitoring and personal protection are given in the Health and Safety Plan for the Remedial Investigation (Montgomery & Associates and CRA, 1988c).

Soil samples for laboratory chemical analyses will be obtained in clean four-inch or six-inch brass tube inserts. After sample collection, the ends of the brass tubes will be sealed with sheets of Teflon or aluminum, and plastic caps, and the samples will be stored on ice until delivery to the laboratory. For each sampling method, samples will be processed, sealed, cooled, and delivered to the laboratory as rapidly as possible to prevent excessive loss of volatile compounds prior to laboratory analysis.

Sampling tools will be cleaned before and after the collection of each sample for laboratory chemical analyses, according to the following procedure:

1. **Clean with hot, high-pressure, tap water spray;**
2. **Wash with trisodiumphosphate solution;**
3. **Rinse with tap water; and**
4. **Rinse with deionized water.**

Water solutions used to clean the sampling tools will be placed in the lined excavation in the hazardous waste area.

Climatological data for Buckeye, Arizona, indicate that the maximum daily temperature exceeds 90°F (degrees Fahrenheit) for more than 20 days per month during the period from May through October each year (Sellers and Hill, 1974). Review of information for heat stress exposure, given by the American Conference of Governmental Industrial Hygienists (1988), and the anticipated level of personal protective equipment indicates that November 1989 is the soonest that field work for the soil boring program should begin. Field operations for the soil boring program are scheduled to be complete three weeks after commencement. Review of laboratory chemical analyses for the soil samples would be complete about 13 weeks after completion of field operations **(Figure 3)**.

TASK F2: GROUNDWATER MONITOR WELLS

TASK F2 will include construction, testing, and equipping as many as five proposed on-site monitor wells. The purpose of these wells is:

- **to obtain data for lateral extent and potential source of contamination at monitor well MW-1UA and abandoned well site HS-1;**
- **to obtain hydrogeologic data, groundwater samples, and aquifer hydraulic parameters;**
- **to provide the basis for determining the need for additional groundwater investigations; and**
- **to provide a basis for selection of a remedial alternative for groundwater contamination.**

Locations for existing monitor wells and tentative locations for proposed monitor wells are shown on **Figure 5** (located in pocket inside back cover). Final locations for the proposed monitor wells will be cleared with

Maricopa County Landfill Department based on location of utilities and other potential hazards or obstructions, and may be modified slightly from the locations shown on **Figure 5**. Final locations will be submitted to EPA for approval. Construction details for the proposed monitor wells are shown on **Figure 6**.

TASK F2 includes construction, developing, testing, equipping, and sampling three to five proposed groundwater monitor wells, which would be completed in Unit A. The proposed monitor well sites are:

Well Site A:	Located approximately 10 to 20 feet downgradient from abandoned monitor well HS-1. The proposed monitor well at Site A will replace abandoned monitor well HS-1 and should provide water level and water quality data representative for Unit A.
Well Site B:	Located approximately 280 feet upgradient from monitor well MW-1UA, to define the lateral extent of groundwater contamination at well MW-1UA in an upgradient direction.
Well Site C:	Located outside the hazardous waste area, approximately 680 feet downgradient from monitor well MW-1UA and approximately 400 feet northwest, along the fence line for the landfill, from monitor well HS-2. Purpose for Site C is to define, together with existing monitor well HS-2, the lateral extent of groundwater contamination at well MW-1UA in a downgradient direction.
Well Site D:	Located on-site approximately 190 feet downgradient from abandoned monitor well HS-1. Site D is optional and will be drilled to define the lateral extent of groundwater contamination in a downgradient direction only if contamination is found in the monitor well constructed at Site A.
Well Site E:	Located approximately 200 feet south-southeast from abandoned monitor well HS-1. Site E is optional and will be drilled to define the lateral extent of groundwater contamination in a downgradient direction only if contamination is found in the monitor well constructed at Site A.

Laboratory chemical analyses for the most recent groundwater samples obtained by Montgomery & Associates from abandoned monitor well HS-1 indicate that volatile organic compounds were present in the groundwater sample at a total concentration of 1,716 micrograms per liter (μg/l). **Figure 7** is a schematic diagram of well construction for monitor well HS-1 prior to abandonment in 1988. Groundwater contamination has occurred at the HS-1 site, but it is inconclusive whether the contamination occurred via natural percolation through the vadose zone, via contaminant movement down the annulus of this monitor well, or via construction operations at the well. The proposed Unit A monitor well at Site A is designed to yield representative groundwater data for Unit A at a location that is near, but down-gradient from the HS-1 site.

Laboratory chemical analyses for the most recent groundwater samples obtained by Montgomery & Associates from existing on-site monitor well MW-1UA (**Figure 5**), indicates that volatile organic compounds were present in the groundwater sample at a concentration of 146 μg/l. **Figure 8** is a schematic diagram of well construction for monitor well MW-1UA. Proposed monitor well Sites B and C are located upgradient and downgradient from well MW-1UA, respectively (**Figure 5**). Results from the monitor wells at Sites B and C will be used to evaluate the upgradient and downgradient extent of the contamination detected in monitor well MW-1UA (**Figure 5**).

Groundwater samples from the proposed monitor well at Site A will be obtained and analyzed during construction of monitor wells at Sites B and C. If volatile organic compounds are not detected in the groundwater samples from the Site A monitor well, monitor wells at Sites D and E (**Figure 5**) will not be drilled. If volatile organic compounds are detected in these samples, monitor wells at Sites D and E will be drilled.

The groundwater sampling results will be used to determine the type and level of treatment needed to remediate groundwater. If no groundwater contamination is discerned from the proposed monitor well array, the wells would function as sentinel wells for early detection of potential future contaminant seepage into groundwater below the landfill.

Field work for TASK F2 can begin on completion of field work for TASK F1. Field work for TASK F2 will be scheduled to be complete within 13 weeks after drilling operations begin.

Well Construction

Technical specifications for construction, development, testing, and equipping of proposed monitor wells are given in Appendix B of the comprehensive Work Plan (Montgomery & Associates and CRA, 1988a). The specifications will be submitted to a selected drilling contractor and a drilling contract will be negotiated. The selected drilling contractor will possess a license from the Arizona Department of Water Resources and will have experience on similar projects. Permits will be obtained from Arizona Department of Water Resources to drill and, if necessary, to test the wells for aquifer parameters.

Montgomery & Associates will provide field inspection of drilling, construction, development, testing, equipping, and sampling operations for the proposed monitor wells. The air-rotary drilling method is preferred, and will be used where possible. If drilling conditions indicate that the wells can not be completed using the air-rotary drilling method, bentonite-base mud-rotary drilling methods will be used. The proposed casing schedule for each monitor well includes: 12-inch diameter blank steel surface casing set and cemented from land surface to a depth of 19 feet; eight-inch diameter blank steel conductor casing set and cemented from land surface to the top of the production interval; and four-inch diameter blank and perforated steel inner casing set, but not cemented, from land surface to total depth of the well. **Figure 6** is a schematic diagram of proposed well construction for the proposed monitor wells, which will be completed in Unit A (sandy silt/silty clay unit). The final zone of production for each well may differ slightly from that shown on **Figure 6**.

During drilling operations, the on-site hydrogeologist will obtain samples of drill cuttings at five-foot intervals and will prepare detailed lithologic descriptions. **Figure 4** shows the general format for lithologic descriptions. The drill cuttings samples either will be placed in containers, labeled, and preserved, or will be disposed in the lined excavation. Other data that will be obtained include: drill penetration rate; borehole geophysical logs; borehole conditions and reaction of rig during drilling; drilling mud viscosity; monitoring of air quality; water levels; quantities and types of materials used for well construction; and schematic diagrams of well construction.

Air quality in the work space will be monitored during drilling operations using a HNU portable gas analyzer. Procedures for air monitoring and personal safety are given in the Health and Safety Plan for the Remedial Investigation. Prior to drilling the first monitor well and after drilling the last monitor well, a sample of water used for drilling operations will be obtained from the driller's water truck and will be analyzed for volatile organic compounds using EPA method 601/602. Individual compounds to be analyzed with this method are listed in the QAPP (Montgomery & Associates and CRA, 1988b). Prior to drilling the first monitor well and after drilling at each monitor well, the drilling tools will be cleaned using a hot, high-pressure, tap water rinse. Drilling mud, together with water solutions used to clean the drilling tools, will be placed in the second lined excavation in the hazardous waste area.

Prior to setting the conductor casing, and again prior to setting the inner casing, borehole geophysical logs will be obtained for each monitor well. The logs will include: single point resistance, focused resistivity, spontaneous potential, natural gamma ray, and caliper. Optional logs may include gamma-gamma density and neutron-neutron porosity. Logging tools will be calibrated prior to logging, and portions of each borehole will be logged twice to check for repeatability of logging tool response. Analysis of borehole geophysical logs and lithologic descriptions of drill cuttings will provide a basis for accurate location of tops and bottoms of hydrogeologic units, for placement of perforated intervals in the wells, and for delineation of permeable strata through which groundwater flow may be concentrated.

Prior to setting the four-inch diameter inner casing, the casing will be washed using a trisodiumphosphate solution, if necessary, and/or cleaned using a hot, high-pressure, tap water rinse. After the inner casing is set, a sand/gravel pack will be installed via tremie pipe in the annular space between the inner casing and the 7-7/8-inch borehole wall (Figure 6). The sand/gravel pack will be clean, containerized material with a high silica content, and will be designed for the casing perforation size.

Well Development

After construction of each monitor well is complete, well development operations will be conducted to remove drilling fluids and to remove fine-grained sediments from the aquifer adjacent to the perforated interval. The monitor wells will be developed by air-lift pumping and surging until the air-lifted water is reasonably clear and sand-free within five minutes after a surge. If submergence is insufficient for air-lift pumping, the wells will be developed by bailing and/or by pumping with an electric submersible pump. On completion of development operations, the wells will be bailed to remove fill. Records will be made of water levels, pumping rate, and appearance and sediment load of pumped water during development operations.

Water removed from each monitor well during development operations will be discharged to an excavation adjacent to the well that is lined with a double layer of six-mil thickness plastic liner. Water discharged to these lined excavations will be allowed to evaporate naturally. Samples of the water removed from each monitor well during development operations will be obtained and analyzed for: volatile organic compounds using EPA method 624; semi-volatile organic compounds using EPA method 625; pesticides and PCBs using EPA method 608; cyanide; routine constituents; trace constituents; pH; and specific electrical conductance. Individual constituents to be analyzed with these EPA methods are listed in the QAPP (Montgomery & Associates and CRA, 1988b). These samples will comprise the TASK F2 sampling round no. 1 **(Table 2)**. For every 10 groundwater samples obtained, a duplicate groundwater sample and a field blank will be analyzed for the same suite of parameters **(Table 2)**. In addition, a trip blank will be analyzed for volatile organic compounds for each sample shipment. Results of these initial groundwater samples (TASK F2 round no. 1) will be used to screen for contaminants and to determine if water removed from the wells during pumping tests and sampling operations should also be contained in the lined excavations. If potential contaminants are not detected or are detected below Maximum Contaminant Levels, the water removed during pumping test and sampling operations will be discharged via a perforated hose or pipe to the land surface for evaporation.

Pumping Test Operations

Technical specifications for pumping test operations for the proposed monitor wells are given in Appendix B of the comprehensive Work Plan (Montgomery & Associates and CRA, 1988a). After development operations are complete, a short-term pumping test will be conducted at two or three monitor wells using an electric submersible test pump. The selection of wells to be tested will be based on pumping rates sustained during well development operations. Pumping test operations will consist of a brief preliminary test to determine potential pumping rates, a 12-hour pumping period, and a 12-hour water level recovery period. During the pumping period, on-site hydrologic personnel will make standard measurements of pumping rate, water levels in the pumped well and nearby wells, and sediment load, conductance, pH, and temperature of pumped water. Water levels will be measured to the nearest 0.01 foot using electrical water level sounders. The water level sounders, conductivity meter, and pH meter will be calibrated prior to the first pumping test and after the last pumping test. Groundwater samples for laboratory chemical analyses will be obtained from each pumped well near the end of the pumping period. Water samples will be obtained in accordance with the Sampling Plan given in **Appendix B**. During the recovery period, measurements of water level recovery will be made. Results of pumping test operations will be analyzed for aquifer transmissivity, storage coefficient, and hydraulic conductivity. These data will be required for computations of groundwater flow velocities, and for evaluation of potential remedial alternatives.

The pumping tests will be designed to meet applicable Arizona Department of Water Resources standards. Capacity of the test pump will be determined based on hydrogeologic conditions encountered during well construction, results of development operations, and depth to water. Components of the pump assembly will be cleaned prior to installation by:

1. Washing in a trisodiumphosphate solution; and
2. Rinsing with a hot, high-pressure, tap water spray.

A rigid one-inch diameter PVC sounder access pipe will be attached to the pump column pipe from land surface to the top of the pump. The sounder access pipe will be capped and perforated in the bottom five to 10 feet. Pre-pumping water level in the proposed monitor wells will be measured prior to starting each test.

The discharge assembly for the pumped well will consist of a horizontal section of steel discharge pipe extending at least 20 feet from the wellhead. If sediment load of the pumped water is negligible, a totalizing flow meter with an instantaneous flow rate indicator needle will be installed on the discharge pipe 10 feet from the wellhead. A 45-degree rise in the discharge pipe will be installed five feet downstream from the flowmeter to ensure full pipe flow through the meter. A pressure gauge will be installed on the top of the discharge pipe at the wellhead. A gate valve to control discharge will be installed between the pressure gauge and the flowmeter. A hose bib for collection of water samples will be installed on the discharge line between the pressure gauge and the gate valve. Pumping rate will be measured using the flowmeter and by measuring the time required to fill a container of known volume.

If contaminants are not detected or are detected below the Maximum Contaminant Levels in the initial TASK F2 water samples obtained from the pumped wells during development operations, then water withdrawn during pumping test operations will be discharged via a perforated hose or pipe to the land surface for evaporation. If contaminants are detected above the Maximum Contaminant Levels in the initial TASK F2 water samples, then water withdrawn during pumping test operations will be discharged to excavations adjacent to the wells that are lined with a double layer of six-mil thickness plastic liner. Water discharged to these lined excavations will be allowed to evaporate naturally.

Near the end of the pumping period for each pumping test, groundwater samples for laboratory chemical analyses will be obtained from the discharge pipe. In addition, groundwater samples will be obtained for TASK F2 from wells that are not selected for conduct of pumping tests. Because a wide range of substances were disposed at the landfill, these TASK F2 round no. 2 groundwater samples will be analyzed for: volatile organic compounds using EPA method 624; semi-volatile organic compounds using EPA method 625; pesticides and PCBs using EPA method 608; cyanide; routine constituents; trace constituents; pH; and specific electrical conductance. Individual constituents to be analyzed with these EPA methods are listed in the QAPP (Montgomery & Associates and CRA, 1988b). For every 10 groundwater samples obtained, a duplicate groundwater sample and a field blank will be analyzed for the same suite of parameters **(Table 2)**. In addition, a trip blank will be analyzed for volatile organic compounds for each sample shipment.

Completion of Wellhead and Permanent Pumps

Technical specifications for completion of wellheads and for equipping the proposed monitor wells are given in Appendix B of the comprehensive Work Plan (Montgomery & Associates and CRA, 1988a). On completion of pumping test operations for selected wells and on completion of development operations for wells not selected for testing, permanent electric submersible pumps will be installed for future collection of groundwater samples. Pump capacity and pump depth setting will be specified after results of the development and pumping test operations have been analyzed. A rigid one-inch diameter PVC sounder access pipe will be attached to the pump column pipe from land surface to the top of the pump, using stainless steel clamps. All wiring will meet local safety codes. The submersible pump assemblies will be suspended from a sanitary well seal. Components of the pump assemblies will be new and will be cleaned prior to installation by:

1. **Washing in a trisodiumphosphate solution; and**
2. **Rinsing with a hot, high-pressure, tap water spray.**

Figure 9 is a schematic diagram for the permanent pump assembly. If nonaqueous hydrocarbon phase liquids are detected in any of the proposed Unit A monitor wells, those wells will not be equipped with permanent submersible pumps.

The wellheads for the proposed monitor wells will be completed above land surface in locking vaults **(Figure 6)**. A six-foot by six-foot by four-inch cement pad will be installed at each wellhead. Altitude and location of each wellhead will be surveyed to the nearest 0.1 foot to provide a datum for water level measurements. Four barrier posts, consisting of four-inch diameter blank steel casing cemented in place, will be constructed around each monitor well to protect the wells from damage by vehicles or landfill equipment. The barrier posts and well vault will be painted to increase visibility.

The identification number for each monitor well will be welded on the outside of the surface vault, and on the four-inch blank steel inner casing that extends above the cement pad.

TASK F3: GROUNDWATER MONITORING PROGRAM

The objective of TASK F3 is to extend the groundwater monitoring program established under TASK G of the comprehensive Work Plan (Montgomery & Associates and CRA, 1988a). Results of the monitoring program will be used to document groundwater quality and to detect changes in rate and direction of groundwater movement. The monitoring program will comprise three rounds of groundwater sampling and measurement of groundwater levels.

TASK F3 sampling round no. 1 will be conducted during summer 1989 and will comprise collection of groundwater samples and measurement of water levels at the 11 existing on-site monitor wells. TASK F3 sampling round no. 2 would be conducted approximately 30 days after completion of field operations for TASK F2, and will comprise collection of groundwater samples and measurement of water levels at the new and existing on-site monitor wells. TASK F3 sampling round no. 3 would be conducted 13 weeks after TASK F3 sampling round no. 2, and would be identical to round no. 2. Results from TASKS F2 and F3 sampling rounds will be given to EPA in monthly data submittals, as required in the Consent Order.

For all TASK F3 sampling rounds, groundwater samples from the 11 existing on-site monitor wells will be analyzed for: volatile organic compounds using EPA method 601/602; routine constituents; selected trace constituents previously detected; pH; and specific electrical conductance. The TASK F3 groundwater samples obtained from new monitor wells constructed under TASK F2 will be analyzed for: volatile organic compounds using EPA method 601/602; routine constituents; pH; specific electrical conductance; and any other constituents detected in groundwater samples obtained during TASK F2. Individual constituents to be analyzed with these EPA methods are listed in the QAPP (Montgomery & Associates and CRA, 1988b).

In addition, selected groundwater samples obtained during TASK F3 sampling round no. 2 and sampling round no. 3 will be analyzed for the following constituents not listed in the QAPP (Montgomery & Associates and

CRA, 1988b): nitrite using EPA method 353.2; total Kjeldahl nitrogen (TKN) using EPA method 351.2; total organic carbon (TOC) using EPA method 415.2; oil and grease using EPA method 413.1; chemical oxygen demand (COD) using modified EPA method 410.4; and biochemical oxygen demand (BOD) using EPA method 405.1. These additional constituents were requested by CRA to provide data for treatability of groundwater. Wells proposed for supplemental sampling and analysis are: Unit A monitor well MW-1UA; proposed Unit A monitor wells A, B, D, and E; and Unit B monitor wells MW-1UB and MW-4UB.

For every 10 groundwater samples obtained, a duplicate groundwater sample and a field blank will be analyzed for the same suite of parameters **(Table 2)**. In addition, a trip blank will be analyzed for volatile organic compounds for each sample shipment.

Groundwater samples will be obtained in accordance with the Sampling Plan given in **Appendix B**. Samples will be pumped from the wells using electric submersible pumps. Field measurements of water level, pumping rate, and pH, conductance, and temperature of pumped water will be made for each well. Water levels will be measured using an electrical sounder. Samples will be obtained when three borehole volumes have been pumped from a well or when conductance and pH of the pumped water have stabilized, whichever takes longer.

If contaminants are not detected in the TASK F2 groundwater samples, or are detected at concentrations below the Maximum Contaminant Levels, then water pumped from the wells during TASK F3 sampling operations will be discharged via a perforated hose or pipe to the land surface for evaporation. If contaminants are detected above the Maximum Contaminant Levels in the TASK F2 water samples, then water pumped from the wells during TASK F3 sampling operations will be discharged to excavations adjacent to the wells that are lined with a double layer of six-mil thickness plastic liner. Water discharged to these lined excavations will be allowed to evaporate naturally.

If nonaqueous hydrocarbon phase liquids occur on the water surface in any Unit A well, that well will not be equipped with a permanent submersible pump and subsequent samples from the well will be obtained by bailing. For these conditions, samples would be bailed from the uppermost five feet of water in the well using a clear Teflon or acrylic bailer. The filled bailer would be visually inspected for thickness and character of the hydrocarbon phase. In addition, an ORS Interface Probe would be used to measure water level and free product thickness in the well. A sample of the hydrocarbons would be analyzed for total petroleum hydrocarbons (TPH) using modified EPA method 8015 and for volatile organic compounds using EPA method 624 **(Table 2)**. Individual compounds to be analyzed by these methods are given in the QAPP (Montgomery & Associates and CRA, 1988b).

TASK F4: STAGE III INVESTIGATION (if necessary)

The necessity and scope of TASK F4 will depend on results of TASKS B2, F1, F2, and F3. The objective of TASK F4 would be to conduct any additional field work necessary for completion of the RI/FS. If TASK F4 would be required, a Stage III Supplemental Work Plan would be prepared and submitted to EPA. The Supplemental Work Plan would delineate the sequence of events leading to review of results for TASK F4 and to finalization of the Remedial Investigation prior to undertaking the report preparation (TASK G).

ESTIMATED PROJECT TIMING

Figure 3 is a schedule graph for estimated project timing, excluding TASK F4. Initial work for TASK B2 of the Remedial Investigation would begin in October 1989. Excluding TASK F4, completion of the Remedial Investigation may require about 155 weeks (36 months) from the effective date of the Consent Order, which was February 19, 1988. In the event that TASK F4 would be required, an additional six to 12 months or more may be necessary for completion of the Remedial Investigation. Completion of the Feasibility Study may occur within about 73 weeks (17 months) after completion of the Remedial Investigation.

The time schedule set forth in the Consent Order includes time for regulatory agency review at key points in the RI/FS and time for the EPA risk assessment. Changes in time allotted for regulatory agency review and comment during the RI/FS, or for the risk assessment, would necessarily require adjustments in the estimated project timing described in the Supplemental Work Plan and shown on **Figure 3**.

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TABLES

TABLE 1. SUMMARY OF WASTES DISPOSED
HASSAYAMPA LANDFILL MARICOPA COUNTY, ARIZONA
(MODIFIED FROM ARIZONA DEPARTMENT OF HEALTH SERVICES, 1985)

		QUANTITY	
PIT	WASTE TYPE DESIGNATED	LIQUID WASTE (gallons)	SOLID WASTE (tons)
SPECIAL PIT	INCOMPATIBLE HAZARDOUS WASTE	134,578	308.64
PIT 1	ORGANICS & OILS	360,805	0
PIT 2	ACIDS & ACID SLUDGES	125,597	0.1
PIT 3	ALKALINE & METALLIC SLUDGES	1,362,636	24.5
PIT 4	PESTICIDES & ALKALINE SLUDGES	1,295,022.2	3,816.46
	TOTAL	3,278,638.25	4,149.7

TABLE 2. SUMMARY OF STAGE II SAMPLING PROGRAM
HASSAYAMPA LANDFILL, MARICOPA COUNTY, ARIZONA

	..INVESTIGATIVE SAMPLES..			..............QA/QC SAMPLES ...DUPLICATE SAMPLES[a]...			......FIELD BLANKS[b].....			......TRIP BLANKS[c]......					
	NUMBER	FREQUENCY	TOTAL	NUMBER	FREQUENCY	TOTAL	NUMBER	FREQUENCY	TOTAL	NUMBER	FREQUENCY	TOTAL	GRAND TOTAL	ASSUMED[d] CONCENTRATION	TYPE OF ANALYSIS[e]
WATER SAMPLES[f]															
Task F2 Round 1															
5 New Wells															
w/o HC phase	5	1	5	1	1	1	1	1	1	1	1	1	8	L	624, 625, 608, cyanide, routine, trace
w/HC phase	5	1	5	1	1	1	1	1	1	1	1	1	8	H	624, 8015 (modified)
Task F2 Round 2															
5 New Wells															
w/o HC phase	5	1	5	1	1	1	1	1	1	1	1	1	8	L	624, 625, 608, cyanide, routine, trace
w/HC phase	5	1	5	1	1	1	1	1	1	1	1	1	8	H	624, 8015 (modified)
Task F3 Round 1															
11 Existing Wells	11	1	11	2	1	2	2	1	2	2	1	2	17	L	601/602, routine, selected trace
Task F3 Round 2															
11 Existing Wells	11	1	11	2	1	2	2	1	2	2	1	2	17	L	601/602, routine, selected trace
7 Selected Wells	7	1	7	1	1	1	1	1	1	0	0	0	9	L	TKN, TOC, COD, BOD, nitrite, oil & grease
5 New Wells															
w/o HC phase	5	1	5	1	1	1	1	1	1	1	1	1	8	L	601/602; routine; (plus any previously detected parameters)
w/HC phase	5	1	5	1	1	1	1	1	1	1	1	1	8	H	601/602, 8015 (modified)
Task F3 Round 3															
11 Existing Wells	11	1	11	2	1	2	2	1	2	2	1	2	17	L	601/602, routine, selected trace
7 Selected Wells	7	1	7	1	1	1	1	1	1	0	0	0	9	L	TKN, TOC, COD, BOD, nitrite, oil & grease
5 New Wells															
w/o HC phase	5	1	5	1	1	1	1	1	1	1	1	1	8	L	601/602; routine; (plus any previously detected parameters)
w/HC phase	5	1	5	1	1	1	1	1	1	1	1	1	8	H	601/602, 8015 (modified)
Drilling Water	1	2	2	0	0	0	0	0	0	1	2	2	4	L	601/602

TABLE 2. SUMMARY OF STAGE II SAMPLING PROGRAM
HASSAYAMPA LANDFILL, MARICOPA COUNTY, ARIZONA

	..INVESTIGATIVE SAMPLES..			....QA/QC SAMPLES....											
				...DUPLICATE SAMPLES[a]...			......FIELD BLANKS[b].....			......TRIP BLANKS[c]......			GRAND	ASSUMED[d]	
	NUMBER	FREQUENCY	TOTAL	NUMBER	FREQUENCY	TOTAL	NUMBER	FREQUENCY	TOTAL	NUMBER	FREQUENCY	TOTAL	TOTAL	CONCENTRATION	TYPE OF ANALYSIS[e]
TASK F1 SOIL SAMPLES															
4 Soil Borings	32	1	32	4	1	4	0	0	0	0	0	0	36	H	8240, 8270, 8080, EP Toxicity metals
Lined Excavation	1	1	1	1	1	1	0	0	0	0	0	0	2	H	8240, 8270, 8080, EP Toxicity, CERCLA characteristics of hazardous waste
AIR SAMPLES	7	1	7	1	1	1	1	1	1	1	1	1	10	L	TO-1, TO-2, 8240

[a] Duplicates of soil samples for laboratory chemical analyses will be prepared by the laboratory

[b] Field blanks for water chemical analyses will be prepared using bottled deionized water

[c] Trip blanks for water chemical analyses will be prepared by the laboratory prior to field operations

[d] H = High
L = Low

[e] Numbers refer to EPA method numbers
TKN = Total Kjeldahl nitrogen
TOC = Total organic carbon
COD = Chemical oxygen demand
BOD = Biochemical oxygen demand

[f] HC - Nonaqueous hydrocarbon phase

NOTE: Frequency indicates the number of times the sample source will be sampled for the indicated sampling round and/or analysis.

TABLE 3. SUMMARY OF SAMPLING REQUIREMENTS
HASSAYAMPA LANDFILL, MARICOPA COUNTY, ARIZONA

PARAMETER (Analyses Method)	MATRIX	CONTAINER	PRESERVATION	MAXIMUM HOLDING TIME FOR PROJECT
Volatile Organic Compounds (EPA methods 624/8240 or 601/602)	Water	Two 40-ml glass vials with Teflon-lined septa	Add 4 drops 1:1 HCl, Refrigerate	14 days
	Soil	400-ml mason jar with Teflon-lined lid, or 4-6 inch brass tube with Teflon/aluminum lined endcaps	Refrigerate	14 days
Semi-Volatile Organics, Pesticides, or PCB's (EPA methods 625/8270 and 608/8080)	Water	Four 1-liter amber glass bottles with Teflon-lined screwcaps	Refrigerate	7 days prior to extraction; 40 days after extraction
	Soil	400-ml mason jar with Teflon/aluminum lined lid	Refrigerate	7 days prior to extraction; 40 days after extraction
Total Petroleum Hydrocarbons (modified EPA method 8015)	Water	Two 40-ml glass vials with Teflon-lined septa	Add 4 drops 1:1 HCl, Refrigerate	14 days
Trace Elements (general)	Water	1-liter plastic bottle	Filter immediately, add 1:1 HNO_3 to pH<2, Refrigerate	28 days
	Soil	One mason jar with Teflon/aluminum lined lid, or 4-6 inch brass tube with Teflon/aluminum lined endcaps	Refrigerate	28 days
Routine Constituents (general)	Water	1-liter plastic bottle	Filter & Refrigerate	28 days
Cyanide (total) (EPA method 335.2)	Water	1-liter plastic bottle	Add NaOH to pH>12 Refrigerate	14 days
Ammonia, Nitrate (EPA methods 350.3 and 353.2)	Water	1-liter	Add 1:1 H_2SO_4 to pH <2 Refrigerate	28 days
Nitrite (EPA method 353.2)	Water	500-ml plastic bottle	Add 1:1 H_2SO_4 to pH <2 Refrigerate	48 hours

TABLE 3. SUMMARY OF SAMPLING REQUIREMENTS
HASSAYAMPA LANDFILL, MARICOPA COUNTY, ARIZONA

PARAMETER (Analyses Method)	MATRIX	CONTAINER	PRESERVATION	MAXIMUM HOLDING TIME FOR PROJECT
Total Kjeldahl Nitrogen (TKN) (EPA method 351.2)	Water	1-liter plastic bottle	Add 1:1 H_2SO_4 to pH <2 Refrigerate	28 days
Total Organic Carbon (TOC) (EPA method 415.2)	Water	250-ml amber glass bottle	Add 1:1 H_2SO_4 to pH <2 Refrigerate	28 days
Phosphate (EPA method 365.3) + Chemical Oxygen Demand (COD) (Modified EPA method 410.4)	Water	1-liter plastic bottle	Add 1:1 H_2SO_4 to pH <2 Refrigerate	28 days
Biochemical Oxygen Demand (BOD) (EPA method 405.1)	Water	1-liter plastic bottle	Refrigerate	48 hours
Oil and Grease (EPA method 413.1)	Water	1-liter glass bottle	Add 1:1 H_2SO_4 to pH <2 Refrigerate	28 days

ILLUSTRATIONS

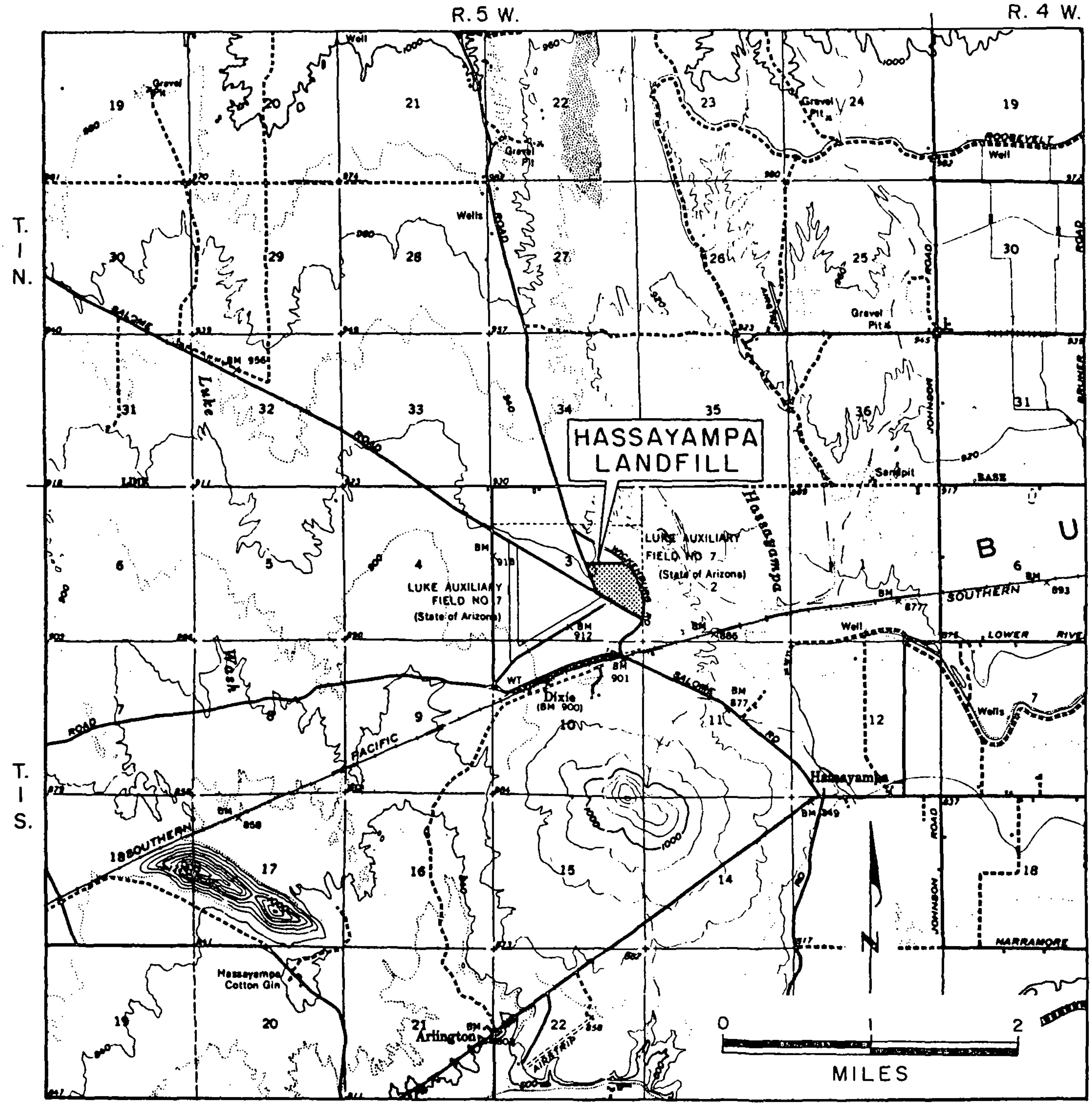
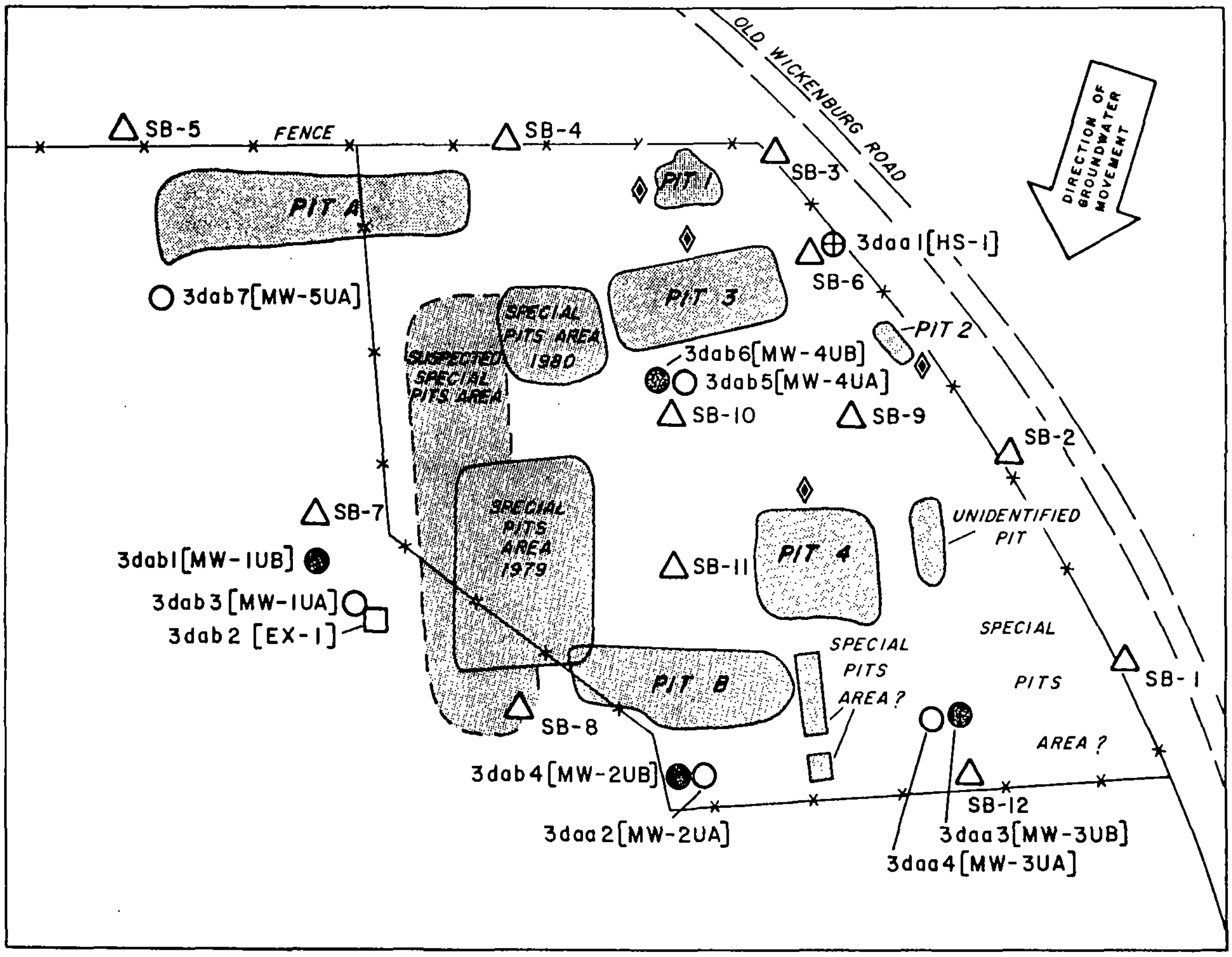
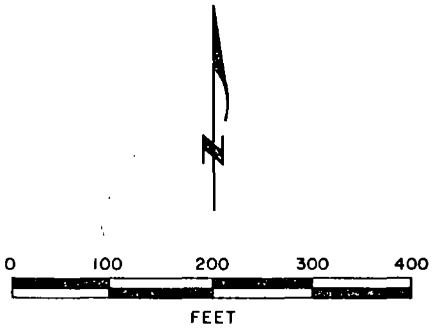


FIGURE 1. REGIONAL LOCATION MAP

ERROL L. MONTGOMERY & ASSOCIATES, INC.
CONSULTANTS IN HYDROGEOLOGY
TUCSON, ARIZONA





EXPLANATION

△ SB-1	SOIL BORING
○ 3dab3 [MW-1UA]	UNIT A MONITOR WELL
● 3dab1[MW-1UB]	UNIT B MONITOR WELL
☐ 3dab2 [EX-1]	EXPLORATION BORING
⊕ 3daa1[HS-1]	ABANDONED MONITOR WELL Constructed by Arizona Department of Health Services
◆	PROPOSED SOIL BORING
PIT 1	DISPOSAL PIT: locations and boundaries of disposal pits are based on analysis of a January 26, 1981, aerial photo and on reports; locations and boundaries are *tentative and approximate*

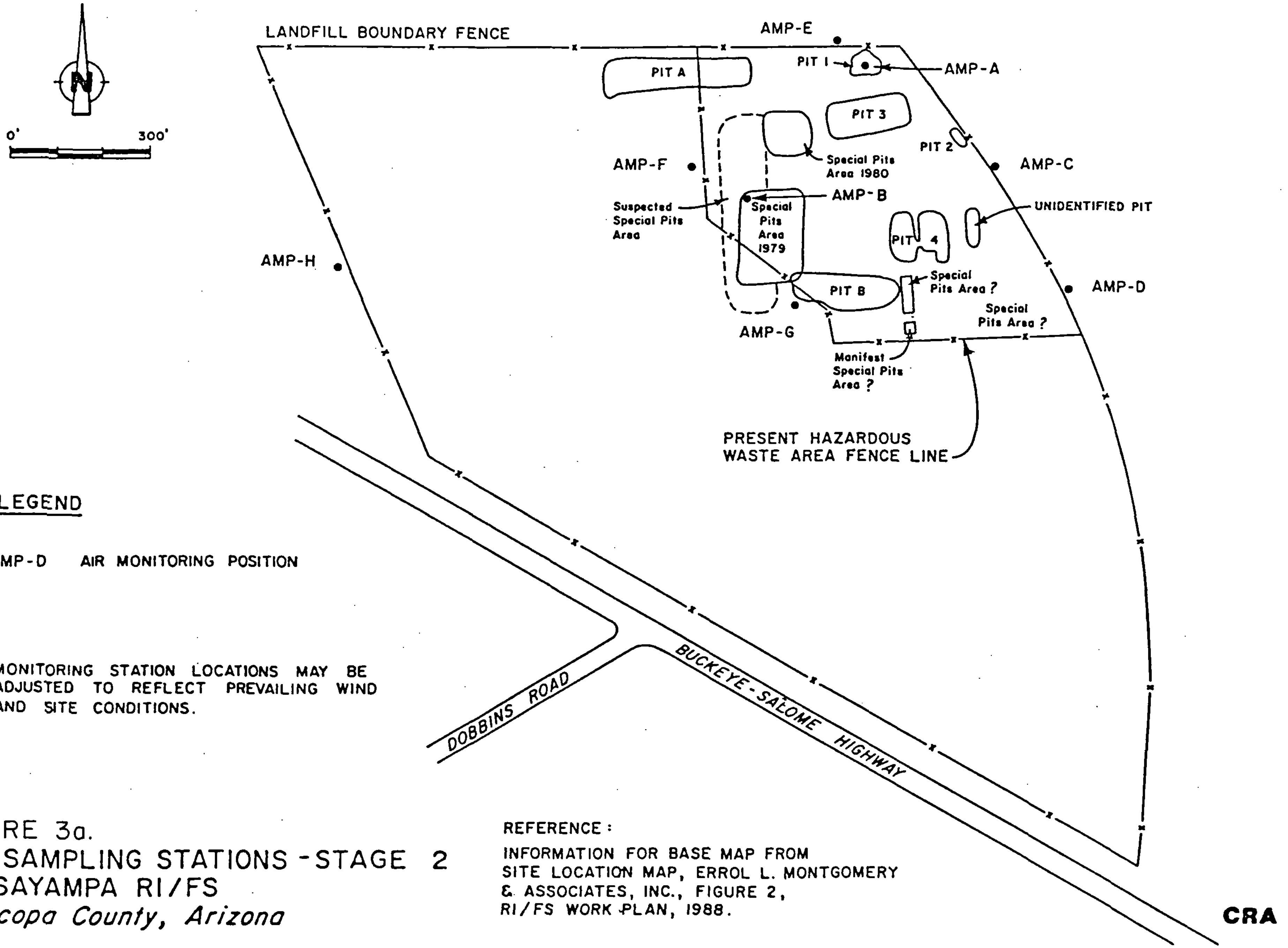
HASSAYAMPA LANDFILL
MARICOPA COUNTY, ARIZONA

LOCATION MAP FOR FORMER HAZARDOUS WASTE AREA

ERROL L. MONTGOMERY & ASSOCIATES, INC.
CONSULTANTS IN HYDROGEOLOGY
TUCSON, ARIZONA

1989

FIGURE 2



LEGEND

● AMP-D AIR MONITORING POSITION

NOTE: MONITORING STATION LOCATIONS MAY BE ADJUSTED TO REFLECT PREVAILING WIND AND SITE CONDITIONS.

FIGURE 3a.
AIR SAMPLING STATIONS - STAGE 2
HASSAYAMPA RI/FS
Maricopa County, Arizona

REFERENCE:
INFORMATION FOR BASE MAP FROM SITE LOCATION MAP, ERROL L. MONTGOMERY & ASSOCIATES, INC., FIGURE 2, RI/FS WORK PLAN, 1988.

CRA

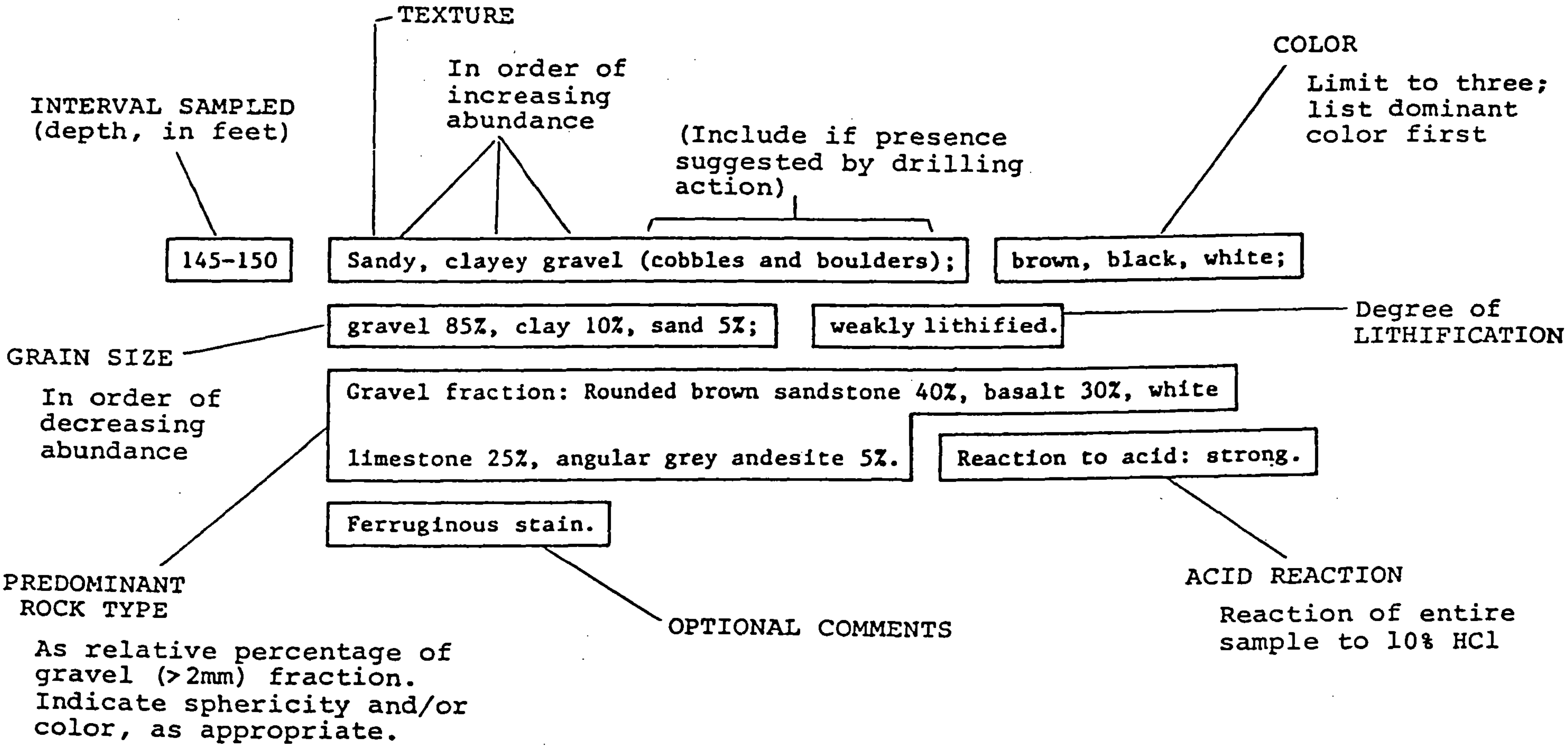
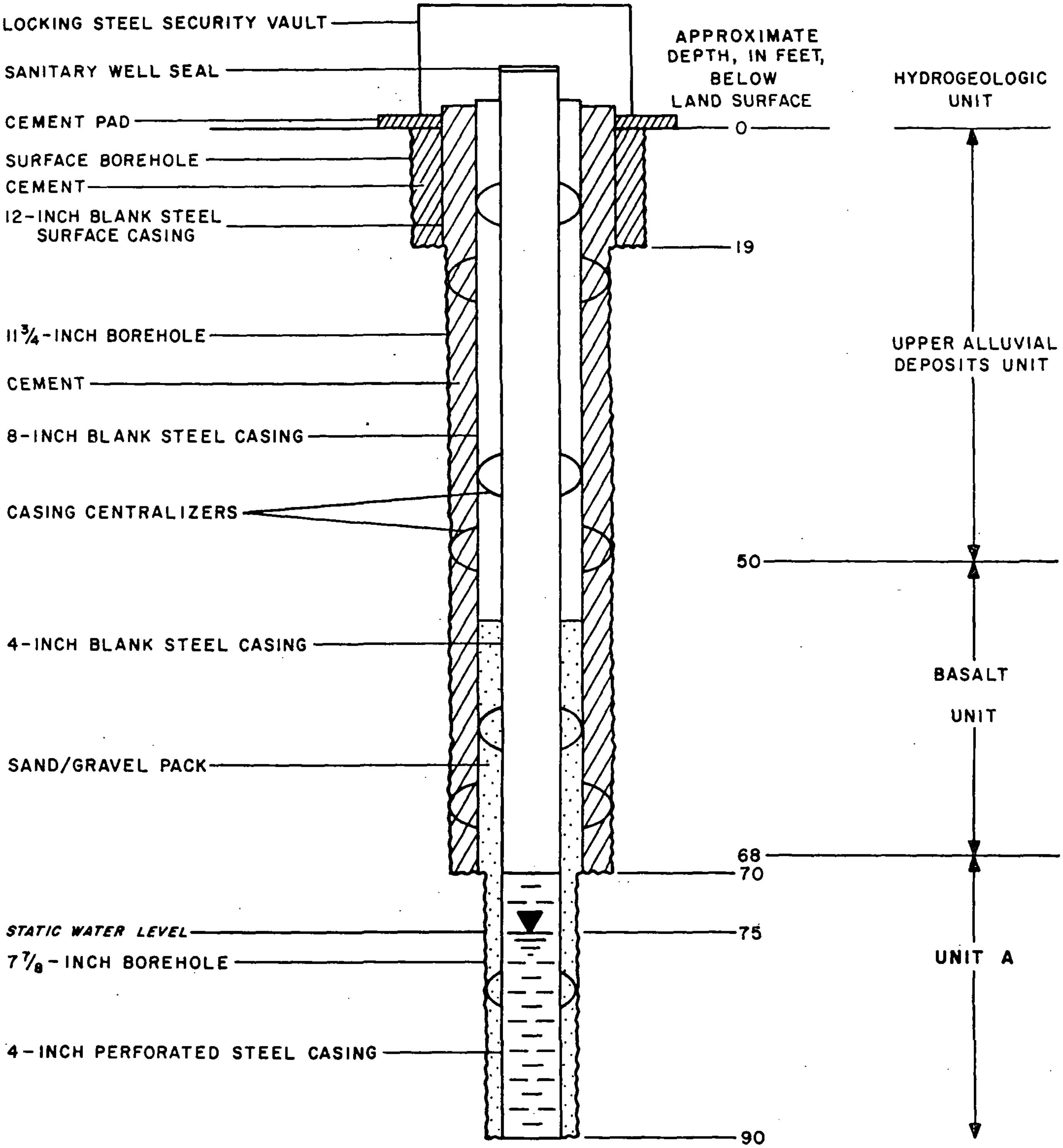
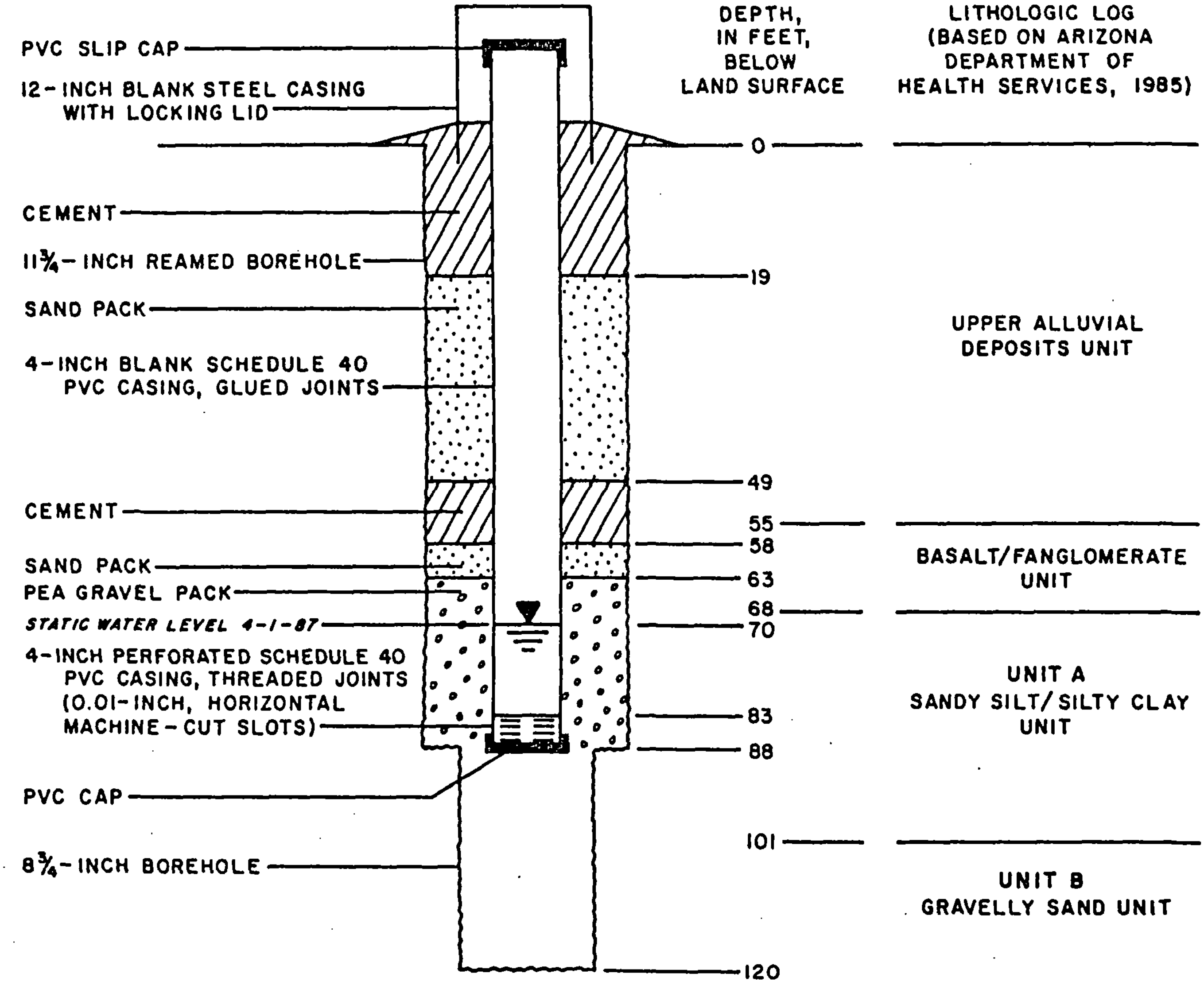


FIGURE 4. GENERAL FORMAT FOR LITHOLOGIC DESCRIPTION



NOTE: CONTRACTOR WILL INSTALL PERMANENT SUBMERSIBLE PUMP

FIGURE 6. SCHEMATIC DIAGRAM OF PROPOSED UNIT A MONITOR WELL



PERFORATED INTERVAL IS BASED ON TV VIDEO SURVEY CONDUCTED 4-1-87

FIGURE 7. SCHEMATIC DIAGRAM OF WELL CONSTRUCTION FOR MONITOR WELL (C-1-5)3daa [HS-1]

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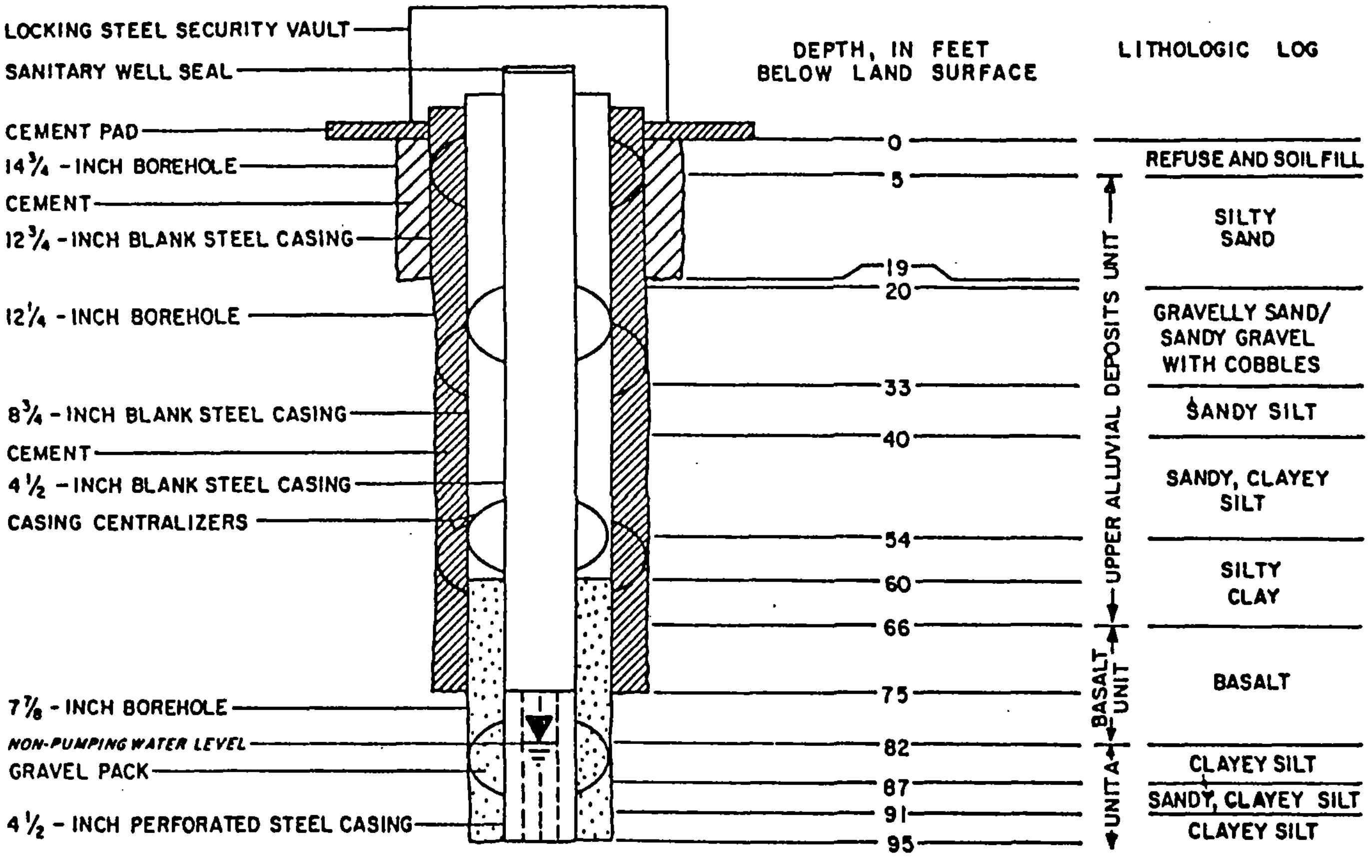


FIGURE 8. SCHEMATIC DIAGRAM OF WELL CONSTRUCTION FOR UNIT A MONITOR WELL (C-1-5)3dab$_3$ [MW-1UA]

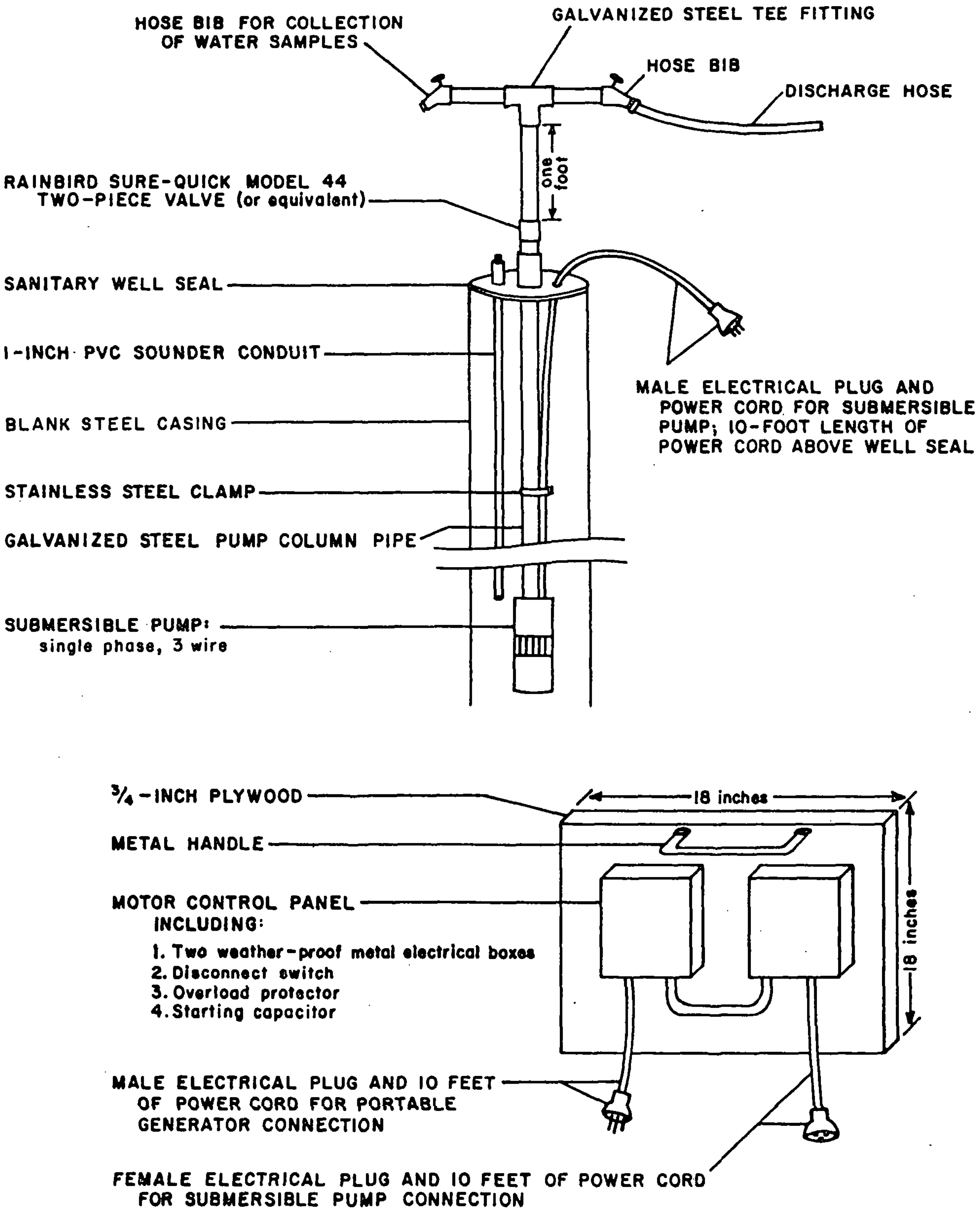


FIGURE 9. SCHEMATIC DIAGRAM FOR PERMANENT WELL HEAD AND PORTABLE MOTOR CONTROL PANEL

Computing minutes required
to pump five B.H. volumes:
(T.D.-P.W.L.)(÷Q)= ________ minutes
(   )(   )
,

ERROL L. MONTGOMERY & ASSOCIATES, INC.

WATER LEVEL RECORD SHEET (Previous measured W.L.____)   Page ______

______ Sampling Round

PUMPED WELL____________________

Computed Sampling
Time ________Hrs.

Measuring Point ______Top of____________________

______which is______________ft. above land surface.

Well Location: T.________, R.__________, Sec.__________

Well Coordinates: ______________________ft N.

Elevation of Measuring Point ____________________ft
above mean sea level.

______________________ft E.

STATIC WATER LEVEL: ______________

Pump Intake ______________ ft.BMP

DATE/TIME AFTER PUMPING STARTED (MINUTES)	HOUR	DEPTH TO WATER (FEET)			PUMPING RATE (GPM)	DRAWDOWN (FT.)		REMARKS (INCLUDE METHOD OF MEASUREMENT)
		HELD	WET	DEPTH				secs per ___gal.discharge
SOUNDER USED: #								
CONDUCTIVITY METER/PROBE USED: # /#								
pH METER/PROBE USED: # /#								

FIGURE 10. FIELD DATA FORM FOR PUMPED WELL

ERROL L. MONTGOMERY & ASSOCIATES, INC.
CONSULTANTS IN HYDROGEOLOGY
1075 EAST FORT LOWELL ROAD, SUITE B
TUCSON, ARIZONA 85719 (602) 881-4912
TELEX: 165597 MONTE TUC

CHAIN OF CUSTODY
TRAFFIC REPORT

Sample Number

Project No. ________

☐ Organic
☐ Inorganic

☐ Grab
☐ Composite

☐ Soil
☐ Water
☐ Other ____________________

Sampling Site Name/Code/Well No. ____________________

Sampling Date ____________________ and Time of Collection ____________________

Sampling Personnel:

Name ____________________ Signature ____________________

Name ____________________ Signature ____________________

Name ____________________ Signature ____________________

Sampling Point ____________________ and Method of Sampling ____________________

Field Observations ____

Sample, Sample Container Data

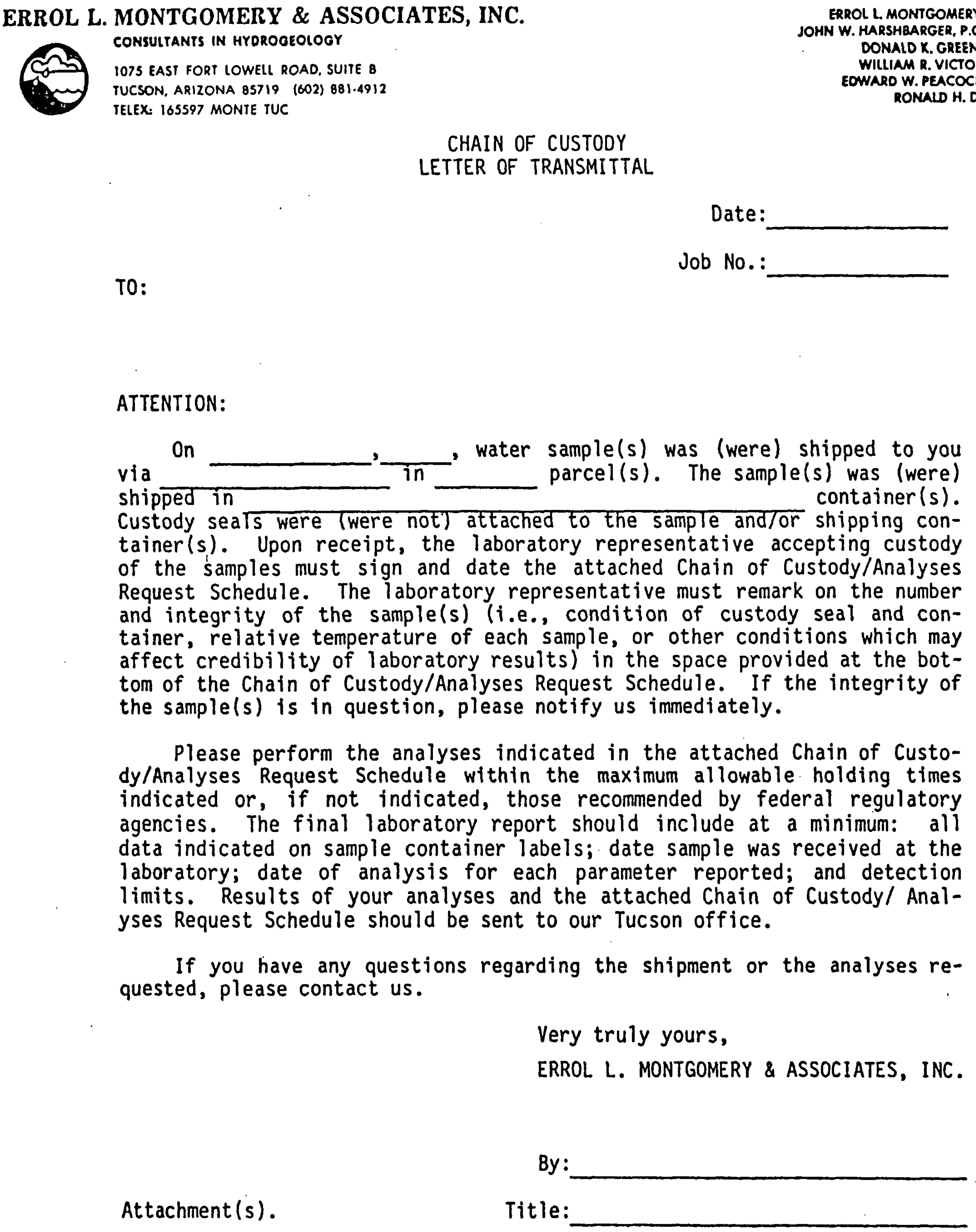
Volume	No. Used	Lot No.	Preservatives	Analyses Needed	Destin.	Ship. Method/Date

Special Handling Procedures ____

____

____

FIGURE 11. CHAIN OF CUSTODY TRAFFIC REPORT



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1075 EAST FORT LOWELL ROAD, SUITE B
TUCSON, ARIZONA 85719 (602) 881-4912
TELEX: 165597 MONTE TUC

ERROL L. MONTGOMERY, P.G.
JOHN W. HARSHBARGER, P.G., P.E.
DONALD K. GREENE, P.E.
WILLIAM R. VICTOR, P.G.
EDWARD W. PEACOCK, P.G.
RONALD H. DEWITT

CHAIN OF CUSTODY
LETTER OF TRANSMITTAL

Date: ______________

Job No.: ______________

TO:

ATTENTION:

On ____________, _____, water sample(s) was (were) shipped to you via _________________ in ________ parcel(s). The sample(s) was (were) shipped in ________________________________ container(s). Custody seals were (were not) attached to the sample and/or shipping container(s). Upon receipt, the laboratory representative accepting custody of the samples must sign and date the attached Chain of Custody/Analyses Request Schedule. The laboratory representative must remark on the number and integrity of the sample(s) (i.e., condition of custody seal and container, relative temperature of each sample, or other conditions which may affect credibility of laboratory results) in the space provided at the bottom of the Chain of Custody/Analyses Request Schedule. If the integrity of the sample(s) is in question, please notify us immediately.

Please perform the analyses indicated in the attached Chain of Custody/Analyses Request Schedule within the maximum allowable holding times indicated or, if not indicated, those recommended by federal regulatory agencies. The final laboratory report should include at a minimum: all data indicated on sample container labels; date sample was received at the laboratory; date of analysis for each parameter reported; and detection limits. Results of your analyses and the attached Chain of Custody/ Analyses Request Schedule should be sent to our Tucson office.

If you have any questions regarding the shipment or the analyses requested, please contact us.

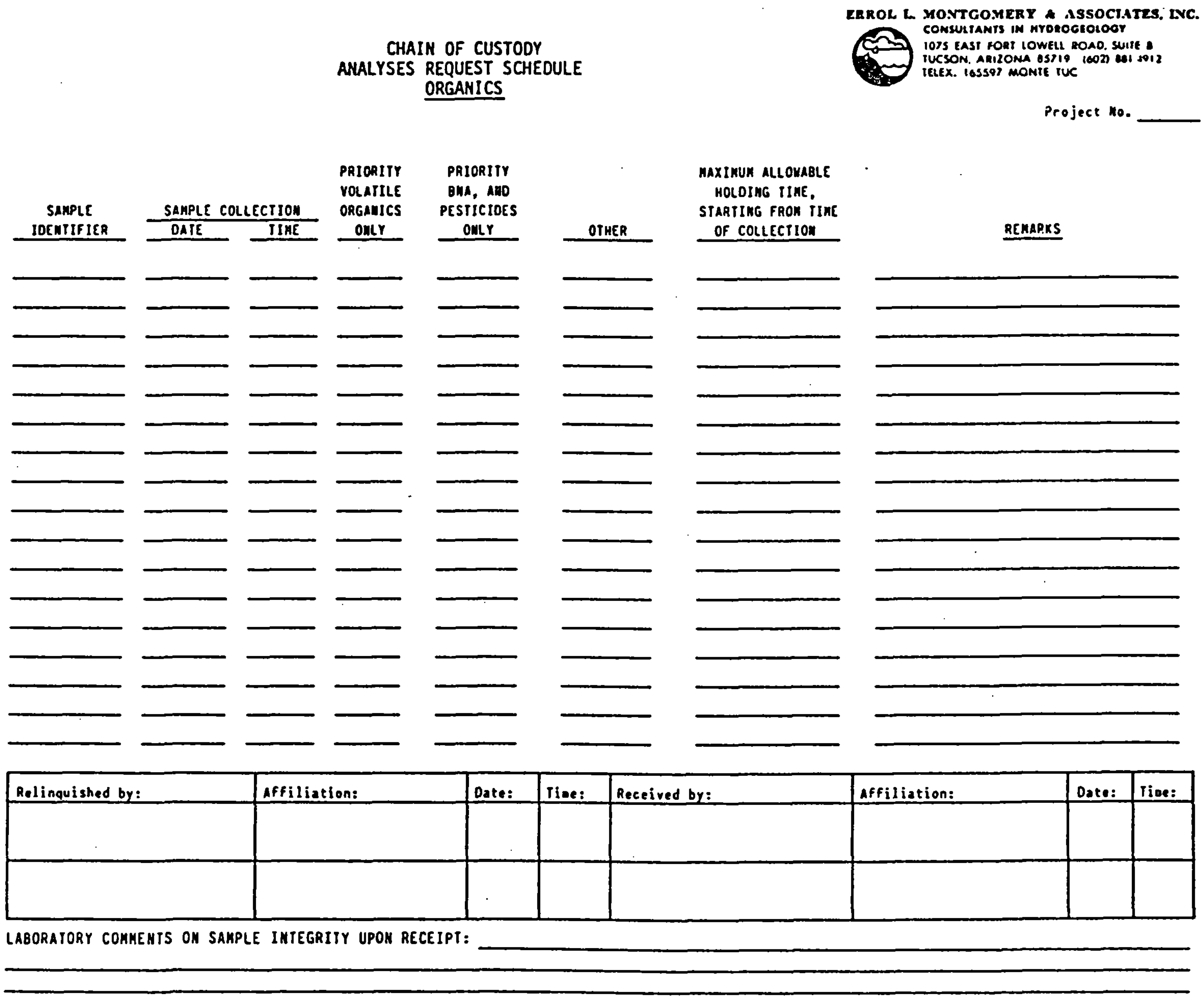
Very truly yours,
ERROL L. MONTGOMERY & ASSOCIATES, INC.

By: ______________________________

Attachment(s).

Title: ______________________________

FIGURE 12. CHAIN OF CUSTODY LETTER OF TRANSMITTAL



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CONSULTANTS IN HYDROGEOLOGY
1075 EAST FORT LOWELL ROAD, SUITE B
TUCSON, ARIZONA 85719 (602) 881 4912
TELEX. 165597 MONTE TUC

CHAIN OF CUSTODY
ANALYSES REQUEST SCHEDULE
ORGANICS

Project No. ________

SAMPLE IDENTIFIER	SAMPLE COLLECTION DATE	SAMPLE COLLECTION TIME	PRIORITY VOLATILE ORGANICS ONLY	PRIORITY BNA, AND PESTICIDES ONLY	OTHER	MAXIMUM ALLOWABLE HOLDING TIME, STARTING FROM TIME OF COLLECTION	REMARKS

Relinquished by:	Affiliation:	Date:	Time:	Received by:	Affiliation:	Date:	Time:

LABORATORY COMMENTS ON SAMPLE INTEGRITY UPON RECEIPT: ____________________

FIGURE 13. CHAIN OF CUSTODY ANALYSES REQUEST SCHEDULE FOR ORGANICS

ERROL L. MONTGOMERY & ASSOCIATES, INC.
CONSULTANTS IN HYDROGEOLOGY
1075 EAST FORT LOWELL ROAD, SUITE B
TUCSON, ARIZONA 85719 (602) 881-4912
TELEX: 165597 MONTE TUC

CHAIN OF CUSTODY
ANALYSES REQUEST SCHEDULE

ROUTINE PARAMETERS

TO:

FROM:________________________

DATE OF SHIPMENT:_______________ NUMBER OF SAMPLES SHIPPED:_______________

SHIPPED VIA:___________________ CONTAINER:___________________________

IDENTIFICATION OF SAMPLES

Sample No. Identification	Sampling Date (Time)	Sample Temp./Conductivity/pH

PRE-TREATMENT OF SAMPLES:

DETERMINATIONS TO BE MADE:

Routine Constituents

Calcium
Magnesium
Sodium
Potassium
Carbonate
Bicarbonate
Chloride

Sulfate
Nitrate
Boron
Fluoride
Electrical Conductance
Total Dissolved Solids
(Residue @ 180°C)

Silica
pH

Relinquished by:	Affiliation:	Date:	Time:
	E.L. Montgomery & Associates, Inc.		
Received by:	Affiliation:	Date:	Time:

LABORATORY COMMENTS ON SAMPLE INTEGRITY
UPON RECEIPT:____

FIGURE 14. CHAIN OF CUSTODY ANALYSES REQUEST SCHEDULE FOR ROUTINE PARAMETERS

ERROL L. MONTGOMERY & ASSOCIATES, INC.
CONSULTANTS IN HYDROGEOLOGY
1075 EAST FORT LOWELL ROAD, SUITE B
TUCSON, ARIZONA 85719 (602) 881-4912
TELEX: 165597 MONTE TUC

CHAIN OF CUSTODY ANALYSES REQUEST SCHEDULE

TRACE ELEMENTS

TO:

FROM: ____________________

DATE OF SHIPMENT: ____________ NUMBER OF SAMPLES SHIPPED: ____________

SHIPPED VIA: ____________ CONTAINER: ____________

IDENTIFICATION OF SAMPLES

Sample No. Identification	Sampling Date (Time)	Sample Temp./Conductivity/pH

PRE-TREATMENT OF SAMPLES:

DETERMINATIONS TO BE MADE:

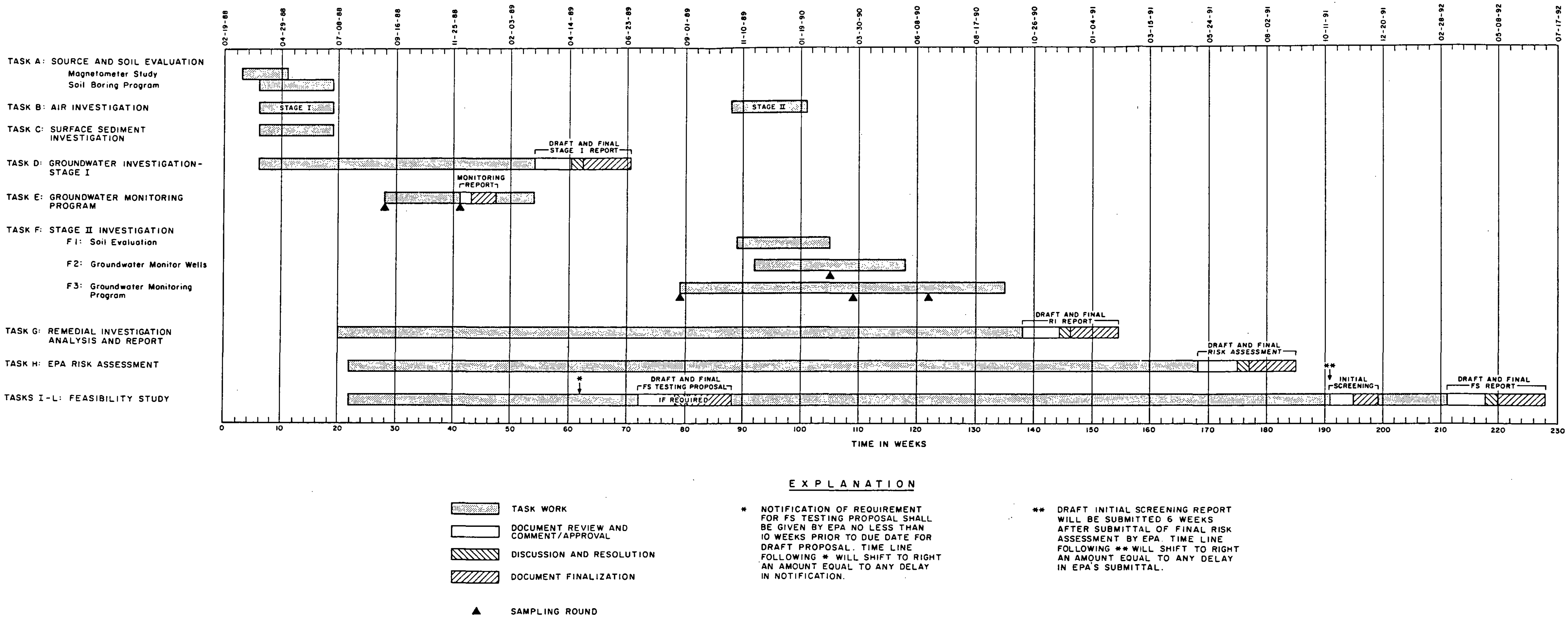
Trace Metals and Other Constituents

- Iron
- Manganese
- Copper
- Molybdenum
- Lead
- Antimony
- Beryllium
- Cadmium
- Total Chromium
- Arsenic
- Silver
- Mercury
- Selenium
- Zinc
- Nickel
- Thallium
- Aluminum
- Barium

Relinquished by:	Affiliation:	Date:	Time:
	E.L. Montgomery & Associates, Inc.		
Received by:	Affiliation:	Date:	Time:

LABORATORY COMMENTS ON SAMPLE INTEGRITY UPON RECEIPT: ____________________

FIGURE 15. CHAIN OF CUSTODY ANALYSES REQUEST SCHEDULE FOR TRACE ELEMENTS



* NOTIFICATION OF REQUIREMENT FOR FS TESTING PROPOSAL SHALL BE GIVEN BY EPA NO LESS THAN 10 WEEKS PRIOR TO DUE DATE FOR DRAFT PROPOSAL. TIME LINE FOLLOWING * WILL SHIFT TO RIGHT AN AMOUNT EQUAL TO ANY DELAY IN NOTIFICATION.

** DRAFT INITIAL SCREENING REPORT WILL BE SUBMITTED 6 WEEKS AFTER SUBMITTAL OF FINAL RISK ASSESSMENT BY EPA. TIME LINE FOLLOWING ** WILL SHIFT TO RIGHT AN AMOUNT EQUAL TO ANY DELAY IN EPA'S SUBMITTAL.

NOTE: If TASK F4 (Stage III Investigation) would be required, all deliverables for TASKS G-L would be delayed from 6 to 12 months or more, except for FS testing proposal.

FIGURE 3. SCHEDULE GRAPH OF ESTIMATED PROJECT TIMING (EXCLUDING TASK F4)

APPENDIX A

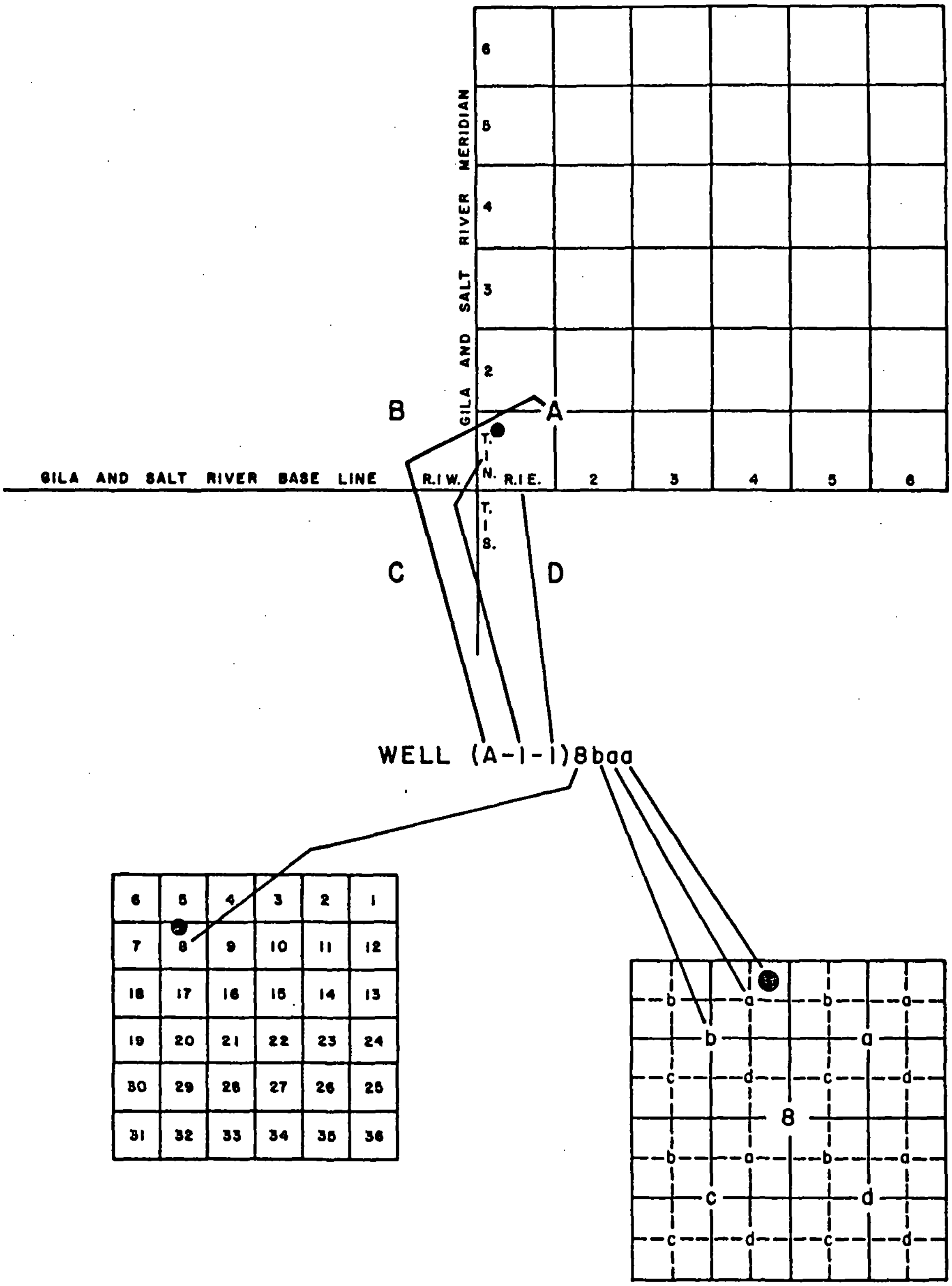
WELL NUMBERING SYSTEM

APPENDIX A

WELL NUMBERING SYSTEM

The well numbers used in this report are in accordance with the Bureau of Land Management's system of land subdivision. The land survey in Arizona is based on the Gila and Salt River meridian and base line, which divide the state into four quadrants. These quadrants are designated, counter-clockwise, by the capital letters A, B, C, and D. All land north and east of the point of origin is in quadrant A; all land north and west of the origin is in quadrant B; all land south and west is in quadrant C; and all land south and east is in quadrant D. The first digit of a well number indicates the township, the second digit the range, and the third digit the section in which the well is located. The lowercase letters a, b, c, and d after the section number indicate the well location within the section. The first letter denotes a particular 160-acre tract or quarter section; the second letter denotes the 40-acre tract or quarter-quarter section; and the third letter denotes the 10-acre tract or quarter-quarter-quarter section. These letters are also assigned in a counter-clockwise direction, beginning in the northeast quarter. As **Figure A-1** shows, well number (A-1-1)8baa designates the well as being located in the Northeast 1/4, Northeast 1/4, Northwest 1/4, Section 8, Township 1 North, Range 1 East. Where more than one well is located within a 10-acre tract, consecutive numbers beginning with "1" are added as suffixes.

For this investigation, additional well identifiers enclosed in brackets are added as suffixes, as is shown on Figure 2. The additional well identifiers are used to identify monitor wells located at the Hassayampa Landfill.



6	5	4	3	2	1
7	8	9	10	11	12
18	17	16	15	14	13
19	20	21	22	23	24
30	29	28	27	26	25
31	32	33	34	35	36

FIGURE A-1. WELL NUMBERING DIAGRAM

APPENDIX B

SAMPLING PLAN FOR STAGE II INVESTIGATION FOR HAZARDOUS WASTE AREA

CONTENTS

Page

APPENDIX B

SAMPLING PLAN FOR STAGE II INVESTIGATION FOR HAZARDOUS WASTE AREA

INTRODUCTION

The following Sampling Plan describes procedures for obtaining soil and water samples for Stage II of the Remedial Investigation for the hazardous waste area at the Hassayampa Landfill. This Sampling Plan should be used in conjunction with the associated Supplemental Work Plan, comprehensive RI/FS Work Plan (Montgomery & Associates and CRA, 1988a), Quality Assurance Project Plan (QAPP) (Montgomery & Associates and CRA, 1988b), and Health and Safety Plan (Montgomery & Associates and CRA, 1988c) to conduct proper sampling operations. **Figure 2** shows locations for soil borings. **Figure 5** (located in pocket inside back cover) shows locations for groundwater monitor wells.

Topography across the Hassayampa Landfill is undulatory due to the frequent reworking of landfill pits in the active part of the property. However, the closed hazardous waste area is covered by a graded soil cover that is relatively flat to gently sloping. Access for vehicles is generally good in the closed hazardous waste area, where surficial soils are relatively compacted and firm. Surficial soils in parts of the active landfill are loose and are generally passable only to off-road vehicles. Access is good to existing monitor wells, proposed monitor wells, and proposed soil borings.

DATA MANAGEMENT

Data management procedures will be required to document results of field operations, chain of custody, laboratory analyses, and other project related activities. Data management will include maintenance of field notebooks, instrument calibration notebooks, Quality Assurance / Quality Control (QA/QC) notebooks for laboratory results, and project files. Field notebooks will be used to record notes on field operations and to record field data obtained during project TASKS. Items to be recorded for data management documentation will include, but not be limited to, the following:

- site conditions, including weather and location;
- personnel on-site during field operations;
- observations during drilling of soil borings and monitor wells;
- lithologic descriptions of drill cuttings;
- all sampling data and forms, including chain of custody and sample control data;
- time that pertinent sampling operations occur and equations used to calculate volume of water pumped prior to sampling wells;
- QA/QC reviews for data;
- pumping test data and analysis;
- well development data; and
- calibration data for field instrumentation, such as water level sounders, pH meters, conductivity meters, etc.

Entries in field notebooks and calibration notebooks will be initialed and dated. Photographs will be taken of pertinent field operations and site areas. All such photographs will be developed and retained in the project files.

SAMPLING PROCEDURES

Sampling and QA/QC procedures for the Remedial Investigation are designed to ensure that collection, identification, preservation, and transportation of samples will result in properly representative data for site conditions. Quantities, types, and frequency of water and soil samples to be obtained during Stage II, including QA/QC samples, are summarized in **Table 2**. A list of sample containers, preservatives, and holding times for parameters to be analyzed is given in **Table 3**. Sampling procedures for the Stage II air investigation (TASK B2) are given in the Supplemental Work Plan and in **Appendix C**.

CHAIN OF CUSTODY AND SAMPLE CONTROL PROCEDURES

Chain of custody and sample control procedures will be required to ensure the integrity and preservation of samples during their collection, transportation, and storage prior to laboratory chemical analysis. Examples of typical chain of custody and sample control documents are shown on **Figures 10 through 15**. These documents will include: field data form **(Figure 10)**; chain of custody traffic report **(Figure 11)**; chain of custody letter of transmittal **(Figure 12)**; chain of custody analysis request schedules with signatures for transfer of custody **(Figures 13, 14, and 15)**; and records and receipts for delivery or shipment of samples. All pertinent data concerning each sample will be recorded on the traffic report **(Figure 11)**, including:

- traffic report sample numbers
- sample description
- sampling personnel
- description of sampling point and sampling methods
- sample site name and number
- date and time of collection
- field observations
- number and volumes of samples

- container lot numbers, if applicable
- analyses required
- method and date of delivery or shipment
- preservatives used
- sample destination
- special handling procedures

Immediately after obtaining a water or soil sample, a unique, pre-printed, pre-numbered, adhesive sample label will be affixed to the sample container and traffic report by the field hydrogeologist. Sample lids and sample labels will be secured with tape, and the samples will be put on ice in an ice chest. Vials for volatile organic analyses will be placed in zip-lock bags and the supply of ice in the ice chest will be maintained to provide proper cooling of the samples. The field hydrogeologist will maintain custody of the samples from the time of collection to time of delivery or shipment to the chemical laboratory. At the end of each sampling day, samples will be hand delivered or will be shipped to the chemical laboratory via bus or via overnight air freight service. If the samples are shipped, receipts for shipment will be obtained. The laboratory will be notified prior to delivery or shipment of samples.

Prior to relinquishing sample custody for shipment, a minimum of two custody seals marked with the sample custodian's initials will be placed across the opening of the shipping container to detect unauthorized opening of the container. Clear tape will be placed over the custody seals to prevent accidental breakage of the seals during shipment. Samples will be preserved by cooling with refrigeration, ice, or artificial substances (such as "Blue Ice") from the time of collection to the time of receipt by the laboratory. Thereafter, the laboratory will preserve the samples in accordance with protocol of analytical methods. Chain of custody and sample control procedures followed by the laboratory will be consistent with the QAPP (Montgomery & Associates and CRA, 1988b).

One original copy of the chain of custody documents will accompany the sample shipping container to the laboratory; the sample custodian will retain a copy of these documents. On receipt of the samples at the laboratory, the laboratory will complete the original chain of custody documents, retain a copy for their records, and forward the completed originals to the Tucson, Arizona, office of Errol L. Montgomery & Associates, Inc.

SAMPLE CONTAINERS

For laboratory chemical analyses of water and soil samples, clean unused sample containers will be provided by the chemical laboratory. Requirements for volume, type, and cleanliness of sample containers will be consistent with requirements of the laboratory and with the analytical methods to be used. A list of sample containers, preservatives, and holding times for parameters to be analyzed is given in **Table 3**.

SOIL SAMPLING METHODS

Soil samples will be obtained from soil borings during TASK F1. In addition, samples of drill cuttings, drilling mud, etc., placed in the second lined excavation in the hazardous waste area will be obtained for laboratory chemical analyses after several months of exposure to the atmosphere. Quantities and frequency of soil samples and QA/QC samples to be obtained are given in **Table 2**.

Soil Boring Samples

Four soil borings will be drilled under TASK F1 of the Supplemental Work Plan. One soil boring will be drilled at an angle to vertical beneath Pits 1, 2, 3, and 4 **(Figure 2)**. Soil samples for laboratory chemical analyses will be obtained from each of the borings at intervals to be selected by the on-site hydrogeologist based on data obtained during drilling; however, 10-foot sampling intervals, beginning at about five feet below land surface, are expected. A maximum of six to eight soil samples for laboratory chemical analyses will be obtained from each soil boring. For every 10 soil samples analyzed, a duplicate sample will be prepared from the soil samples by the chemical laboratory **(Table 2)**. Zones of low permeability, where contaminants in the vadose zone may tend to accumulate, will be targeted for sampling.

All soil samples obtained for laboratory chemical analyses from soil borings will be analyzed for: volatile organic compounds using EPA method 8240; semi-volatile organic compounds using EPA method 8270; pesticides and polychlorinated biphenyls (PCBs) using EPA method 8080; and eight metals (arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver) using the EPA EP Toxicity method. Duplicate soil samples will also be analyzed using these methods. Organic compounds to be analyzed with these methods are listed in the QAPP (Montgomery & Associates and CRA, 1988b).

The soil borings will be drilled using a hollow-stem flight auger, preferably with the capability for continuous sampling. Prior to drilling the first soil boring and after drilling at each site, the auger drill stem and drilling tools will be cleaned using a hot, high-pressure, tap water rinse. Water solutions used to clean the drilling tools will be placed in the lined excavation in the hazardous waste area. Soil samples for lithologic descriptions will be obtained at five-foot intervals. Lithologic descriptions will also be prepared by the on-site hydrogeologist for soil samples obtained for laboratory chemical analyses. Soil moisture will be monitored closely by visual inspection. Drill cuttings samples, cores, and split-spoon samples that are not used for laboratory analyses, either will be placed in containers, labeled, and preserved, or will be disposed in the lined excavation. If split-spoon samplers are used, a record will be made of the number of blows required to drive the samplers for each depth interval sampled.

Soil samples for laboratory chemical analyses will be obtained in clean four-inch or six-inch brass tube inserts. After the sampler has been advanced to the specified depth, the core barrel, California modified sampler, or split-spoon sampler will be removed from the auger, and will be opened at a sample processing station located near the drill rig. The brass inserts will be removed from the core barrel, and a lithologic description will be prepared for soils in the barrel or split-spoon. Based on appearance and texture of soils in the brass inserts, brass insert samples considered to be representative for the depth sampled will be selected for laboratory chemical analyses. Each selected insert will be sealed on both ends with sheets of Teflon or aluminum foil, and plastic caps, secured with tape, marked with sample identifiers, and put in clean glass mason jars or sealable plastic bags. The chain of custody and procedures described in the previous section titled "<u>CHAIN OF CUSTODY AND SAMPLE CONTROL PROCEDURES</u>" will be followed. After the brass inserts are removed, the samplers will be cleaned and equipped with additional clean brass inserts for the collection of subsequent soil samples.

All brass tube inserts will be pre-cleaned by the chemical laboratory, and will be used once and not reused. The core barrel, split-spoon samplers, and other sampling tools will be cleaned before and after the collection of each sample for laboratory chemical analyses, according to the following procedure:

1. **Clean with hot, high-pressure, tap water spray;**
2. **Wash with trisodiumphosphate solution;**
3. **Rinse with tap water; and**
4. **Rinse with deionized water.**

Water solutions used to clean the sampling tools will be placed in the lined excavation in the hazardous waste area.

Lined Excavation Samples

At the start of field operations, a second lined excavation will be made near the existing Stage I lined excavation and will be used for placement of drill cuttings, drilling fluids, and rinsate generated during Stage II. Materials in this lined excavation will remain exposed to the atmosphere for a period of several months, preferably summer months, after which a composite sample of the materials will be obtained.

The composite sample will be obtained using a stainless steel scoop, a stainless steel bowl, and clean wide-mouth glass jars. Scoops of material will be obtained from a minimum of 10 evenly spaced locations along the length of the excavation. The scooped material will be placed in a clean stainless steel bowl and the contents of the bowl will then be thoroughly mixed. A jar will be filled with this mixture as completely as practicable to minimize air space, and will be sealed with a Teflon-lined or aluminum-lined lid. Procedures described in the previous section titled "CHAIN OF CUSTODY AND SAMPLE CONTROL PROCEDURES" will be followed. A description of the sampled material will be prepared. A duplicate sample for laboratory chemical analyses will be prepared by the chemical laboratory from the samples submitted. The composite sample and duplicate sample will be analyzed for: volatile organic compounds using EPA method 8240; semi-volatile organic compounds using EPA method 8270; pesticides and PCBs using EPA method 8080; the characteristic of EP Toxicity; and appropriate tests for determining characteristics of hazardous wastes.

Sampling tools will be cleaned before and after collection of the sample according to the following procedure:

1. **Rinse with tap water;**
2. **Wash with trisodiumphosphate solution;**
3. **Rinse with tap water; and**
4. **Rinse with deionized water.**

WATER SAMPLING METHODS

Groundwater samples will be obtained during three sampling rounds as follows:

> <u>TASK F2 ROUNDS 1 AND 2</u>: All new monitor wells will be sampled once during development operations (round 1) and once near the end of TASK F2 field operations (round 2). Groundwater samples will be analyzed for: volatile organic compounds using EPA method 624; semi-volatile organic compounds using EPA method 625; pesticides and PCBs using EPA method 608; cyanide; routine constituents; trace constituents; pH; and specific electrical conductance.
>
> <u>TASK F3 ROUND 1</u>: Eleven existing on-site monitor wells will be sampled during summer 1989. Groundwater samples will be analyzed for: volatile organic compounds using EPA method 601/602; routine constituents; selected trace constituents that have been detected previously; pH; and specific electrical conductance.
>
> <u>TASK F3 ROUNDS 2 and 3</u>: All on-site monitor wells will be sampled once 30 days after the end of TASK F2 field operations and once three months later. Groundwater samples from 11 existing monitor wells will be analyzed for: volatile organic compounds using EPA method 601/602; routine constituents; selected trace constituents that have been detected previously; pH; and specific electrical conductance. Groundwater samples from new monitor wells will be analyzed for: volatile organic compounds using EPA method 601/602; routine constituents; pH; and specific electrical conductance; and any other constituents detected previously. Additional parameters will be analyzed for selected groundwater samples.

Individual constituents to be analyzed with these EPA methods are listed in the QAPP (Montgomery & Associates and CRA, 1988b).

Selected groundwater samples obtained during TASK F3 sampling rounds no. 2 and 3 will be analyzed for the following constituents <u>not</u> listed in the QAPP (Montgomery & Associates and CRA, 1988b): nitrite using EPA method 353.2; total Kjeldahl nitrogen (TKN) using EPA method 351.2; total organic carbon (TOC) using EPA method 415.2; oil and grease using EPA method 413.1; chemical oxygen demand (COD) using modified EPA method 410.4; and, biochemical oxygen demand (BOD) using EPA method 405.1. These additional constituents were requested by CRA to provide data for treatability of groundwater. Wells proposed for this supplemental sampling and analysis are: Unit A monitor well MW-1UA; proposed monitor wells A, B, D, and E; and Unit B monitor wells MW-1UB and MW-4UB.

For every 10 groundwater samples obtained for organic and/or inorganic analyses, a duplicate and a field blank will be obtained and will be analyzed for the same parameters as the groundwater samples. As a check for possible cross contamination or third source contamination, a trip blank prepared by the chemical laboratory will accompany each group of samples submitted for volatile organic analysis. Field blanks will be prepared by the sampling personnel using bottled deionized water. Quantities and frequency of groundwater samples and QA/QC samples to be obtained during Stage II are given in **Table 2**. A list of sample containers, preservatives, and holding times for parameters to be analyzed is given in **Table 3**.

If nonaqueous hydrocarbon phase liquids occur in a new Unit A monitor well, samples of the nonaqueous phase will be bailed from the well and will be analyzed solely for: volatile organic compounds using EPA method 624; and TPH (Total Petroleum Hydrocarbons) using modified EPA method 8015.

The following procedures will be followed for collection of groundwater samples from monitor wells:

1. At the beginning of each day of a sampling round, operation of large-capacity wells located within one-half mile from the monitor wells to be sampled will be observed and recorded.
2. With the possible exception of groundwater samples obtained during well development operations (TASK F2 round 1), each well will be sampled using a submersible pump. A water level measurement using an electrical water level sounder will be obtained prior to pumping each well. The wellhead assembly for sampling operations at the new monitor wells is shown on **Figure 9**. A pump will be dedicated to each well.

3. A minimum volume of water equal to three borehole volumes will be pumped from each well prior to sampling. The minimum volume, in gallons, will be calculated using the following equation:

   71 x (hole radius, in ft.)^2 x (height of water in hole, in ft.)

   Time when pumping starts and stops will be recorded in a field notebook.

4. During the pumping period, measurements of water level, pumping rate, and pH, temperature, and specific electrical conductance of pumped water will be obtained at intervals determined by the pumping rate and the volume to be pumped. Pumping rate will be determined by measuring the time required to fill a container of known volume. After measurements of specific electrical conductance are stable (within +/- 10 percent of the average), and after a minimum of three borehole volumes have been pumped, water samples will be obtained from the discharge line. Temperature, pH, and conductance of pumped water will be measured immediately before samples for laboratory chemical analyses are obtained; these data will be considered representative for the samples.

5. All samples will be put on ice at the time of collection and procedures described in the previous section titled "<u>CHAIN OF CUSTODY AND SAMPLE CONTROL PROCEDURES</u>" will be followed. After groundwater samples are collected, a final water level measurement will be obtained and the pump will be turned off.

6. On arrival at a monitor well, the well vault, lock, and protective barrier posts will be inspected for security, damage, and vandalism. The well vault will be locked whenever authorized sampling personnel are not present.

7. If nonaqueous hydrocarbon phase liquids occur on the water surface in a new monitor well, the well will not be equipped with a permanent submersible pump and samples will be obtained from the well by bailing. Bailers will be dedicated to each of these wells.

   a. Prior to sampling, a measurement of water level and free product thickness will be made using an ORS Interface Probe.

   b. Samples will be obtained by bailing using a dedicated two-inch by five-foot clear Teflon or acrylic bailer equipped with a check valve. Water withdrawn with the first full bailer will be inspected for character and thickness of the nonaqueous phase. A sample for laboratory chemical analyses will then be obtained from the hydrocarbon phase in the first full bailer and from as many subsequent bails as are necessary to obtain a sufficient volume of the hydrocarbon phase.

To minimize contact of sampling equipment with surficial soils, sampling equipment will be placed on the cement pad at each well site or on the tailgate of the sampling vehicle.

Water removed from each monitor well during development operations (TASK F2 round 1) will be discharged to a lined excavation adjacent to the well and will be allowed to evaporate naturally. Results of laboratory chemical analyses for the TASK F1 round 1 groundwater samples will be used to screen for contaminants and to determine if water removed from the wells during subsequent pumping test and sampling operations should also be contained in the lined excavations. If potential contaminants are not detected or are detected at concentrations below Maximum Contaminant Levels in the most recent sample from a well, water removed during subsequent sampling operations at the well will be discharged via a perforated hose or pipe to the land surface for evaporation.

Drill Water Samples

As a precautionary check and documentation for drilling water to be used during construction of monitor wells, water samples from the water truck used for drilling operations will be obtained prior to drilling the first monitor well and after drilling the last TASK F2 monitor well. These samples will be analyzed for volatile organic compounds using EPA method 601/602. Individual compounds to be analyzed with this method are listed in the QAPP (Montgomery & Associates and CRA, 1988b).

Measurement of Groundwater Levels

Groundwater level measurements will be made using an electrical water level sounder. Prior to groundwater level measurement, the sounder will be rinsed with deionized water and wiped with a clean paper towel. Groundwater levels will be recorded to the nearest 0.01 foot on water level record forms

(Figure 10). Site identifier, weather conditions, date and time of measurement, elevation and description of measuring point, and distance of measuring point from land surface will be included in the information recorded. Sounders will be dedicated to the project. The sounders will be calibrated with a steel surveyor chain before each round of water level measurements and when repairs are made. A calibration notebook will be maintained for each sounder and will include: date and time calibrated; points of calibration; personnel conducting the calibrations; and method of calibration. In addition, manufacturer-recommended maintenance of the instruments will be conducted and results recorded.

Parameters Measured in the Field

Specific electrical conductance, temperature, and pH of water will be measured in the field during pumping test and sampling operations. Specific electrical conductance of water will be measured using a Beckman Solu Bridge conductivity meter, or equivalent. Measurements of pH will be made using a Beckman pHI 20 or pHI 21 digital pH meter, or equivalent. These pH meters also measure temperature. Measurements of pH and temperature will be verified using pH paper and a laboratory grade thermometer. The conductivity meter and pH meter will be calibrated with standard solutions before each pumping test and sampling round. Notes from the calibrations will be recorded in the field notebook. In addition, manufacturer-recommended maintenance of the instruments will be conducted and results recorded.

Water samples for measurement of these parameters in the field will be obtained in a wide-mouth one-liter polyethylene bottle. The bottle will be rinsed three times with the water to be sampled. After rinsing, the bottle will be filled and measurements of the parameters will be made and recorded. Before and after each measurement, the meter probes and the thermometer will be rinsed with deionized water.

Samples for Organic Analyses

Water samples for volatile organic analyses will be obtained from each monitor well in two 40-milliliter screwcap glass vials fitted with Teflon-coated silicon septa. The vials (no. 13074) and septa (no. 12722) are sold by Pierce Chemical Company, Rockford, Illinois, and will be obtained from the chemical laboratory in a clean and new condition. Sampling will be conducted so as to minimize exposure of the sample to air. First, the vial and cap will be rinsed three times with the water stream to be sampled. After rinsing, if EPA sampling policy requires, four drops of reagent grade 1:1 hydrochloric acid will be added to the vial. The vial will then be filled with the sample water to attain a convex meniscus at the top of the vial. Only the sample water will contact the inside of the vial or cap. The vial will be sealed immediately after filling by placing the septum, Teflon side down, on the meniscus and screwing the cap firmly in place. The vial will be checked for trapped air by inverting the vial, tapping it gently, and inspecting for headspace (air bubbles). If headspace is present, the vial will be emptied and the process will be repeated until no headspace is observed.

If it is necessary to analyze for TPH (Total Petroleum Hydrocarbons) for any monitor well, samples for TPH analyses will be obtained in the same manner as water samples for volatile organic analyses.

Groundwater samples for analyses of semi-volatile organic compounds, pesticides, and PCBs will be obtained in four one-liter, screwcap, amber glass bottles with Teflon-coated caps. Sampling will be conducted so as to minimize exposure of the samples to air. Methods for filling the bottles will be the same as described above for the vials, except that hydrochloric acid will not be used, a septum will not be used, and the occurrence of headspace will not be cause for refilling the bottle.

Samples for Analysis of Routine Constituents, Trace Constituents, and Cyanide

Groundwater samples for analysis of routine constituents, trace constituents, and cyanide will be obtained in new, clean, one-liter polyethylene bottles. The bottles will have relatively long screwcaps and a positive seal lip on the bottle. Prior to filling, the bottle and cap will be rinsed three times with the water stream to be sampled. After rinsing, the bottle will be filled and sealed immediately by screwing the cap firmly in place. Only the sample water will contact the inside of the bottle or cap. Separate bottles will be used for each type of analysis.

Groundwater samples for analysis of trace constituents will be filtered immediately in the field and will be acidified by adding a sufficient amount of reagent grade 1:1 nitric acid to each bottle to lower the pH to less than two. The bottles will be shaken gently after capping to evenly disperse the acid. Acid preservation will be noted in the sample custody documents.

Groundwater samples for analysis of routine constituents will be filtered immediately in the field and not preservatives will be used.

Groundwater samples for analysis of nitrate, phosphate, and ammonia will be filtered immediately in the field and will be acidified by adding a sufficient amount of reagent grade 1:1 sulfuric acid to each bottle to lower the pH to less than two. The bottles will be shaken gently after capping to evenly disperse the acid. Acid preservation will be noted in the sample custody documents.

Groundwater samples for analysis of cyanide will not be filtered in the field, but will be treated with sodium hydroxide to raise the pH to 12. The bottles for cyanide analyses will be shaken gently after capping to evenly disperse the sodium hydroxide. Method of preservation for the cyanide sample will be noted in the sample custody documents.

Supplemental Analyses

Additional analyses were requested by CRA to provide data for treatability of groundwater. Selected groundwater samples obtained during TASK F3 sampling rounds no. 2 and 3 will be analyzed for the following constituents not listed in the QAPP (Montgomery & Associates and CRA, 1988b): nitrite using EPA method 353.2; total Kjeldahl nitrogen (TKN) using EPA method 351.2; total organic carbon (TOC) using EPA method 415.2; oil and grease using EPA method 413.1; chemical oxygen demand (COD) using modified EPA method 410.4; and biochemical oxygen demand (BOD) using EPA method 405.1. Wells proposed for supplemental sampling and analysis are: Unit A monitor well MW-1UA; proposed Unit A monitor wells A, B, D, and E; and Unit B monitor wells MW-1UB and MW-4UB. Laboratory methods and sampling procedures for these analyses will be in accordance with applicable EPA protocol.

LABORATORY PROCEDURES

All samples submitted for analyses during this project will be handled and analyzed by the chemical laboratories in accordance with standard procedures and methods established by the laboratories and in accordance with the QAPP (Montgomery & Associates and CRA, 1988b). These procedures and methods include requirements for: purity of standards, solvents, and reagents; glassware; analytical methods; data requirements; laboratory performance; and analytical data review. Detailed discussions for these procedures and methods are given in the QAPP (Montgomery & Associates and CRA, 1988b). The chemical laboratories selected for the Remedial Investigation are:

LABORATORY	INTENDED USE
Analytical Technologies, Inc. 2113 South 48th Street, Suite 108 Tempe, Arizona 85282	Principal laboratory for analyses of organic and inorganic parameters in water and soil samples.
Clayton Environmental Conslts, Inc. 1252 Quarry Lane Pleasanton, California 94566	Alternate laboratory for analyses of organic and inorganic parameters in water and soil samples.
Brown and Caldwell 373 South Fair Oaks Avenue Pasadena, California 91105	Alternate laboratory for analyses of organic and inorganic compounds in water and soil samples.
BC Laboratories, Inc. 4100 Pierce Road Bakersfield, California 93308	Alternate laboratory for analyses inorganic parameters in water and soil samples.

The laboratories will follow QA/QC procedures and methods, and will provide QA/QC documentation, which provide reliability of data equivalent to that intended by the EPA Contract Laboratory Program. All laboratory chemical analyses will be conducted in accordance with standard protocols applicable to each method.

QA/QC protocols for the principal laboratory (Analytical Technologies, Inc.) are given in **"Analytical Technologies, Inc. Laboratory Quality Assurance Plan"**. This document is available for review on request. In addition, the QA/QC protocols for the principal laboratory and the alternate laboratories will be consistent with the QAPP (Montgomery & Associates and CRA, 1988b) and with the intent of the following publications:

1. **"Laboratory Data Validation Functional Guidelines for Evaluating Organics Analyses"**, Technical Directive Document No. HQ-8410-01, prepared for the Hazardous Site Control Division of the U. S. Environmental Protection Agency, April 11, 1985.
2. **"Laboratory Data Validation Functional Guidelines for Evaluating Inorganics Analyses"**, U. S. Environmental Protection Agency Office of Emergency and Remedial Response.
3. **"Statement of Work for Organics Analysis"**, U. S. Environmental Protection Agency Contract Laboratory Program, October 1986.
4. **"Statement of Work for Inorganics Analysis"**, U. S. Environmental Protection Agency Contract Laboratory Program, SOW No. 787, July 1987.

ANALYTICAL METHODS

Methods to be used for laboratory chemical analyses for Stage II water and soil samples are listed in **Table 2**; individual constituents to be analyzed using these methods are listed in the QAPP (Montgomery & Associates and CRA, 1988b).

APPENDIX C

AIR SAMPLING PROCEDURES FOR EPA METHODS TO-1 AND TO-2

METHOD FOR THE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR USING [redacted]ADSORPTION AND GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

1. Scope

1.1 The document describes a generalized protocol for collection and determination of certain volatile organic compounds which can be captured on Tenax® GC [redacted] and determined by thermal desorption GC/MS techniques. Specific approaches using these techniques are described in the literature (1-3).

1.2 This protocol is designed to allow some flexibility in order to accommodate procedures currently in use. However, such flexibility also results in placement of considerable responsibility with the user to document that such procedures give acceptable results (i.e. documentation of method performance within each laboratory situation is required). Types of documentation required are described elsewhere in this method.

1.3 Compounds which can be determined by this method are nonpolar organics having boiling points in the range of approximately 80° - 200°C. However, not all compounds falling into this category can be determined. Table 1 gives a listing of compounds for which the method has been used. Other compounds may yield satisfactory results but validation by the individual user is required.

2. Applicable Documents

2.1 ASTM Standards:

D1356	Definitions of Terms Related to Atmospheric Sampling and Analysis.
E355	Recommended Practice for Gas Chromatography Terms and Relationships.

2.3 Other documents:

Existing procedures (1-3).
U.S. EPA Technical Assistance Document (4).

3. Summary of Protocol

3.1 Ambient air is drawn through a cartridge containing ∿1-2 grams of Tenax and certain volatile organic compounds are trapped on the resin while highly volatile organic compounds and most inorganic atmospheric constituents pass through the cartridge. The cartridge is then transferred to the laboratory and analyzed.

3.2 For analysis the cartridge is placed in a heated chamber and purged with an inert gas. The inert gas transfers the volatile organic compounds from the cartridge onto a cold trap and subsequently onto the front of the GC column which is held at low temperature (e.g. - 70°C). The GC column temperature is then increased (temperature programmed) and the components eluting from the column are identified and quantified by mass spectrometry. Component identification is normally accomplished, using a library search routine, on the basis of the GC retention time and mass spectral characteristics. Less sophistacated detectors (e.g. electron capture or flame ionization) may be used for certain applications but their suitability for a given application must be verified by the user.

3.3 Due to the complexity of ambient air samples only high resolution (i.e. capillary) GC techniques are considered to be acceptable in this protocol.

4. Significance

4.1 Volatile organic compounds are emitted into the atmosphere from a variety of sources including industrial and commercial facilities, hazardous waste storage facilities, etc. Many of these compounds are toxic; hence knowledge of the levels of such materials in the ambient atmosphere is required in order to determine human health impacts.

4.2 Conventional air monitoring methods (e.g. for workspace monitoring) have relied on carbon adsorption approaches with subsequent solvent desorption. Such techniques allow subsequent injection of only a small portion, typically 1-5% of the sample onto the GC system. However, typical ambient air concentrations of these compounds require a more sensitive approach. The thermal desorption process, wherein the entire sample is introduced into the analytical (GC/MS) system fulfills this need for enhanced sensitivity.

5. Definitions

Definitions used in this document and any user prepared SOPs should be consistent with ASTM D1356(6). All abbreviations and symbols are defined with this document at the point of use.

6. INTERFERENCES

6.1 Only compounds having a similar mass spectrum and GC retention time compared to the compound of interest will interfere in the method. The most commonly encountered interferences are structural isomers.

6.2 Contamination of the Tenax cartridge with the compound(s) of interest is a commonly encountered problem in the method. The user must be extremely careful in the preparation, storage, and handling of the cartridges throughout the entire sampling and analysis process to minimize this problem.

7. Apparatus

7.1 Gas Chromatograph/Mass Spectrometry system - should be capable of subambient temperature programming. Unit mass resolution or better up to 800 amu. Capable of scanning 30-440 amu region every 0.5-1 second. Equipped with data system for instrument control as well as data acquisition, processing and storage.

7.2 Thermal Desorption Unit - Designed to accommodate Tenax cartridges in use. See Figure 2a or b.

7.3 Sampling System - Capable of accurately and precisely drawing an air flow of 10-500 ml/minute through the Tenax cartridge. (See Figure 3a or b.)

7.4 Vacuum oven - connected to water aspirator vacuum supply.

7.5 Stopwatch

7.6 Pyrex disks - for drying Tenax.

7.7 Glass jar - Capped with Teflon-lined screw cap. For storage of purified Tenax.

7.8 Powder funnel - for delivery of Tenax into cartridges.

7.9 Culture tubes - to hold individual glass Tenax cartridges.

7.10 Friction top can (paint can) - to hold clean Tenax cartridges.

7.11 Filter holder - stainless steel or aluminum (to accommodate 1 inch diameter filter). Other sizes may be used if desired. (optional)

7.12 Thermometer - to record ambient temperature.

7.13 Barometer (optional).

7.14 Dilution bottle - Two-liter with septum cap for standards preparation.

7.15 Teflon stirbar - 1 inch long.

7.16 Gas-tight glass syringes with stainless steel needles - 10-500 µl for standard injection onto GC/MS system.

7.17 Liquid microliter syringes - 5,50 µL for injecting neat liquid standards into dilution bottle.

7.18 Oven - 60 ± 5°C for equilibrating dilution flasks.

7.19 Magnetic stirrer.

7.20 Heating mantel.

7.21 Variac

7.22 Soxhlet extraction apparatus and glass thimbles - for purifying Tenax.

7.23 Infrared lamp - for drying Tenax.

7.24 GC column - SE-30 or alternative coating, glass capillary or fused silica.

7.25 Psychrometer - to determine ambient relative humidity. (optional).

8. Reagents and Materials

8.1 Empty Tenax cartridges - glass or stainless steel (See Figure 1a or b).

8.2 Tenax 60/80 mesh (2,6-diphenylphenylene oxide polymer).

8.3 Glasswool - silanized.

8.4 Acetone - Pesticide quality or equivalent.

8.5 Methanol - Pesticide quality, or equivalent.

8.6 Pentane - Pesticide quality or equivalent.

8.7 Helium - Ultra pure, compressed gas. (99.9999%)

8.8 Nitrogen - Ultra pure, compressed gas. (99.9999%)

8.9 Liquid nitrogen.

8.10 Polyester gloves - for handling glass Tenax cartridges.

8.11 Glass Fiber Filter - one inch diameter, to fit in filter holder. (optional)

8.12 Perfluorotributylamine (FC-43).

8.13 Chemical Standards - Neat compounds of interest. Highest purity available.

8.14 Granular activated charcoal - for preventing contamination of Tenax cartridges during storage.

9. Cartridge Construction and Preparation

9.1 Cartridge Design

9.1.1 Several cartridge designs have been reported in the literature (1-3). The most common (1) is shown in Figure 1a. This design minimizes contact of the sample with metal surfaces, which can lead to decomposition in certain cases. However, a disadvantage of this design is the need to rigorously avoid contamination of the <u>outside</u> portion of the cartridge since the entire surface is subjected to the purge gas stream during the desorption porcess.

Clean polyester gloves must be worn at all times when handling such cartridges and exposure of the open cartridge to ambient air must be minimized.

9.1.2 A second common type of design (3) is shown in Figure 1b. While this design uses a metal (stainless steel) construction, it eliminates the need to avoid direct contact with the exterior surface since only the interior of the cartridge is purged.

9.1.3 The thermal desorption module and sampling system must be selected to be compatible with the particular cartridge design chosen. Typical module designs are shown in Figures 2a and b. These designs are suitable for the cartridge designs shown in Figures 1a and 1b, respectively.

9.2 Tenax Purification

9.2.1 Prior to use the Tenax resin is subjected to a series of solvent extraction and thermal treatment steps. The operation should be conducted in an area where levels of volatile organic compounds (other than the extraction solvents used) are minimized.

9.2.2 All glassware used in Tenax purification as well as cartridge materials should be thoroughly cleaned by water rinsing followed by an acetone rinse and dried in an oven at 250°C.

9.2.3 Bulk Tenax is placed in a glass extraction thimble and held in place with a plug of clean glasswool. The resin is then placed in the soxhlet extraction apparatus and extracted sequentially with methanol and then pentane for 16-24 hours (each solvent) at approximately 6 cycles/hour. Glasswool for cartidge preparation should be cleaned in the same manner as Tenax.

9.2.4 The extracted Tenax is immediately placed in an open glass dish and heated under an infrared lamp for two hours in a hood. Care must be exercised to avoid over heating of the Tenax by the infrared lamp. The Tenax is then placed in a vacuum oven (evacuated using a water aspirator) without heating for one hour. An inert gas (helium or nitrogen) purge of 2-3 ml/minute is used to aid in the removal of solvent vapors. The oven temperature is then increased to 110°C, maintaining inert gas flow and held for one hour. The oven temperature control is then shut off and the oven is allowed to cool to room temperature. Prior to opening the oven, the oven is slightly pressurized with nitrogen to prevent contamination with ambient air. The Tenax is removed from the oven and sieved through a 40/60 mesh sieve (acetone rinsed and oven dried) into a clean glass vessel. If the Tenax is not to be used immediately for cartridge preparation it should be stored in a clean glass jar having a Teflon-lined screw cap and placed in a desiccator.

9.3 Cartridge Preparation and Pretreatment

9.3.1 All cartridge materials are pre-cleaned as described in Section 9.2.2. If the glass cartridge design shown in Figure 1a is employed all handling should be conducted wearing polyester gloves.

9.3.2 The cartridge is packed by placing a 0.5-1cm glasswool plug in the base of the cartridge and then filling the cartridge to within approximately 1 cm of the top. A 0.5-1cm glasswool plug is placed in the top of the cartridge.

9.3.3 The cartridges are then thermally conditioned by heating for four hours at 270°C under an inert gas (helium) purge (100 - 200 ml/min).

9.3.4 After the four hour heating period the cartridges are allowed to cool. Cartridges of the type shown in Figure 1a are immediately placed (without cooling) in clean culture tubes having Teflon-lined screw caps with a glasswool cushion at both the top and the bottom. Each tube should be shaken to ensure that the cartridge is held firmly in place. Cartridges of the type shown in Figure 1b are allowed to cool to room temperature under inert gas purge and are then closed with stainless steel plugs.

9.3.5 The cartridges are labeled and placed in a tightly sealed metal can (e.g. paint can or similar friction top container). For cartridges of the type shown in Figure 1a the culture tube, not the cartridge,is labeled.

9.3.6 Cartridges should be used for sampling within 2 weeks after preparation and analyzed within two weeks after sampling. If possible the cartridges should be stored at -20°C in a clean freezer (i.e. no solvent extracts or other sources of volatile organics contained in the freezer).

10. Sampling

10.1 Flow rate and Total Volume Selection

10.1.1 Each compound has a characteristic retention volume (liters of air per gram of adsorbent) which must not be exceeded. Since the retention volume is a function of temperature, and possibly other sampling variables, one must include an adequate margin of safety to ensure good collection efficiency. Some considerations and guidance in this regard are provided in a recent report (5). Approximate breakthrough volumes at 38°C (100°F) in liters/gram of Tenax are provided in Table 1. These retention volume data are supplied only as rough guidance and are subject to considerable variability, depending on cartridge design as well as sampling parameters and atmospheric conditions.

10.1.2 To calculate the maximum total volume of air which can be sampled use the following equation:

$$V_{MAX} = \frac{V_b x W}{1.5}$$

where

V_{MAX} is the calculated maximum total volume in liters.

V_b is the breakthrough volume for the least retained compound of interest (Table 1) in liters per gram of Tenax.

W is the weight of Tenax in the cartridge, in grams.

1.5 is a dimensionless safety factor to allow for variability in atmospheric conditions. This factor is appropriate for temperatures in the range of 25-30°C. If higher temperatures are encountered the factor should be increased (i.e. maximum total volume decreased).

10.1.3 To calculate maximum flow rate use the following equation:

$$Q_{MAX} = \frac{V_{MAX}}{t} \times 1000$$

where

Q_{MAX} is the calculated maximum flow rate in milliliters per minute.

t is the desired sampling time in minutes. Times greater than 24 hours (1440 minutes) generally are unsuitable because the flow rate required is too low to be accurately maintained.

10.1.4 The maximum flow rate Q_{MAX} should yield a linear flow velocity of 50-500 cm/minute. Calculate the linear velocity corresponding to the maximum flow rate using the following equation:

$$B = \frac{Q_{MAX}}{\pi r^2}$$

where

B is the calculated linear flow velocity in centimeters per minute.

r is the internal radius of the cartridge in centimeters.

If B is greater than 500 centimeters per minute either the total sample volume (V_{MAX}) should be reduced or the sample flow rate (Q_{MAX}) should be reduced by increasing the collection time. If B is less than 50 centimeters per minute the sampling rate (Q_{MAX}) should be increased by reducing the sampling time. The total sample value (V_{MAX}) cannot be increased due to component breakthrough.

10.1.4 The flow rate calculated as described above defines the maximum flow rate allowed. In general, one should collect additional samples in parallel, for the same time period but at lower flow rates. This practice yields a measure of quality control and is further discussed in the literature (5). In general, flow * rates 2 to 4 fold lower than the maximum flow rate should be employed for the parallel samples. In all cases a constant flow rate should be achieved for each cartridge since accurate integration of the analyte concentration requires that the flow be constant over the sampling period.

10.2 Sample Collection

10.2.1 Collection of an accurately known volume of air is critical to the accuracy of the results. For this reason the use of mass flow controllers, rather than conventional needle valves or orifices is highly recommended, especially at low flow velocities (e.g. less than 100 milliliters/minute). Figure 3a illustrates a sampling system utilizing mass flow controllers. This system readily allows for collection of parallel samples. Figures 3b shows a commercially available system based on needle valve flow controllers.

10.2.2 Prior to sample collection insure that the sampling flow rate has been calibrated over a range including the rate to be used for sampling, with a "dummy" Tenax cartridge in place. Generally calibration is accomplished using a soap bubble flow meter or calibrated wet test meter. The flow calibration device is connected to the flow exit, assuming the entire flow system is sealed. ASTM Method D3686 describes an appropriate calibration scheme, not requiring a sealed flow system downstream of the pump.

10.2.3 The flow rate should be checked before and after each sample collection. If the sampling interval exceeds four hours the flow rate should be checked at an intermediate point during sampling as well. In general, a rotameter should be included, as showed in Figure 3b, to allow observation of the sampling flow rate without disrupting the sampling process.

10.2.4 To collect an air sample the cartridges are removed from the sealed container just prior to initiation of the collection process. If glass cartridges (Figure 1a) are employed they must be handled only with polyester gloves and should not contact any other surfaces.

10.2.5 A particulate filter and holder are placed on the inlet to the cartridges and the exit end of the cartridge is connected to the sampling apparatus. In many sampling situations the use of a filter is not necessary if only the total concentration of a component is desired. Glass cartridges of the type shown in Figure 1a are connected using teflon ferrules and Swagelok (stainless steel or teflon) fittings. Start the pump and record the following parameters on an appropriate data sheet (Figure 4): data, sampling location, time, ambient temperature, barometric pressure, relative humidity, dry gas meter reading (if applicable) flow rate, rotameter reading (if applicable), cartridge number and dry gas meter serial number.

10.2.6 Allow the sampler to operate for the desired time, periodically recording the variables listed above. Check flow rate at the midpoint of the sampling interval if longer than four hours.

At the end of the sampling period record the parameters listed in 10.2.5 and check the flow rate and record the value. If the flows at the beginning and end of the sampling period differ by more than 10% the cartridge should be marked as suspect.

10.2.7 Remove the cartridges (one at a time) and place in the original container (use gloves for glass cartridges). Seal the cartridges or culture tubes in the friction-top can containing a layer of charcoal and package for immediate shipment to the laboratory for analysis. Store cartridges at reduced temperature (e.g. - 20°C) before analysis if possible to maximize storage stability.

10.2.8 Calculate and record the average sample rate for each cartridge according to the following equation:

$$Q_A = \frac{Q_1 + Q_2 + \ldots Q_N}{N}$$

where

Q_A = Average flow rate in ml/minute.

$Q_1, Q_2, \ldots Q_N$ = Flow rates determined at beginning, end, and immediate points during sampling.

N = Number of points averaged.

10.2.9 Calculate and record the total volumetric flow for each cartridge using the following equation:

$$V_m = \frac{T \times Q_A}{1000}$$

where

V_m = Total volume sampled in liters at measured temperature and pressure.

T_2 = Stop time.

T_1 = Start time.

T = Sampling time = $T_2 - T_1$, minutes

10.2.10 The total volume (V_s) at standard conditions, 25°C and 760 mmHg, is calculated from the following equation:

$$V_s = V_m \times \frac{P_A}{760} \times \frac{298}{273 + t_A}$$

where

P_A = Average barometric pressure, mmHg

t_A = Average ambient temperature, °C.

11. GC/MS Analysis

11.1 Instrument Set-up

11.1.1 Considerable variation from one laboratory to another is expected in terms of instrument configuration. Therefore each laboratory must be responsible for verifying that their particular system yields satisfactory results. Section 14 discusses specific performance criteria which should be met.

11.1.2 A block diagram of the typical GC/MS system required for analysis of Tenax cartridges is depicted in Figure 5. The operation of such devices is described in 11.2.4. The thermal desorption module must be designed to accommodate the particular cartridge configuration. Exposure of the sample to metal surfaces should be minimized and only stainless steel, or nickel metal surfaces should be employed.

The volume of tubing and fittings leading from the cartridge to the GC column must be minimized and all areas must be well-swept by helium carrier gas.

11.1.3 The GC column inlet should be capable of being cooled to -70°C and subsequently increased rapidly to approximately 30°C. This can be most readily accomplished using a GC equipped with subambient cooling capability (liquid nitrogen) although other approaches such as manually cooling the inlet of the column in liquid nitrogen may be acceptable.

11.1.4 The specific GC column and temperature program employed will be dependent on the specific compounds of interest. Appropriate conditions are described in the literature (1-3). In general a nonpolar stationary phase (e.g. SE-30, OV-1) temperature programmed from 30°C to 200°C at 8°/minute will be suitable. Fused silica bonded phase columns are preferable to glass columns since they are more rugged and can be inserted directly into the MS ion source, thereby eliminating the need for a GC/MS transfer line.

11.1.5 Capillary column dimensions of 0.3 mm ID and 50 meters long are generally appropriate although shorter lengths may be sufficient in many cases.

11.1.6 Prior to instrument calibration or sample analysis the GC/MS system is assembled as shown in Figure 5. Helium purge flows (through the cartridge) and carrier flow are set at approximately 10 ml/minute and 1-2 ml/minute respectively. If applicable, the injector sweep flow is set at 2-4 ml/minute.

11.1.7 Once the column and other system components are assembled and the various flows established the column temperature is increased to 250°C for approximately four hours (or overnight if desired) to condition the column.

11.1.8 The MS and data system are set according to the manufacturer's instructions. Electron impact ionization (70eV) and an electron multiplier gain of approximately 5×10^4 should be employed. Once the entire GC/MS system has been setup the system is calibrated as described in Section 11.2. The user should prepare a detailed standard operating procedure (SOP) describing this process for the particular instrument being used.

11.2 Instrument Calibration

11.2.1 Tuning and mass standarization of the MS system is performed according to manufacturer's instructions and relevant information from the user prepared SOP. Perfluorotributylamine should generally be employed for this purpose. The material is introduced directly into the ion source through a molecular leak. The instrumental parameters (e.g. lens voltages, resolution, etc.) should be adjusted to give the relative ion abundances shown in Table 2 as well as acceptable resolution and peak shape. If these approximate relative abundances cannot be achieved, the ion source may require cleaning according to manufacturer's instructions. In the event that the user's instrument cannot achieve these relative ion abundances, but is otherwise operating properly, the user may adopt another set of relative abundances as performance criteria.

However, these alternate values must be repeatable on a day-to-day basis.

11.2.2 After the mass standarization and tuning process has been completed and the appropriate values entered into the data system the user should then calibrate the entire system by introducing known quantities of the standard components of interest into the system. Three alternate procedures may be employed for the calibration process including 1) direct syringe injection of dilute vapor phase standards, prepared in a dilution bottle, onto the GC column, 2) Injection of dilute vapor phase standards into a carrier gas stream directed through the Tenax cartridge, and 3) introduction of permeation or diffusion tube standards onto a Tenax cartridge. The standards preparation procedures for each of these approaches are described in Section 13. The following paragraphs describe the instrument calibration process for each of these approaches.

11.2.3 If the instrument is to be calibrated by direct injection of a gaseous standard, a standard is prepared in a dilution bottle as described in Section 13.1. The GC column is cooled to -70°C (or, alternately, a portion of the column inlet is manually cooled with liquid nitrogen). The MS and data system is set up for acquisition as described in the relevant user SOP. The ionization filament should be turned off during the initial 2-3 minutes of the run to allow oxygen and other highly volatile components to elute. An appropriate volume (less than 1 ml) of the gaseous standard is injected onto the GC system using an accurately calibrated gas tight syringe.

The system clock is started and the column is maintained at -70°C (or liquid nitrogen inlet cooling) for 2 minutes. The column temperature is rapidly increased to the desired initial temperature (e.g. 30°C). The temperature program is started at a consistent time (e.g. four minutes) after injection. Simultaneously the ionization filament is turned on and data acquisition is initiated. After the last component of interest has eluted acquisiton is terminated and the data is processed as described in Section 11.2.5. The standard injection process is repeated using different standard volumes as desired.

11.2.4 If the system is to be calibrated by analysis of spiked Tenax cartridges a set of cartridges is prepared as described in Sections 13.2 or 13.3. Prior to analysis the cartridges are stored as described in Section 9.3. If glass cartridges (Figure 1a) are employed care must be taken to avoid direct contact, as described earlier. The GC column is cooled to -70°C, the collection loop is immersed in liquid nitrogen and the desorption module is maintained at 250°C. The inlet valve is placed in the desorb mode and the standard cartridge is placed in the desorption module, making certain that no leakage of purge gas occurs. The cartridge is purged for 10 minutes and then the inlet valve is placed in the inject mode and the liquid nitrogen source removed from the collection trap. The GC column is maintained at -70°C for two minutes and subsequent steps are as described in 11.2.3. After the process is complete the cartridge is removed from the desorption module and stored for subsequent use as described in Section 9.3.

11.2.5 Data processing for instrument calibration involves determining retention times, and integrated characteristic ion intensities for each of the compounds of interest. In addition, for at least one chromatographic run, the individual mass spectra should be inspected and compared to reference spectra to ensure proper instrumental performance. Since the steps involved in data processing are highly instrument specific, the user should prepare a SOP describing the process for individual use. Overall performance criteria for instrument calibration are provided in Section 14. If these criteria are not achieved the user should refine the instrumental parameters and/or operating procedures to meet these criteria.

11.3 Sample Analysis

11.3.1 The sample analysis process is identical to that described in Section 11.2.4 for the analysis of standard Tenax cartridges.

11.3.2 Data processing for sample data generally involves 1) qualitatively determining the presence or absence of each component of interest on the basis of a set of characteristic ions and the retention time using a reverse-search software routine, 2) quantification of each identified component by integrating the intensity of a characteristic ion and comparing the value to that of the calibration standard, and 3) tentative identification of other components observed using a forward (library) search software routine. As for other user specific processes, a SOP should be prepared describing the specific operations for each individual laboratory.

12. Calculations

12.1 Calibration Response Factors

12.1.1 Data from calibration standards is used to calculate a response factor for each component of interest. Ideally the process involves analysis of at least three calibration levels of each component during a given day and determination of the response factor (area/nanogram injected) from the linear least squares fit of a plot of nanograms injected versus area (for the characteristic ion). In general quantities of component greater than 1000 nanograms should not be injected because of column overloading and/or MS response nonlinearity.

12.1.2 In practice the daily routine may not always allow analysis of three such calibration standards. In this situation calibration data from consecutive days may be pooled to yield a response factor, provided that analysis of replicate standards of the same concentration are shown to agree within 20% on the consecutive days. One standard concentration, near the midpoint of the analytical range of interest, should be chosen for injection every day to determine day-to-day response reproducibility.

12.1.3 If substantial nonlinearity is present in the calibration curve a nonlinear least squares fit (e.g. quadratic) should be employed. This process involves fitting the data to the following equation:

$$Y = A + BX + CX^2$$

where

Y = peak area
X = quantity of component, nanograms
A, B, and C are coefficients in the equation

12.2 Analyte Concentrations

12.2.1 Analyte quantities on a sample cartridge are calculated from the following equation:

$$Y_A = A + BX_A + CX_A$$

where

Y_A is the area of the analyte characteristic ion for the sample cartridge.

X_A is the calculated quantity of analyte on the sample cartridge, in nanograms.

A,B, and C are the coefficients calculated from the calibration curve described in Section 12.1.3.

12.2.2 If instrumental response is essentially linear over the concentration range of interest a linear equation (C=0 in the equation above) can be employed.

12.2.3 Concentration of analyte in the original air sample is calculated from the following equation:

$$C_A = \frac{X_A}{V_S}$$

where

C_A is the calculated concentration of analyte in nanograms per liter.

V_S and X_A are as previously defined in Section 10.2.10 and 12.2.1, respectively.

13. Standard Preparation

13.1 Direct Injection

13.1.1 This process involves preparation of a dilution bottle containing the desired concentrations of compounds of interest for direct injection onto the GC/MS system.

13.1.2 Fifteen three-millimeter diameter glass beads and a one-inch Teflon stirbar are placed in a clean two-liter glass septum capped bottle and the exact volume is determined by weighing the bottle before and after filling with deionized water. The bottle is then rinsed with acetone and dried at 200°C.

13.1.3 The amount of each standard to be injected into the vessel is calculated from the desired injection quantity and volume using the following equation:

$$W_T = \frac{W_I}{V_I} \times V_B$$

where

W_T is the total quantity of analyte to be injected into the bottle in milligrams

W_I is the desired weight of analyte to be injected onto the GC/MS system or spiked cartridge in nanograms

V_I is the desired GC/MS or cartridge injection volume (should not exceed 500) in microliters.

V_B is total volume of dilution bottle determined in 13.1.1, in liters.

13.1.4 The volume of the neat standard to be injected into the dilution bottle is determined using the following equation:

$$V_T = \frac{W_T}{d}$$

where

V_T is the total volume of neat liquid to be injected in microliters.

d is the density of the neat standard in grams per milliliter.

13.1.6 The bottle is placed in a 60°C oven for at least 30 minutes prior to removal of a vapor phase standard.

13.1.7 To withdraw a standard for GC/MS injection the bottle is removed from the oven and stirred for 10-15 seconds. A suitable gas-tight microber syring warmed to 60°C, is inserted through the septum cap and pumped three times slowly. The appropriate volume of sample (approximately 25% larger than the desired injection volume) is drawn into the syringe and the volume is adjusted to the exact value desired and then immediately injected over a 5-10 seconds period onto the GC/MS system as described in Section 11.2.3.

13.2 Preparation of Spiked Cartridges by Vapor Phase Injection

13.2.1 This process involves preparation of a dilution bottle containing the desired concentrations of the compound(s) of interest as described in 13.1 and injecting the desired volume of vapor into a flowing inert gas stream directed through a clean Tenax cartridge.

13.2.2 A helium purge system is assembled wherein the helium flow 20-30 mL/minute is passed through a stainless steel Tee fitted with a septum injector. The clean Tenax cartridge is connected downstream of the tee using appropriate Swagelok fittings. Once the cartridge is placed in the flowing gas stream the appropriate volume vapor standard, in the dilution bottle, is injected through the septum as described in 13.1.6. The syringe is flushed several times by alternately filling the syringe with carrier gas and displacing the contents into the flow stream, without removing the syringe from the septum. Carrier flow is maintain through the cartridge for approximately 5 minutes after injection.

13.3 Preparation of Spiked Traps Using Permeation or Diffusion tubes

13.3.1 A flowing stream of inert gas containing known amounts of each compound of interest is generated according to ASTM Method D3609(6). Note that a method of accuracy maintaining temperature within ± 0.1°C is required and the system generally must be equilibrated for at least 48 hours before use.

13.3.2 An accurately known volume of the standard gas stream (usually 0.1-1 liter) is drawn through a clean Tenax cartridge using the sampling system described in Section 10.2.1, or a similar system. However, if mass flow controllers are employed they must be calibrated for the carrier gas used in Section 13.3.1 (usually nitrogen). Use of air as the carrier gas for permeation systems is not recommended, unless the compounds of interest are known to be highly stable in air.

13.3.3 The spiked cartridges are then stored or immediately analyzed as in Section 11.2.4.

14. Performance Criteria and Quality Assurance

This section summarizes quality assurance (QA) measures and provides guidance concerning performance criteria which should be achieved within each laboratory. In many cases the specific QA procedures have been described within the appropriate section describing the particular activity (e.g. parallel sampling).

14.1 Standard Opreating Procedures (SOPs)

14.1.1 Each user should generate SOPs describing the following activities as they are performed in their laboratory:

1) assembly, calibration, and operation of the sampling system,
2) preparation, handling and storage of Tenax cartridges,
3) assembly and operation of GC/MS system including the thermal desorption apparatus and data system, and
4) all aspects of data recording and processing.

14.1.2 SOPs should provide specific stepwise instructions and should be readily available to, and understood by the laboratory personnel conducting the work.

14.2 Tenax Cartridge Preparation

14.2.1 Each batch of Tenax cartridges prepared (as described in Section 9) should be checked for contamination by analyzing one cartridge immediately after preparation. While analysis can be accomplished by GC/MS, many laboratories may chose to use GC/FID due to logistical and cost considerations.

14.2.2 Analysis by GC/FID is accomplished as described for GC/MS (Section 11) except for use of FID detection.

14.2.3 While acceptance criteria can vary depending on the components of interest, at a minimum the clean cartridge should be demonstrated to contain less than one fourth of the minimum level of interest for each component. For most compounds the blank level should be less than 10 nanograms per cartridge in order to be acceptable. More rigid criteria may be adopted, if necessary, within a specific laboratory. If a cartridge does not meet these acceptance criteria the entire lot should be rejected.

14.3 Sample Collection

14.3.1 During each sampling event at least one clean cartridge will accompany the samples to the field and back to the laboratory, without being used for sampling, to serve as a field blank. The average amount of material found on the field blank cartridge may be subtracted from the amount found on the actual samples. However, if the blank level is greater than 25% of the sample amount, data for that component must be identified as suspect.

14.3.2 During each sampling event at least one set of parallel samples (two or more samples collected simultaneously) will be collected, preferably at different flow rates as described in Section 10.1. If agreement between parallel samples is not generally within ± 25% the user should collect parallel samples on a much more frequent basis (perhaps for all sampling points). If a trend of lower apparent concentrations with increasing flow rate is observed for a set of parallel samples one should consider using a reduced flow rate and longer sampling interval if possible. If this practice does not improve the reproducibility further evaluation of the method performance for the compound of interest may be required.

14.3.3 Backup cartridges (two cartridges in series) should be collected with each sampling event. Backup cartridges should contain less than 20% of the amount of components of interest found in the front cartridges, or be equivalent to the blank cartridge level, whichever is greater. The frequency of use of backup cartridges should be increased if increased flow rate is shown to yield reduced component levels for parallel sampling. This practice will help to identify problems arising from breakthrough of the component of interest during sampling.

14.4 GC/MS Analysis

14.4.1 Performance criteria for MS tuning and mass calibration have been discussed in Section 11.2 and Table 2. Additional criteria may be used by the laboratory if desired. The following sections provide performance guidance and suggested criteria for determining the acceptability of the GC/MS system.

14.4.2 Chromatographic efficiency should be evaluated using spiked Tenax cartridges since this practice tests the entire system. In general a reference compound such as perfluorotoluene should be spiked onto a cartridge at the 100 nanogram level as described in Section 13.2 or 13.3. The cartridge is then analyzed by GC/MS as described in Section 11.4. The perfluorotoluene (or other reference compound) peak is then plotted on an expanded time scale so that its width at 10% of the peak can be calculated, as shown in Figure 6. The width of the peak at 10% height should not exceed 10 seconds. More stringent criteria may be required for certain applications. The assymmetry factor (See Figure 6) should be between 0.8 and 2.0. The assymmetry factor for any polar or reactive compounds should be determined using the process described above. If peaks are observed that exceed the peak width or assymmetry factor criteria above, one should inspect the entire system to determine if unswept zones or cold spots are present in any of the fittings and is necessary. Some laboratories may chose to evaluate column performance separately by direct injection of a test mixture onto the GC column. Suitable schemes for column evaluation have been reported in the literature (7). Such schemes cannot be conducted by placing the substances onto Tenax because many of the compounds (e.g. acids, bases, alcohols) contained in the test mix are not retained, or degrade, on Tenax.

14.4.3 The system detection limit for each component is calculated from the data obtained for calibration standards. The detection limit is defined as

$$DL = A + 3.3S$$

where

DL is the calculated detection limit in nanograms injected.

A is the intercept calculated in Section 12.1.1 or 12.1.3.

S is the standard deviation of replicate determinations of the lowest level standard (at least three such determinations are required.

In general the detection limit should be 20 nanograms or less and for many applications detection limits of 1-5 nanograms may be required. The lowest level standard should yield a signal to noise ratio, from the total ion current response, of approximately 5.

14.4.4 The relative standard deviation for replicate analyses of cartridges spiked at approximately 10 times the detection limit should be 20% or less. Day to day relative standard deviation should be 25% or less.

14.4.5 A useful performance evaluation step is the use of an internal standard to track system performance. This is accomplished by spiking each cartridge, including blank, sample, and calibration cartridges with approximately 100 nanograms of a compound not generally present in ambient air (e.g. perfluorotoluene). The integrated ion intensity for this compound helps to identify problems with a specific sample. In general the user should calculate the standard deviation of the internal standard response for a given set of samples analyzed under identical tuning and calibration conditions. Any sample giving a value greater than ± 2 standard deviations from the mean (calculated excluding that particular sample) should be identified as suspect. Any marked change in internal standard response may indicate a need for instrument recalibration.

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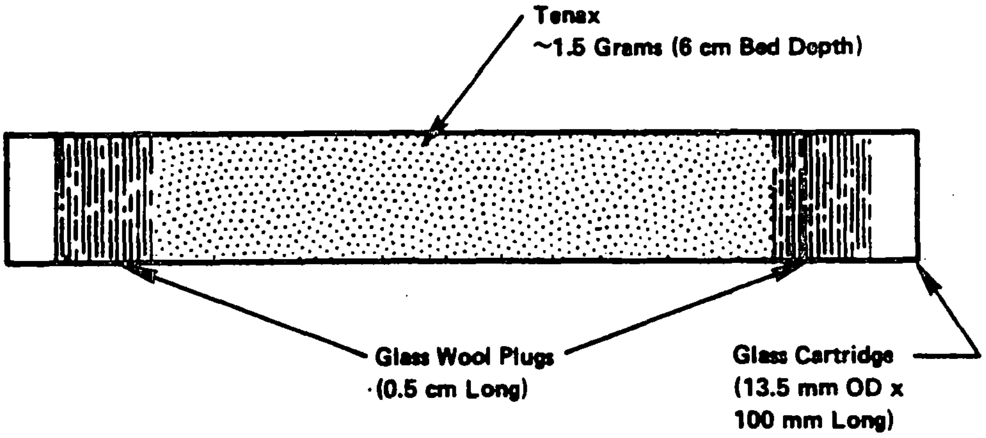
TABLE 1. RETENTION VOLUME ESTIMATES FOR COMPOUNDS ON TENAX

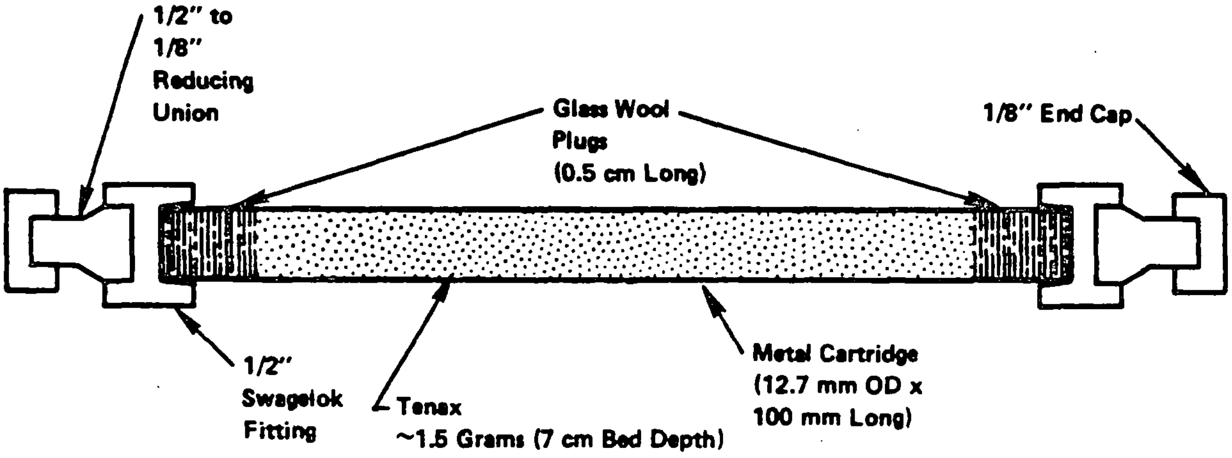
COMPOUND	ESTIMATED RETENTION VOLUME AT 100°F (38°C)-LITERS/GRAM
Benzene	19
Toluene	97
Ethyl Benzene	200
Xylene(s)	∿ 200
Cumene	440
n-Heptane	20
1-Heptene	40
Chloroform	8
Carbon Tetrachloride	8
1,2-Dichloroethane	10
1,1,1-Trichloroethane	6
Tetrachloroethylene	80
Trichloroethylene	20
1,2-Dichloropropane	30
1,3-Dichloropropane	90
Chlorobenzene	150
Bromoform	100
Ethylene Dibromide	60
Bromobenzene	300

TABLE 2. SUGGESTED PERFORMANCE CRITERIA FOR RELATIVE ION ABUNDANCES FROM FC-43 MASS CALIBRATION

M/E	% RELATIVE ABUNDANCE
51	1.8 ± 0.5
69	100
100	12.0 ± 1.5
119	12.0 ± 1.5
131	35.0 ± 3.5
169	3.0 ± 0.4
219	24.0 ± 2.5
264	3.7 ± 0.4
314	0.25 ± 0.1

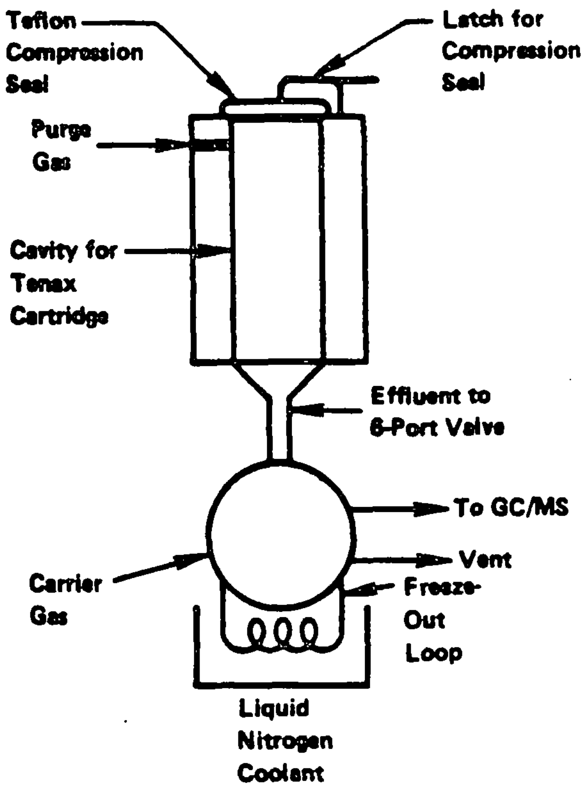


(a) Glass Cartridge

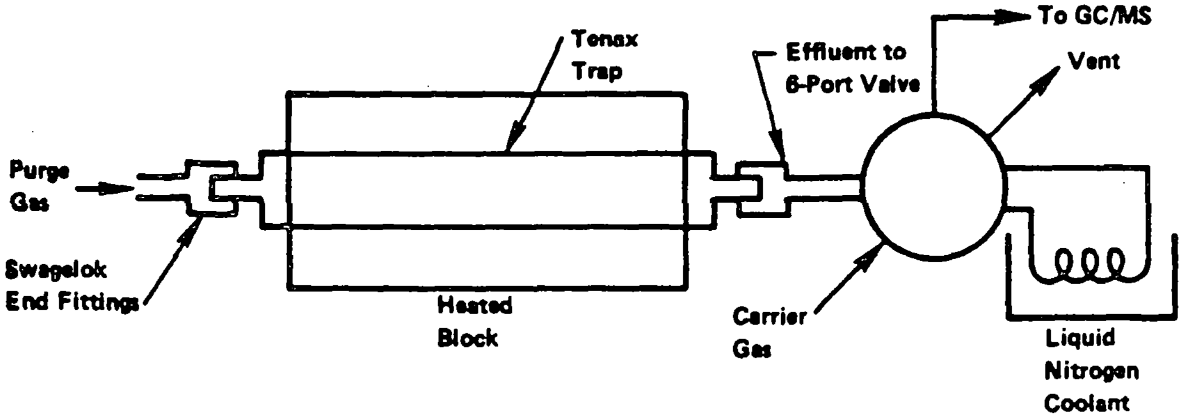


(b) Metal Cartridge

FIGURE 1. TENAX CARTRIDGE DESIGNS

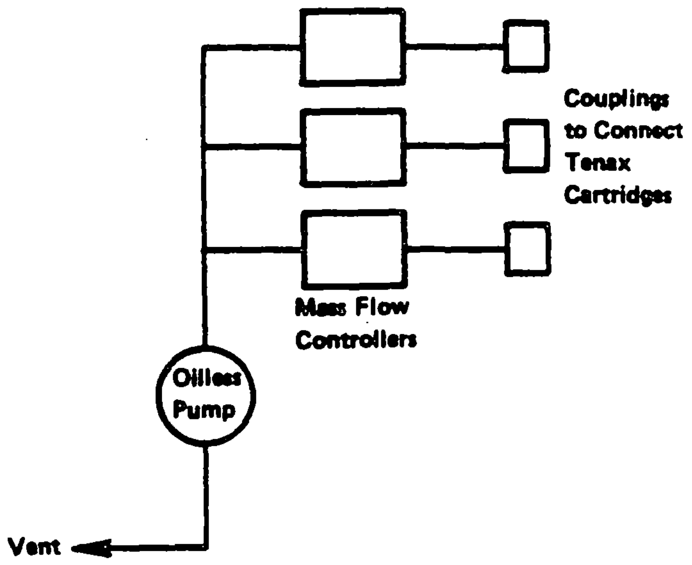


(a) Glass Cartridges (Compression Fit)

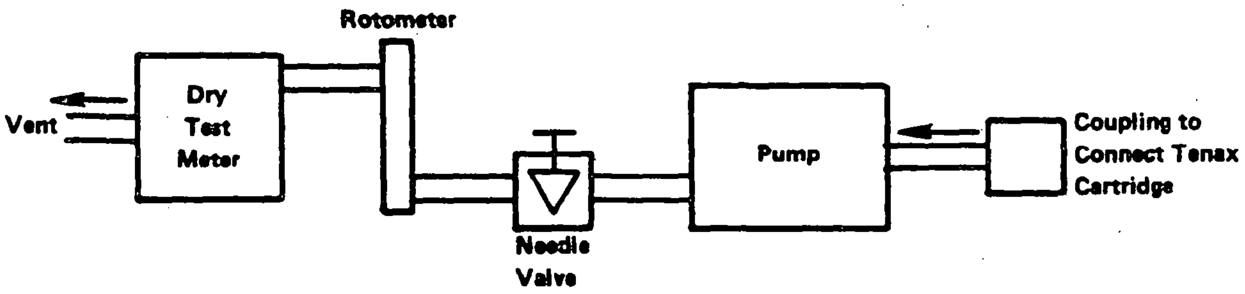


(b) Metal Cartridges (Swagelok Fittings)

FIGURE 2. TENAX CARTRIDGE DESORPTION MODULES



(a) Mass Flow Control



(b) Needle Valve Control

FIGURE 3. TYPICAL SAMPLING SYSTEM CONFIGURATIONS

SAMPLING DATA SHEET
(One Sample Per Data Sheet)

PROJECT: ____________________

SITE: ____________________

LOCATION: ____________________

INSTRUMENT MODEL NO: ____________

PUMP SERIAL NO: ______________

DATE(S) SAMPLED: ____________________

TIME PERIOD SAMPLED: ________________

OPERATOR: ____________________

CALIBRATED BY: ____________________

SAMPLING DATA

Sample Number: ____________________

Start Time: ________ Stop Time: ________

Time	Dry Gas Meter Reading	Rotameter Reading	Flow Rate,*Q ml/Min	Ambient Temperature °C	Barometric Pressure, mmHg	Relative Humidity, %	Comments
1.							
2.							
3.							
4.							
N.							

Total Volume Data**

V_m = (Final - Initial) Dry Gas Meter Reading, or = ______ Liters

$$= \frac{Q_1 + Q_2 + Q_3 \ldots Q_N}{N} \times \frac{1}{1000 \times (\text{Sampling Time in Minutes})} = \_\_\_\_\_\_ \text{ Liters}$$

* Flowrate from rotameter or soap bubble calibrator (specify which).

** Use data from dry gas meter if available.

FIGURE 4. EXAMPLE SAMPLING DATA SHEET

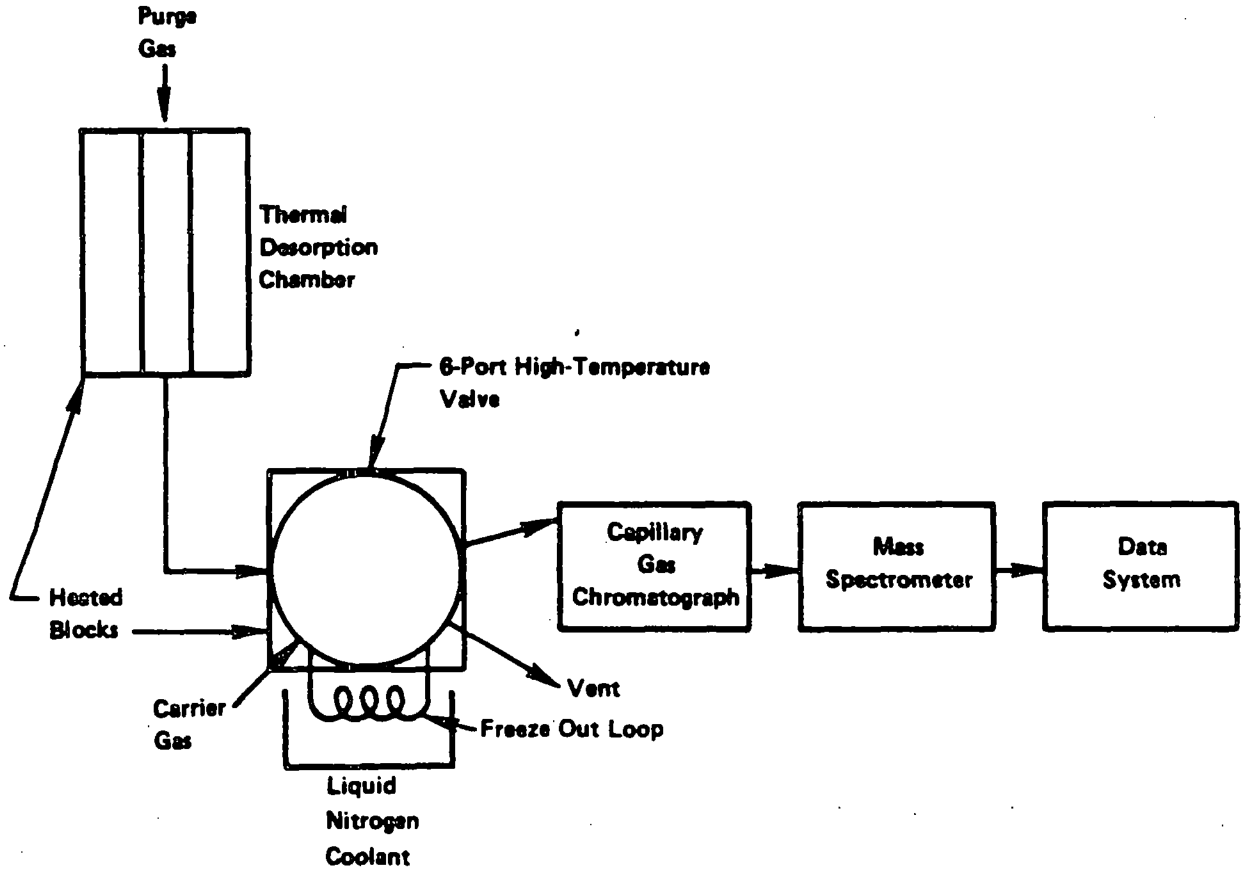
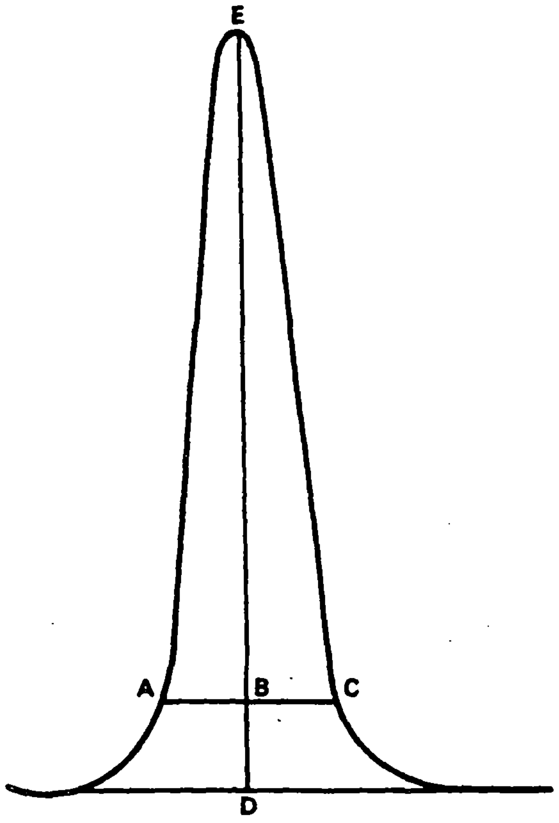


FIGURE 5. BLOCK DIAGRAM OF ANALYTICAL SYSTEM



$$\text{Asymmetry Factor} = \frac{BC}{AB}$$

Example Calculation:

Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

Therefore: Asymmetry Factor $= \frac{12}{11} = 1.1$

FIGURE 6. PEAK ASYMMETRY CALCULATION

METHOD FOR THE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR BY CARBON MOLECULAR SIEVE ADSORPTION AND GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

1. Scope

1.1 This document describes a procedure for collection and determination of selected volatile organic compounds which can be captured on carbon molecular sieve (CMS) adsorbents and determined by thermal desorption GC/MS techniques.

1.2 Compounds which can be determined by this method are nonpolar and nonreactive organics having boiling points in the range -15 to +120°C. However, not all compounds meeting these criteria can be determined. Compounds for which the performance of the method has been documented are listed in Table 1. The method may be extended to other compounds but additional validation by the user is required. This method has been extensively used in a <u>single</u> laboratory. Consequently, its general applicability has not been thoroughly documented.

2. Applicable Documents

2.1 ASTM Standards

D 1356 Definitions of Terms Related to Atmospheric Sampling and Analysis.

E 355 Recommended Practice for Gas Chromatography Terms and Relationships.

2.2 Other Documents

Ambient Air Studies (1,2).

U.S. EPA Technical Assistance Document (3).

3. Summary of Method

3.1 Ambient air is drawn through a cartridge containing ∿0.4 of a carbon molecular sieve (CMS) adsorbent. Volatile organic compounds are captured on the adsorbent while major inorganic atmospheric constituents pass through (or are only partially retained). After sampling, the cartridge is returned to the laboratory for analysis.

3.2 Prior to analysis the cartridge is purged with 2-3 liters of pure, dry air (in the same direction as sample flow) to remove adsorbed moisture.

3.3 For analysis the cartridge is heated to 350°-400°C, under helium purge and the desorbed organic compounds are collected in a specially designed cryogenic trap. The collected organics are then flash evaporated onto a capillary column GC/MS system (held at -70°C). The individual components are identified and quantified during a temperature programmed chromatographic run.

3.4 Due to the complexity of ambient air samples, only high resolution (capillary column) GC techniques are acceptable for most applications of the method.

4. Significance

4.1 Volatile organic compounds are emitted into the atmosphere from a variety of sources including industrial and commercial facilities, hazardous waste storage and treatment facilities, etc. Many of these compounds are toxic; hence knowledge of the concentration of such materials in the ambient atmosphere is required in order to determine human health impacts.

4.2 Traditionally air monitoring methods for volatile organic compounds have relied on carbon adsorption followed by solvent desorption and GC analysis. Unfortunately, such methods are not sufficiently sensitive for ambient air monitoring, in most cases, because only a small portion of the sample is injected onto the GC system. Recently on-line thermal desorption methods, using organic polymeric adsorbents such as Tenax® GC, have been used for ambient air monitoring. The current method uses CMS adsorbents (e.g. Spherocarb®) to capture highly volatile organics (e.g. vinyl chloride) which are not collected on Tenax®. The use of on-line thermal desorption GC/MS yields a sensitive, specific analysis procedure.

5. Definitions

Definitions used in this document and any user prepared SOPs should be consistent with ASTM D1356 (4). All abbreviations and symbols are defined with this document at the point of use.

6. Interferences

6.1 Only compounds having a mass spectrum and GC retention time similar to the compound of interest will interfere in the method. The most commonly encountered interferences are structural isomers.

6.2 Contamination of the CMS cartridge with the compound(s) of interest can be a problem in the method. The user must be careful in the preparation, storage, and handling of the cartridges through the entire process to minimize contamination.

7. Apparatus

7.1 Gas Chromatograph/Mass Spectrometry system - must be capable of subambient temperature programming. Unit mass resolution to 800 amu. Capable of scanning 30-300 amu region every 0.5-0.8 seconds. Equipped with data system for instrument control as well as data acquisition, processing and storage.

7.2 Thermal Desorption Injection Unit - Designed to accommodate CMS cartridges in use (See Figure 3) and including cryogenic trap (Figure 5) and injection valve (Carle Model 5621 or equivalent).

7.3 Sampling System - Capable of accurately and precisely drawing an air flow of 10-500 ml/minute through the CMS cartridge. (See Figure 2a or b.)

7.4 Dewar flasks - 500 mL and 5 liter.

7.5 Stopwatches.

7.6 Various pressure regulators and valves - for connecting compressed gas cylinders to GC/MS system.

7.7 Calibration gas - In aluminum cylinder. Prepared by user or vendor. For GC/MS calibration.

7.8 High pressure apparatus for preparing calibration gas cylinders (if conducted by user). Alternatively, custom prepared gas mixtures can be purchased from gas supply vendors.

7.9 Friction top can (e.g. one-gallon paint can) - With layer of activated charcoal to hold clean CMS cartridges.

7.10 Thermometer - to record ambient temperature.

7.11 Barometer (optional).

7.12 Dilution bottle - Two-liter with septum cap for standard preparation.

7.13 Teflon stirbar - 1 inch long

7.14 Gas tight syringes - 10-500 µl for standard injection onto GC/MS system and CMS cartridges.

7.15 Liquid microliter syringes - 5-50 µL for injecting neat liquid standards into dilution bottle.

7.16 Oven - 60 ± 5°C for equilibrating dilution bottle.

7.17 Magnetic stirrer.

7.18 Variable voltage transformers - (120 V and 1000 VA) and electrical connectors (or temperature controllers) to heat cartridge and cryogenic loop.

7.19 Digital pyrometer - 30 to 500°C range.

7.20 Soap bubble flow meter - 1, 10 and 100 mL calibration points.

7.21 Copper tubing (1/8 inch) and fittings for gas inlet lines.

7.22 GC column - SE-30 or alternative coating, glass capillary or fused silica.

7.23 Psychrometer (optional).

7.24 Filter holder - stainless steel or aluminum (to accommodate 1 inch diameter filter). Other sizes may be used if desired. (optional)

8. Reagents and Materials

8.1 Empty CMS cartridges - Nickel or stainless steel (See Figure 1).

8.2 CMS Adsorbent, 60/80 mesh- Spherocarb® from Analabs Inc., or equivalent.

8.3 Glasswool - silanized.

8.4 Methylene chloride - pesticide quality, or equivalent.

8.5 Gas purifier cartridge for purge and GC carrier gas containing charcoal, molecular sieves, and a drying agent. Available from various chromatography supply houses.

8.6 Helium - Ultra pure, (99.9999%) compressed gas.

8.7 Nitrogen - Ultra pure, (99.9999%) compressed gas.

8.8 Liquid nitrogen or argon (50 liter dewar).

8.9 Compressed air, if required - for operation of GC oven door.

8.10 Perfluorotributylamine (FC-43) for GC/MS calibration.

8.11 Chemical Standards - Neat compounds of interest. Highest purity available.

9. Cartridge Construction and Preparation

9.1 A suitable cartridge design in shown in Figure 1. Alternate designs have been reported (1) and are acceptable, provided the user documents their performance. The design shown in Figure 1 has a built-in heater assembly. Many users may choose to replace this heater design with a suitable separate heating block or oven to simplify the cartridge design.

9.2 The cartridge is assembled as shown in Figure 1 using standard 0.25 inch O.D. tubing (stainless steel or nickel), 1/4 inch to 1/8 inch reducing unions, 1/8 inch nuts, ferrules, and endcaps. These parts are rinsed with methylene chloride and heated at 250°C for 1 hour prior to assembly.

9.3 The thermocouple bead is fixed to the cartridge body, and insulated with a layer of Teflon tape. The heater wire (constructed from a length of thermocouple wire) is wound around the length of the cartridge and wrapped with Teflon tape to secure the wire in place. The cartridge is then wrapped with woven silica fiber insulation (Zetex or equivalent). Finally the entire assembly is wrapped with fiber glass tape.

9.4 After assembly one end of the cartridge is marked with a serial number to designate the cartridge inlet during sample collection.

9.5 The cartridges are then packed with ∿0.4 grams of CMS adsorbent. Glasswool plugs (∿0.5 inches long) are placed at each end of the cartridge to hold the adsorbent firmly in place. Care must be taken to insure that no strands of glasswool extend outside the tubing, thus causing leakage in the compression endfittings. After loading the endfittings (reducing unions and end caps) are tightened onto the cartridge.

9.6 The cartridges are conditioned for initial use by heating at 400°C overnight (at least 16 hours) with a 100 mL/minute purge of pure nitrogen. Reused cartridges need only to be heated for 4 hours and should be reanalyzed before use to ensure complete desorption of impurities.

9.7 For cartridge conditioning ultra-pure nitrogen gas is passed through a gas purifier to remove oxygen,moisture and organic contaminants. The nitrogen supply is connected to the unmarked end of the cartridge and the flow adjusted to ∿50 mL/minute using a needle valve. The gas flow from the inlet (marked) end of the cartridge is vented to the atmosphere.

9.8 The cartridge thermocouple lead is connected to a pyrometer and the heater lead is connected to a variable voltage transformer (Variac) set at 0 V. The voltage on the Variac is increased to ∿15 V and adjusted over a 3-4 minute period to stabilize the cartridge temperature at 380-400°C.

9.9 After 10-16 hours of heating (for new cartridges) the Variac is turned off and the cartridge is allowed to cool to ∿30°C, under continuing nitrogen flow.

9.10 The exit end of the cartridge is capped and then the entire cartridge is removed from the flow line and the other endcap immediately installed. The cartridges are then placed in a metal friction top (paint) can containing ∿2 inches of granulated activated charcoal (to prevent contamination of the cartridges during storage) in the bottom, beneath a retaining screen. Clean paper tissues (e.g. Kimwipes) are placed in can to avoid damage to the cartridges during shipment.

9.11 Cartridges are stored in the metal can at all times except when in use. Adhesives initially present in the cartridge insulating materials are "burnt off" during initial conditioning. Therefore, unconditioned cartridges should not be placed in the metal can since they may contaminate the other cartridges.

9.12 Cartridges are conditioned within two weeks of use. A blank from each set of cartridges is analyzed prior to use in field sampling. If an acceptable blank level is achieved, that batch of cartridges (including the cartridge serving as the blank) can be used for field sampling.

10. Sampling

10.1 Flow Rate and Total Volume Selection

10.1.1 Each compound has a characteristic retention volume (liters of air per unit weight of adsorbent). However, all of the compounds listed in Table 1 have retention volumes (at 37°C) in excess of 100 liters/cartridge (0.4 gram CMS cartridge) except vinyl chloride for which the value is ~30 liters/cartridge. Consequently, if vinyl chloride or similarly volatile compounds are of concern the maximum allowable sampling volume is approximately 20 liters. If such highly volatile compounds are not of concern, samples as large as 100 liters can be collected.

10.1.2 To calculate the maximum allowable sampling flow rate the following equation can be used:

$$Q_{Max} = \frac{V_{Max}}{t} \times 1000$$

where

Q_{Max} is the calculated maximum sampling rate in mL/minute.

t is the desired sampling time in minutes.

V_{Max} is the maximum allowable total volume based on the discussion in 10.1.1.

10.1.3 For the cartridge design shown in Figure 1 Q_{Max} should be between 20 and 500 mL/minute. If Q_{Max} lies outside this range the sampling time or total sampling volume must be adjusted so that this criterion is achieved.

10.1.4 The flow rate calculated in 10.1.3 defines the maximum allowable flow rate. In general, the user should collect additional samples in parallel, at successive 2- to 4-fold lower flow rates. This practice serves as a quality control procedure to check on component breakthrough and related sampling and adsorption problems, and is further discussed in the literature (5).

10.2 Sample Collection

10.2.1 Collection of an accurately known volume of air is critical to the accuracy of the results. For this reason the use of mass flow controllers, rather than conventional needle valves or orifices is highly recommended, especially at low flow rates (e.g. less than 100 milliliters/minute). Figure 2a illustrates a sampling system based on mass flow controllers which readily allows for collection of parallel samples. Figure 2b shows a commercially available sampling system based on needle valve flow controllers.

10.2.2 Prior to sample collection the sampling flow rate is calibrated near the value used for sampling, with a "dummy" CMS cartridge in place. Generally calibration is accomplished using a soap bubble flow meter or calibrated wet test meter connected to the flow exit, assuming the entire flow system is sealed. ASTM Method D 3686 (4) describes an appropriate calibration scheme, not requiring a sealed flow system downstream of the pump.

10.2.3 The flow rate should be checked before and after each sample collection. Ideally, a rotemeter or mass flow meter should be included in the sampling system to allow periodic observation of the flow rate without disrupting the sampling process.

10.2.4 To collect an air sample the cartridges are removed from the sealed container just prior to initiation of the collection process.

10.2.5 The exit (unmarked) end of the cartridge is connected to the sampling apparatus. The endcap is left on the sample inlet and the entire system is leak checked by activating the sampling pump and observing that no flow is obtained over a 1 minute period. The sampling pump is then shut off.

10.2.6 The endcap is removed from the cartridge, a particulate filter and holder are placed on the inlet end of the cartridge, and the sampling pump is started. In many situations a particulate filter is not necessary since the compounds of interest are in the vapor state. However, if, large amounts of particulate matter are encountered, the filter may be useful to prevent contamination of the cartridge. The following parameters are recorded on an appropriate data sheet (Figure 4): date, sampling location, time, ambient temperature, barometric pressure, relative humidity, dry gas meter reading (if applicable), flow rate, rotometer reading (if applicable), cartridge number, pump, and dry gas meter serial number.

10.2.7 The samples are collected for the desired time, periodically recording the variables listed above. At the end of the sampling period the parameters listed in 10.2.6 are recorded and the flow rate is checked. If the flows at the beginning and end of the sampling period differ by more than 10%, the cartridge should be marked as suspect.

10.2.8 The cartridges are removed (one at a time), the endcaps are replaced, and the cartridges are placed into the original container. The friction top can is sealed and packaged for immediate shipment to the analytical laboratory.

10.2.9 The average sample rate is calculated and recorded for each cartridge according to the following equation:

$$Q_A = \frac{Q_1 + Q_2 + \ldots Q_N}{N}$$

where

Q_A = Average flow rate in ml/minute.

Q_1, Q_2,...Q_N = Flow rates determined at beginning, end, and immediate points during sampling.

N = Number of points averaged.

10.2.10 The total volumetric flow is obtained directly from the dry gas meter or calculated and recorded for each cartridge using the following equation:

$$V_m = \frac{T \times Q_A}{1000}$$

where

V_m = Total volume sampled in liters at measured temperature and pressure.

T = Sampling time = T_2-T_1, minutes.

10.2.11 The total volume sampled (V_s) at standard conditions, 760 mm Hg and 25°C, is calculated from the following equation:

$$V_s = V_m \times \frac{Pa}{760} \times \frac{298}{273 + ta}$$

where

Pa = Average barometric pressure, mm Hg

ta = Average ambient temperature, °C.

11. Sample Analysis

11.1 Sample Purging

11.1.1 Prior to analysis all samples are purged at room temperature with pure, dry air or nitrogen to remove water vapor. Purging is accomplished as described in 9.7 except that the gas flow is in the same direction as sample flow (i.e. marked end of cartridge is connected to the flow system).

11.1.2 The sample is purged at 500 mL/minute for 5 minutes. After purging the endcaps are immediately replaced. The cartridges are returned to the metal can or analyzed immediately.

11.1.3 If very humid air is being sampled the purge time may be increased to more efficiently remove water vapor. However, the sum of sample volume and purge volume must be less than 75% of the retention volume for the most volatile component of interest.

11.2 GC/MS Setup

11.2.1 Considerable variation from one laboratory to another is expected in terms of instrument configuration. Therefore, each laboratory must be responsible for verifying that their particular system yields satisfactory results. Section 14 discusses specific performance criteria which should be met.

11.2.2 A block diagram of the analytical system required for analysis of CMS cartridges is depicted in Figure 3. The thermal desorption system must be designed to accommodate the particular cartridge configuration. For the CMS cartridge design shown in Figure 1, the cartridge heating is accomplished as described in 9.8. The use of a desorption oven, in conjunction with a simplier cartridge design is also acceptable. Exposure of the sample to metal surfaces should be minimized and only stainless steel or nickel should be employed. The volume of tubing leading from the cartridge to the GC column must be minimized and all areas must be well-swept by helium carrier gas.

11.2.3 The GC column oven must be capable of being cooled to -70°C and subsequently temperature programmed to 150°C.

11.2.4 The specific GC column and temperature program employed will be dependent on the compounds of interest. Appropriate conditions are described in the literature (2). In general, a nonpolar stationary phase (e.g. SE-30, OV-1) temperature programmed from -70 to 150°C at 8°/minute will be suitable. Fused silica, bonded-phase columns are preferable to glass columns since they are more rugged and can be inserted directly into the MS ion source, thereby eliminating the need for a GC/MS transfer line. Fused silica columns are also more readily connected to the GC injection valve (Figure 3). A drawback of fused silica, bonded-phase columns is the lower capacity compared to coated, glass capillary columns. In most cases the column capacity will be less than 1 microgram injected for fused silica columns.

11.2.5 Capillary column dimensions of 0.3 mm ID and 50 meters long are generally appropriate although shorter lengths may be sufficient in many cases.

11.2.6 Prior to instrument calibration or sample analysis the GC/MS system is assembled as shown in Figure 3. Helium purge flow (through the cartridge) and carrier flow are set at approximately 50 mL/minute and 2-3 mL/minute respectively. When a cartridge is not in place a union is placed in the helium purge line to ensure a continuous inert gas flow through the injection loop.

11.2.7 Once the column and other system components are assembled and the various flows established the column temperature is increased to 250°C for approximately four hours (or overnight if desired) to condition the column.

11.2.8 The MS and data system are set up according to the manufacturer's instructions. Electron impact ionization (70eV) and an electron multiplier gain of approximately 5×10^4 should be employed. Once the entire GC/MS system has been setup the system is calibrated as described in Section 11.3. The user should prepare a detailed standard operating procedure (SOP) describing this process for the particular instrument being used.

11.3 GC/MS Calibration

11.3.1 Tuning and mass standardization of the MS system is performed according to manufacturer's instructions and relevant user prepared SOPs. Perfluorotributylamine (FC-43) should generally be employed as the reference compound. The material is introduced directly into the ion source through a molecular leak. The instrumental parameters (e.g., lens voltages, resolution, etc.) should be adjusted to give the relative ion abundances shown in Table 2, as well as acceptable resolution and peak shape. If these approximate relative abundances cannot be achieved, the ion source may require cleaning according to manufacturer's instructions. In the event that the user's instrument cannot achieve these relative ion abundances, but is otherwise operating properly, the user may adopt another set of relative abundances as performance criteria. However, these alternate values must be repeatable on a day-to-day basis.

11.3.2 After the mass standardization and tuning process has been completed and the appropriate values entered into the data system, the user should then calibrate the entire GC/MS system by introducing known quantities of the components of interest into the system. Three alternate procedures may be employed for the calibration process including 1) direct injection of dilute vapor phase standards, prepared in a dilution bottle or compressed gas cylinder, onto the GC column, 2) injection of dilute vapor phase standards into a flowing inert gas stream directed onto a CMS cartridge, and 3) introduction of permeation or diffusion tube standards onto a CMS cartridge. Direct injection of a compressed gas cylinder (aluminum) standard containing trace levels of the compounds of interest has been found to be the most convenient practice since such standards are stable over a several month period. The standards preparation processes for the various approaches are described in Section 13. The following paragraphs describe the instrument calibration process for these approaches.

11.3.3 If the system is to be calibrated by direct injection of a vapor phase standard, the standard, in either a compressed gas cylinder or dilution flask, is obtained as described in Section 13. The MS and data system are setup for acquisition, but the ionizer filament is shut off. The GC column oven is cooled to -70°C, the injection valve is placed in the <u>load</u> mode, and the cryogenic loop is immersed in liquid nitrogen or liquid argon. Liquid argon is required for standards prepared in nitrogen or air, but not for standards prepared in helium. A known volume of the standard (10-1000 mL) is injected through the cryogenic loop at a rate of 10-100 mL/minute.

11.3.4 Immediately after loading the vapor phase standard, the injection valve is placed in the inject mode, the GC program and system clock are started, and the cryogenic loop is heated to 60°C by applying voltage (15-20 volts) to the thermocouple wire heater surrounding the loop. The voltage is adjusted to maintain a loop temperature of 60°C. An automatic temperature controller can be used in place of the manual control system. After elution of unretained components (∿3 minutes after injection) the ionizer filament is turned on and data acquisition is initiated. The helium purge line (set at 50 mL/minute) is connected to the injection valve and the valve is returned to the load mode. The loop temperature is increased to 150 °C, with helium purge, and held at this temperature until the next sample is to be loaded.

11.3.5 After the last component of interest has eluted, acquisition is terminated and the data is processed as described in Section 11.3.8. The standard injection process is repeated using different standard concentrations and/or volumes to cover the analytical range of interest.

11.3.6 If the system is to be calibrated by analysis of standard CMS cartridges, a series of cartridges is prepared as described in Sections 13.2 or 13.3. Prior to analysis the cartridges are stored (no longer than 48 hours) as described in Section 9.10. For analysis the injection valve is placed in the load mode and the cryogenic loop is immersed in liquid nitrogen (or liquid argon if desired). The CMS cartridge is installed in the helium purge line (set at 50 mL/minute) so that the helium flow through the cartridge is opposite to the direction of sample flow and the purge gas is directed through the cryogenic loop and vented to the atmosphere. The CMS cartridge is heated to 370-400°C and maintained at this temperature for 10 minutes (using the temperature control process described in Section 9.8). During the desorption period, the GC column oven is cooled to -70°C and the MS and data system are setup for acquisition, but the ionizer filament is turned off.

11.3.7 At the end of the 10 minute desorption period, the analytical process described in Sections 11.3.4 and 11.3.5 is conducted. During the GC/MS analysis heating of the CMS cartridge is discontinued. Helium flow is maintained through the CMS cartridge and cryogenic loop until the cartridge has cooled to room temperature. At that time, the cryogenic loop is allowed to cool to room temperature and the system is ready for further cartridge analysis. Helium flow is maintained through the cryogenic loop at all times, except during the installation or removal of a CMS cartridge, to minimize contamination of the loop.

11.3.8 Data processing for instrument calibration involves determining retention times, and integrated characteristic ion intensities for each of the compounds of interest. In addition, for at least one chromatographic run, the individual mass spectra should be inspected and compared to reference spectra to ensure proper instrumental performance. Since the steps involved in data processing are highly instrument specific, the user should prepare a SOP describing the process for individual use. Overall performance criteria for instrument calibration are provided in Section 14. If these criteria are not achieved, the user should refine the instrumental parameters and/or operating procedures to meet these criteria.

11.4 Sample Analysis

11.4.1 The sample analysis is identical to that described in Sections 11.3.6 and 11.3.7 for the analysis of standard CMS cartridges.

11.4.2 Data processing for sample data generally involves 1) qualitatively determining the presence or absence of each component of interest on the basis of a set of characteristic ions and the retention time using a reversed-search software routine, 2) quantification of each identified component by integrating the intensity of a characteristic ion and comparing the value to that of the calibration standard, and 3) tentative identification of other components observed using a forward (library) search software routine. As for other user specific processes, a SOP should be prepared describing the specific operations for each individual laboratory.

12. Calculations

12.1 Calibration Response Factors

12.1.1 Data from calibration standards is used to calculate a response factor for each component of interest. Ideally the process involves analysis of at least three calibration levels of each component during a given day and determination of the response factor (area/nanogram injected) from the linear least squares fit of a plot of nanograms injected versus area (for the characteristic ion). In general, quantities of components greater than 1,000 nanograms should not be injected because of column overloading and/or MS response nonlinearity.

12.1.2 In practice the daily routine may not always allow analysis of three such calibration standards. In this situation calibration data from consecutive days may be pooled to yield a response factor, provided that analysis of replicate standards of the same concentration are shown to agree within 20% on the consecutive days. In all cases one given standard concentration, near the midpoint of the analytical range of interest, should be injected at least once each day to determine day-to-day precision of response factors.

12.1.3 Since substantial nonlinearity may be present in the calibration curve, a nonlinear least squares fit (e.g. quadratic) should be employed. This process involves fitting the data to the following equation:

$$Y = A + BX + CX^2$$

where

Y = peak area
X = quantity of component injected nanograms
A, B, and C are coefficients in the equation.

12.2 Analyte Concentrations

12.2.1 Analyte quantities on a sample cartridge are calculated from the following equation:

$$Y_A = A + BX_A + CX^2$$

where Y_A is the area of the analyte characteristic ion for the sample cartridge.
X_A is the calculated quantity of analyte on the sample cartridge, in nanograms.
A, B, and C are the coefficients calculated from the calibration curve described in Section 12.1.3.

12.2.2 If instrumental response is essentially linear over the concentration range of interest, a linear equation (C=0 in the equation above) can be employed.

12.2.3 Concentration of analyte in the original air sample is calculated from the following equation:

$$C_A = \frac{X_A}{V_s}$$

where

C_A is the calculated concentration of analyte in ng/L.

V_s and X_A are as previously defined in Section 10.2.11 and 12.2.1, respectively.

13. Standard Preparation

13.1 Standards for Direct Injection

13.1.1 Standards for direct injection can be prepared in compressed gas cylinders or in dilution vessels. The dilution flask protocol has been described in detail in another method and is not repeated here (6). For the CMS method where only volatile compounds (boiling point <120°C) are of concern, the preparation of dilute standards in 15 liter aluminum compressed gas cylinders has been found to be most convenient. These standards are generally stable over at least a 3-4 month period and in some cases can be purchased from commercial suppliers on a custom prepared basis.

13.1.2 Preparation of compressed gas cylinders requires working with high pressure tubing and fittings, thus requiring a user prepared SOP which ensures that adequate safety precautions are taken. Basically, the preparation process involves injecting a predetermined amount of neat liquid or gas into an empty high pressure cylinder of known volume, using gas flow into the cylinder to complete the transfer.

The cylinder is then pressurized to a given value (500-1000 psi). The final cylinder pressure must be determined using a high precision gauge after the cylinder has thermally equilibrated for a 1-2 hour period after filling.

13.1.2 The concentration of components in the cylinder standard should be determined by comparison with National Bureau of Standards reference standards (e.g. SRM 1805-benzene in nitrogen) when available.

13.1.3 The theoretical concentration (at 25°C and 760 mm pressure) for preparation of cylinder standards can be calculated using the following equation:

$$C_T = \frac{V_I \times d}{V_c} \times \frac{14.7}{P_c + 14.7} \times 24.4 \times 1000$$

where C_T is the component concentration, in ng/mL at 25°C and 760 mm Hg pressure.

V_I is the volume of neat liquid component injected, in µL.

V_c is the internal volume of the cylinder, in L.

d is the density of the neat liquid component, in g/mL.

P_c is the final pressure of the cylinder standards, in pounds per square inch gauge (psig).

13.2 Preparation of Spiked Traps by Vapor Phase Injection

This process involves preparation of a dilution flask or compressed gas cylinder containing the desired concentrations of the compound(s) of interest and injecting the desired volume of vapor into a flowing gas stream which is directed onto a clean CMS cartridge. The procedure is described in detail in another method within the Compendium (6) and will not be repeated here.

13.3 Preparation of Spiked Traps Using Permeation or Diffusion Tubes

13.3.1 A flowing stream of inert gas containing known amounts of each compound of interest is generated according to ASTM Method D3609 (4). Note that a method of accurately maintaining temperature within ± 0.1°C is required and the system generally must be equilibrated for at least 48 hours before use.

13.3.2 An accurately known volume of the standard gas stream (usually 0.1-1 liter) is drawn through a clean CMS cartridge using the sampling system described in Section 10.2.1, or a similar system. However, if mass flow controllers are employed, they must be calibrated for the carrier gas used in Section 13.3.1 (usually nitrogen). Use of air as the carrier gas for permeation systems is not recommended, unless the compounds of interest are known to be highly stable in air.

13.3.3 The spiked traps are then stored or immediately analyzed as in Sections 11.3.6 and 11.3.7.

14. Performance Criteria and Quality Assurance

This section summarizes the quality assurance (QA) measures and provides guidance concerning performance criteria which should be achieved within each laboratory. In many cases the specific QA procedures have been described within the appropriate section describing the particular activity (e.g. parallel sampling).

14.1 Standard Operating Procedures (SOPs)

14.1.1 Each user should generate SOPs describing the following activities as accomplished in their laboratory: 1) assembly, calibration and operation of the sampling system, 2) preparation, handling and storage of CMS cartridges, 3) assembly and operation of GC/MS system including the thermal desorption apparatus and data system, and 4) all aspects of data recording and processing.

14.1.2 SOPs should provide specific stepwise instructions and should be readily available to, and understood by the laboratory personnel conducting the work.

14.2 CMS Cartridge Preparation

14.2.1 Each batch of CMS cartridges, prepared as described in Section 9, should be checked for contamination by analyzing one cartridge, immediately after preparation. While analysis can be accomplished by GC/MS, many laboratories may chose to use GC/FID due to logistical and cost considerations.

14.2.2 Analysis by GC/FID is accomplished as described for GC/MS (Section 11) except for use of FID detection.

14.2.3 While acceptance criteria can vary depending on the components of interest, at a minimum the clean cartridge should be demonstrated to contain less than one-fourth of the minimum level of interest for each component. For most compounds the blank level should be less than 10 nanograms per cartridge in order to be acceptable. More rigid criteria may be adopted, if necessary, within a specific laboratory. If a cartridge does not meet these acceptance criteria, the entire lot should be rejected.

14.3 Sample Collection

14.3.1 During each sampling event at least one clean cartridge will accompany the samples to the field and back to the laboratory, having been placed in the sampler but without sampling air, to serve as a field blank. The average amount of material found on the field blank cartridges may be subtracted from the amount found on the actual samples. However, if the blank level is greater than

25% of the sample amount, data for that component must be identified as suspect.

14.3.2 During each sampling event at least one set of parallel samples (two or more samples collected simultaneously) should be collected, preferably at different flow rates as described in Section 10.1.4. If agreement between parallel samples is not generally within ±25% the user should collect parallel samples on a much more frequent basis (perhaps for all sampling points). If a trend of lower apparent concentrations with increasing flow rate is observed for a set of parallel samples one should consider using a reduced sampling rate and longer sampling interval, if possible. If this practice does not improve the reproducibility further evaluation of the method performance for the compound of interest might be required.

14.3.3 Backup cartridges (two cartridges in series) should be collected with each sampling event. Backup cartridges should contain less than 10% of the amount of components of interest found in the front cartridges, or be equivalent to the blank cartridge level, whichever is greater.

14.4 GC/MS Analysis

14.4.1 Performance criteria for MS tuning and mass standardization have been discussed in Section 11.2 and Table 2. Additional criteria can be used by the laboratory, if desired. The following sections provide performance guidance and suggested criteria for determining the acceptability of the GC/MS system.

14.4.2 Chromatographic efficiency should be evaluated daily by the injection of calibration standards. A reference compound(s) should be chosen from the calibration standard and plotted on an expanded time scale so that its width at 10% of the peak height can be calculated, as shown in Figure 6. The width of the peak at 10% height should not exceed 10 seconds. More stringent criteria may be required for certain applications. The asymmetry factor (see Figure 6) should be between 0.8 and 2.0. The user should also evaluate chromatographic performance for any polar or reactive compounds of interest, using the process described above. If peaks are observed that exceed the peak width or asymmetry factor criteria above, one should inspect the entire system to determine if unswept zones or cold spots are present in any of the fittings or tubing and/or if replacement of the GC column is required. Some laboratories may chose to evaluate column performance separately by direct injection of a test mixture onto the GC column. Suitable schemes for column evaluation have been reported in the literature (7).

14.4.3 The detection limit for each component is calculated from the data obtained for calibration standards. The detection limit is defined as

$$DL = A + 3.3S$$

where

DL is the calculated detection limit in nanograms injected.

A is the intercept calculated in Section 12.1.3.

S is the standard deviation of replicate determinations of the lowest level standard (at least three such determinations are required). The lowest level standard should yield a signal to noise ratio (from the total ion current response) of approximately 5.

14.4.4 The relative standard deviation for replicate analyses of cartridges spiked at approximately 10 times the detection limit should be 20% or less. Day to day relative standard deviation for replicate cartridges should be 25% or less.

14.4.5 A useful performance evaluation step is the use of an internal standard to track system performance. This is accomplished by spiking each cartridge, including blank, sample, and calibration cartridges with approximately 100 nanograms of a compound not generally present is ambient air (e.g. perfluorotoluene). Spiking is readily accomplished using the procedure outlined in Section 13.2, using a compressed gas standard. The integrated ion intensity for this compound helps to identify problems with a specific sample. In general the user should calculate the standard deviation of the internal standard response for a given set of samples analyzed under identical tuning and calibration conditions. Any sample giving a value greater than ± 2 standard deviations from the mean (calculated excluding that particular sample) should be identified as suspect. Any marked change in internal standard response may indicate a need for instrument recalibration.

14.5 Method Precision and Recovery

14.5.1 Recovery and precision data for selected volatile organic compounds are presented in Table 1. These data were obtained using ambient air, spiked with known amounts of the compounds in a dynamic mixing system (2).

14.5.2 The data in Table 1 indicate that in general recoveries better than 75% and precision (relative standard deviations) of 15-20% can be obtained. However, selected compounds (e.g. carbon tetrachloride and benzene) will have poorer precision and/or recovery. The user must check recovery and precision for any compounds for which quantitative data are needed.

References

1. Kebbekus, B. B. and J. W. Bozzelli. Collection and Analysis of Selected Volatile Organic Compounds in Ambient Air. Proceedings of Air Pollution Control Association, Paper No. 82-65.2, Air Pollution Control Association, Pittsburgh, Pennsylvania, 1982.

2. Riggin R. M. and L. E. Slivon. Determination of Volatile Organic Compounds in Ambient Air Using Carbon Molecular Sieve Adsorbants, Special Report on Contract 68-02-3745 (WA-7), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, September, 1983.

3. Riggin, R. M., "Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air", EPA-600/4-83-027, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1983.

4. Annual Book of ASTM Standards, Part 11.03, "Atmospheric Analysis: Occupational Health and Safety", American Society for Testing and Materials, 1983.

5. Walling, J. F., Berkley, R. E., Swanson, D. H., and Toth, F. J. "Sampling Air for Gaseous Organic Chemical-Applications to Tenax", EPA-600/7-54-82-059, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1982.

6. This Methods Compendium - Tenax Method (TO 1).

7. Grob, K., Jr., Grob, G., and Grob, K., "Comprehensive Standardized Quality Test for Glass Capillary Columns", J. Chromatog., 156 1-20, 1978.

TABLE 1. VOLATILE ORGANIC COMPOUNDS FOR WHICH THE CMS ADSORPTION METHOD HAS BEEN EVALUATED

Compound	Retention Time, Minutes(a)	Characteristic Mass Fragment Used For Quantification	Method Performance Data(b)		
			Concentration, ng/L	Percent Recovery	Standard Deviation
Vinyl Chloride	6.3	62	17	74	19
Acrylonitrile	10.8	53	20	85	18
Vinylidene Chloride	10.9	96	36	94	19
Methylene Chloride	11.3	84	28	93	16
Allyl Chloride	11.4	76	32	72	19
Chloroform	13.8	83	89	91	12
1,2-Dichloroethane	14.5	62	37	85	11
1,1,1-Trichloroethane	14.7	97	100	75	9.1
Benzene	15.4	78	15	140	37
Carbon Tetrachloride	15.5	117	86	55	2.9
Toluene	18.0	91	4.1	98	5.4

a) GC conditions as follows:

Column - Hewlett Packard, crosslinked methyl silicone, 0.32 mm ID x 50 mm long, thick film, fused silica.

Temperature Program - 70°C for 2 minutes then increased at 8°C/minute to 120°C.

b) From Reference 2. For spiked ambient air.

TABLE 2. SUGGESTED PERFORMANCE CRITERIA FOR RELATIVE ION ABUNDANCES FROM FC-43 MASS CALIBRATION

M/E	% Relative Abundance
51	1.8 ± 0.5
69	100
100	12.0 ± 1.5
119	12.0 ± 1.5
131	35.0 ± 3.5
169	3.0 ± 0.4
219	24.0 ± 2.5
264	3.7 ± 0.4
314	0.25 ± 0.1

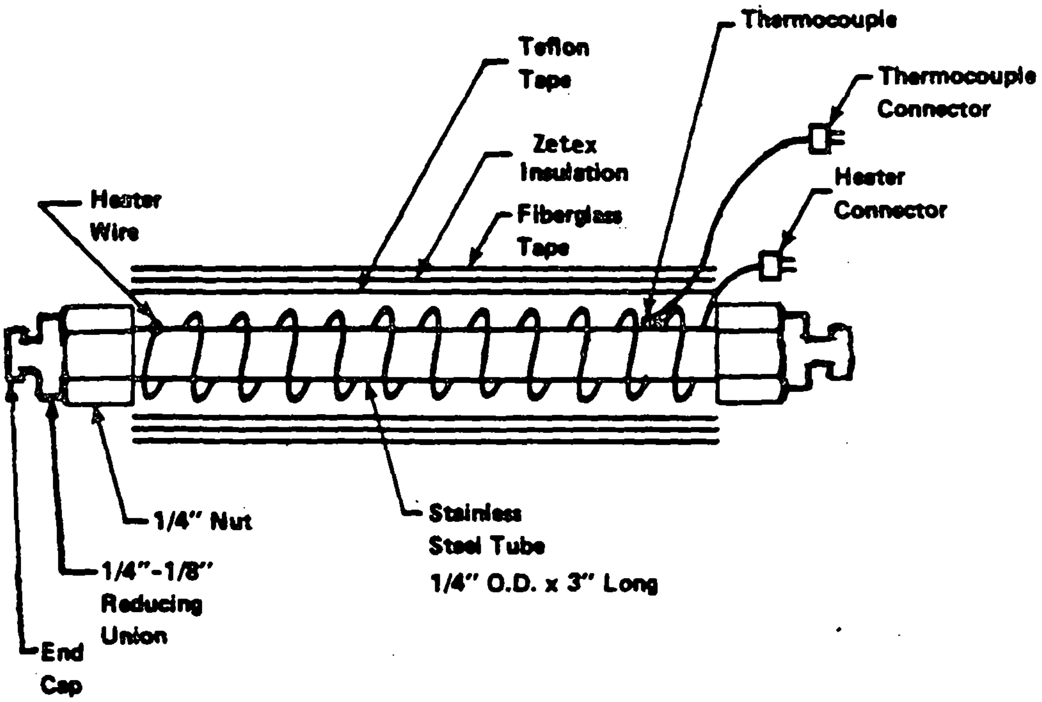
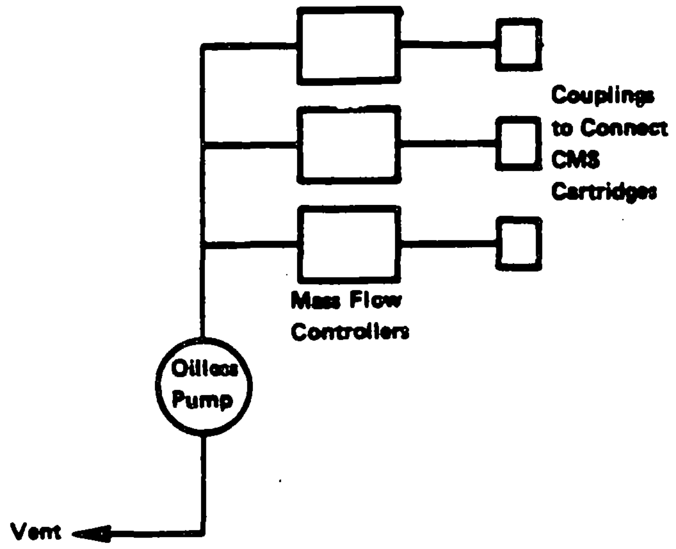
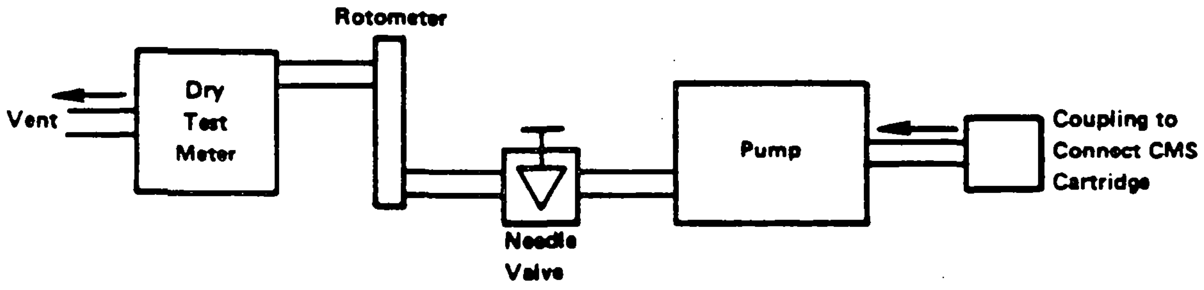


FIGURE 1. DIAGRAM SHOWING CARBON MOLECULAR SIEVE TRAP (CMS) CONSTRUCTION

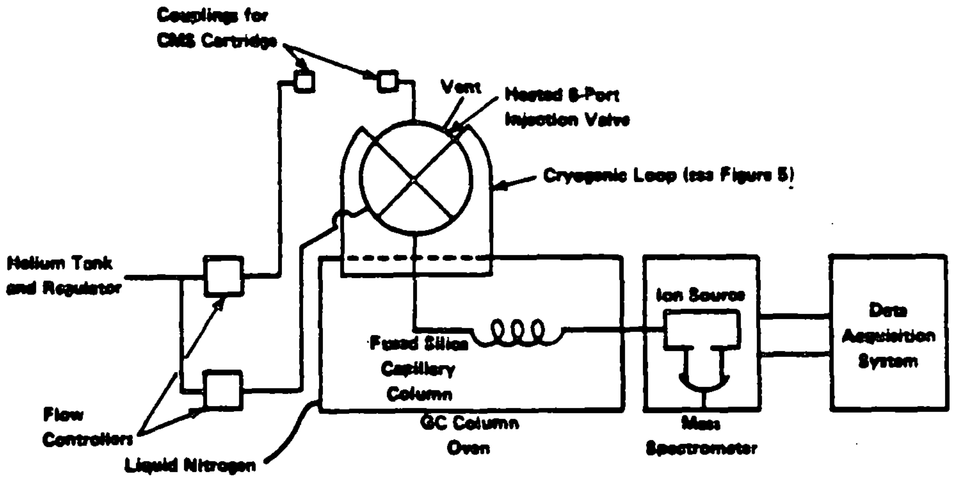


(a) Mass Flow Control

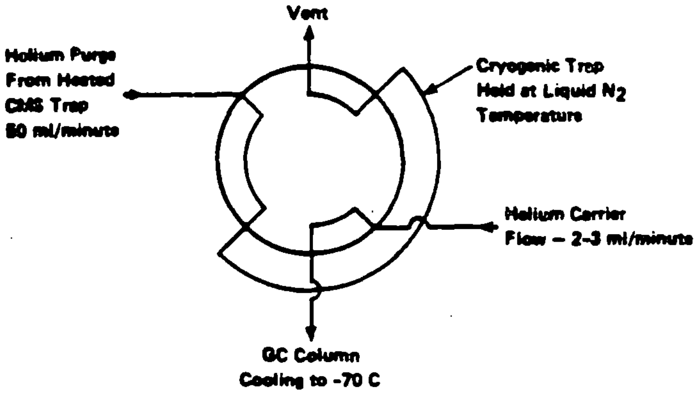


(b) Needle Valve Control

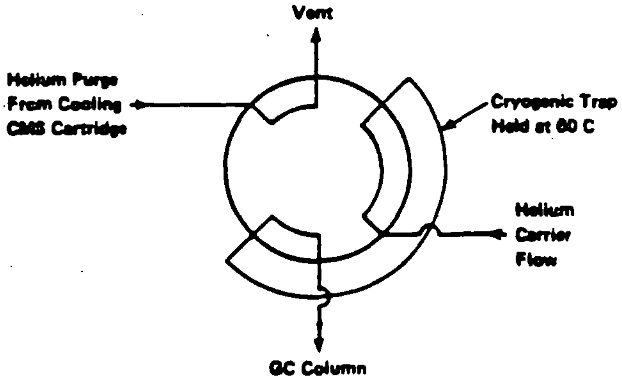
FIGURE 2. TYPICAL SAMPLING SYSTEM CONFIGURATIONS



(a) Overall System



(b) Valve – Load Mode



(c) Valve – Inject Mode

FIGURE 3. GC/MS ANALYSIS SYSTEM FOR CMS CARTRIDGES

SAMPLING DATA SHEET
(One Sample Per Data Sheet)

PROJECT:____________________ DATE(S) SAMPLED:____________________

SITE:____________________ TIME PERIOD SAMPLED:____________________

LOCATION:____________________ OPERATOR:____________________

INSTRUMENT MODEL NO:____________________ CALIBRATED BY:____________________

PUMP SERIAL NO:____________________

SAMPLING DATA

Sample Number:____________________

Start Time: __________ Stop Time: __________

Time	Dry Gas Meter Reading	Rotameter Reading	Flow Rate,*Q ml/Min	Ambient Temperature °C	Barometric Pressure, mmHg	Relative Humidity, %	Comments
1.							
2.							
3.							
4.							
N.							

Total Volume Data**

V_m = (Final - Initial) Dry Gas Meter Reading, or = ______ Liters

$$\frac{Q_1 + Q_2 + Q_3 \ldots Q_N}{N} \times \frac{1}{1000 \times \text{(Sampling Time in Minutes)}} = \_\_\_\_\_\_ \text{ Liters}$$

* Flowrate from rotameter or soap bubble calibrator (specify which).

** Use data from dry gas meter if available.

FIGURE 4. EXAMPLE SAMPLING DATA SHEET

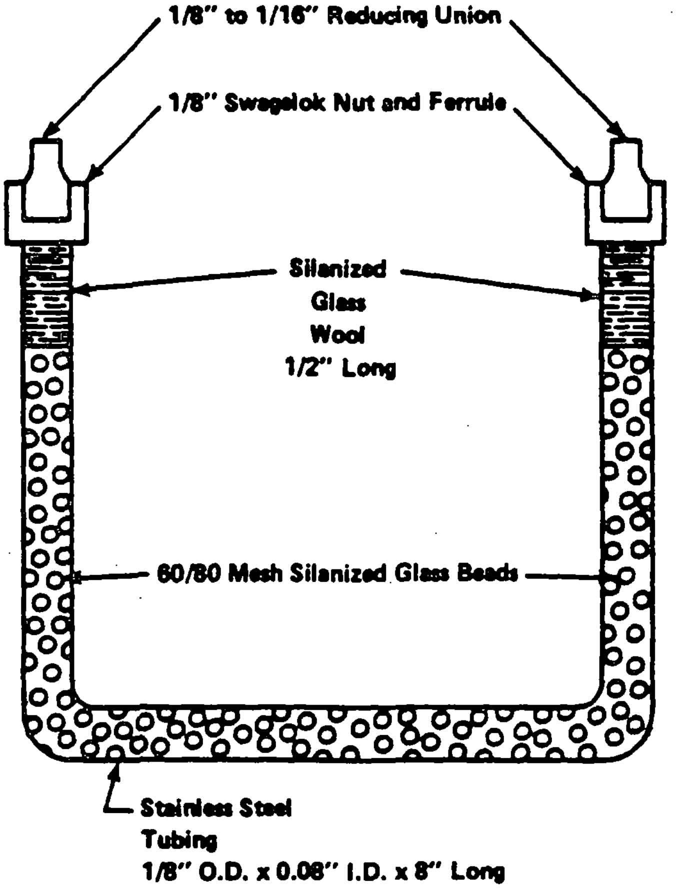
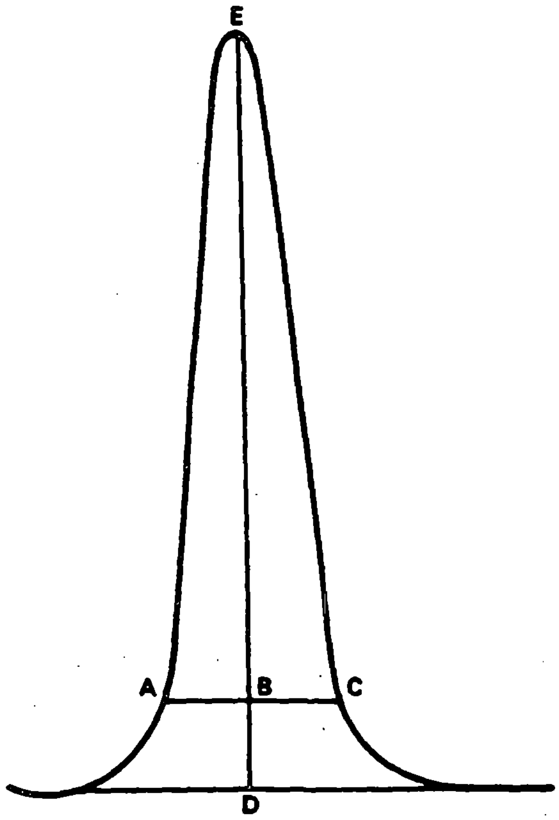


FIGURE 5. CRYOGENIC TRAP DESIGN

glass $27.50
steel $44.00

steel $44.00



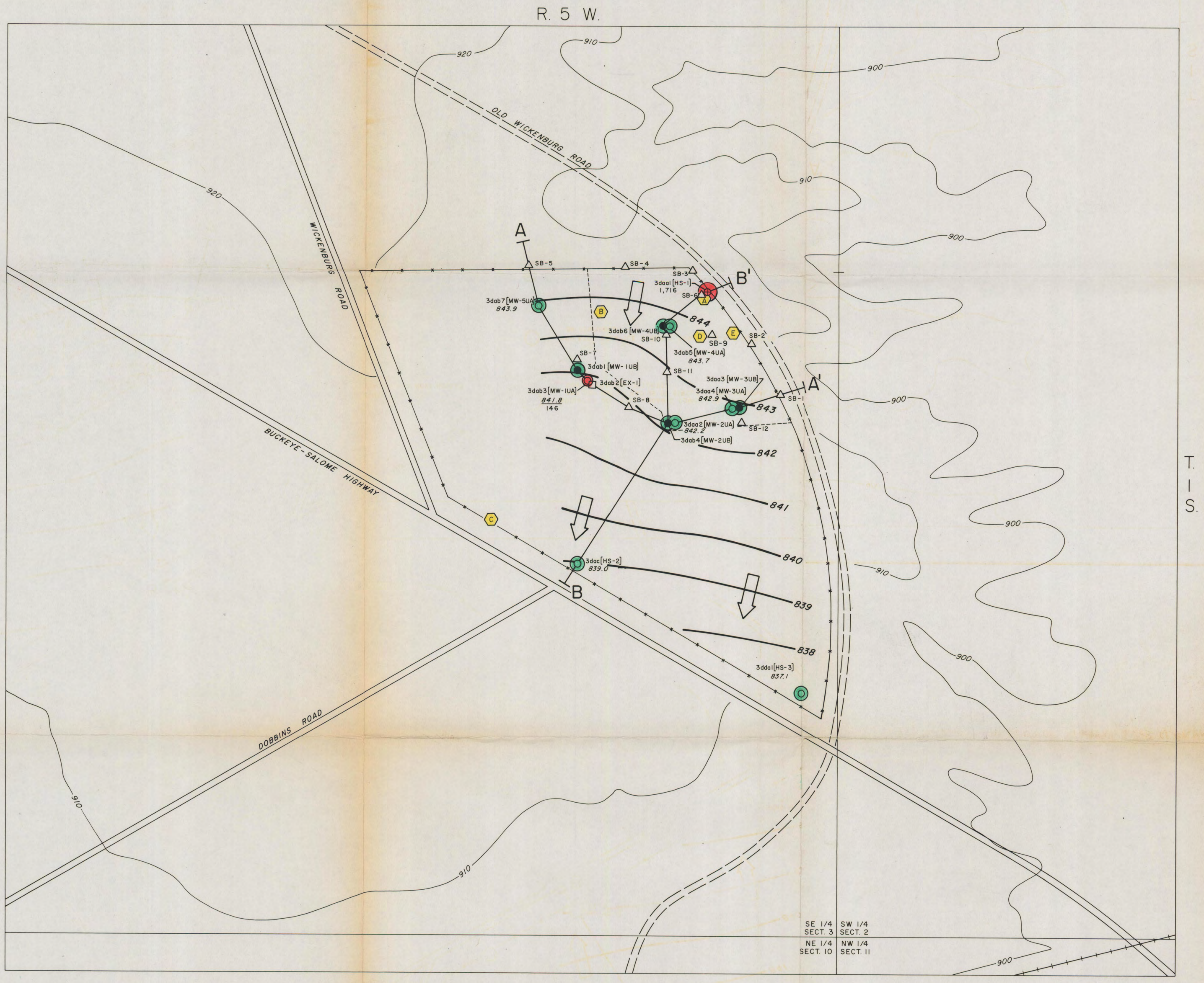
$$\text{Asymmetry Factor} = \frac{BC}{AB}$$

Example Calculation:

Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

$$\text{Therefore: Asymmetry Factor} = \frac{12}{11} = 1.1$$

FIGURE 6. PEAK ASYMMETRY CALCULATION



EXPLANATION

△ SB-1	SOIL BORING LOCATION AND IDENTIFIER
○ 3dab3 [MW-1UA]	UNIT A MONITOR WELL AND IDENTIFIER
841.8	WATER LEVEL ALTITUDE: DECEMBER 1988, IN FEET MSL
146	TOTAL CONCENTRATION OF VOLATILE ORGANIC COMPOUNDS IN MOST RECENT GROUNDWATER SAMPLE, IN MICROGRAMS PER LITER
● 3dab1 [MW-1UB]	UNIT B MONITOR WELL AND IDENTIFIER
☐ 3dab2 [EX-1]	EXPLORATION BORING AND IDENTIFIER
⊕ 3daa1 [HS-1]	ABANDONED MONITOR WELL AND IDENTIFIER
—— 842 ——	WATER LEVEL CONTOUR: DECEMBER 1988, UNIT A; IN FEET MSL
⇨	INDICATES DIRECTION OF GROUNDWATER MOVEMENT IN UNIT A
A├──┤A'	LOCATION OF HYDROGEOLOGIC SECTION
🔴	INDICATES VOLATILE ORGANIC COMPOUNDS DETECTED AND CONFIRMED: RADIUS OF CIRCLE IS PROPORTIONAL TO CONCENTRATION DETECTED
🟢	INDICATES VOLATILE ORGANIC COMPOUNDS NOT DETECTED OR CONFIRMED
⬡ C	PROPOSED UNIT A MONITOR WELL; LETTER INDICATES SEQUENTIAL ORDER OF CONSTRUCTION

0 100 200 300 400 500
FEET

N

HASSAYAMPA LANDFILL
MARICOPA COUNTY, ARIZONA

WATER LEVEL CONTOURS
DECEMBER 1988
UNIT A

1989

ERROL L. MONTGOMERY & ASSOCIATES, INC.
CONSULTANTS IN HYDROGEOLOGY
TUCSON, ARIZONA

FIGURE 5