MONITORING TECHNOLOGIES FOR WELLHEAD PROTECTION

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Work Assignment Manager
S.P. Gardner
Environmental Monitoring Systems Laboratory
Advanced Monitoring Systems Divisions U.S.
Environmental Protection Agency
P.O. Box 93578
Las Vegas, NV 89193-3478

US ENVIRONMENTAL PROTECTION AGENCY
ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
LAS VEGAS, NEVADA 89193-3478

Task Lead

E. Eschner[1]

Contributing Authors

R. M. Bochicchio[2]
W. H. Cole, III[1]
D. Eastwood[1]
W. H. Englemann[3]
R. L Lidberg[1]
E. L Miller[1]
B. A Moore[1]
E. J. Poziomek[4]
S. R. Schroedel[1]
R. J. White[1]
S. M. I-I. Klainer[5]
E. Eschner[1]

[1] Lockheed Engineering & Sciences Company
[2] Desert Research Institute, University of Nevada, Las Vegas
[3] U. S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory
[4] Environmental Research Center, University of Nevada, Las Vegas
[5] FiberChem, Inc.

NOTICE

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ABSTRACT

The scope of this document is bifocal, highlighting potential wellhead protection field technologies, as well as recent, applicable literature. The technologies are classified into four groups: *in situ* and in-line monitoring technologies, portable monitoring technologies, mobile monitoring technologies, and technologies currently under development. *In situ* and in-line technologies monitor general physical and chemical parameters at a site, such as electrical conductivity, oxidation reduction potential, turbidity, temperature, water level, dissolved oxygen, pH, and salinity. Portable monitoring technologies are those which can be hand-carried into the field, such as geophysics, immunoassays, soil-analysis, test kits, X-ray fluorescence, and gas analysis equipment. Mobile monitoring technologies use equipment that is transported to the field in a trailer or a mobile laboratory. Mobile monitoring technologies include gas chromatography, mass spectroscopy, analytical x-ray fluorescence, and atomic absorption. Innovative monitoring technologies presently in the laboratory-development stage include: ion Mobility Spectrometry, Molecular Optical Spectrometry, extraction membranes, surface acoustic wave probes and quartz-crystal microbalances, spectroelectrochemistry, and biosensors.

The document also contains case studies of water agencies that employ innovative monitoring technologies for ground-water and surface water quality monitoring as early-warning contaminant detection. The case studies describe technology applications of the Orange County Water District, California and the State of Florida.

TABLE OF CONTENTS

1 INTRODUCTION

2 WELLHEAD PROTECTION MONITORING DESIGN CONSIDERATIONS

3 AVAILABLE IN SITU AND IN-LINE MONITORING TECHNOLOGIES

TABLE OF CONTENTS (continued)

4 PORTABLE MONITORING METHODS

TABLE OF CONTENTS (continued)

5 MOBILE MONITORING METHODS

6 MONITORING TECHNOLOGIES UNDER DEVELOPMENT

TABLE OF CONTENTS (continued)

TABLE OF CONTENTS (continued)

FIGURES

FIGURES (continued)

TABLES

ABBREVIATIONS AND ACRONYMS

ABBREVIATIONS

AA	atomic absorption
AC	alternating current
ASTM	American Society for Testing and Materials
bgs	below ground surface
BOD	biochemical oxygen demand
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
COD	chemical oxygen demand
CV	coefficient of variation
DC	direct current
DO	dissolved oxygen
DQOs	data quality objectives
EC	electrical conductance
ELISA	enzyme-linked immunosorbent immunoassay
EM	electromagnetic
FID	flame ionization detector
FOCs	fiber optic chemical sensors
FPXRF	field-portable, X-ray fluorescence
FTIR	Fourier Transform IR Spectrophotometer
GC	gas chromatography
GC/MS	gas chromatography/mass spectroscopy
gpm	gallons per minute
GPR	ground penetrating radar
HPLC	high performance liquid chromatography
ICP/AES	inductively coupled plasma discharge/atomic emission spectroscopy
IMS	ion mobility spectrometer
IR	infrared
LC-MS	liquid chromatography-mass spectroscopy
OCWD	Orange County Water District
OVAS	organic vapor analyzers
OVMS	organic vapor meters
PAHS	polyaromatic hydrocarbons
PC	personal computer
PCBS	polychlorinated biphenyls
PID	photoionization detector
PPb	parts per billion
pph	parts per hundred
wm	parts per million
PPt	parts per trillion

ABBREVIATIONS AND ACRONYMS (continued)

ppth□	parts per thousand
QA/QC	quality assurance/quality
QCM□	control quartz-crystal
redox□	microbalance
RCRA	oxidation reduction
RIA	Resource Conservation and Recovery Act
SAW	radioimmunoassay
SCADA	surface acoustic wave
SERS	Supervisor Control and Data Acquisition
SITE	surface-enhanced Raman spectroscopy
SMCU	Superfund Innovative Technology Evaluation
SP	surface memory and control unit spontaneous
SSC□	potential
TCE	site-specific calibration
TDS	standards trichloroethylene
TOC	total dissolved solids
TSS	total organic carbon
UV-vis	total suspended solids
VISA	ultraviolet-visible
VOC	very intense study area
WHPA	volatile organic compound
WHPP	wellhead protection area
WRMS	wellhead protection program
XRF	Water Resources Management System
	X-ray fluorescence

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The preparation of the case studies also required the support of numerous individuals.
Portions of the Orange County Water District (OCWD) case study are reprinted with permission of the Association of Ground Water Scientists and Engineers, a division of the National Water Well Association. Individuals at OCWD who provided assistance on this case study are K L. Brill, R. L. Herndon, M. D. West, and J. k Goodrich. G. Florence and G. H. Kinsman (Southwest Florida Water Management District), R. Copeland (Florida Department of Environmental Regulation), K Rohrer (Sarasota Ecological Monitoring District) and J. Kite (Saint John*s River Water Management District) were instrumental in preparing the Florida case study.

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SECTION 1

INTRODUCTION

The increasing threat of chemical contamination to public water supply wells has created a new political and technical awareness of ground-water protection programs. Management of both contaminant sources and public water supplies is necessary to prevent and minimize ground-water quality degradation. In 1986, the Safe Drinking Water Act was amended to include Section 1428. This amendment called for the creation of a wellhead protection program (WHPP), thus establishing a legal framework to protect public water supply wells, wellfields, and springs from contamination. Elements of a WHPP include, at a minimum (EPA, 1989a):

- Specifying the roles and duties of cooperating agencies.
- Delineating the wellhead protection area (WHPA) for each wellhead or spring.
- Identifying sources of contamination within and in proximity to each wellhead or spring.
- Developing management approaches to protect the water supply within WHPAs from contaminants.
- Developing contingency plans in response to wellhead or spring contamination.
- Siting new wells properly to maximize yield and to minimize contamination.
- Ensuring public participation.

An important technical and management element of WHPP implementation is the monitoring of chemical and physical parameters in WHPAs. A WHPA is defined as the surface and subsurface areas surrounding a well, wellfield, or spring, through which contaminants could pass and reach that portion of the ground water which is contributing to the water supply. Figure l-l depicts a simplified WHPA with it*s potential source (landfill) and the water well to be protected.

A monitoring strategy for a WHPA is generally designed to perform three functions - source release detection, ambient trend monitoring, and early warning detection (Carter et al., 1987). The function that a monitoring device performs depends, in part, on its position along the flow path from the potential source to the wellhead.

The source release detection function determines if contamination has begun migrating from the source material. Monitoring devices would be situated below or immediately down-gradient of the potential source area. The ambient trend monitoring function assesses the temporal and spatial trends in ground-water quality in the bulk of the WHPA between the source area and the wellhead. A dispersed array of monitoring devices situated along flow paths is required for this purpose. The early warning detection function provides advance notice of the need to enact contingency response plans to prevent public exposure to contaminants. This function is performed by monitoring devices a relatively short distance up-gradient of the wellhead.

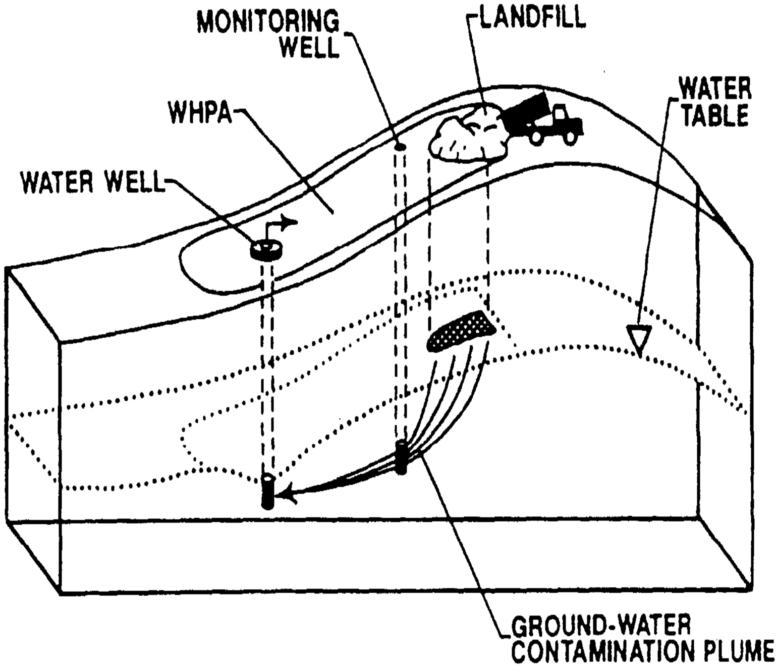

Figure l-l. Schematic drawing of a wellhead protection area.

This document focuses on field analytical techniques which may be incorporated into the WHPA monitoring strategy to perform one or more of the monitoring functions described. Numerous field technologies that mezisure chemical and physical parameters in soil and water have been evaluated, but to date, an examination of the relationship of these technologies to WHPA monitoring has not been compiled. This document is intended to fill that gap, presenting methods that mmplement traditional laboratory analyses and that are especially useful for rapid field screening of ground-water, soil, and soil-gas samples. As such, many of the technologies described are useful tools in the characterization and monitoring of WHPAs.

As monitoring techniques, field methods have several advantages over conventional, analytical laboratory analyses. For example, they can provide timely, on-site information that can be used immediately to make decisions about additional sampling needs. This eliminates the frustration of waiting several weeks for laboratory results. Field technologies are also more portable and less expensive than laboratory methods.

There are, however, several drawbacks to field methods. The detection limits and accuracy of field methods (especially methods currently under development) are not always as reliable as laboratory methods. This is especially critical, for example, if the detection limit of the field method does not meet water quality criteria or regulatory requirements. Nevertheless, even less accurate field methods might be useful to screen samples prior to confirmatory laboratory analyses.

The scope of this document is bifocal, highlighting potential WHPP applications of field technologies, as well as recent, applicable literature. It is written for technical personnel (engineers, geologists, and chemists) from local water departments and utility companies who are responsible for the implementation of WHPP monitoring and the protection of public water supplies. The document includes a description of WHPA monitoring design considerations (Section 2) and discussions of a variety of field measurement technologies, These include in situ and in-line monitoring technologies for general chemical and physical parameters (Section 3), portable monitoring technologies (Section 4), technologies that can be used in field laboratories (Section 5), and technologies currently under development (Section 6). Section 7 contains descriptions of applications of monitoring technologies by local water districts.

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SECTION 2

WELLHEAD PROTECTION MONITORING DESIGN CONSIDERATIONS

Ground water can become contaminated by numerous hazardous materials such as fertilizers, pesticides, septic tank effluent, and organic and inorganic industrial waste. Ground-water systems can vary greatly in the nature of their flow and assimilative characteristics. It is clear that a monitoring strategy that effectively addresses the physical, chemical, and microbial threats to an adequately characterized ground-water system is essential to protect against the danger of well contamination.

In this section, the considerations in the design of a WHPA monitoring strategy are briefly discussed. Those considerations include the hydrogeologic assessment, the source assessment, the selection of monitoring parameters, and the selection of monitoring technologies. It is not the intent to reproduce information which is provided in other existing or developing WHPP guidance documents, but to develop the framework for the discussion of field analytical techniques in subsequent sections.

2.1 HYDROGEOLOGIC ASSESSMENT

Characterization of the WHPA hydrogeologic system is a prerequisite to the development of the contaminant transport conceptual model and the design of an effective monitoring system. Elements of the conceptual model include the sources, migration pathways, and receptors. In a WHPP, the receptor is the public water supply well, wellfield, or spring. During the initial stages of program implementation, potential contaminant sources are identified, characterized, and prioritized. Concurrently, WHPAs are delineated based on a site-specific, ground-water flow and contaminant transport assessment.

2.2 SOURCE ASSESSMENT

A critical first step in the design of an effective monitoring system is the assessment of potential sources of aquifer contamination. A wide variety of anthropogenic contaminant sources may threaten ground-water supplies. A list of common sources of ground-water contamination is provided in Table 2-l. General guidance for inventorying, prioritizing, and characterizing potential contamination sources for wellhead protection is in the following U.S. EPA documents:

- Tools for Local Governments (1989a).
- Practical Guide for Assessing and Remediating Contaminated Ground Water (1989b).
- Guide to Water-Supply Contingency Planning for Local and State Governments (1990a).

TABLE 2-1. COMMON SOURCES OF GROUND-WATER CONTAMINATION

AGRICULTURAL

Animal burial areas
Animal feedlots
Chemical application
  (e.g., pesticides, fungicides, and fertilizers)
Chemical storage areas
Irrigation
Manure spreading and pits

COMMERCIAL

Airports
Auto repair shops
Boat yards
Construction areas
Car washes
Cemeteries
Dry cleaning establishments
Educational institutions (e.g., labs, lawns, and
  chemical storage areas)
Gas stations
Golf courses (chemical application)
Jewelry and metal plating
Laundromats
Medical institutions
Paint shops
Photography establishments/printers
Railroad tracks and yards/maintenance
Research laboratories
Road deicing operations (e.g., road salt)
Road maintenance depots
Scrap and junkyards
Storage tanks and pipes (i.e., above-ground,
  below-ground, underground)

INDUSTRIAL

Asphalt plants
Chemical manufacture, warehousing, and
  distribution activities
Electrical and electronic products and
  manufacturing
Electroplaters and metal fabricators
Foundaries
Machine and metalworking shops
Manufacturing and distribution sites for
  cleaning supplies
Mining (surface and underground) and
  mine drainage
Petroleum products production, storage,
  and distribution centers
Pipelines (e.g., oil, gas, coal slurry)
Septage lagoons and sludge
Storage tanks (ie.e., above-ground,
  below-ground, underground)
Toxic and hazardous spills
Wells - operating and abandoned
  (e.g., oil, gas, water supply, injection,
  monitoring and exploration)
Wood Preserving facilities

RESIDENTIAL

Fuel storage systems
Furniture and wood strippers and refinishers
Household hazardous products
Household lawns (chemical application)
Septic systems, cesspools, water softeners
Sewer lines
Swimming pools (e.g., chlorine)

WASTE MANAGEMENT

Fire training facilities
Hazardous waste management units
  (e.g., landfills, land treatment areas, surface
  impoundments, waste piles, incinerators,
  treatment tanks)
Municipal incinerators
Municipal landfills
Municipal wastewater and sewer lines
Open burning sites
Recycling and reduction facilities
Stormwater drains, retention basins,
  transfer stations

- A Review of Sources of Ground- Water Contamination from Light-Industry (1990b).
- The Risk Ranking and Screening System (RRSS), Volumes I, II, and III (In Review).

2.3 SELECTION OF MONITORING PARAMETERS

After the contaminant sources are identified, optimal monitoring sites are determined based on the prioritization of sources. Next, monitoring parameters for early-warning detection and source assessment can be selected from a comprehensive list of known and suspected contaminants associated with specific sources. Tailoring the monitoring objectives based on the source assessment and choosing the appropriate monitoring parameters enhances protection and characterization, improves efficiency, and reduces the cost of the program.

It is important to choose chemical parameters for WHPP ground-water monitoring based on the potential contaminants from sources identified as the most serious threat to specific WHPAs. However, if a wide variety of potential sources are within a WHPA, the number of monitoring parameters ultimately must be balanced against the number of samples analyzed and the cost of the analyses. Therefore, when possible, indicator parameters are sought that will be effective for detecting the presence of ground-water contamination and signaling when more comprehensive laboratory analysis is needed.

2.3.1 General Water Quality Parameters

Ground water contains natural chemical constituents; the type and quantity of these constituents depends on the geochemical environment, migration, and source of the ground water (Todd et al., 1976). The most common inorganic chemical constituents, which are usually analyzed as part of the broad category of general water quality parameters, include the major cations (calcium, magnesium, potassium, and sodium) and major anions (bicarbonate, chloride, nitrate, and sulfate).

Analyses of environmental isotopes, such as Tritium, can be a valuable aid in a WHPP. These data may allow the investigator to distinguish age zones within the system and to estimate the average linear velocity of ground-water flow.

Other general indicators of water quality include temperature, electrical conductivities, pH, dissolved oxygen (DO), biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), specific conductance, oxidation reduction (redox) potential, total suspended solids (TSS), and turbidity.

By analyzing and graphing the inorganic chemical composition of ground water, interpretations are made concerning the classification, age, origin, source of the water, ground-water flow paths, and interconnections between aquifers. These geochemical interpretations are used to refine the hydrogeologic conceptual model of the study area. Data visualization methods, such as Stiff diagrams, Piper diagrams, and other graphical techniques are commonly used for interpreting water chemistry data (Davis and DeWeist, 1966, Freeze and Cherry, 1979; Hem, 1970).

2.3.2 Site-Specific Monitoring Parameters

Approaches for choosing indicator monitoring parameters were developed for characterizing hazardous waste sites. The Resource Conservation and Recovery Act (RCRA) interim status regulations identified four indicator parameters for use in detection monitoring for ground-water contamination: specific conductance, pH, total organic carbon, and total organic halides (EPA, 1989c). Plumb (1985,1987) and Plumb and Pitchford (1985) showed that volatile organic compounds (VOCs) were the single most abundant class of organic contaminants detected in ground water due to releases from hazardous waste sites. They proposed using a VOC scan as a cost-effective monitoring approach to detect ground-water contamination and suggested more comprehensive laboratory analyses at both RCRA and Super-fund sites. Rosenfeld (1990a,b) documented groundwater contamination at hazardous waste disposal sites and other industries and proposed using site-specific monitoring parameters that are customized for different source industries.

The chemical parameters in Table 2-2 are suggested as an approach for monitoring the broad categories of sources typically found within or in proximity to WHPAs. This list is only a general guideline, and it is

TABLE 2-2. MONITORING PARAMETERS FOR VARIOUS SOURCES WITHIN A WHPA

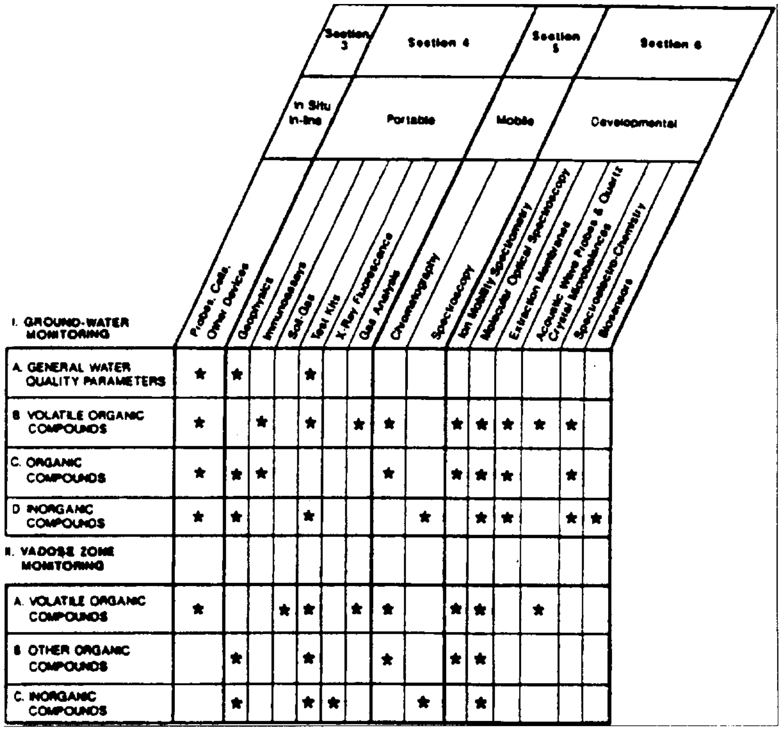
Source	Monitoring Parameters
Agricultural	General water-quality (cations, anions, TDS, pH, specific conductance, temperature, DO, redox) Nutrients (nitrate, nitrite, ammonia, phosphate) Pesticides, insecticides, herbicides VOC scan (optional)
Commercial and Industrial Facilities	General water-quality Trace metals VOC scan Other Priority pollutants (optional) Gross alpha and beta (optional)
Residential	General water-quality Nutrients VOC scan (optional) Trace Metals (optional)
Waste Management	General water-quality VOC scan Trace metals Other priority pollutants (optional) Gross alpha and beta (optional)

TDS = total dissolved solid
DO = dissolved oxygen
VOC = volatile organic compound

The suggested approach is based primarily on using the VOC scan as an indicator of leakage events at commercial, industrial, and waste management sites. Trace metals should also be monitored for those sources to check for inorganic contamination; organic priority pollutants (other than VOCs) and radioactivity screening may also be necessary, depending on site-specific conditions. Nutrient and pesticide analyses are suggested monitoring parameters for agricultural source and residential septic system identification. Additionally, general water quality parameters can potentially be useful for all types of sources, not only for source assessment, but also for refinement of the hydrogeologic conceptual model.

2.4 SELECTION OF MONITORING TECHNOLOGIES

The field monitoring technologies presented in this document can be used for measurements of many of the suggested monitoring parameters. Figure 2-l lists the monitoring technologies described in this document and shows the general classes of monitoring parameters that can be detected by each technology. Many of the technologies are used primarily for analyzing water samples, but some of the technologies are more useful for source assessment activities because of their applications for measurements of soil and soil-gas properties. Figure 2-l can be used as a reference index to the remaining sections of this document to find information on either a specific type of instrumentation or class of monitoring parameter.



	Section 3	Section 4						Section 5		Section 6					
	In Situ In-line	Portable						Mobile		Developmental					
I. GROUND-WATER MONITORING	Probes, Cells, Other Devices	Geophysics	Immunoassays	Soil-Gas	Test Kits	X-Ray Fluorescence	Gas Analysis	Chromatography	Spectroscopy	Ion Mobility Spectrometry	Molecular Optical Spectroscopy	Extraction Membranes	Acoustic Wave Probes & Quartz Crystal Microbalances	Spectroelectro-Chemistry	Biosensors
A. GENERAL WATER QUALITY PARAMETERS	★	★			★										
B. VOLATILE ORGANIC COMPOUNDS	★		★		★		★	★		★	★	★	★	★	
C. ORGANIC COMPOUNDS	★	★	★					★		★	★	★		★	
D. INORGANIC COMPOUNDS	★	★			★				★		★	★		★	★
II. VADOSE ZONE MONITORING															
A. VOLATILE ORGANIC COMPOUNDS	★			★	★		★	★		★	★		★		
B. OTHER ORGANIC COMPOUNDS		★			★			★		★	★				
C. INORGANIC COMPOUNDS		★			★	★			★		★				

Figure 2-l. Monitoring technologies and general classes of monitoring parameters.

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SECTION 3

AVAILABLE IN SITU AND IN-LINE MONITORING TECHNOLOGIES

3.1 INTRODUCTION

Current water quality monitoring practices generally involve costly and time consuming annual, biannual, or quarterly ground-water sample collection and analysis activities. The use of field screening technologies to monitor selected parameters may indicate the need for ground-water sampling in response to a baseline change rather than as a part of a predetermined sampling schedule. This will provide a more timely detection of the changes in water quality.

General indicators of ground-water quality were provided in Section 2.3.1. Because these indicator parameters are useful for dictating when sampling should occur, it is imperative to establish a data base containing baseline values of clean (uncontaminated) or ambient ground water.

These indicator parameters are sensitive to changes in pressure, temperature, agitation, and exposure to atmospheric gases (Gillham et al., 1983); therefore, it is advantageous to obtain *in situ* sample readings (Gamer, 1988; EPA 1986). *In situ* monitoring devices possess some form of sensor or probe which is designed to be placed in the medium to be monitored (i.e., ground water or soil). This sensor reacts to certain chemical or physical parameters in the medium and transmits information regarding the magnitude of that reaction by means of an electrical current (etc.) to a meter or a recorder. Several companies produce *in situ,* multiparameter probes and data transmitter packages for continuous water quality monitoring (e.g., Hydrolab Corporation; Martek Instruments, Incorporated).

The use of *in situ* monitoring devices in wells, however, is limited to certain conditions. The rate of aquifer flow through the well screen must be adequate enough so that the well is self-flushing and no purging procedure is necessary. This flow-through rate is controlled by the aquifer properties and the design of the well. An adequate flow-through rate would be analyte-specific and would not have been quantified.

When *in situ* monitoring is infeasible or impractical, measurements from in-line, flow-through cells at the wellhead can be used to reduce the effects of atmospheric gaseous contamination (Walton-Day et al., 1990, Gamer, 1988, Torstensson and Petsonk, 1988; Barcelona et al., 1985; Nacht, 1983; Gibb et al., 1981). In utilizing such a device, ground water is pumped to the surface in a closed system. The ground water is directed to flow through a device (cell) which is designed to react to certain chemical or physical parameters. The magnitude of these reactions are transmitted to a meter or a recorder. Multiparameter, in-line, flow-through cells can be fabricated with commercially available materials (Walton-Day et al., 1990), or purchased from commercial vendors (e.g., YSI Incorporated, Hydrolab Corporation). Additionally, a variety of manufacturers provide standard water quality instruments for measuring temperature, electrical conductivity, pH, and turbidity.

Ion-specific electrodes, available from various vendors, are capable of measuring specific analytes of interest and are commonly used in the waste-water industries. However, many ion-specific electrodes are sensitive to various environmental factors and are not easily useable in continuous monitoring applications for wellhead protection.

Water level monitoring technologies are also useful in WHPA applications. Water level monitoring devices are classified into three main categories: float recorders, acoustic devices, and pressure transducers. By using these methods, continuous water level measurements can be made.

3.2 THEORY OF OPERATION

3.2.1 In Situ. Monitoring& Multiparameter Probes

Commercially available probes. are equipped with a sensor for measuring temperature and a six electrode cluster for measuring specific conductance, salinity, pH, DO, oxygen, and redox potential. Additionally, the probes are equipped with a pressure transducer for measuring depth or water level.

Three types of sensors can be used for measuring temperature; these include thermistors, thermocouples, and resistance temperature detectors (Ritchey, 1986). Specific conductance, or conductivity, is measured with a multi-electrode cell that is calibrated with standard potassium chloride or seawater solutions, and the measurement is automatically temperature-compensated because conductivity varies with temperature. Salinity is automatically calculated from the conductivity measurement. The pH is generally determined with a glass membrane electrode cell. The pH electrode is calibrated using standard pH buffer solutions and is automatically temperature-compensated. Dissolved oxygen is measured with an ion-specific electrode and a membrane cell calibrated using saturated air, saturated water, or the Winkler titration method. The measurement is automatically temperature- and salinity-calibrated. The redox potential is measured using a platinum electrode. Water level or depth is measured using a pressure sensitive, strain-gauge transducer that is automatically compensated for specific conductance. The sensors must be calibrated before the probe is submerged in the water well to the desired depth of the screened interval of interest.

3.2.2 In-Line Monitoring. Multiparameter. Flow-Through Cells

Flow-through cells can be purchased from several manufacturers to monitor temperature, temperature-compensated conductivity, temperature-compensated pH, and redox potential. One manufacturer supplies an attachable flow cup for the multiparameter probe that allows in-line measurement of salinity, DO, and pressure.

Water extracted from the desired depth in the well is pumped through the inlet port of the cell chamber where the measuring sensors are located. The chamber is generally constructed of durable, clear acrylic so the water flow and turbidity conditions are observable. Electronically, the water flowing through the chamber is continuously monitored by the sensors, and the values can be stored using a data logger or a computer.

3.2.3 Ion-Specific Electrodes

Electrodes are constructed of a metal wire coated with an insoluble salt of the metal. If the electrode is dipped into a liquid solution containing a low concentration of the metal ion or a high concentration of the negative ion of the insoluble salt, the metal wire will tend to react to form the insoluble salt. Conversely, if the water solution contains a high concentration of the metal ion, or a low concentration of the negative ion, the insoluble salt will tend to form the metal. In these reactions, electrons are added to or removed from the metal wire, changing the electrical charge on the wire. By measuring the voltage of a calibrated electrode, the concentration of the metal ion or negative ion in the solution can be calculated.

The silver chloride and the silver sulfide electrodes are the most common electrodes used in the manufacture of ion-selective electrodes. The silver chloride electrode consists of a silver wire coated with insoluble silver chloride, which is immersed in a solution containing chloride ions. The silver chloride electrode can be used to measure the concentration of silver ions or chloride ions dissolved in water. The principle of operation of the silver sulfide electrode is identical to that of the silver chloride electrode, but the construction of the silver sulfide electrode is simpler because it is not immersed in a solution containing the negative ion of the insoluble salt (sulfide, in this case). If another metal sulfide is dispersed in the silver sulfide matrix, the electrode can be used to measure the concentration of that metal dissolved in water. For example, by mixing lead sulfide with the silver sulfide, the electrode can be used to determine lead dissolved in water. If an insoluble silver salt is dispersed in the silver sulfide, the electrode can be used to measure the concentration of the negative ion of the silver salt dissolved in water. A cyanide-sensing electrode can be made by mixing silver cyanide with the silver sulfide (Willard et al., 1974).

Perhaps the most familiar type of ion-selective electrode is the glass membrane electrode, which is used for measuring the pH of water samples (Figure 3-la). The pH electrode uses a silver chloride internal reference electrode immersed in a chloride internal filling solution surrounded by a thin glass membrane (Figure 3-lb). When immersed in an alkaline solution, positive hydrogen ions are removed from the outer surface of the bulb, leaving the bulb with a negative charge. The negative charge on the bulb repels negatively charged chloride ions dissolved in the solution within the bulb. The chloride ions cluster around the silver wire, increasing the local chloride concentration, thus making the electrode voltage more negative. When immersed in an acidic solution, hydrogen ions are added to the surface of the glass bulb, giving it a positive charge. The positively charged bulb attracts chloride ions and decreases their concentration around the silver wire. The electrode voltage is charged according to the pH.

The pH electrode forms the basis of other electrodes which can be used to measure the concentration of certain gases dissolved in water. In the ammonia electrode, for example, the glass sensing element of a pH electrode is surrounded by an internal filling solution contained by a porous membrane (Figure 3-2a). The membrane repels liquid water but permits the free passage of gases. When this electrode is dipped into water that contains ammonia, the ammonia passes through the electrode membrane and is dissolved in the solution surrounding the glass bulb. The ammonia changes the pH of the solution; this, in turn, changes the voltage of the electrode. In addition to ammonia, electrodes can be used to measure the concentration of other gases dissolved in water, including carbon dioxide, oxides of nitrogen, and oxygen.

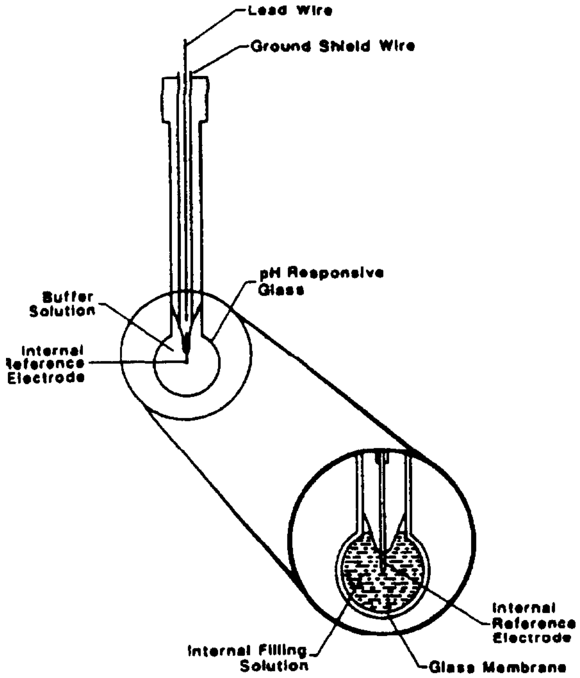

Figure 3-la. pH electrode which requires an external reference electrode.

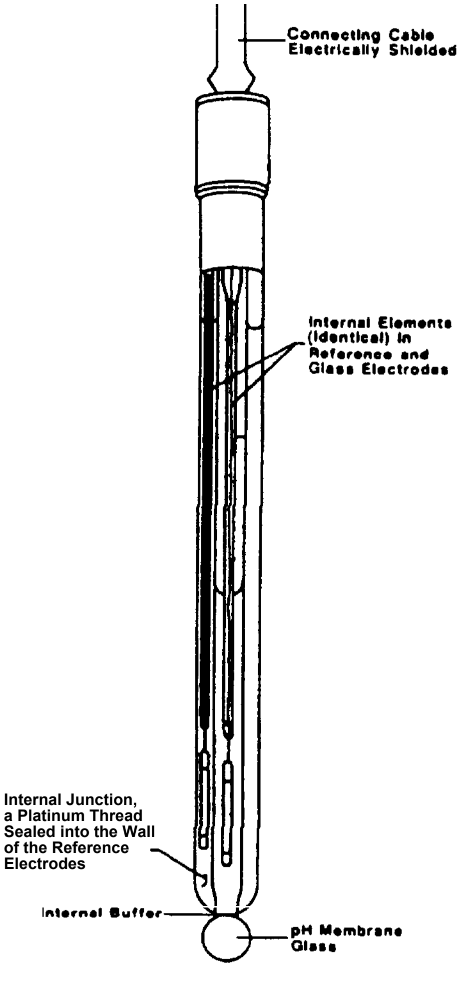

Figure 3-lb. "Combination" pH electrode with internal reference electrode.

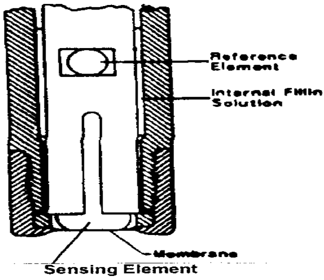

Figure 3-2a. Gas-sensing electrode.

Modified gas-sensing electrodes can be used to measure the concentration of numerous organic compounds dissolved in water. This is accomplished by coating the gas-sensing electrode membrane with an enzyme or catalyst which converts a specific organic compound to the gas that is measured by the electrode (Figure 3-2b). The most common example is the urea electrode in which the enzyme urease is applied to an ammonia electrode membrane. The urease converts urea to ammonia, which is then detected by the ammonia electrode.

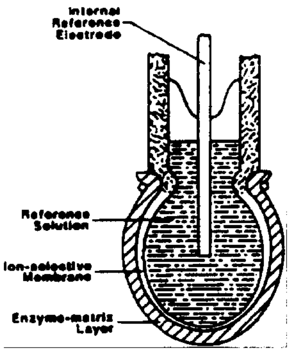

Figure 3-2b. Enzyme electrode.

The fluoride ion electrode is similar in construction to the pH electrode. Instead of a glass membrane, however, the fluoride electrode uses a crystal of the insoluble solid-state ionic conductor lanthanum fluoride, and the internal filling solution contains fluoride as well as chloride ions (Figure 3-2c). When dipped into a solution more concentrated in fluoride than the internal solution, negative fluoride ions enter the crystal, giving it a negative charge. As in the case of the pH electrode, the negatively charged crystal increases the chloride concentration in the vicinity of the silver wire and makes its voltage more negative. When dipped into a more dilute solution, fluoride ions leave the crystal, giving it a positive charge. The chloride concentration in the vicinity of the silver wire is decreased, and the voltage of the wire becomes more positive. Other ion-selective electrodes are based on the silver

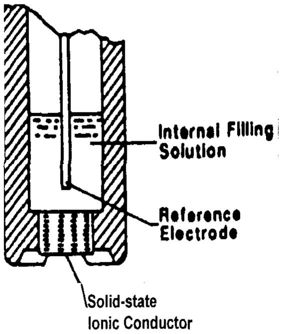

Figure 3-2c. Fluoride electrode.

3.2.4 Water-Level Monitoring

Several different types of devices can be used to monitor water-level measurements. These include float and weight systems, acoustic devices, or pressure transducers that can be connected to a chart recorder, digital encoder and data loggers, or a modem.

Float systems installed in the well require a float that is connected to a weight by a beaded cable or a graduated tape that rests on a pulley. The changing water level in the well causes the float to rise or fall with the water in the well. The change in the position of the float causes the pulley to rotate proportionally, and if the pulley is linked to a clock-controlled chart recorder, a pen records the water level change on a scaled chart. Alternatively, a digital encoder may be linked to the pulley so that the water level change produces a digital signal that is recorded using a data logging device, or the logger may be linked to a modem and the data relayed to a centralized location for analysis and computer storage and use.

Acoustic devices installed in the wellhead produce short pulses of sound waves that reflect off the water surface. The acoustic device receives the reflected sound wave, and the elapsed time between pulse transmission and the reception of the reflected wave is converted to a distance measurement. The water level in the well is periodically monitored by the device, which is linked to a data logger or modem (Figure 3-3).

Transducers, installed in the well beneath the water surface, use pressure/strain relationships to create an electrical signal to measure water level or depth. The electrical signal is transmitted from the transducer and is relayed up a coaxial cable to the wellhead.

3.3 METHODOLOGY

3.3.1 In Situ, Monitoring. Multiparameter Probes

The probe is calibrated at the wellhead using the appropriate standard solutions that include the ranges of values anticipated for the temperatures expected in the well water to be monitored. Next, the probe is lowered into the well using a cable that mounts to a bracket attached to the probe.

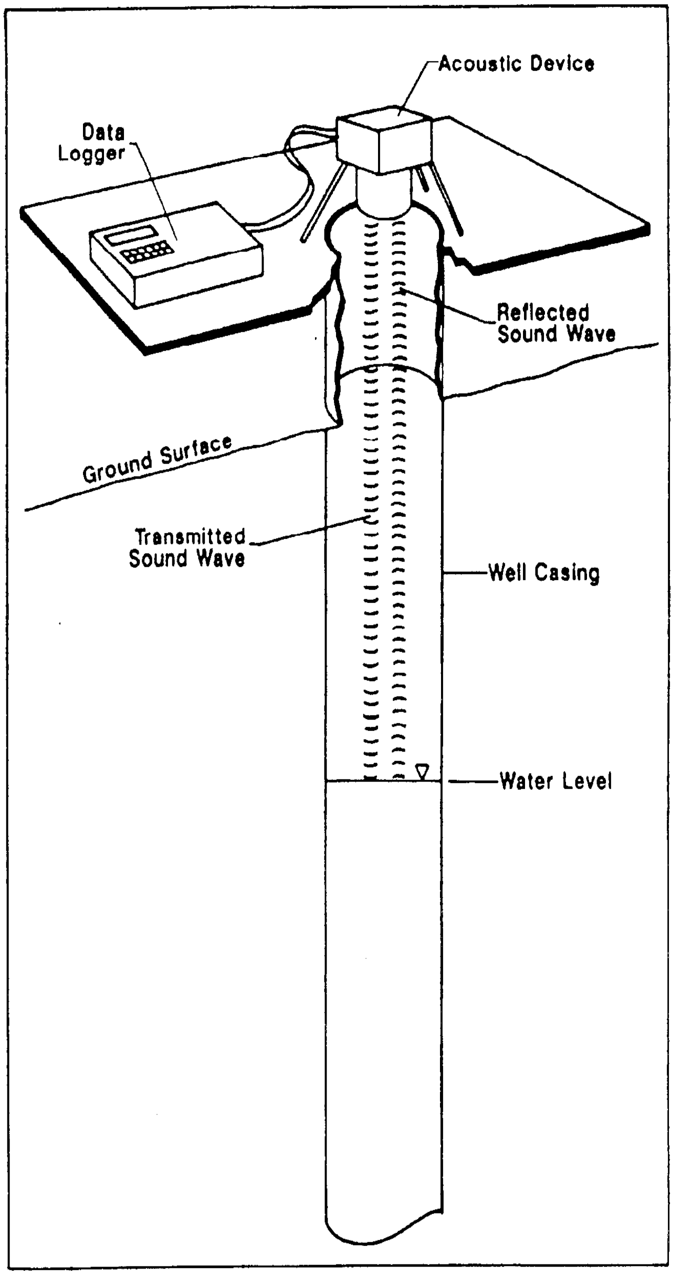

Figure 3-3. Acoustic device installed in a well and linked to a data logger.

Parameter values are manually queried at the wellhead with a rotating switch on the display unit, or the data may be stored on a digital, field data, logging device for manual or unattended data storage. Another device, called a data management unit, is needed to transfer the data from the logging device to any RS-232-C compatible printer, data terminal, or computer. Therefore, unattended monitoring can be performed, and the data can be stored at the monitoring site and retrieved by a site visit, or the data may be transmitted to the centralized data base via modem or telemetry.

3.3.2 In-Line, Monitoring, Multiparameter. Flow-Through Cells

Plow-through cells are calibrated at the wellhead using the appropriate standard solutions tailored to the ambient water conditions. The in-line, multiparameter, flow-through cell is then connected with inert tubing to a device such as a bladder pump. Water is pumped from the well at a flow rate that minimizes agitation of the water. The sensors should be allowed several minutes to adjust to the change in temperature and parameter values (Gamer, 1988). Also, the stagnant casing water should be purged from the well in order to allow fresh aquifer water to be drawn into the pumping system and into the cell. Purging should continue until temperature, pH, and electrical conductivity measurements of the purged water have stabilized. These measurements can also be conducted with the use of an appropriate in-line, flow-through cell.

3.3.3 Ion-Specific Electrodes

Electrodes are calibrated by measuring the response voltage to at least two solutions containing different known concentrations of the analyte of interest. This calibration procedure defines the response (voltage) of the electrode within that concentration range of the analyte of interest. To measure the apparent concentration of the analyte of interest in any other solution, the electrode is placed in an apparatus such as a down-hole probe or a flow-through cell and placed in contact with the ground water to be monitored in the appropriate manner, and the electrode voltage is measured using a metering device. The concentration which corresponds to that voltage can then be determined from the calibration data (Kolthof et al., 1971). However, interfering constituents present in some ground water makes proper calibration a difficult task in some situations (Ritchey, 1986).

3.3.4 Water-Level Monitoring

The “Methodology” and the ‘Theory of Operation” of these water-level monitoring devices are essentially inseparable. Refer to Section 3.2.4 for this information.

3.4 APPLICATION TO WHPA MONITORING

3.4.1 *In Situ*. Monitoring, Multiparameter Probes

The in situ probe can be installed in two-inch or larger diameter monitoring wells to continuously monitor indicator parameters. If the ground water in the monitoring well is uncontaminated and the water remains uncontaminated for several years, then valuable information can be obtained and used to model the natural, temporal, and spatial variation of the ambient water conditions. Such a record of ambient water quality conditions can be used for recognizing when additional chemical analyses of water samples may be needed. As a result, the early-detection of contamination may be accomplished, leading to early corrective action, thus protecting valuable water resources, expensive water extraction systems, and the consumer.

3.4.2 In-Line, Monitoring, Multiparameter, Flow-Through Cells

The flow-through cell technology is also used for monitoring ambient water conditions to establish an historical data base to be used for the early-detection of ground-water contamination. The flow-through cell concept can feasibly be implemented through a manual, monthly, monitoring schedule. Additionally, the cells can be used to obtain the basic physical and chemical condition of water collected for routine analysis or to determine when well-development procedures are effective.

3.4.3 Ion-Selective Electrodes

Ion-selective electrodes are available for the measurement of a large number of parameters of interest in WHPPs, including ammonia, bromide, cadmium, calcium, carbon dioxide, chloride, copper, cyanide, fluoride, hardness, lead, nitrate, nitrite, oxygen, pH, sodium, and sulfide (Baxter Healthcare Corp., 1989). Ion selective electrodes could be installed in a flow-through cell or a probe (Figure 3-4).

The silver sulfide-based electrodes (cadmium, copper, cyanide, lead, chloride, and sulfide) are solid, so they may be placed at depths of thousands of feet without being adversely affected by high water pressures. The silver chloride-based electrodes contain liquid reservoirs; they must be manufactured of flexible materials which can be slightly compressed without damage, in order to equalize pressures inside and outside the electrode body. Some electrodes are constructed to withstand high pressures and can be installed at almost any desired depth within a well. Of course, water samples can be pumped from any depth and analyzed at the surface. However, this may compromise the accuracy of the measurements of dissolved gases such as oxygen and carbon dioxide (Lattimer, 1982).

3.4.4 Water-Level Monitoring

Many manufacturers produce equipment for continuous water level monitoring using floats, acoustic devices, or pressure transducers linked to data loggers or telemetry equipment. The information obtained from these systems is valuable for mapping apparent flow direction, seasonal water-level fluctuation, and long-term, water-level changes.

3.5 LIMITATIONS/PERFORMANCE

3.51 In Situ. Monitoring, Multiparameter Probes

Multiparameter probes have limited applicability in situations such as long-term monitoring for DO because the membrane on the electrode can become fouled. Additional sensor calibrations must be performed according to manufacturer specifications, Also, without an external power source the probe has limited continuous data recording capability. Table 3-l shows some of the probe specifications. The most serious limitation for current instrumentation is that many of the sensors have predicted stability for a

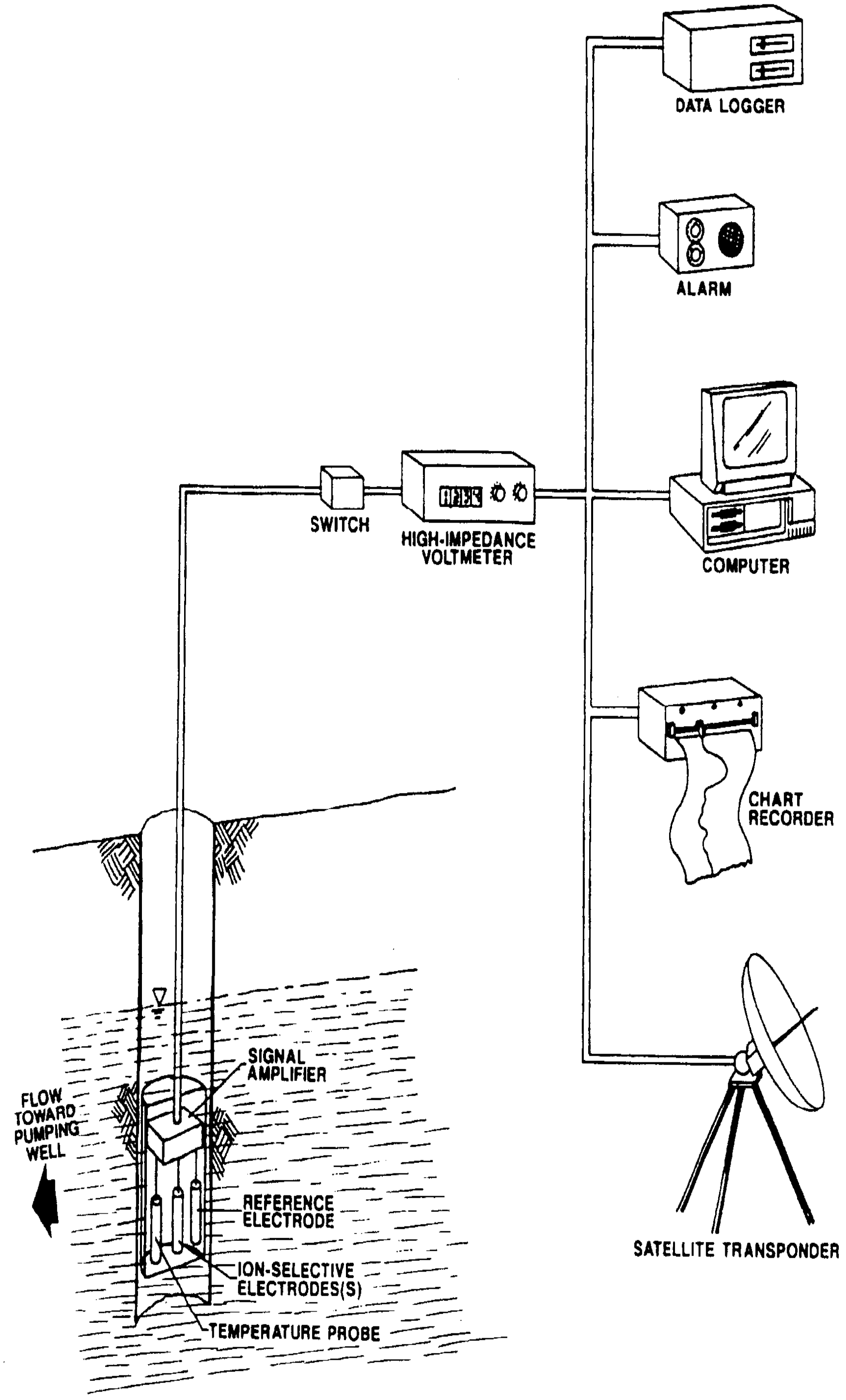

Figure 3-4. Conceptual drawing of a well monitoring system using ion-selective electrodes.

TABLE 3-1. EXAMPLES OF IN SITU PROBE SPECIFICATIONS*

PARAMETER	RANGE	ACCURACY	SENSOR	COMPENSATIONS	RESOLUTION	CALIBRATION	RESPONSE TIME	STABILITY	OUTPUT OPTIONS
TEMPERATURE	-5 to 50°C	±0.15°C	thermistor	none req'd	0.01 °C	none req'd	two minutes	three years	output in deg F.
SPECIFIC CONDUCTANCE	0 to 100 mS/cm	*1% of range	6-electrode cell	automatic for temp (25°C)	4 digits	KCl or seawater standards	one minute	six months	output in salinity, conductivity, TDS, or resistivity; output in μS/cm
pH	0 to 14 units	*0.2 units	glass pH; rebuildable or low ionic strength reference electrode	automatic for temperature	0.01 unit	pH 7 buffer, plus one slope buffer	two minutes	one month	none
DISSOLVED OXYGEN	0 to 20 mg/L	*0.2 mg/L	rebuildable polarographic; 1 mil Teflon™ or *LoFlow* ™	automatic for temp & salinity	0.01 mg/L	saturated air, Winkler, or saturated water	two minutes	one month	w/o salinity correction, % Saturation
REDOX	-999 to 999 mV	*20 mV	Platinum electrode	none req'd	1 mV	quinhydrone or transfers	two minutes	one month	none
DEPTH	0 to 100 m	*0.45 m	strain-gauge transducer	automatic for sp. conductance	0.1 m	set zero in air	one minute	one month	output in feet
LEVEL	0 to 10 m	*0.09 m	stain-gauge transducer	automatic for sp. conductance	0.01 m	set zero in air	one minute	one month	output in feet
SALINITY	0 to 70 ppt	*0.2 ppt	calculated from specific conductance	none req'd	0.1 ppt	uses calibration from specific conductance	two minutes	one month	none

(Continued

*(From Hydrolab Corporation) specifications for probe capable of monitoring four-inch or larger diameter wells. Can also be used for flow-through capability with addition of attachable flow-cup

TABLE 3-1. Continued*

PARAMETER	RANGE	ACCURACY	SENSOR TYPE
Temperature	0-50°C	±0.1°C	Thermolinear array
Conductivity	0-10 mmho/cm 0-100 mmho/cm	±0.01 mmho/cm ±0.1 mmho/cm	5 electrode stainless steel
Temperature Corrected Conductivity	Variable	±2% of range selected	
Salinity	0-50 ppt	±0.5 ppt	
pH	0-14	±0.1 pH	Combination pH electrode with internal silver-silver chloride reference electrode
Dissolved Oxygen	0-20 ppm	±0.1 at temperature of calibration	Galvanic electrode with automatic temperature compensation and in-situ stirrer
ORP	±2000 meters	±0.05 of actual voltage	Combination platinum electrode with silver-silver chloride reference electrode
Depth	0-300 meters	±1% of range	Silicon strain gauge-temperature compensated

*(from Martek Instruments, Inc) probe capable of monitoring two-inch or larger diameter wells.

35.2 In-Line. Monitoring. Multiparameter. Flow-Through Cells

Pumping individual monitoring wells and using in-line cells for monitoring wells on a regular schedule requires manual labor hours that may impose logistical and cost restrictions on the monitoring program. As with multiparameter probes, sensors on the flow-through cells must be manually calibrated according to manufacturer directions. Table 3-2 shows some general specifications of a commercially available unit.

TABLE 3-2 EXAMPLE OF COMMERCIALLY AVAILABLE FLOW-THROUGH CELL SPECIFICATIONS*

	RANGE	ACCURACY	SENSOR TYPE	COMPENSATIONS	CALIBRATIONS	RESPONSE TIME
Temperature	-5 to 50 °C	± 0.4 °C	thermistor	none required	none required	95% in 10 seconds
Conductivity	0 to 100 MS/CM	± 3% to ± 6% Depending on range	2 electrode	automatic for temperature (25 °C)	conductivity calibrator solution	95% in 10 seconds
PH	0 to 14 units	Depends on calibration	glass electrode	automatic for temperature	pH buffer	95% in 10 seconds
ORP	-1500 to 1500 mv	± 2% of reading plus 1 count	platinum electrode	none required	Zobell solution	95% in 10 seconds

* (From YSI Incorporated)

3.5.3 Ion-Specific Electrodes

Ion-specific electrodes must be used with an internal or an external reference electrode. Fortunately, a single reference electrode can be used with any number of ion-selective electrodes as long as they are immersed in the same solution.

Ion-selective electrodes have a very high internal resistance, thus the voltage of an ion-selective electrode must be measured with a very sensitive (high input impedance) voltmeter. Such voltmeters, which may be used with any number of electrodes, are readily available from electrode manufacturers. Some voltmeters display concentrations of detected substances directly, thus eliminating the need for manual calculations using an electrode calibration chart. Ion-specific electrodes produce a voltage response. As a result, they can be connected to chart recorders or data storage devices such as computers to provide continuous monitoring of the analyte concentrations in the water being analyzed. Electrodes respond relatively quickly (generally within two minutes) to sudden changes in the concentration. If desired, an electrode can be connected to an alarm system set to a pre-selected contaminant level. Practical limits of detection for several electrodes are listed in Table 3-3.

The response of an electrode is affected by temperature changes. Thus, electrodes must be calibrated in solutions having the same temperature as the water to be analyzed. Furthermore, the water to be analyzed must remain at a relatively constant temperature. However, the effect of temperature changes on electrode responses is well-known. Thus, a temperature measuring device should be used to provide a correction to the electrode response.

There are, of course, some important limitations on the use of ion-specific electrodes. Perhaps the most important is the non-selective nature of such electrodes. That is, some electrodes may respond to more than one substance. For example, a chloride-sensing electrode will also respond to

TABLE 3-3. PRACTICAL LIMITS OF DETECTION FOR SEVERAL ION-SELECTIVE AND GAS-SENSING ELECTRODES.

Electrode	Detection Limit (ppm)
Ammonia	0.01
Bromide	0.4
Cadmium	0.01
Calcium	0.02
Carbon Dioxide	5
Chloride	2
Chlorine	0.01
Copper	0.001
Cyanide	0.2
Chloride	0.02
Hardness	20 gpg
Lead	0.2
Nitrate nitrogen	0.1
Oxides of nitrogen	0.2
Oxygen	0.5
pH	2-12 pH units
Potassium	0.04
Silver	0.01
Sodium	0.3
Sulfide	0.005

cyanide and sulfide (Orion Research Inc., 1986a). The cyanide and sulfide electrodes will not respond if the water is too acidic (Orion Research Inc., 1986b, 1988). A chemical analysis of the well water will provide information regarding the suitability of using particular electrodes to analyze the water. In some monitoring situations, their use may be inadvisable (Ritchey, 1986).

To obtain maximum accuracy, electrodes must be recalibrated on a regular basis. This procedure requires that the electrodes be withdrawn from a well to the surface, calibrated, and re-inserted into the well. The frequency of recalibration (weekly, monthly, semi-annually, etc.) depends on the quality of the water in the well being monitored and the tendency for the electrode to drift off calibration. Electrodes used to monitor relatively clean water will require infrequent recalibration, while electrodes used to monitor water containing abundant biological activity or suspended oils may need frequent cleaning and recalibration. Probably the best method for determining the optimum recalibration frequency for electrodes used to monitor a particular well is to maintain and regularly review recalibration data.

If electrodes are used in deep wells, their signals must be amplified to overcome the resistance of the long electrical cables required. Electrode systems have been designed to utilize small radio transmitters to broadcast the electrode signal (Lattimer, 1982).

Personnel assigned to install a well-monitoring system utilizing electrodes must be thoroughly familiar with the uses and limitations of electrodes. The team should include an experienced chemist and personnel trained in electronics in order to interface the electrodes with the desired electronic equipment. Although off-the-shelf, computer interfacing hardware and software are available, some computer programming experience may be useful.

3.54 Water-Level Monitoring

Float systems and submersible strain-gauge type pressure transducers are relatively simple to install in monitoring wells, and they can be linked to data logging or telemetry equipment.
Studies performed to test the accuracy of water level monitoring devices have shown that over approximately a one-year period the average absolute error for selected float systems and pressure transducers is 0.027 feet and 0.098 feet, respectively (Rosenberry, 1990). The accuracy of acoustic devices is reported to be approximately & 1 foot (Ritchey, 1986).

Measurement inaccuracies are caused by a number of factors, including systematic errors (e.g. site-specific problems, instrument breakdown, surveying errors) or random errors such as weather conditions or instrument calibration (Sweet et al., 1990).

3.6 SUMMARY

Multiparameter probes are available from several commercial manufacturers for ***in situ*** monitoring in two-inch or larger diameter wells, depending on the model. These probes can be used at multiple sites or used in a single well to continuously monitor changes in general chemical and physical parameters. Linking the continuous monitoring probe to a modem or telemetry system allows rapid data transmission and the application of computer software that will signal an alarm if parameter values reach predetermined levels. Field sampling and analysis procedures may be warranted if the monitored values reach action levels. Monthly sensor calibration is necessary.

In-line, flow-through cells can be constructed in-house or purchased commercially. Flow cells are used at the wellhead to periodically monitor ambient ground-water conditions. Sensor calibration is necessary.

Ion-selective electrodes are currently available for measuring a wide variety of organic and inorganic water contaminants. These electrodes are small, rugged, non-contaminating, inexpensive compared to other analytical methods, and relatively simple to use. They can be used for analyses in wells at great depths, or they can be used to measure contaminants in-line with water samples which have been pumped to the surface. Applications are limited by various interferences, depending on the water chemistry. A chemical analysis of the well water will indicate which electrodes would be useable in any particular situation.

Several different types of continuous water level monitoring devices are commercially available for monitoring temporal and spatial water level changes and apparent ground-water flow directions. Float recorders have been routinely used in monitoring programs for many years while acoustic devices and pressure transducers are relatively new on the market. The three types can be linked to data loggers or used with modems for data transmission.

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SECTION 4

PORTABLE MONITORING METHODS

Portable monitoring methods involve light-weight equipment that can be readily carried into the field by the user. Portable methods are applicable for WHPA monitoring by indirect sensing, or analysis of the vadose zone, or by direct analysis of ground-water samples. The methods described in this section include geophysics, immunoassays, soil-gas sampling and analysis, test hits, X-ray fluorescence spectroscopy, and gas analysis equipment.

4.1 GEOPHYSICS

4.1.1 Introduction

Physical property changes related to some kinds of contaminants can be remotely sensed using geophysical monitoring systems. Because geophysical measurements detect the effect rather than the contaminant, the physical characteristics in a WHPA must be characterized before the monitoring system is installed to establish a basis for identifying changes occurring in an aquifer. A properly designed geophysical monitoring system provides the ability to detect contaminants before they reach a production well. It also provides a mechanism to monitor the movement of contaminants so that pumping rates within the wellhead protection area can be adjusted, and contaminants can be removed through recovery wells with minimal effects on adjacent areas.

Surface and borehole geophysical measurements are useful components of any WHPA monitoring strategy. Each has advantages and limitations; however, the use of both methods may provide the investigator with more comprehensive information than possible with either method alone.

Surface geophysical techniques may be noninvasive and can often provide data along lines over large areas. Different methods can be used to remotely sense subsurface physical property contrasts such as electrical properties, density, and magnetic susceptibility. Data interpretations are used to relate physical properties to geologic or hydrologic objectives, including estimates of depth to water level, stratigraphic thickness, location and movement of contaminated substances, and location of buried objects that influence the movement of contaminants. The primary WHPA targets of interest are the location and movement of contaminants.

Borehole geophysical techniques (or geophysical well-logging) are invasive; however, these can provide the investigator with information that may not be obtainable with surface methods. For example, the borehole tool can be lowered to known depths in a well, making it a good “ground truth” tool. The tool is in close proximity to subsurface formations of interest; therefore, it can produce better resolution than surface-based measurements. Borehole techniques can be used to obtain information about lithology and to identify physical properties of the rock matrix. They can also provide information about the thickness, *porosity,* bulk *density, resistivity, and* percent saturation *of* aquifers and confining beds. (Keys, 1927).

4.1.2 Theory of Operation

A. Surface Techniques

Direct Current Resistivity--Direct current (DC) resistivity methods measure subsurface distribution of electrical properties. Electrical current passes into the ground via two electrodes connected to an electrical current source Resistivity is related to ohmic losses that occur when an electric current flows through the earth. Depth of current penetration is related to the separation between current electrodes and potential electrodes (Figure 4-l).

Resistivity is an intrinsic property that remains constant for a homogeneous isotropic material, regardless of the amount of material measured or the electrode configuration (Bisdorf, 1985). The subsurface generally will not consist of homogeneous isotropic material. Apparent resistivity or average resistivity of all material through which current flows will be a function of the true resistivities. depths, and thicknesses of the different subsurface materials down to the limit of current penetration.

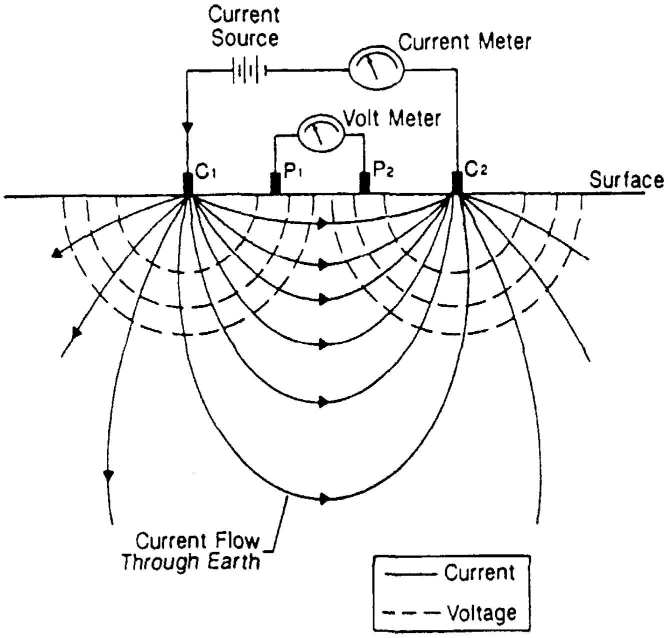

Figure 4-l. Diagram showing basic concept of resistivity measurement.

Electromagnetic Methods--Electromagnetic (EM) techniques, like DC resistivity methods, are sensitive to changes in subsurface electrical properties. EM techniques make use of an inductively induced electromagnetic field to measure conductivity changes (Figure 4-2). Conductivities are measured by inductively inducing secondary eddy currents in the earth and measuring the associated magnetic field at some location. The apparent conductivity is not a true conductivity except when measurements are taken over a homogeneous, isotropic medium. Otherwise it is a composite value which averages effects from different materials with varying thicknesses, depths, and conductivities found within its range of detection. Depth of penetration is related to these parameters, but also depends on signal frequency and the distance between source and receiver.

Ground Penetrating Radar--Ground penetrating radar (GPR) uses high frequency electromagnetic energy transmitted into the ground by antenna to map conductivity contrasts in the subsurface. GPR differs from the other electromagnetic methods discussed because of the high frequency of the signal. At radar frequencies, electromagnetic induction is not the dominant propagation mechanism. Instead, the energy travels through the subsurface like a wave. This wave is reflected, refracted, diffracted, or transmitted at the water table and other subsurface interfaces where there are changes of complex permittivity. Reflected energy is detected with a receiver antenna and is used to create a continuous cross-sectional profile of the subsurface. A representation of transmitted and reflected energy is shown in Figure 4-3.

Depth of investigation is dependent on the depth that the wave and its reflections can travel before they are attenuated by various loss mechanisms. These loss mechanisms are controlled by the electrical conductivity of the formation, clay content, water content, and particle size. Also, for given subsurface conditions, depth of penetration generally decreases as frequency increases.

B. Borehole Geophysics

Borehole geophysical methods comprise three general categories: mechanical, passive, and active-source devices. Mechanical-source borehole tools use moving parts to obtain information about the borehole environment. Passive-source borehole methods involve those tools that are sensitive to a particular property, but have no active source. Active-source borehole tools contain both source and receiver. Table 4-l summarizes the suite of borehole tools and their capabilities.

4.1.3 Methodology

A. Surface Techniques

Direct Current Resistivity--Several different electrode configurations, called arrays, are commonly used for resistivity surveys. Three of the most widely used are the Schlumberger, Wenner, and dipole-dipole arrays (Violette, 1987, Zohdy, 1974).

Resistivity surveys can be used to conduct vertical depth soundings or horizontal profiling. The objective of the former is to locate changes in electrical properties with depth. It is accomplished by expanding the array symmetrically about a central point. The objective of horizontal profiling is to locate lateral variations in resistivity at a particular depth. In horizontal profiling, a fixed-spaced array is moved across the surface of the earth. Array configuration in both horizontal and vertical

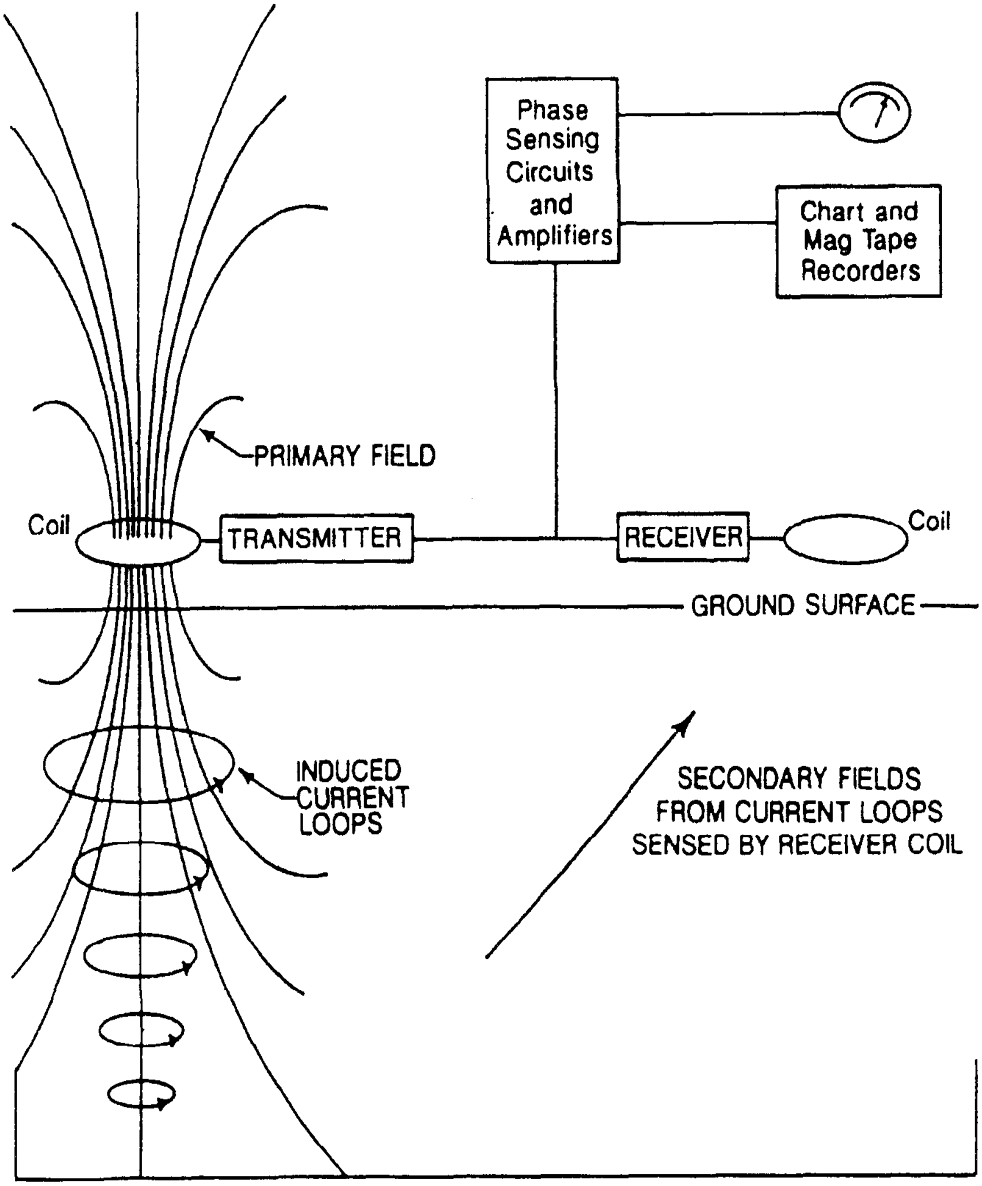

Figure 4-2. Illustration showing EM principle of operations.

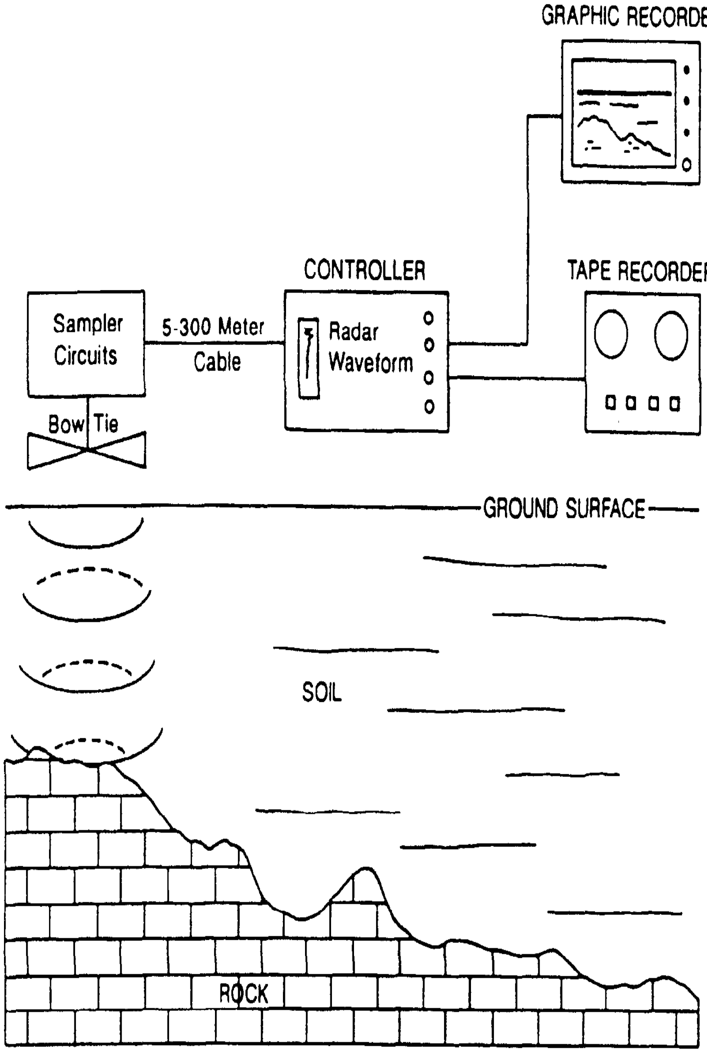

Figure 4-3. Illustration of ground penetrating radar system. Radar waves are relected from soil/rock interface.

TABLE 4-1. SUMMARY OF LOG APPLICATIONS

Required information on the properties of rocks, fluid, wells, or the groundwater system.	Widely available logging techniques which might be utilized.
Lithology and stratigraphic correlation of aquifers and associated rocks	Electric, sonic, or caliper logs made in open holes, calibrated neutron or gamma-gamma logs in open or cased holes
Total porosity or bulk density not resisting	Calibrated long-normal resistivity logs
Clay or shale content	Gamma logs
Permeability	No direct measurement by logging; may be related to porosity, injectivity, sonic amplitude
Secondary permeability--fractures, solution openings	Caliper sonic, borehole televiewer, or television logs
Location of water level or saturated zones	Electric, temperature, or fluid conductivity in open hole or inside casing. Neutron or gamma-gamma logs in open hole or outside casing.
Moisture content	Calibrated neutron logs.
Infiltration	Time-interval neutron logs under special circumstances or radioactive tracers.
Direction, velocity, and path of groundwater flow	Single-well tracer techniques--point dilution and single-well pulse. Multiwell tracer techniques.
Dispersion, dilution, and movement of waste	Fluid conductivity and temperature logs. Gamma logs for some radioactive wastes, fluid sampler.
Source and movement of water in a well	Injectivity profile; flowmeter or tracer logging during pumping or injection; temperature logs
Chemical and physical characteristics of water, including salinity, temperature, density, and viscosity	Calibrated fluid conductivity and temperature in the well; neutron chloride logging outside casing; multielectrode resistivity
Determining construction of existing wells, diameter and position of casing, perforations, screens	Gamma-gamma, caliper, collar, perforation locator, and borehole television

(continued)

TABLE 4-1. Continued

Guide to screen setting	All logs providing data on the lithology, water-bearing characteristics, and correlation and thickness of aquifers
Cementing	Caliper, temperature, gamma-gamma; acoustic for cement bond
Casing corrosion	Under some conditions caliper, or collar locator
Casing leaks and (or) plugged screen	Tracer and flowmeter

investigations is determined by depth of interest. The dipoledipole array allows a combination of sounding and profiling.

The process of converting measured values (in this case apparent resistivities and electrode spacings) to a subsurface model is called inversion. Inversion is accomplished using specialized algorithms that have in some cases been made user friendly and adapted for use on personal computers (PCs).

Electromagnetic Methods--Though there are several types of EM induction methods, this discussion focuses on frequency-domain and transient (time-domain) EM. The source of the time-varying EM field is an alternating or AC current (as opposed to the direct current of DC resistivity techniques) flowing through the transmitter loop. A receiver loop is used to detect secondary field effects. The loop may be moved across the surface, or one loop may be held fixed while the second is moved. EM measurements can be used either for vertical soundings or as a tool for horizontal profiling at a particular depth. This is a fairly tedious process, and the resulting data reduction and interpretation must be done by a skilled geophysicists. Even then, resolution is often not great enough to delineate targets with required resolution.

Ground Penetrating Radar--The transmitting antenna is moved across the surface of the earth. The moving antenna continuously transmits pulses of high frequency energy into the subsurface. Reflected energy is captured by a receiving antenna. The receiving antenna may be the same antenna that is used as a transmitting antenna; an alternative is to have a separate receiver antenna at a fixed distance from the transmitting antenna. It is advantageous to operate in the bistatic mode to minimize noise.

The GPR systems allow for continuous data acquisition. It is important, however, to have a system for locating the survey area on a map for later analysis purposes. GPR systems use a broadband antenna with a particular center frequency. The higher frequency antennas have greater resolution but are limited to detection of shallow targets. Resolution is reduced when lower frequency antennas are used; however, detection depth is often increased. The larger antennas can weigh more than 70 kilograms, which makes them unwieldy.

Graphic recorders and video displays make it possible to monitor data as it is collected. The data can be displayed in various formats to show the position and amplitude of reflecting interfaces. Usually data are presented with survey distance and two-way travel time as the two axes, similar to the presentation of seismic data. In many cases, this is all the data processing that is necessary for interpretation. It is also possible to use a magnetic tape recorder. This allows the data to be saved and displayed on the graphic recorder at a later time. It also allows them to be used as input for computer processing, which may be desirable for more complex interpretations. This will increase the cost of the survey. Both digital and analog tape recording systems are available.

B. Borehole Geophysics

Mechanical Devices--A good example of a mechanical logging device is the caliper log, which measures the average diameter of the borehole by using two or more caliper arms (Walenco, Inc). This tool is used to obtain information for hole-diameter corrections for other log interpretations and for information on possible fracture zones, casing conditions, and volume for cementing. Another mechanical log is the flowmeter, used for flow zone identification and flow rate measurements. Mechanical flowmeters often are not capable of measuring flow rates if the well is not being pumped. A fairly recent development is the low velocity, heat-pulsed flowmeter (Hess, 1982; Paillet et al., 1987). This device uses a resistance-wire heating grid (activated by a pulsed electrical current) and temperature-sensitive resistors to measure flow rates of as low as 2 liters per minute.

Passive Devices--This section discusses three standard passive borehole devices: the natural gamma log, the spontaneous potential (SP) log, and the temperature log. The natural gamma log measures the naturally occurring gamma emissions from the formation surrounding the borehole (Walenco, Inc). Gamma emissions are often related to clay minerals present in the formation; therefore, the natural gamma log is useful for determining the location of clay layers and other materials like coal. The SP log measures DC voltage (or potential) differences between a moveable electrode down the hole and a fixed electrode at the surface. Potential differences develop at the contact between shale or clay beds and sandy aquifers; they are dependent on conductivity differences between formation fluid and the fluid in the borehole. It is usually necessary to have a conductive fluid, such as drilling mud, in the borehole. The log is used to determine lithology, shale/clay content, and water quality. Response is more complex when used in a hole without a conductive drilling fluid. The log should generally be interpreted by someone with log analysis expertise.

Active Source Devices--Resistivity logs, sonic (or acoustic) logs, including the acoustic televiewer, and the remaining nuclear logs are examples of active methods. The resistivity log operates on the same principle as its surface counterpart. It is useful for determination of lithology and pore fluid quality. The acoustic logs measure the time it takes for a pulsed, compressional sound wave to travel a known distance from source to receiver. These devices are useful for determination of porosity and for fracture detection. The active nuclear devices, both the gamma-gamma and the neutron logs, are used for porosity, bulk density, and moisture content information.

4.1.4 Application to WHPA Monitoring

A Surface Techniques

Direct Current Resistivity--The electrical resistivity of ground water is usually the controlling factor in formation resistivity. Changes in the electrical resistivity of ground water can sometimes be linked to changes in ground-water quality. The presence of some (mostly inorganic) contaminants can alter the resistivity of ground water enough to be detected with DC resistivity techniques. If an initial resistivity survey were conducted during the wellhead protection area delineation phase, then conducting subsequent surveys will serve to detect any changes in formation resistivity with time. Resistivity might be used to trigger ground-water sampling for electrically conductive contaminants in the area. Examples which demonstrate the use of the resistivity method for detection of ground-water contamination include Fink and Aulenbach (1974), Roux (1975), Sweeney (1984), and Urish (1983).

Electromagnetic Methods- Commercially available EM tools are portable and easy to operate by one or two technicians, under the supervision of a geophysicists. In addition, some instruments allow measurements at several depths. These are suitable for environmental applications. This, along with their ability to detect lateral changes in electrical conductivity, makes EM tools a logical choice for a surface monitoring tool. These tools can cover large areas fairly rapidly. If a careful survey grid is made in the wellhead protection area, periodic EM measurements can be repeated in the same location and then compared. Any anomalous readings can be followed up with other monitoring techniques for confirmation.

Ground Penetrating Radar--Applications of GPR to monitoring wellhead protection areas is dependent on the method*s ability to detect organic contaminants floating on the water table. It has been suggested by Olhoeft (1986) and others that some types of hydrocarbons, if present in the subsurface in sufficient quantity, will prevent the radar energy from further penetration. These areas would appear on the radar record as being nearly blank, since little or no energy would penetrate. The presence of hydrocarbons in the saturated zone would also attenuate the signal, but not to such a large degree. Therefore, it may be possible to locate areas where hydrocarbons are present above the water table.

B. Borehole Geophysics

Recently-developed tools have been developed with the hydrological or environmental application in mind. A slimhole EM induction tool has been developed (Taylor, 1990, Bochicchio, 1990). The induction log can be used for many of the same applications as the single-point resistance and multi-electrode resistivity logs. With the induction tool, however, it is possible to log in dry holes, fluid-filled holes, and nonsteel-cased holes. The small diameter of the sonde makes measurements in two-inch monitoring wells possible.

Another significant advance for wellhead monitoring strategy is a new logging application used for the fluid conductivity logging tool (Pedler et al., 1990, Tsang et al., 1990). This device is used to measure the electrical conductivity of the borehole fluid. With the new application, the borehole fluid is replaced with a deionized fluid before logging takes place. Then slug testing or continuous pumping is used to draw the native formation fluid back in the borehole. Variation in fluid electrical conductivity with depth is used to determine the presence of fracture zones or even of individual fractures which have much greater hydraulic conductivity than the surrounding formation. In addition, this technique can provide information about fluid electrical conductivity, temperature, and pH (Pedler et al., 1990).

A third interesting development is the increasing use of the cone penetrometer for ground water sampling and monitoring applications. Cone penetrometers have traditionally been used for determining engineering soil properties such as plasticity values, stress data, and load-bearing capabilities. More recently, new adaptations are allowing it to be used as a sampling device (Bergren et al., 1990) and a geophysical tool (Erchul, 1990). The cone penetrometer is of interest because data can be acquired relatively inexpensively without having to drill boreholes.

4.1.5 Limitations/Performance

A. Surface Techniques

Direct Current Resistivity--The limitations of the resistivity method are listed below:

- The presence of nearby power lines, metal fences, railroad tracks, and buried utilities can alter the surface current distribution and cause erroneous interpretations.
- Resistivity is a site-specific property; values which can indicate contaminated ground water at one location may not do so in another nearby location.
- The technique requires a relatively large, costly field effort. It also requires experienced workers (as working with current and voltage can be dangerous if done improperly).
- An understanding of physics is necessary.
- Hydrocarbons and organic contaminants usually do not change the electrical resistivity enough to be detectable.

Electromagnetic Methods--Many of the limitations of the DC resistivity technique also apply to the EM techniques, as shown below:

- The presence of nearby power lines, metal fences, railroad tracks, and buried utilities can alter the eddy current distribution and cause erroneous interpretations.
- Conductivity is a site-specific property; values which can indicate contaminated ground water at one location may not do so in another, nearby location.
- Geophysical expertise is necessary for proper data reduction and interpretation.
- Hydrocarbons and organic contaminants usually do not change the electrical conductivity enough to be detectable.
- The method may not work if the near-surface is conductive.

The limitations of time-domain EM are, for the most part, similar to those of frequency-domain EM, with the exception of poor vertical resolution. An added limitation of time-domain EM is that the complexity of the set-up procedures and the necessity of computer-aided reduction and interpretation means that time-domain EM cannot be used as a quick reconnaissance tool like the frequency-domain instrumentation. This may be a disadvantage for wellhead protection, an effort that requires frequent monitoring.

Ground Penetrating Radar--Limitations of GPR are listed below:

- Depth of penetration in rock/soil is usually limited to under 10 meters.
- Radar signals are attenuated by the presence of moisture and conductive subsurface material.
- Radar signals are severely attenuated by the presence of some clays.
- Gobble-sized and boulder-sized particles cause scattering of radar signals.
- The presence of nearby overhead power lines and metallic features on the surface can interfere with measurements.

B. Borehole Geophysics

When deciding on which well logging methods are correct for an application, it is important to consider the condition of the borehole or well. Some logs (such as resistivity and acoustic logs) can only be run in fluid-filled holes. Resistivity, SP, and acoustic logs must also be run in non-cased ("open") holes, unless information about the casing is desired. The induction logger, magnetic susceptibility tools, and the borehole deviation log cannot be run in a steel-cased hole. Induction logs are used in air-filled holes. Additionally, logging tools with active nuclear sources (gamma-gamma density log, neutron-thermal neutron log) are subject to various regulations and licensing procedures that vary from state to state. Table 4-2 is a summary of the conditions affecting the different well logging devices (Colog, Inc.).

4.1.6 Summary

Surface and borehole geophysical techniques are remote sensing methods that can be applied to WHPA monitoring. The surface applications include direct current resistivity and electromagnetic methods that can be used to detect and monitor the movement of electrically conductive or resistive contaminants. In addition, ground-penetrating radar can be used to detect organic contaminants floating on the ground-water table. Many types of borehole geophysical instruments (i.e. caliper, flowmeter, natural gamma, spontaneous potential, temperature, resistivity, sonic, acoustic televiewer, gamma-gamma and neutron logs) can be lowered down the well bore to provide depth-specific hydrogeologic information such as lithologic characteristics and water quality

TABLE 4-2. SUMMARY OF CONDITIONS AFFECTING WELL LOGGING DEVICES

MEASUREMENTS-METHOD INFORMATION DESIRED	Acoustic Amp. and Δ T	Acoustic Waveform	Spontaneous Potential (SP)	Single Point Resistance	Short Normal (16") Res.	Long Normal (64") Res.	Guard Resistivity	Induced Polarization	Fluid Resistivity	Lateral Resistivity	Induction	Magnetic Susceptibility	Natural Gamma	Focused G-G Density	4 pi G-G Density	Neutron-Thermal Neutron	Temperature	Caliper	Borehole Deviation	Casing Collar Locator	Flowmeter
Borehole Fluid Quality									■								■				
Casing Features	■	■		■					■					△	△		■	□		+	■
Cement Features or Bond	■	■												△	△	△	■	o			
Coal Thickness					●	●	●				★			△	△	△		o	★		
Coal Quality	●	●			●	●	●	●			★	★	□	△	△	△		o			
Densities	●	●												△	△	△		o			
Depositional Environment	●	●	●	●	●	●	●			●	★	★	□	△	△	△		o			
Elastic Modulii	●	●												△				o			
Fluid Flow			●														■				■
Formation Water Res. (Rw)	●		●			●	●		■	●	★		□	△		△		o			
Formation Res. (Rt)						●	●		●	●	★							o			
Fracture Detection	●	●			●	●	●								△	△	■	o			
Geologic Structure	●	●	●	●	●	●	●				★		□	△	△	△		o	★		
Geotechnical Studies	●	●	●	●	●	●	●				★		□	△	△	△		o	★		
Hazardous Waste Studies	●	●	●	●	●	●	●	●	■	●	★		□	△	△	△	■	o		+	■
Industrial Mineral Expl.	●	●	●	●	●	●	●	●			★	★	□	△	△	△		o	★		
Lithology - Stratigraphy	●	●	●	●	●	●	●			●	★		□	△		△		o			
Mineral Identification	●		●					●				★	□	△	△	△		o			
Permeability Estimates	●	●	●		●	●	●			●			□	△	△	△	■	o			■
Porosity	●	●			●	●	●			●			□	△	△	△		o			
Precious Metal Expl.	●	●	●	●	●	●	●	●		●	★	★	□	△	△	△		o	★		
Rock Properties	●	●			●	●	●	●		●		★	□	△		△		o			
Shaliness Evaluation	●		●		●	●	●							△	△	△		o			
Hydrocarbon Investigation	●	●	●		●	●	●	●	●	●	★	★	□	△		△		o			
Uranium Exploration	●		●	●	●	●	●	●	●	●	★	★	□	△		△	■	o	★		
Water Investigations	●		●	●	●	●	●		●		★		□	△	△	△	■	o	★		■
Water Saturation	●	●			●	●	●		●		★			△		△		o			

o Open Hole Only

● Open Fluid Filled Hole Only

\+ Steel Casing Only

□ No Restriction on Hole

■ Cased or Open Fluid Filled Hole

△ Active Nuclear Log to be Run Only in Stable or Cased Holes Only

★ Open or Non-Steel Casing Only - Dry or Fluid Filled

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4.2 IMMUNOASSAYS

4.2.1 Introduction

Immunoassays are analytical techniques based on protein molecules called antibodies. The binding of a specific antibody to its target analyte can be used to quantitate the extent of contamination in an environmental sample. Specific antibodies can be developed to detect a single analyte or a small group of related compounds.

Antibodies are proteins that are produced in animals in response to the introduction of a foreign substance, known as an antigen. When challenged with an antigen, an animals*s immune system responds by synthesizing antibodies in blood cells known as B-Lymphocytes. Injections of an antigen into an animal induce the formation of a broad spectrum of antibody molecules, subsets of which react with different regions of the antigen molecule. Each antibody subset has the ability to recognize and bind to a specific portion, or site, of the antigen. (White and Van Emon, 1989).

Immunoassays offer advantages over other ground-water monitoring applications. These advantages include speed, sensitivity, specificity, and cost effectiveness. Immunoassays, designed as rapid, field-portable, semiquantitative methods or as standard quantitative laboratory procedures, can be used for the analysis of a wide variety of compounds. They are well suited for the analysis of large numbers of samples and often obviate lengthy sample preparation. Immunoassays can be used as screening methods to identify which samples need to be further analyzed by classical analytical chemistry methods. The technology is especially applicable in situations where the analysis of an analyte by conventional methods is not possible or cost effective (White and Van Emon, 1989).

4.2.2 Theory of Operation

There are two basic categories of immunoassays, isotopic, and nonisotopic Each category is based on the type of label used for detecting the antigen-antibody complex. Isotopic methods, such as radioimmunoassays (RIAs), use radioactive isotopes as labels. Nonisotopic methods include those that have enzymatic, fluorescent, or chemiluminescent labels (White and Van Emon, 1989). Enzyme immunoassays are the most commonly used immunoassays for analysis of toxic environmental compounds.

Radioimmunoassays-

RIA tests provide sensitive, quantitative, analytical techniques that are well-suited to analyzing trace levels of toxic compounds. To conduct an RIA test, a radioactively labeled antigen is used as the label for detection. This radioactively labeled analyte competes with the analyte in the sample for binding sites on the specific antibody. At higher concentrations of analyte in the sample, an increasing amount of labeled antigen is displaced from the antibody. The antibody-bound antigen is displaced from the free analyte and the radioactivity of each fraction is measured (Kimball, 1986).

Enzyme Immunoassays-

Enzyme immunoassays use an enzyme label acting on a calorimetric or fluorescent substrate. The enzyme label provides sensitivity through amplification. Depending on the assay format chosen, either the specific antibody, the analyte, or a nonspecific secondary antibody can be labeled with the enzyme (Engvall and Perlmann, 1971 a,b; Van Weeman and Schuurs, 1971). The process involved in a typical enzyme immunoassay is shown in Figure 4-4.

For typical enzyme immunoassay formats, the rate of color formation by enzymatic action on the substrate is inversely proportional to the analyte concentration in the sample. Higher analyte concentration in the sample inhibits the formation of colored, enzyme product (White and Van Emon, 1989).

Fluorescent and Chemiluminescent Immunoassays

Immunoassays that employ fluorescent or chemiluminescent labels offer the highest sensitivity. Fluorescent enzymatic substrates have been used to enhance the sensitivity of a variety of enzymes commonly used for enzyme immunoassays. The major difficulty with this type of label is that it is subject to interference and quenching from substance contained in the sample matrix A variety of approaches to limiting interference have been successfully demonstrated (Soini and Hemmilla, 1979; Elkins, 1985).

4.2.3. Methodology

Some environmental immunoassays are rapid, field-portable tests, which can be run in 5 to 30 minutes and are usually qualitative or semiquantitative. With some assays, 5 to 10 tests can be run simultaneously, an advantage that allows an analyst to run as many as 20 to 30 assays per hour. These tests come in a variety of formats with antibody (or antigen) coated tubes, membranes, microparticles, or other solid phases. In some cases, tests are read visually. Others require a portable calorimeter or spectrophotometer. Rapid field screening tests, however, are not as accurate or precise as the laboratory-based tests. A typical field analysis kit is depicted in Figure 4-5.

Other environmental immunoassays are laboratory tests. These include laboratory enzyme linked immunosorbent immunoassay (ELISA) and RIA tests. For ELISA tests, a plate reader containing a variable wavelength spectrophotometer (Figure 4-6) is required. A counter is necessary to run RIA tests. These laboratory tests are quantitative and usually have much better accuracy and precision than the field-portable tests. Between-laboratory coefficients of variation (CVs) are usually in the 10 to 15 percent range, and in some studies (Harrison et al., 1989) reasonably good correlation (r=O.9 or above) has been found in comparing laboratory plate ELISA tests with a conventional analytical method. Quantitative ELISA and RIA tests usually cost from $10 to $15 per test (as of writing, 1991). Laboratory-based ELISA and RIA tests usually take several hours (to overnight) to run, but sample throughput is high because 10 to 15 samples can be run on each plate. One analyst could run 30 to 40 samples a day (in triplicate). In addition, the instrumentation necessary to fully automate the assays with robotic systems is available commercially. With these systems, even higher sample throughput is possible.

4.2.4 Application to WHPA Monitoring

The key to successfully applying immunoassay technology for WHPA monitoring lies in understanding the advantages and limitations of the methods (Section 4.2.5) and in applying them in

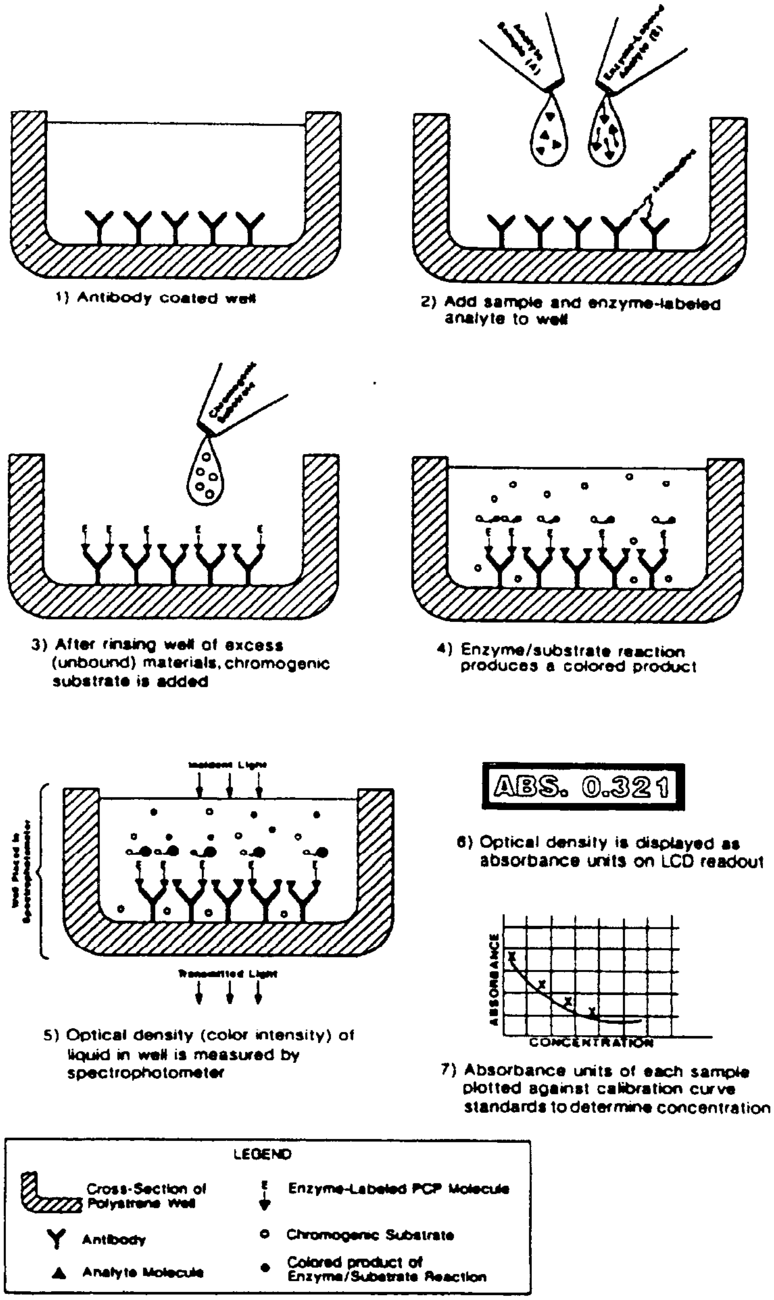

Figure 4-4. Enzyme Immunoassay.

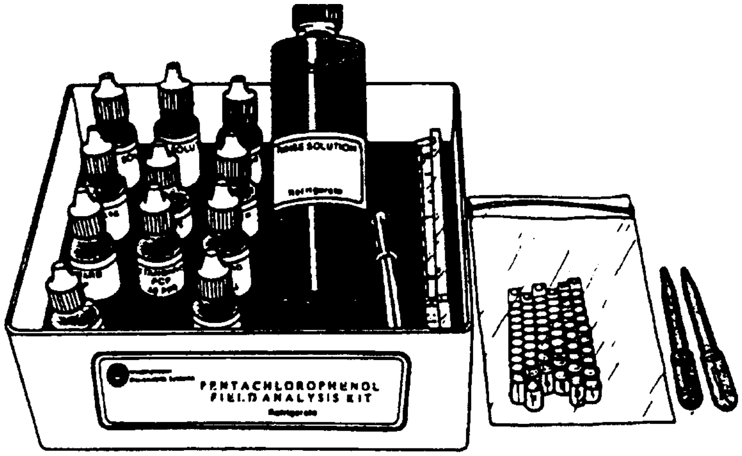

Figure 4-5. A typical field analysis kit.

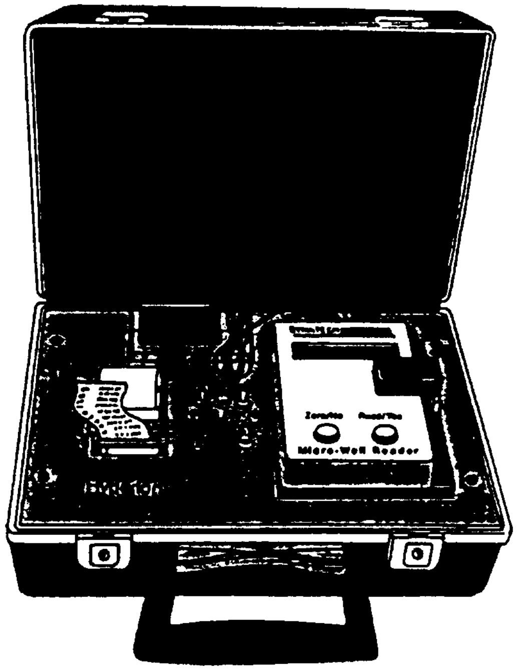

Figure 4-6. Field portable spectrophotometer.

TABLE 4-3. APPLICATION OF IMMUNOASSAYS TO WHPA MONITORING

Analytical Situation	Applicable	Applicable When Used to Complement Conventional Methods	May be Applicable in Some Situations	Not Applicable
Unknown contaminant or complex mixture				QLI RFPI
Highly accurate and precise analysis required		QLI		RFPI
Analysis of compounds difficult or costly to analyze by other methods	QLI RFPI			
Screening large numbers of samples rapidly and inexpensively	QLI RFPI			
Determining the presence of a suspected contaminant	QLI RFPI			
Determining the level of a contaminant		QLI	RFPI	
Determining the source and distribution of a contaminant	QLI RFPI			
Determining whether additional investigation is necessary at a site		QLI RFPI		
Determining the design for appropriate corrective action		QLI RFPI		
Determining the effectiveness of corrective action		QLI RFPI		
Quantitation of a contaminant in a sample with high levels of interfering substances			QLI RFPI	

RFPI = Rapid Field Portable Immunoassay
QLI = Quantitative Laboratory Immunoassay

Immunoassay methods are most applicable to the analysis of organic compounds that are difficult or costly to analyze by other methods. They are also very useful in situations where characterization of a contaminated site involves screening large numbers of samples rapidly and inexpensively.

Immunoassays are not useful for analyzing samples containing unknown contaminants or complex mixtures. If extremely accurate and precise measurements are required (such as those involving litigation or enforcement), quantitative laboratory immunoassays would be useful only if used to complement conventional chemical analytical methods.

Full acceptance and implementation of immunoassay technology for environmental monitoring relies on extensive validation and performance evaluation. Validation of the immunoassays involves analyzing spiked and real samples, doing comparison studies with conventional methods, and conducting thorough performance evaluations. Immunoassay accuracy, precision, specificity, sensitivity and other performance characteristics must also be investigated. Other issues to address include interferences and matrix effects, cross-reactivity, ease-of-use, and ruggedness (White and Van Emon, 1989). Guidelines for evaluation studies have been developed (Van Emon, 1989).

Table 4-4 presents a list of commercially available immunoassays developed for environmental contaminant measurements. Table 4-5 lists immunoassays that have been developed but are not yet commercially available. Cross-reactants refer to compounds that are closely related to the target analyte with which the test*s antibody interacts. The manufacturer can be contacted for additional information on these tests.

4.2.5 Limitations/Performance

Table 4-6 delineates the advantages and limitations of immunoassays. The following text supplements the information presented in the table.

Immunoassays offer the following advantages for environmental analyses: speed, sensitivity, specificity, simplicity, and savings.

> Speed–Immunoassays have a much higher sample throughput than most conventional analytical methods (Van Emon, 1986). For laboratory plate ELISAs, such as those developed for the analysis of molinate in rice field water (Harrison et al., 1989) batches of 80 samples per day could be analyzed. Rapid field-portable immunoassays such as the Res-I-Mune® series (marketed by Immunosystems, Inc., of Scarborough, NE) require only seven minutes per test, and as many as five teats can be run simultaneously.
>
> The instrumentation to fully automate laboratory plate ELISAs using robotics is commercially available. With these systems, even higher sample throughput is possible.
>
> **Sensitivity--Many** immunoassay teats are sensitive down to the ppb and sub-ppb range. Even greater sensitivity is possible through fluorescent-labeling, enzyme application, and other methods.

TABLE 4-4. COMMERCIALLY AVAILABLE IMMUNOASSAYS FOR ENVIRONMENTAL CONTAMINANT MEASUREMENTS

PRODUCT	ALYTES	ASSAY	AVAILABILITY	CHIEF CR CPDS.	MDLA^a	MATRIX	SRC.	INSTRUMENTATION^e	HR.^cc
RIM Triazines	a e	field	now	cyanazine	0.1-1.0 ppb	water, soil	ISI	visual or handheld reader	32
	a ne			terbutylazine					
	p zine			trietazine					
	a yne			hydroxyatrazine					
	a yne			desethylatrazine					
	p tryne								
	p ton								
RIM Aldicarb	a rb	field	now	aldicarb sulfoxide	1.0 ppb	water, soil	ISI	visual or handheld reader	32
	a rb sulfone								
RIM Benomyl	B nyl	field	now	thiophanate	0.2ppb	water	ISI	visual or handheld reader	16
	c ndazim (			thiophanate-methyl					
				thiabendazole					
RIM Alachlor	a or	field	now	metalachlor	0.1 ppb	water, soil	ISI	visual or handheld reader	16
				metalaxyl					
RIM 2, 4-D	2	field	now	2, 4, 5-T	0.5 ppb	water, soil	ISI	visual or handheld reader	16
				some 2, 4-D esters					
				dichlorprop					
				MCPA					
				Silvex					
RIM Cyclodienes	c lane	field	now		0.5-3.0 ppb	water, soil	ISI	visual or handheld reader	32
	a								
	d in								
	e								
	h chlor								
	e ulfan								
RIM Carbofuran	c furan	field	now	five metabolites	0.1 ppb	water, soil	ISI	visual or handheld reader	32
RIQ Triazines	a ne	lab/field	now	cyanazine	0.02-1 ppb	water, soil	ISI	visual, handheld, or lab reader	30
	a ine			terbutylazine					
	p zine			trietazine					
	a yne			hydroxyatrazine					
	a ryne			desethylatrazine					

(Continued)

TABLE 4-4. Continued

	prometryne								
	prometon								
RIQ Alachlor	alachlor	lab/field	now	metalachlor	0.1 ppb	water, soil	ISI	visual, handheld, or lab reader	30
RIQ Aldicarb	aldicarb	lab/field	now	aldicarb sulfoxide	0.4-1.0 ppb	water, soil	ISI	visual, handheld, or lab reader	30
	aldicarb sulfone								
RIQ Benomyl	Benomyl	lab/field	now	thiophanate	0.1 ppb	water	ISI	visual, handheld, or lab reader	30
	carbendazim (MBC)			thiophanate-methyl					
				thiabendazole					
RIQ 2, 4-D	2, 4-D	lab/field	now	as for RIM 2, 4-D	1.0 ppb	water, soil	ISI	visual, handheld, or lab reader	30
	metalaxyl	lab/field	now	alachlor	0.1 ppb	water	ISI	visual, handheld, or lab reader	30
				metalachlor					
RIQ Captan	captan	lab/field	now	tetrahydrophthalimide	100-200 ppb	water	ISI	visual, handheld, or lab reader	30
RIQ Methoprene	methoprene	lab/field	now		1 ppb - 1 ppm	water	ISI	visual, handheld, or lab reader	30
RIQ Reldan	chlorpyrifos-methyl	lab/field	near future		0.05 ppb	water	ISI	visual, handheld, or lab reader	30
RIQ Picloram	picloram	lab/field	near future		1 ppb	water	ISI	visual, handheld, or lab reader	30
RIQ PCB	polychlorinated	lab/field	near future		50 ppb	water, soil	ISI	visual, handheld, or lab reader	30
	biphenyls								
RIQ Pentachlorophenol	pentachlorophenol								
Antox Equate™ water screen	aromatic hydrocarbon	field-portable, coated tube	now	halogenated aromatic	1 - 5 ppm	water	Antox	portable colorimeter	4

[a]MDL = minimum detectable level for analyte(s).
[b]Handheld readers (both battery powered and portable): for RIM is handheld tube reader, for RIQ is handheld strip-well. Laboratory reader is benchtop, microplate reader.
[c]Time for procedure is 7 or 15 min. (RIM) or 90 min. (RIQ). Values given are for sequential batches of 4 (RIM) or 44 (RIQ) samples.

TABLE 4-5 SOME IMMUNOASSAYS FOR ENVIRONMENTAL CONTAMINANT MEASUREMENTS (NOT YET COMMERCIALLY AVAILABLE)

Compound	Method	Detection Limit	Matrix	Reference
Aldicarb	RIA	0.3 ppm	Water	Brady et al., 1989
Aldrin	ELISA	22 pmol	Aqueous	Lagone and Van Vunakis, 1975
Alochlors	RIA	1 ng/mL	Aqueous	Luster et al., 1979
Dieldrin	RIA	4.2 pmol	Aqueous	Lagone and Van Vunakis, 1975
Endosulfan	ELISA	3 ng/mL	Aqueous	Dreher and Podratzki, 1988
Molinate	ELISA	15 ng/mL	Agricultural wastewater	Gee et al., 1988
Paraquat	ELISA	0.1-10 mg/mL	Air filters	Van Emon et al., 1986
Pentachlorophenol	ELISA	3 ppb	Water	Unpublished data
s-Triazine	ELISA	1 ppb	Water	Goodrow et al., 1988, 1989
Terbutryn	ELISA	4.8 ng	Lake and pond water	Huber and Hock, 1985
Thiobencarb	ELISA	1 ppb	Water	Cheung et al., 1988
2,4-D 2,4,5-T	RIA	0.1 ng/mL (D) 20 μg/mL (T)	Surface water	Rinder and Fleeker, 1981

TABLE 4-6. ADVANTAGES AND LIMITATIONS OF IMMUNOASSAYS

ADVANTAGES	LIMITATIONS
• Offers speed, sensitivity, specificity, simplicity, and savings • Versatile: can be designed as a rapid field screening method or a quantitative laboratory method • Amenable to automation and analysis of large numbers of samples • Effective for analysis of some compounds difficult to analyze by other methods • Can be used to detect and measure a wide variety of environmental contaminants	• Requires long lead time for making antibodies and developing immunoassay • Immunoassay reproducibility is sometimes a problem • Cannot be used for identifying an unknown compound or complex mixture of compounds in environmental samples • Immunoassay performance affected by antibody cross-reactivity and certain types of matrix interference • Requires a constant, stable supply of antibody

Specificity–Immunoassays can be made very specific if the proper antibody can be obtained (through careful design of hapten and immunization scheme). An immunoassay which is selective for a single isomer of the pesticide allethrin has been developed and investigated (Wing et al., 1978).

Simplicity–Immunoassays such as the Antox Equate® hydrocarbon water screen or the Res-I-Mune® tests are short and simple tests which require little training to run. The Antox Equate® is a field-portable ELISA for BTX (benzene, toluene, and xylene) and related compounds. The immunoassay is based on an antibody-coated tube, and a portable calorimeter is used to measure enzymatic color development.

Immunoassay methods require much simpler and shorter sample preparation than conventional techniques. As a result, they are suited for compounds such as aldicarb (Brady et al., 1989) and paraquat (Van Emon et al., 1987) which are difficult to extract and analyze.

Savings-Immunoassays typically cost $5.00 to $15.00 a test, which is substantially less than some of the conventional analytical methods,.

As with any other method, immunoassays have disadvantages. Unlike GC/MS, immunoassays cannot be used if the environmental sample contains an unknown compound or a complex mixture of compounds. In some cases, immunoassays may not be as accurate and precise as conventional analytical procedures. Due to the nature of antibodies, they are subject to interferences (from matrix) and cross-reactivity with compounds other than the target analyte. More lead time is required for the development of immunoassays because antibodies must be produced and characterized (White and Van Emon, 1989).

The accuracy and precision of an immunoassay test depends on a number of factors, including the type of assay, the protocol and how carefully it is followed, the quality assurance/quality control (QA/QC) procedures and guidelines, and the extent of matrix interference. Optimal performance can only be reached when protocols are carefully written and followed, and QA/QC procedures and guidelines are integrated into all phases of the development and manufacture of the tests.

Quantitative laboratory ELISA and RIA tests generally perform with greater accuracy and precision than rapid, field-portable tests. Between-run and between-laboratory CVs (which vary with concentration) generally range from 3 to 15 percent under controlled conditions. Accuracy is difficult to define when comparison is made with a confirmatory method because the two methods may not be measuring the same thing and are subject to different interferences.

Rapid, field-portable assays are designed to be qualitative or semiquantitative. They are intended to be used to determine the approximate concentration range of analyte in a sample (within &50 percent for example). If results indicate that a sample has a pollutant near or above a critical concentration range, the sample can be sent back to the laboratory for analysis by a more quantitative method. As with laboratory-based immunoassays, the reproducibility is highly dependent on the protocol, the QA/QC guidelines, and the extent of matrix interference. Coefficients of variation can range from 5 to 50 percent, depending on these factors.

4.2.6 Summary

Immunoassay methods offer important advantages for WHPA monitoring, Immunoassays for analysis of a variety of widely-used pesticides are now commercially available. Among the chief advantages of immunoassays are their speed, sensitivity, specificity, simplicity, and savings.

To some extent, the specificity of the immunoassay tests can be controlled by producing antibodies that are selective for a single compound, small groups of related compounds, or classes of compounds. The specificity of an antibody can sometimes be a problem if the antibody cross-reacts with unwanted compounds that are analogs of a target analyte.

The variety of types and formats of immunoassay tests have particular advantages and disadvantages. Generally, tests can be placed in two major categories: rapid, field-portable tests and quantitative, laboratory-based tests. The field-portable tests are designed for rapid, qualitative, field screening; the laboratory tests have the level of accuracy and precision necessary for quantitation.

T*he key to successfully implementing immunoassays for WHPA monitoring lies in understanding the advantages and limitations of various kinds of immunoassay tests. With this understanding, it is possible to apply the tests in situations where they will perform optimally and provide the greatest benefit. Immunoassays are especially useful for high-volume, sample analysis or for testing for specific compounds that are difficult or costly to measure using other methods.

42.7 References

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4.3 SOIL-GAS SAMPLING AND ANALYSIS

4.3.1 Introduction

"Soil gas" refers to the atmosphere present in the subsurface soil pore spaces of the unsaturated or vadose zone. The soil atmosphere is a diverse mixture of inorganic and organic gases that varies in composition depending on localized conditions. With sufficient soil porosity, soil gases can be collected easily and analyzed to determine component identities and relative concentrations. For example, at sites where contamination by organic compounds (e.g., fuel spills) exists, volatile contaminants such as benzene, toluene, and xylene can be present initially in the gas phase. These contaminants can also undergo a transition to the gas phase from the liquid phase to become part of the soil atmosphere. Soil-gas compounds can also originate from the volatilization of liquid organic contaminants such as fuels and solvents in the subsurface (Figure 4-7).

Soil-gas measurement can be used as a field screening technique. Soil-gas results indirectly indicate contamination; therefore, the method should not be used to replace sampling and analysis of the primary contaminated material such as soil or ground water. Volatile organic compound (VOC) concentrations detected in soil gases are dependent on a variety of factors, including source characteristics and site-specific conditions such as soil matrix, distance from the source, temperature, pressure, barriers to diffusion, and conditions that might cause degradation of target compounds. These subsurface conditions cannot be controlled and their contribution to detected compounds and concentrations is difficult to estimate. Because of these uncertainties, soil-gas results do not provide absolute measures of contamination. Rather, they provide an indication of trends and patterns of contamination such as the location, identity, extent, and relative magnitude of contamination at a site or area of interest (EPA, 1991).

4.3.2 Theory of Operation

Soil-gas sampling and analysis consists of collecting a sample of gas from the vadose zone and analyzing the sample for components that are indicative of contamination.

Contaminant Source. The contaminant source, as depicted schematically in Figure 4-7, can be soil or ground water contaminated by a variety of compounds. Table 4-7 lists the most frequently identified compounds at Superfund sites that are amenable to soil-gas analysis. For a compound to be detectable in the soil gas, it must be present in sufficient quantity and must be able to partition into the gas phase to achieve a vapor concentration that is high enough to exceed the detection limits of the analytical equipment being used. The properties of the contaminants that most affect soil-gas concentrations are vapor pressure (tendency of a compound to partition into the gas phase), aqueous solubility (tendency of a compound to dissolve in water), and gas-phase diffusivity. The ratio of vapor pressure to aqueous solubility is termed the Henry*s Law Constant. This constant is useful in determining the potential for a compound to produce a large enough vapor concentration to be detected by soil-gas sampling and analysis. Because diffusion is the primary mechanism for gas transport in soils (Mathess, 1982, Lappola and Thompson, EW), the diffusivity of the gas-phase compound indicates the tendency of the gas-phase contaminant to be transported away from the source so that it can be detected in the soil-gas sample.

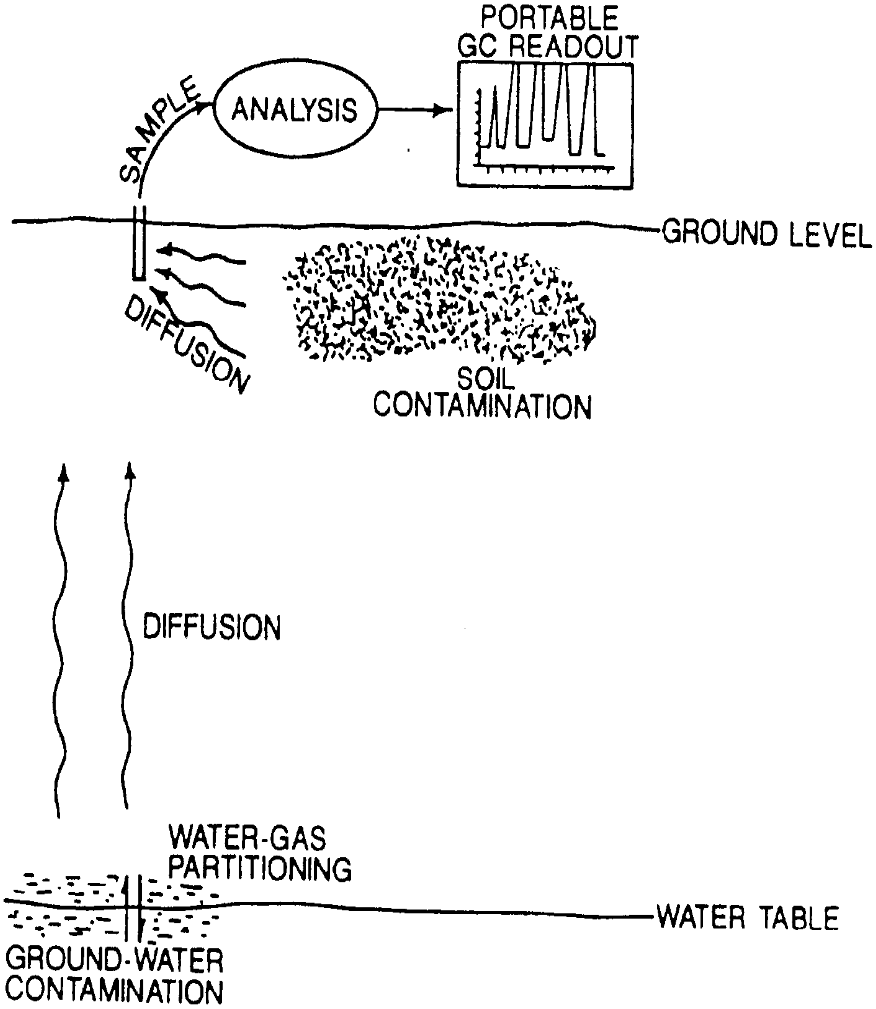

Figure 4-7. Contaminant volatilization and detection by soil-gas sampling and analysis.

TABLE 4-7. MOST FREQUENTLY IDENTIFIED CONTAMINANTS AT 546 SUPERFUND SITES AND THE COMPOUNDS AMENABLE TO DETECTION BY SOIL-GAS SAMPLING AND ANALYSIS.

Rank (Based on detection frequency)	Substance	Henry's Law Constant (ppbv•L/μg)[a]	Percent of Sites
1	Trichloroethylene[*]	72	33
2	Lead and Compounds	NA	30
3	Toluene[*]	56	28
4	Benzene[*]	71	26
5	Polychlorinated biphenyls (PCBs)	<<1	22
6	Chloroform[*]	40	20
7	Tetrachloroethylene[*]	123	16
8	Phenol	<<1	15
9	Arsenic and compounds	NA	15
10	Cadmium and compounds	NA	15
11	Chromium and compounds	NA	15
12	1,1,1-Trichloroethane[*]	30	14
13	Zinc and compounds	NA	14
14	Ethylbenzene[*]	59	13
15	Xylene[*]	43	13
16	Methylene chloride[*]	23	12
17	trans-1,2-Dichloroethylene[*]	570	11
18	Mercury and compounds[b]	NA	10
19	Copper and compounds	NA	9
20	Cyanides (soluble salts)	<<1	8
21	Vinyl chloride[*]	5,100	8
22	1,2-Dichloroethane[*]	88	8
23	Chlorobenzene[*]	32	8
24	1,1-Dichloroethane[*]	420	8
25	Carbon tetrachloride[*]	3,600	7

[a] Henry's Law constant is the equilibrium gas concentration of a volatile compound divided by its concentration in water at 25 °C.

[b] Some mercury compounds are detectable using soil-gas techniques.

[*] Compounds amenable to detection by soil-gas anlaysis; some mercury compounds are amenable (adapted form McCoy, 1985).

NA = Not Applicable

Gas Sampling. Active and passive sampling techniques can be used to collect soil gases. The active soil-gas sampling method involves driving a sampling probe to a measured depth and withdrawing a sample using a pump or evacuated container. Probes are commercially available in a variety of models or can be fabricated from readily available materials. The basic design is a steel tube less than an inch in diameter with one or several openings near the bottom end (Figure 4-8). The probe is driven to the desired depth and a purging/sampling manifold is connected to the surface end. The sample is collected through the manifold into a container. Syringes are good sample containers if analysis is within a short time of sample collection. When samples are to be held for long periods of time or shipped elsewhere for analysis, gas containers (e.g., steel canisters or glass sampling tubes) provide longer holding times (EPA, 1991). The passive sampling technique makes use of samplers that have a sorbent with an affinity for the target analytes in the ground for a measured period of time. The most common passive sampling method consists of digging a hole approximately one foot in diameter and one to five feet deep at a sampling location. A passive collection device such as a badge or wire coated with activated carbon is either placed in the hole beneath an impermeable plate or hung inside an inverted can (Figure 4-9). The badge is allowed to collect VOCs for a period of time (often on the scale of days to weeks) and then is removed and analyzed for VOCs.

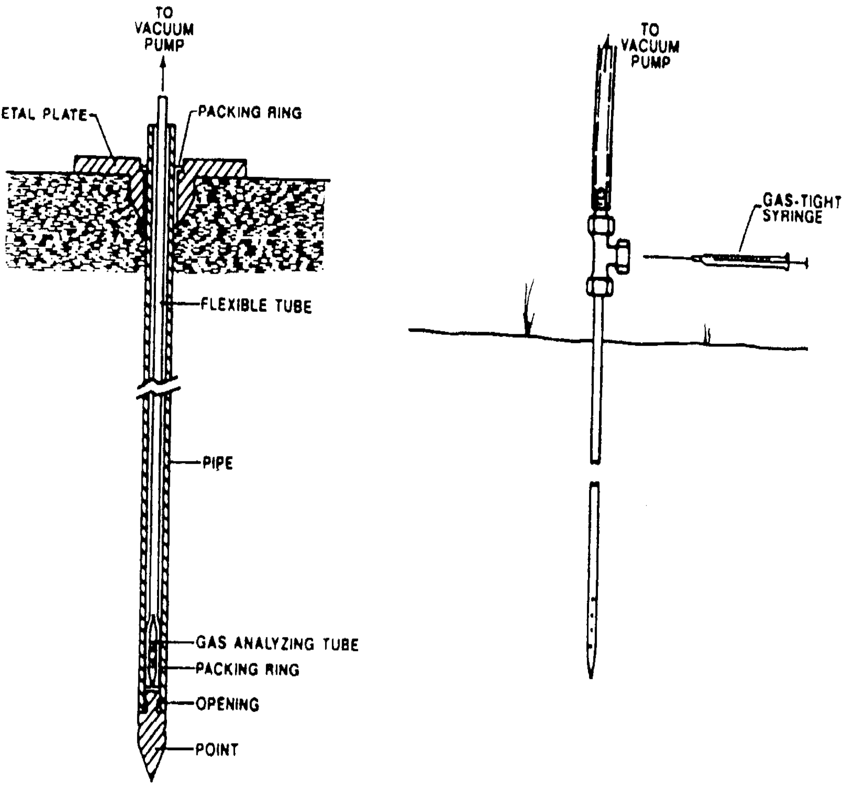

Figure 4-8. Various active soil-gas sampling probe designs.

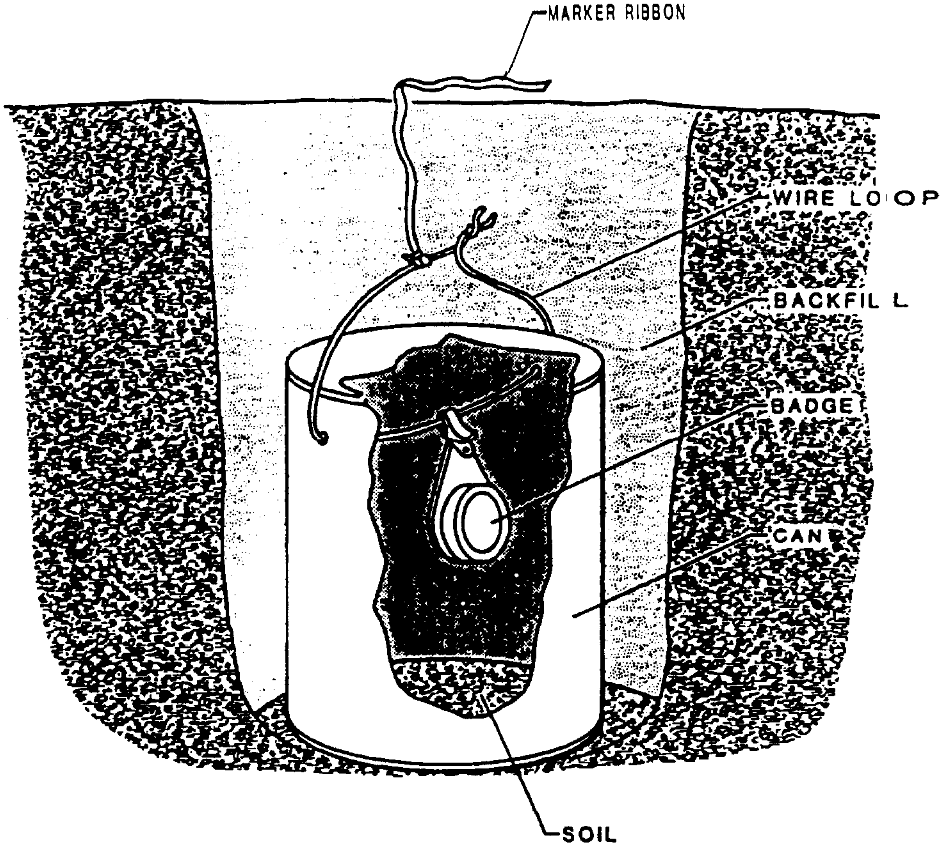

Figure 4-9. Passive soil-gas sampling using a sorbent badge and an inverted can.

Soil-Gas Analysis. Soil-gas samples are most often analyzed using GC (EPA, 1991). These analyses can provide qualitative and quantitative information regarding the constituents of the soil-gas sample. Analysis methods such as detector tubes and Portable organic vapor analyzers have also been used to provide rapid, on-site results. These rapid methods often have larger analytical errors than the GC analyses, but are less expensive and more portable.

Site Characteristics. Site characteristics that influence soil-gas concentrations are numerous and can be categorized as chemical or physical in nature. The chemical constituents of the vadose zone can interact with the contaminants to decrease soil,-gas concentrations or product alteration or degradation products. Physical characteristics such as barriers to diffusion, sorption capacity of the soil, surface-elevation changes, and meteorologic influences can affect soil-gas concentrations.

4.3.3 Methodology

The application of soil-gas sampling requires a comprehensive sampling plan and a data interpretation scheme that accommodates site-specific characteristics and sampling and analysis effects.

Sampling Plan. A sampling plan should include the expected target analyte(s), a detailed sampling technique, an analytical method, the expected initial sampling locations, and the desired data quality objectives (DQQs). Since most soil-gas survey objectives require the comparison of data among points to determine patterns of relative concentration, the difference in values needs to be determined as real or as a function of method precision or site-specific influences (EPA, 1991). The QA/QC measures should include at least replicate samples, sample splits, blank samples, and depth profiles.

Data Interpretation. The diffusion transport of the contaminants can produce a decreasing vapor-phase concentration gradient with increasing distance from the source, resulting in predictable VOC soil-gas concentrations. However, additional site-specific conditions such as localized impervious zones, an impermeable surface layer, or other conditions can provide different concentration gradients. As a result, QA/QC measures are extremely critical in decreasing sampling analytical variability as a factor in soil-gas data interpretation.

4.3.4 Application to WHPA Monitoring

Applications of soil-gas measurement to WHPPs include site characterization activities such as screening potential sources of contamination, delineating contaminant plumes, guiding placement of soil borings and/or monitoring wells, and testing storage tanks and pipelines for leakage. Soil-gas measurements can also be used for monitoring the progress of remedial efforts and long-term, periodic monitoring for early warning systems. Soil-gas surveys for site characterization usually can be completed in a period of days to weeks using temporary probe installations.

The application of soil-gas sampling and analysis to monitoring remediation operations or early warning detection of contamination requires committed sampling probes at points that encompass suspected contaminant migration paths and various depths. Long-term monitoring also requires QA/QC measures to ensure that fluctuations in soil-gas concentrations are real and not a function of fluctuations in background concentrations or other unrelated events (Yamaguchi et al., 1%2). Also, unknown factors can affect the value of the site-specific, soil-gas results. Unknown factors include the vapor transport rate versus the liquid transport rate (i.e., when a component is detected in the vapor phase, how far behind is the liquid phase?), the influence of vapor-phase contamination on ground-water contaminant concentrations (i.e., can vapor-phase contaminants contaminate ground water?), and subsurface conditions capable of contaminant degradation resulting in altered and potentially undetectable compounds.

4.3.5 Limitations/Performance

Although the use of soil-gas sampling and analysis for contaminant characterization is widespread (Kerfoot, 1988), the indirect nature of the technique produces limitations as to the correlation between soil-gas concentrations and proximity to contamination. As a result, thorough QA/QC procedures are required to identify variabilities in the analysis method, the sampling method,

4.3.6 Summary

Soil-gas sampling and analysis is an indirect, field screening technique that applies accepted gas analysis methods to samples collected from the gas or atmosphere contained in the vadose zone. Soil-gas measurements enable investigators to determine the location, identity, extent, and relative magnitude of VOC contamination at a site. The technique can also be used as a long-term, monitoring method. Due to the indirect nature of the technique, soil-gas sampling and analysis requires QA/QC measures to provide data with a reasonable confidence level to determine patterns of relative subsurface contaminant concentrations.

4.3.7 References

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4.4 TEST KITS

4.4.1 Introduction

The term “test kits,” as used in this document, refers to commercially available, self-contained systems for qualitative and/or semiquantitative measurements of individual compounds or groups of related compound classes in solids, liquids, and gases. These kits can be used for quick and inexpensive field screening of environmental samples, and usually require little technical background to operate. Most test kits contain a complete set of sample handling and analysis containers, utensils, and pre-packaged analytical reagents (Figure 4-10). Positive results are usually indicated by a color change that occurs as the result of a reaction between the analyte and the test reagents. Quantititative or semiquanitative results are usually based on comparison of the color intensity of the sample with color intensities of scaled standards. Some kits require the use of simplified wet chemistry techniques. Others incorporate indicator reagents impregnated on paper, plastic films, or other appropriate **materials,** or use reagent-filled tubes through which the sample is drawn. The development of test kits is an area of active research interest, and continued advancement in this area is expected.

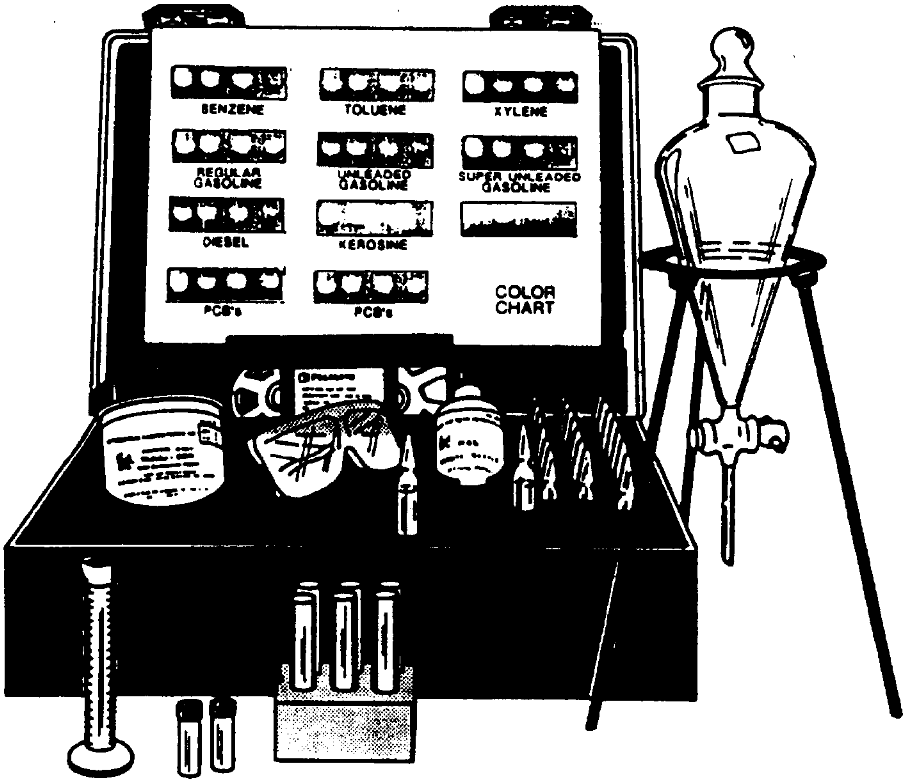

Figure 4-10. Typical test kit equipment

4.4.2 Theory of Operation

The reagents from the kits react with the target analyte, causing either a color change that indicates the presence of the target analyte or a specific color intensity that indicates the quantity of target analyte present.

Wet Chemistry Kits. Analysis using wet chemistry kits involves the addition of reagents to liquid samples or sample extracts. The kits are used to analyze water directly; they can be used on soils if the soils are first treated to extract analytes. Wet chemistry kits are packaged in several styles. Glass sample containers and pre-packaged, color-indicating solutions and extractants characterize the most common wet chemistry kits. Table 4-8 provides a summary of analytes that can be detected by commercially available wet-chemistry test kits.

Detector Tubes. Detector tubes are used for the analysis of gas-phase samples. Detector tubes are generally glass tubes approximately 4 inches in length and l/4 inch in diameter that are filled with calorimetric reagent and sealed at both ends (Figure 4-11). In the most common use of the tube, the ends are broken off, and a measured amount of gas-phase sample is drawn through the tube using a hand-held pump. As the sample contacts the reagent inside the tube, the reagent changes color. The results are read directly from a calibrated scale imprinted on the glass tube with the length of the color being proportional to the concentration of analyte.

Badges. Badges which are used for detection of analytes in the gas phase, consist of indicator paper or cards that are saturated with indicating reagents. The badge is exposed to the atmosphere to be sampled, and the corresponding color change resulting from diffusion of the target analyte onto the badge indicates the presence and concentration of the target analyte as a function of exposure time. Table 4-8 summarizes the analytes that can be detected by commercially available badges.

Test Papers. Test papers are used for analysis of liquids such as water or liquid extracts The test paper is dipped into the liquid, and the color change and intensity indicate the presence and concentration of the analyte. A number of analytes can be detected by commercially available test papers. These analytes include aluminum, ammonium, arsenic, ascorbic acid, bismuth, calcium, chlorine/cyanide, chromate, cobalt, copper, fluoride, formaldehyde, iron, manganese, molybdenum, nickel, nitrate, nitrite, oil, peroxide, potassium, silver, sulfate, sulfite, tartaric acid, tin, total hardness, and zinc.

Water-Test Kits. Water-teat kits allow analysis by either a calorimetric method or a titrimetric method. With the calorimetric method, one or more reagents is added to the sample to produce a color proportional to the concentration of analyte in the sample. The titrimetric method uses the addition of an indicator to the sample to produce a color. A titrant is then added in small increments until the color changes. The results are obtained by converting the amount of titrant used to an analyte concentration value. Analytes that can be detected by commercially available water-test kits are listed in Table 4.8.

TABLE 4-8 COMMERCIALLY AVAILABLE WET-CHEMISTRY KITS, BADGES, AND WATER-TEST KITS AND RESPECTIVE TARGET ANALYTES.

ANALYTE	WET-CHEMISTRY KIT	BADGE	WATER-TEST KIT
Acidity			L
Alkalinity (hydrate)			L
Alkalinity (total)			L
Aluminum			L
Ammonia	G, L	G	L
Antimony			L
Aromatic Amines		G	
Aromatics	S, L		
Carbonate Pesticides	S, L, G		
Carbon Dioxide			L
Carbon Monoxide	G	G	
Chloride	G, L		L
Chlorine	G, L	G	L
Chromate (total)			L
Chromic Acid	G,L		
Color			L
Copper (total soluble)			L
Cyanide (free)			L
Diphenylamine			L
Fluoride	G, L		L
Formaldehyde		G	L
4,4-Methylene Diphenylene	G		
Glycol			L
Hardness (calcium)			L
Hardness (total)			L
Hydrazene		G	L
Hydrogen Pesticide			L
Hyrogen Sulfide	G	G	L

(Continued)

TABLE 4-8. Continued

ANALYTE	WET CHEMISTRY KIT	BADGE	WATER TEST KIT
Iodine			L
Iron (total)			L
Iron (total soluble)			L
Lead	G		L
Magnesium			L
Manganese			L
Mercaptobenzothiazole			L
Mercury	G	G	
Molybdate (low-range)			L
Nickel			L
Nitrate			L
Nitrite			L
Nitrogen Dioxide	G	G	
Organophosphate Pesticides	S, L, G		
Oxygen (dissolved)			L
Ozone		G	L
PCBs	S		
Phenol			L
Phosgene		G	
Phosphate			L
Phosphorus			L
Quaternary Ammonium Comps			L
Salinity			L
Silica			L
Silver			L
Sulfate			L
Sulfide (total soluble)			L
Sulfite			L
Sulfur Dioxide	G		
Tetraethyl Lead	G		

(Continued)

TABLE 4-8. Continued

ANALYTE	WET CHEMISTRY KIT	BADGE	WATER TEST KIT
Tetramethyl Lead	G		
Thiophosphate Pesticides	S, L, G		
Thiosulfate			L
Toluene Diisocyanate (TDI)	G	G	
Total Oxidants	G		
Turbidity			L
Zinc			L

S = solid
L = liquid
G = gas

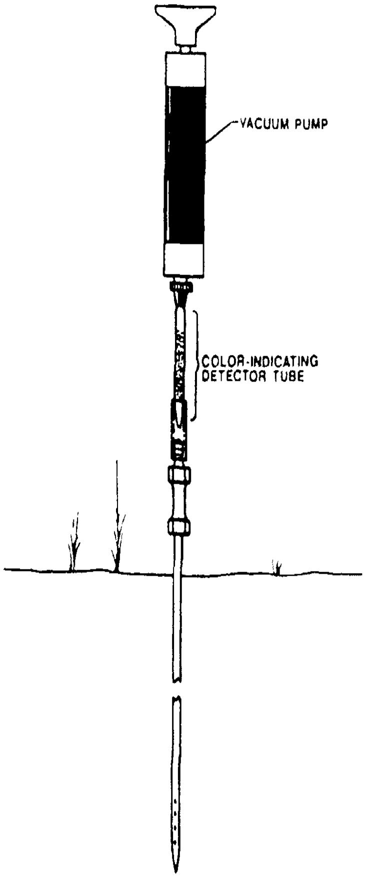

Figure 4-11. Schematic drawing of a detector tube.

4.4.3 Methodology

Test kit methods vary because the objective of the test is to make physical contact between the sample and the indicator compound. These methods include direct contact between the sample and the analytical media and extraction of the sample and analysis of the extract. Test kit analysis can be performed by technician-level personnel.

Direct Contact. Direct contact between a sample and the analytical reagents is the most common type of test kit. Examples include test papers dipped into liquid samples, gas-phase samples drawn through detector tubes, and pre-measured calorimetric indicating reagents added to liquid samples.

Analysis of Extract. Analysis of extracts from the sample media are used if the sample media cannot be analyzed directly by the analysis kit. Solids such as vegetation or soils are the main target for such extractions; however, water samples are also extracted for some test kits. The resulting extract can then be treated as a sample for direct contact analysis. An advantage to extraction is that for some test kits, concentration of low-level samples is positive.

4.4.4 Application to WHPA Monitoring

The use of the kits should be limited to screening efforts, providing qualitative information indicating the need for more rigorous sampling and quantitative analyses. Test kit applications include direct analyses of ground water from monitoring wells, surface waters, soils, and soil-gas analyses to determine potential source areas.

Many of the manufacturers describe additional applications of the test kits such as ground water headspace analyzed by detector tubes or badges. Caution should be taken when using the test kits in these additional applications because the component being analyzed may not be indicative of the conditions associated with the target analyte.

4.4.5 Limitations/Performance

Test kit limitations usually result from interferences due to operating conditions from the pressure of other compounds in the sample that affect test results. Chemical interferences can cause either inbarred or diminished response, leading to false positive or false negative results. Limitations and detection limits (generally in the low ppm range) of the test kits are generally provided by the manufacturers.

Results may be misleading because many of the test kit manufacturers have not rigorously compared their results to results from EPA-approved methods. Test kit results are collected under specific conditions and of a specific media. Extrapolation of such results to environmental conditions should be done with caution, noting any assumptions or limitations.

4.4.6 Summary

Test kits are generally inexpensive, fully self-contained field screening kits that require a low level of technical experience to operate. The kits, which are available from numerous manufacturers, target organic and inorganic compounds in solids such as vegetation and soil, liquids such as water and extracts, and gases. Lower detection limits are generally in the low-ppm range. Interference compounds or conditions that may result in false positives or false negatives are usually noted by the manufacturers. Innovative applications of the kits beyond the originally intended application may be noted by the manufacturer or discovered by the user, however, research is needed to ensure the results obtained from innovative applications are both consistent with the capability of the test kit and the conditions at the site.

4.4.7 References

AQUAQUANT Reagent Test Kits, EM Science, P.O. Box 70,480 Democrat Road, Gibbstown, New Jersey, 08027, (800) 222-0342.

CHEMets Test Kits, Chemetrics Incorporated, Route 28, Calverton, Virginia, 22016, (703) 788-9026.

CHLOR-N-SOL 50, Dexsil Corporation, One Hamden Park Drive, P.O. Box 6556, Hamden, Connecticut, 06517, (2030 288-3509.

COLORTEC Hydrogen Sulfide Detector, VICI Metronics, 2991 Corvin Drive, Santa Clara, California, 95951, (408) 737-0550.

Drager Detector Tubes, National Drager Incorporated, Ecolyzer Division, P.O. Box 120, Pittsburgh, Pennsylvania, 15230, (412) 787-8383.

EM Quant Test Snips, EM Science, P.O. Box 70,480 Democrat Road, Gibbstown, New Jersey, 08027, (800) 222-0342.

EnviroGard Triazine Test Kit, Millipore Corporation, 80 Ashby Road, Bedford, Massachusetts, 01730, (617)275-9200.

EnzyTec Pesticide Biosensor, EnzyTec Incorporated, 8805 Long, Lenexa, Kansas, 66215, (800) 634-2607.

Field Test Kit, Hanby Analytical Laboratories, 4400 South Wayside, Suite 107, Houston, Texas, 77087, (713) 649-4500.

Gallard-Schlesinger Industries Incorporated, 584 Mineola Avenue, Carle Place, New York, 11514, (516) 333-5600.

Hach Water Test Kits, Hach Company, P.O. 389, Loveland, Colorado, 80539, (800) 227-4224.

Hanna Water Analysis Test Kits, Hanna Instruments of America Incorporated, 584 Park East Drive, P.O. Box 849-P, Woonsocket, Rhode Island, 02895, (401) 765-7500.

LaMotte Air Pollution Test Kit, LaMotte Chemical Products Company, P.O. Box 329, Chesterton, Maryland, 21620, (800) 344-3100.

LaMotte Water Test Sets, LaMotte Chemical Products Company, P.O. Box 329, Chestertown, Maryland, 21620, (800) 344-3100.

Leak-Tee Badges, American Gas Chemical Company Limited, 220 Pegasus Avenue, North Vale, New Jersey, 07647, (800) 288-3647.

Matheson De&ion Tubes, Matheson Gas Products, 8800 Utica Avenue, Cucamonga, California, 91730, (714) 9874611.

Mercury Vapor Detector, Lab Safety Supply Incorporated, P.O. Box 1368, Janesville, Wisconsin, 53547-1368, (800) 3560783.

MSA Detector Tubes, Mine Safety Appliances Company, 1775 North Surveyor Avenue, Simi Valley, California, 93063, (800) 672-2222.

Optochemical Research Incorporated, P.O. Box 33637, Raleigh, North Carolina, (919) 821-1724.

Sensidyne Gastec Detector Tubes and Sensidyne Dosimeter Tubes, Se&dyne Incorporated, 12345 Starkley Road, Suite E, Large, Florida, 33543, (800) 451-9444.

SpectoKit Reagent Systems for Water Analysis, Milton Roy Company, Analytical Products Division, **820** Linden Avenue, Rochester, New York, 14625.

Sure-Spot TDI Dosimeter and Phosgene Dosimeter Series 500, GMD Systems Incorporated, Old Route 519, Hendersonville, Pennsylvania, 15339, (412) 746-3600.

TDI/MDI Analyzer Kit, Sensidyne Incorporated, 12345 Starkley Road, Suite E, Large, Florida, 33543, (800) 451-9444.

TEL/TML Analyzer Kit, Sensidyne Incorporated, 12345 Starkley Road, Suite E, Large, Florida, 33543, (800) 451-9444.

4.5. X-RAY FLUORESCENCE SPECTROSCOPY

4.51 Introduction

The field-portable, X-ray fluorescence system (FPXRF) is used for real-time identification and quantitation of inorganic contaminants. The sampling strategy for FPXRF is optimized through the use of geostatistics in order to obtain representative samples and to minimize the estimation error in producing the concentration isopleth maps. The FPXRF is easily carried and is sealed so that it can be decontaminated in the field (Figure 4-12).

The analyte range for F*FPXRF is from chlorine to uranium. Detection limits, quantitation ranges, and accuracy of the measurements vary depending on the sample matrix and the isotope source used for the analysis. Detection limits generally fall in the range of 200 to 400 mg/kg for most analytes. A precise, site-specific, detection limit for each analyte for each matrix can be calculated only after the conclusion of the field work.

Prior to using the FPXRF, site-specific, intrusive samples (physical samples from the media of concern (EPA, 1987) must be collected. These samples, which are representative of the physical and chemical matrices of the various soil types, are totally digested and analyzed in a laboratory. The laboratory results are used to develop site-specific calibration standards (SSC) in order to minimize the matrix-specific, enhancement/absorption effects encountered on any unique site.

Accuracy and precision data for each sampling effort can be determined from the results of the quality control check samples analyzed periodically during the sampling. The short analysis time (30 seconds) and low per sample mst allow data to be collected from many measurement points. This approach provides a high degree of representativeness for the spatial distribution of contaminants over the waste site.

Though the methodology described in this section addresses the analysis of soil matrices, the measurement procedure can be modified for aqueous samples, sludges, and other solid wastes (Clark & Thornton, 1989, Piorek & Rhodes, 1980).

4.5.2 Theory of Operation

X-ray fluorescence is based on the principle that photons produced from an X-ray tube or radioactive source bombard a sample to generate fluorescence (Jenkins et al., 1981). The incident photon bombardment creates vacancies in one or more of the inner electron shells, and the vacancies cause instability within the atom. As the outer shell electrons seek stability by filling the vacancies in the inner electron shells, the atom emits energy (fluorescence), which is characteristic of the atom (Figure 4-13). Most elements under the photon bombardment fluoresce simultaneously to produce a spectrum of characteristic radiation. It is this spectrum that the FPXRF detector senses and counts.

There are two types of X-ray fluorescence spectrometers, energy dispersive and wavelength dispersive. The principal differences between these two types of instruments are the method of detecting the fluorescent energies of specimen and the method of quantifying the analytes of interest. The portable

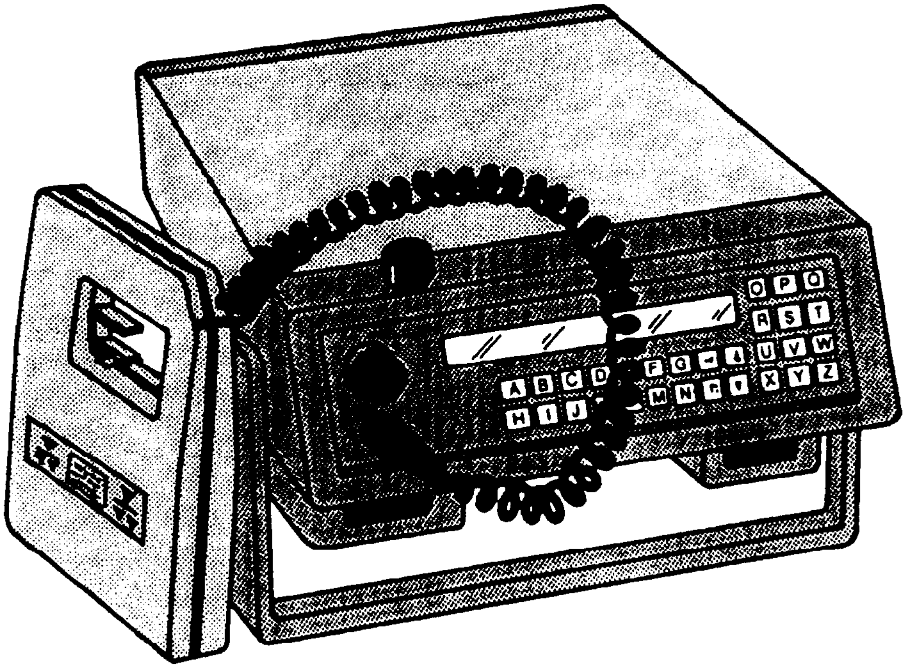

Figure 4-12. The field-portable, X-ray fluorescence system (FPXRF).

The X-MET 880, marketed by Outokumpu Electronics, Inc., in Prinaton, New Jersey, is the only XRF instrument on the market that is truly portable and that can be wet-decontaminated. The unit weighs 85 kg and is self-contained, battery powered, and microprocessor-based. The X-MET 880 is hermetically sealed and can be decontaminated with soap and water. The instrument*s surface analysis probe is specifically designed for field use; it includes one or two of four available radioisotope sources (Fe-55, Curium-244, Cd-109, Am-241), a gas proportional counter, and the associated electronics. The source is protected by a safety shutter approved by the Nuclear Regulatory Commission.

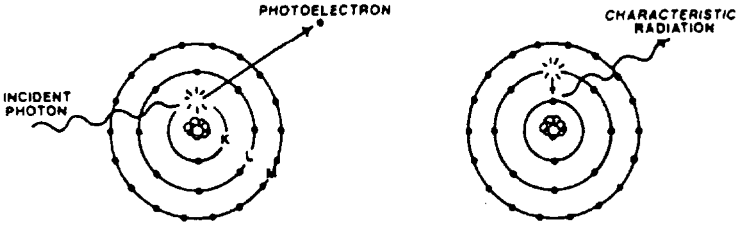

Figure 4-13. Bohr model atomic excitation.

The electronic unit has 32 calibration memories called “models.” Each model can be calibrated independently for as many as six elements. and can be used to measure elements from chlorine to uranium if the proper isotope source is available. The measured sample intensities are regressed against the calibration curves to yield concentrations.

4.5.3 Methodology

Site-Specific Calibration Standards-

A suite of 10 to 30 samples (depending on the number of analytes), spanning the concentration range of the analytes of interest, must be obtained from the site in question. These samples are sent to a laboratory for total digestion and analysis. If previously characterized, total digestion samples exist, then a suitable selection of these samples will suffice. These samples become the SSC standards.

The FPXRF instrument can be used during a site reconnaissance to assist in selecting samples to be characterized for SSC standards. The instrument is calibrated with a suite of natural or spiked soil standards containing the analytes of interest. With the generically calibrated instrument, a relative range of the analytes of interest can be determined, and a suitable suite of samples can be selected for characterization as SSC standards.

SSC standards are characterized for the elements on the EPA*s inorganic Target Analyte List (Table 4-9) in an approved laboratory by a total digestion method (Bernas, 1968, Buckley and Cranston, 1971). Characterization is by U.S. EPA Contract Laboratory Program (CLP) protocol instrument analysis (EPA, 1989). The digestion is performed in an oven or microwave (U.S. Bureau of Mines, 1983) digestion bomb with aqua regia and hydrofluoric acid. The total digestion is necessary because XRF yields a total elemental analysis regardless of the phase (mineralogy) or speciation (oxidation state) of the analyte, whereas the standard CLP extraction (EPA, 1989) produces partial extraction results as a function of the mineralogy. Incomplete elemental characterization of the SC standards yields biased calibration curves in the FPXRF instrument.

TABLE 4-9. THE INORGANIC TARGET ANALYTE (TAL)

Aluminum*	Calcium	Magnesium	Silver
Antimony	Chromium	Manganese	Sodium*
Arsenic	Cobalt	Mercury	Thallium
Barium	Copper	Nickel	Vanadium
Beryllium*	Iron	Potassium	Zinc
Cadmium	Lead	Selenium	Cyanide*

- Unattainable analytes using the X-MET 880 (EPA, 1989).

After the SSC samples have been characterized, the FPXRF instrument is calibrated. The calibration procedure is outlined in the manufacturer*s operations manual (Outokumpu Electronics,

Sampling Procedure-

A grid of arbitrary spacing is established on the site. *In situ* (in place, i.e., probe placed on the ground) FPXRF measurements are taken at each sample point. These data are used to determine semivariograms for optimization of a spatial sampling scheme which must satisfy the project DQQs. *In situ* sample analysis is performed by placing the probe on the ground as near the sample stake as possible and activating the analysis by pulling the trigger on the probe. Analysis can be preprogrammed for any time span, but generally is set for 30 seconds. Quality control check samples and other quality assurance samples are analyzed as needed. The analytical results can be recorded in a field log book or by an electronic data logger for subsequent data processing.

The results of routine sample analyses are computer processed to produce planimetric maps, showing sampling locations and concentration values. Using geostatistics (kriging methods), concentration isopleth maps are produced (Figure 4-14).

4.5.4 Application to WHPA Monitoring

The application of XRF to WHPA monitoring is most useful for rapid field screening of soils within the WHPA that are suspected of containing inorganic contamination. Field screening using XRF is commonly used for delineating contaminated areas and for monitoring remediation efforts at hazardous waste sites including, lead battery recycling and manufacturing facilities, landfills, ore processing facilities, metal plating sites, and mine tailings (Raab et al., 1991). The XRF technology provides a fast and relatively inexpensive method to detect, delineate, and remediate known or suspected sites of inorganic contamination within the WHPA. Recent studies in preconcentrations of H_2O samples have produced results directly applicable to WHPAS (Meltzer & King, 1990).

4.55 Limitations/Performance

The greatest advantage of the FPXRF *in situ* method is the quick analytical turnaround time (approximately 100 sample locations per day). This allows for optimization of sampling designs

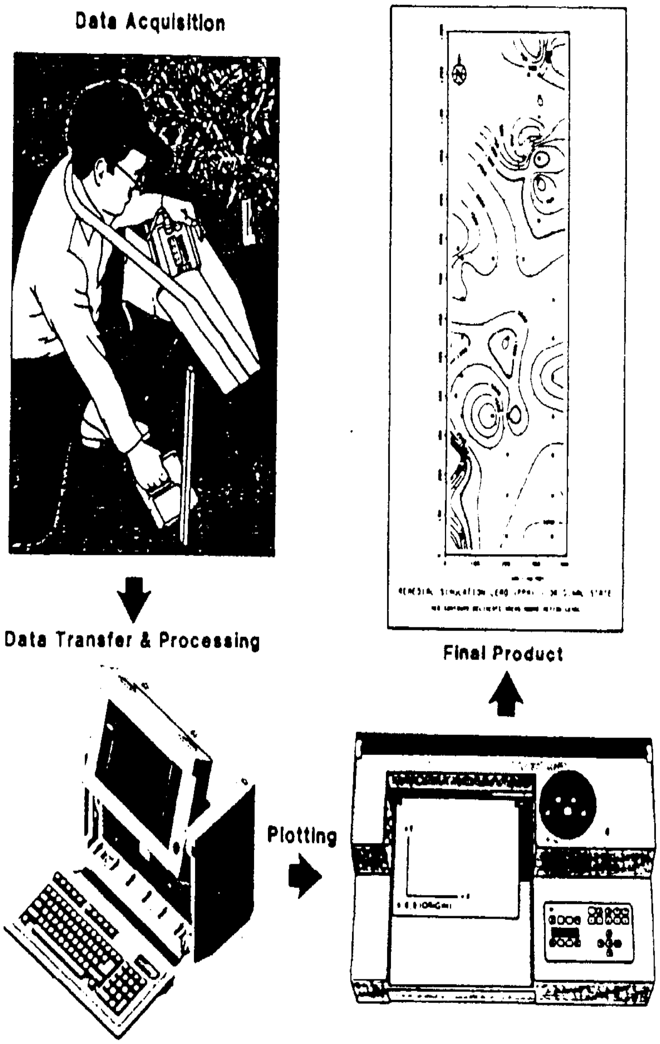

Figure 4-14. Wellhead protection screening with FPXRF.

because more measurements can be taken with the FPXRF units than by conventional sampling and analytical methods. Another advantage is that the FPXRF *in situ* measurement eliminates sample collection, handling, and preparation, thereby reducing the overall sampling error. Increased sampling density and reduction of the sampling error, combined with the spatial interpolation by the geostatistical software produces a representative model of the contaminant distribution on the site.

The moat significant limitation of FPXRF is its relatively high detection limits. Instrument detection limits generally fall between 200 and 400 mg/kg for most analytes, but the limit of quantitation (ACS Committee on Environmental Quality, 1983) can run as high as 800 mg/kg. These value-s must be compared to the remediation levels on the site in question.

4.5.6 Summary

The microprocessor-based FPXRF instrument is self-contained, battery- powered, and *weighs* 8.5 kg. The X-MET 880 has the advantage of being hermetically sealed, which allows it to be decontaminated in the field with soap and water. (It is currently the only FPXRF on the market that can be decontaminated). The specially designed surface-analysis probe includes one or two radioisotope sources (depending upon the analytes in question), a gas-filled tube proportional counter, and the associated electronics. Source protection is afforded by an NRC-approved safety shutter.

The FPXRF instrument can be taken directly into the field, where it can be used immediately to determine the metal content of the soil. Therefore, it is not necessary to wait several weeks for the results from a laboratory. With the X-MET 880, the instrument probe is placed directly on the ground (ti sip), and a measurement is made. Results are available immediately, and many measurements can be taken quickly. Time and money can be saved, resulting in a more thorough characterization because site remediation can be guided by results of previous sampling activities.

The X-MET 880 must be properly calibrated to accommodate the conditions of each site prior to in ***situ*** measurements so that it can provide an accurate analysis. The *in* ***situ*** measurements are made by placing the probe directly on the soil and opening the shutter. After 30 seconds the shutter is closed. The X-MET 880 built-in software now processes the signals it has received, and displays the concentration value for each analyte. During data collection, two standards are measured periodically to monitor accuracy and precision of the instrument and to determine the detection limit for each analyte. One of these standards is as near to a zero value as possible, and the other is a mid-calibration range value. In addition, a complete QA/QC program must be used to determine accuracy, precision, and detection limits. This QA/QC program, in conjunction with operational analyses, establishes the basis for generation of data of known quality. Final data processing results in the production of a representative contour map of contaminant distribution over the site.

The XRF method can be used as a rapid screening tool for WHPAS. The method is useful for detecting, delineating, and remediating known or suspected sites of inorganic contamination.

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4.6 GAS-ANALYSIS EQUIPMENT

4.6.1 Introduction

Portable-gas analysis equipment is designed for rapid qualitative and quantitative analysis of gas-phase samples for specific target compounds (Mine Safety Appliances Co., 1987). Organic vapor meters (OVMs) and organic vapor analyzes (OVAs) have detectors which operate like a GC and are commonly used as screening instruments for VOCs.

4.6.2 Theory of Operation

OVMs and OVAs house a pump, a detector, a power supply, and electronics. A gas-phase sample is pumped past the detector that registers the target, gas-phase compound and indicates its concentration.

OVMs utilize a photoionization detector (PID) that responds to organic vapors including hydrocarbons and chlorinated compounds. The PID requires calibration with a standard calibration gas, usually benzene. The OVM pump moves the sample into the sample chamber where the sample is metered and passed by the detector as a single slug. The resulting reading is the total response to all detectable compounds in parts per million (ppm) equivalents of the calibration gas.

The OVA uses a flame ionization detector (FID) that responds to volatile hydrocarbons. Unlike the PID, all detectable compounds generally respond equally to the FID detector; therefore, the resulting measurement is similar to the total of the actual values of the compounds. This allows a particular OVA to be operated in a chromatographic mode in addition to the survey mode (Foxborro, 1985). A pump in the OVA draws the sample into a sample chamber and moves the entire sample through the detector en masse. Results are expressed as a total detector response in ppm equivalents of the calibration gas. The OVA in chromatographic mode requires that the sample pass through a chromatographic column for separation. The sample then moves past the detector for detection. Sampling and analyzing a multicomponent standard can provide elution times of compounds for identification and quantification ratios.

4.6.3 Methodology

The application of these gas analyzers requires the introduction of a sample into the instrument and contact between the sample and the detector. OVMs and OVAs have a hand-held sampling probe for sampling specific locations (Figure 4-15). The OVM and the OVA (operated in survey mode) have an internal pump that continuously draws the sample through the probe and into the instrument. The instruments continuously read the total detectable compounds in the sample stream and register their concentration in ppm. When the OVA is operated in the chromatographic mode, the sample is drawn through the probe into a set-volume sample loop. The sample volume is separated into its individual components as it passes through a modified chromatographic column mounted on the outside of the instrument. The separated components are then carried past the detector. A strip-chart recorder or electronic integrator can be used to record the detector output and allow identification and quantification of the compounds.

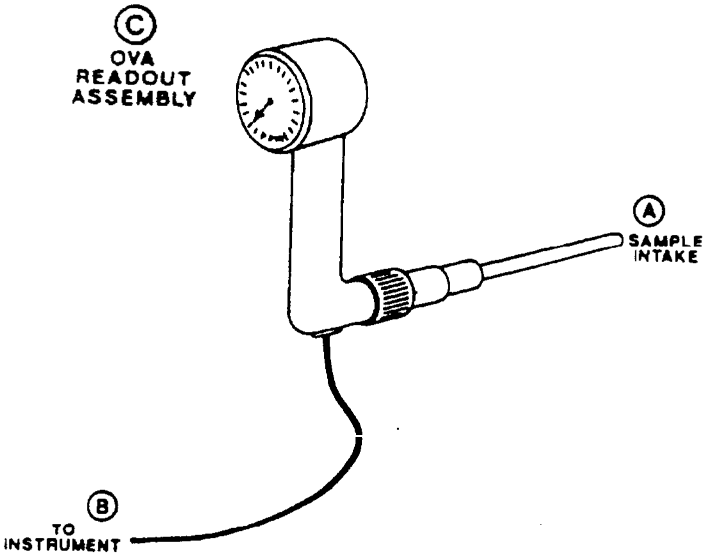

Figure 4-15. Hand-held sampling probe.

46.4 Application to WHPA Monitoring

The primary use of OVMs and OVAs in wellhead protection is the screening of wellhead space and collected samples for VOCs. OVMs and OVAs are most commonly used to monitor worker safety during drilling operations and to screen soil cores for high VOC concentrations. Other more recently proposed uses of OVAs (Robbins, 1990) include analysis of soil-gas samples collected in sample bags and head-space analysis of ground-water samples.

4.6.5 Limitations/Performance

Lower detection limits (generally 0.1 ppm), upper detection limits (2,000 to 20,000 ppm), and operating condition limits of OVMs and OVAs (operating in either mode) are specified by the manufacturers. The OVAs are sensitive to low oxygen conditions because the FID detector uses oxygen from the sample to mix with hydrogen to create a flame. A low-oxygen sample may extinguish the flame. For example, a low-oxygen condition can be produced when the OVA directly measures the gas from a soil-gas probe.

Although both OVMs and OVAs provide a readout (in survey mode) of total detectable compounds in ppm equivalents of standard, the total value from the OVA is more representative than that of the OVM. This discrepancy results from the differing **responses of the PID and FID to** compounds. When a series of detectable compounds passes a PID detector, the PID responds differently for each compound. In contrast, the FID response to most detectable compounds is nearly the same.

Using the OVA for chromatographic analysis requires considerable attention to operating conditions and component identification. Since the chromatographic column is attached to the exterior of the instrument, this can cause considerable variability in retention times of components if the column is not maintained at a constant temperature.

The application of OVMs and OVAs to samples other than ambient-air samples will require defining the ranges of variability resulting from the combined sampling and analysis methodology. This variability is determined with QA/QC procedures such as performing duplicate analyses, analyzing split samples, and assessing the variability of standards.

4.6.6 Summary

OVMs and OVAs are small, self-contained, portable instruments. They are capable of quantitative and qualitative analysis of gas-phase samples for VOCs using gas chromatographic-type detectors. OVMs have a PID that is sensitive to hydrocarbons and chlorinated compounds; OVAs have an FID that is sensitive to hydrocarbons. Roth detectors require calibration before use. The most common use of both instruments is as a survey or screening instrument in which a sample is drawn into the instrument by an internal pump and analyzed as a single slug, providing a total detector response within seconds. In addition to the survey application, a particular OVA can be adapted with a short chromatographic column and a strip-chart recorder to provide chromatographic separation of samples.

The instruments, though originally intended for analyzing ambient-air samples, can be used to screen soil-core, soil-gas, and ground-water samples. Appropriate QA/QC measures must be used to quantify the variability of sample and analysis methods.

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SECTION 5

MOBILE MONITORING METHODS

5.1 INTRODUCTION

The need for rapid sample analysis during emergency responses to accidents involving regulated substances and the management of remediation efforts under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and the Resource Conservation and Recovery Act (RCRA) has underscored the need for mobile laboratories for environmental analysis (EPA, 1984). Mobile monitoring methods are different from portable methods. The equipment is close to laboratory quality and is to heavy to hand-carry to the field. The use of a mobile laboratory as a WHPA monitoring method enables real-time analyses for target compounds and provides data quality at or near the level of an analytical laboratory. Mobile laboratories can contain dedicated analytical instrumentation or can employ a modular arrangement to allow adaptation of instrumentation for specific analytical purposes.

Current chemical analysis methods of solids, liquids, and gases for organic and inorganic compounds involve the use of several major analytical instruments and some associated sample-preparation units. Most of these instruments have associated EPA-approved methodologies that describe their use in a standard method so that results from different laboratories can be compared. Although these analytical instruments were originally designed for use in a controlled laboratory environment, the development of rugged, efficient, and compact electronics has allowed some laboratory-only analytical equipment to be adapted to unconventional laboratory environments. The mobility of the instrumentation requires at a minimum, a consistent power supply and appropriate supplies such as carrier gases. Samples for mobile analysis often require collection into an intermediate device before introduction into the instrument; however, some instrumentation may be capable of analyzing the sample *in situ*. The type of instrumentation installed in the mobile laboratory is determined by the types of analytes expected. This section lists some of the more common instrumentation and describes chromatographic and spectrometric techniques.

5.2 THEORY OF OPERATION

A mobile laboratory can either be leased through a consulting or contracting firm or owned by the agency responsible for monitoring the WHPA The physical arrangement of a mobile laboratory can range from a converted passenger van to a stand-alone trailer. The support services such as electricity, running water, gas hookups, fume hoods, and solvent cabinets can easily be adapted for the scale of vehicles. Mobile laboratories can be fitted with committed analytical and support equipment in order to provide a specific service or can be arranged generically to accommodate a variety of instrumentation sizes and requirements (Figure 5-l). In any mobile laboratory application,

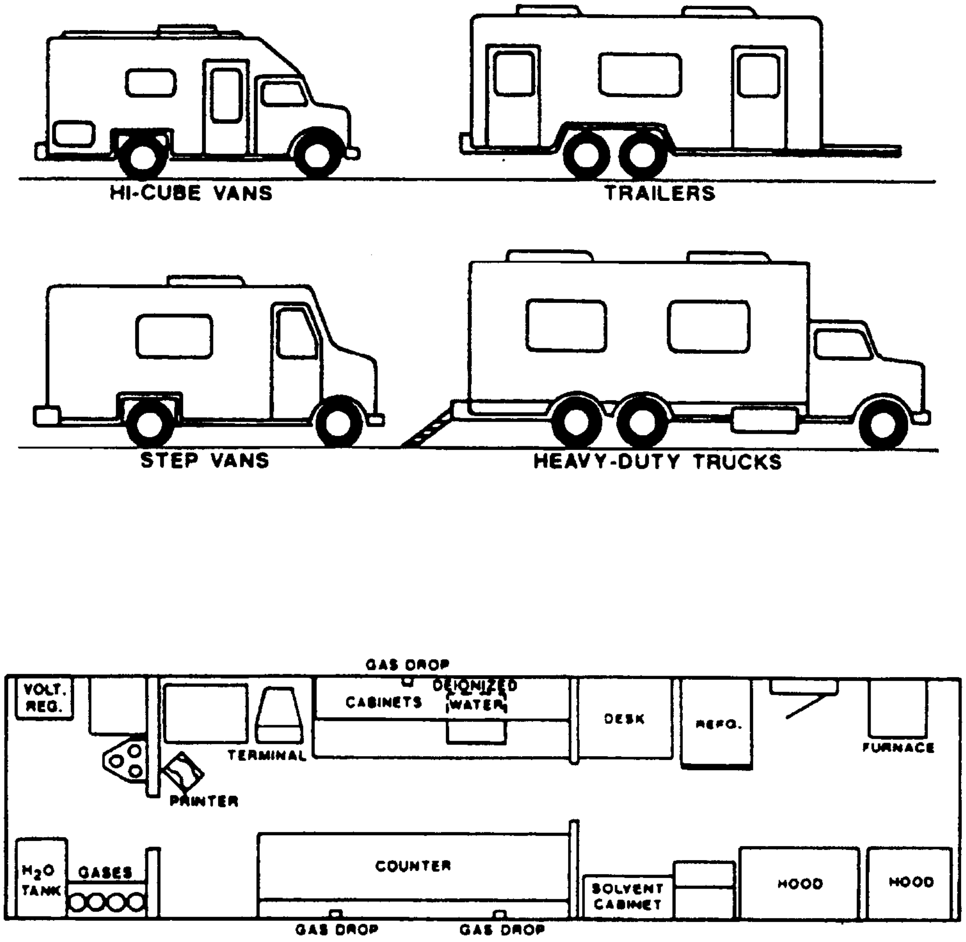

Figure 5-l. Modular mobile analysis laboratory arranged to accommodate a variety of analytical equipment. The laboratory is contained within a 42* x 7* stand-alone trailer (EPA, 1984).

the desired sample matrix, number of samples, sample preparation, sample analyses, and DQOs till dictate the appropriate equipment and instrumentation to be included in the laboratory.

Most analytical instrumentation was originally intended for use in fixed, laboratory environments due to the size of the instrumentation or the dependence of the instrumentation on a stable or sterile operating environment, and most existing EPA-approved analytical methods are targeted towards these particular instruments.. The instrumentation in mobile laboratories consists of either normal laboratory equipment or redesigned laboratory instrumentation which has been modified for portability and ease of operation.

Table 5-l lists standard analytical instrumentation that could be modified for application in a mobile laboratory. The table also delineates the type of compound that each instrument can detect

TABLE 5-l. DEGREE OF LABORATORY INDEPENDENCE OF INSTRUMENTATION USED FOR CHEMICAL ANALYSES

	Instrument Use		Compounds Detected			
Chromatographic Techniques	Lab	Mobile	Organics	Inorganics	Matrix	EPA Method
Gas Chromatograph	X	X	X		G[1]	Yes
Gas Chromatograph w/ Mass Spectrometer	X	X	X		G	Yes
Gas Chromatograph w/ Purge and Trap	X	X	X		S, L	Yes
Gas Chromatograph w/ Thermal Desorption	X	X	X		S	No
High Performance Liquid Chromatography	X	X	X		L	Yes
Spectrometric Techniques						
Ion Mobility Spectroscopy	X	X		X	S, L	Yes
Atomic Aborption (Furnace and Flame)	X	X		X	S, L	Yes
ICP-AES[2]	X	X		X	S	Yes
X-Ray Fluorescence	X	X		X	S	Yes
Fiber Optic Chemical Sensors	X	X		X	S, L, G	No

[2] ICP/AES = Inductively coupled plasma discharge/atomic emission spectroscopy

(organic or inorganic), the necessary sample matrix for the instrumentation, and the existence of an EPA-approved analytical method utilizing the instruments.

5.2.1 chromatogaphic Techniques

Chromatographic instruments that could be modified for mobile application include GCs, GC/MSs, GCs with purge-and-trap instruments, GCs with thermal desorption units, and high performance liquid chromatography (HPLC) instruments.

GCs are capable of analyzing only gas-phase samples of VOCs. Mobile GCs generally have dimensions similar to that of portable computer equipment. The controlling aspect of the mobile GC is the need for supply gases such as the carrier gas and the detector gases. Nevertheless, the ruggedness of certain detectors and the availability of supply gases in transportable sizes allow the GC to be used in either a stationary field analytical laboratory or in a mobile laboratory.

The use of mass spectrometry for chemical analyses is based on the ability to detect gas-phase ions produced from the molecules of the analyte. GC/MS instruments have been used in mobile applications as stationary and vehicle-mounted instruments. The stationary application involves the use of conventional laboratory GUMS instrumentation in fixed, field laboratories. The use of GC/MS units in field applications is still not common, although the instrumentation is physically adaptable. Several manufacturers have recently redesigned GUMS instrumentation in order to make it fit within a vehicle such as a van and to increase its stability and ruggedness. The advantage of the vehicle-mounted GUMS is the ability to bring the analytical instrumentation to the sample location and provide *in situ* GUMS analyses.

Sample preparation instrumentation such as purge-and-trap and thermal absorption units generally have dimensions that are amenable to mobile application and can be readily integrated with a mobile GC A purge-and-trap instrument can be used to prepare water and soil samples that contain VOC compounds for analysis by GC. The thermal desorption unit enables one to use GC to analyze solid-phase material for VOWS. The performance of these mobile sample preparation techniques has not been thoroughly evaluated.

HPLC is a chromatographic-separation technique used primarily for non-volatile organic liquids or extracts (e.g., herbicides, pesticides). Some HPLC instruments are suited for use in fixed, field laboratories, but the performance of the instrument has not been thoroughly evaluated.

5.2.2 Spectrometric Techniques

Analytical instrumentation generally reserved for inorganic compounds is based on spectrometric techniques that measure the energy peaks resulting from the impact of radiation, These techniques include AA, inductively coupled plasma/atomic emission spectroscopy (ICP/AES), XRF, and fiber optic chemical sensors (FOCs).

Atomic absorption is an EPA-approved method for the analysis of inorganic liquid samples, and ICP/AES is an EPA-approved method for the analysis of inorganic compounds. Though both units can be fitted for use in mobile applications, their effectiveness has not been evaluated.

X-ray fluorescence involves bombarding a prepared solid sample with X-rays and reading the remitted, characteristic X-ray remediation. Field-portable XRF is discussed in Section 4.6. Laboratory instrumentation and smaller field instruments have also been used in mobile applications.

Fiber optic chemical sensors involve transmitting light to a sensor in contact with an analyte. The interaction between the sensor and the analyte results in the light being absorbed or refracted or can result in the occurrence of fluorescence The resulting altered light is collected and returned to a spectrometer for spectral analysis. Detail regarding theory, application, and mobile use can be found in Section 6.4.

5.3 METHODOLOGY

The use of the analytical instrumentation in a mobile setting consists of the particular instrumentation and the method chosen for analysis, Inherent specifications of the instrumentation naturally dictate the sample matrix and potential operating conditions. Sampling and analytical methods can be determined by EPA-approved methods or can be customized applications.

Most mobile analytical instrumentation is complicated; therefore, an experienced operator should be employed. This provides a measure of assurance that analytical results are a function of the sample constituents and the analytical methodology, and not a function of the instrumentation. If custom analysis methods are used, appropriate QA/QC measures must be included to ensure the validity of the analytical results.

5.4 APPLICATION TO WHPA MONITORING

Analytical instrumentation contained within a mobile laboratory is capable of analyzing, within a short time frame, soil, liquid, and gas samples. The instrumentation can also provide data quality ranging from EPA-approved methods to rapid screening. Soil-core, ground-water, and soil-gas samples can be taken during WHPA monitoring activities or source characterization surveys. Although the variability associated with the analytical methodology and instrumentation is easily determined and controlled, the variability associated with the collection and handling of specific samples can be quite large. As a result, appropriate sample collection methods and QA/QC measures are mandatory for maintaining sample representativeness and identity.

5.5 LIMITATIONS/PERFORMANCE

All of the instrumentation listed above has associated detection limits or sensitivities, and the analytical variability can be determined easily. The use of instrumentation in mobile conditions could require adaptations that alter the expected detection limits or sensitivities. Variability in results may also result from sampling and sample-handling methods.

5.6 SUMMARY

Mobile laboratories provide on-site, analytical capabilities that can produce real-time results of inorganic and organic compounds in soils, liquids, and gases. Instrumentation originally designed for laboratory application has been utilized under mobile conditions either by redesigning instruments or by adapting existing instrumentation to the mobile laboratory conditions.

The use of the instrumentation can follow EPA-approved methods which detail the instrument operation and QA/QC measures, or custom analysis methods can be created which would require similar detail as EPA-approved methods. Some EPA-approved methods are easily adapted for mobile use; others require considerable preparation equipment that is not amenable to mobile use. Application of analytical instrumentation to WHPA monitoring includes soil, ground-water, and soil-gas analyses for screening and monitoring activities.

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SECTION 6

MONITORING TECHNOLOGIES UNDER DEVELOPMENT

Monitoring technologies are continuously being advanced. For example, advances in medicine, warfare agent monitoring, contraband sensing, and forensics are being applied to ground-water monitoring capabilities. This section provides an overview of some technologies that are expected to be commercially available within the decade. Some of the most promising technologies are ion mobility spectrometry, molecular optical spectroscopy, electrochemical sensors, mass sensitive sensors, extraction membranes, and biosensors.

6.1 ION MOBILITY SPECTROMETRY

6.1.1 Introduction

Ion mobility spectrometry, which has also been known as gaseous electrophonesis and plasma chromatography, is used to detect and characterize organic compounds as vapors at parts-per-billion (ppb) concentrations in air (Eiceman, in press). The IMS output is a mobility spectrum which is useful in compound identification (Bell et al., in prep.). IMSs, ranging from hand-held to laboratory bench models, are becoming available commercially.

The applications of IMSs as mobility detectors in chromatography, environmental sensing, the detection of chemical warfare agents, forensic uses, and contraband sensing were briefly outlined by E&man (1991). The first expansive use of IMS technology was the deployment by the U.S. Army of hand-held chemical agent monitors produced by Graseby Ionics, Ltd. Designed for vapor detection, these military units pointed out that IMS technology could be the basis of simple-to-use, field analyzers.

Recent research indicates a growing interest in the use of IMS for field applications. Dam (1984) demonstrated that IMS was suitable for monitoring certain toxic industrial chemical vapors. Carrico et al. (1986) mentioned that compact IMS systems should be able to function as portable alarms for several classes of organic vapors. Eiceman et al. (1990) showed in field trials that the military configuration of IMS was useful as a point vapor sensor for establishing the presence of contaminated patches of soils. Plume shapes and boundaries were also determined. Reategui et al. (1988) discussed applications for IMS as a vapor monitor for field screening applications, though details were not provided. In addition, six papers on the subject were presented at the preliminary program for the Second International Symposium on Field Screening Methods for Hazardous Wastes and Toxic Chemicals (Burroughs, 1991; Davis, 1991; Hoffland and Shoff, 1991; Bell and Eiceman, 1991; Richter, 1991; Snyder et al., 1991).

A series of experiments (Poziomek et al., 1990) was made in an attempt to identify the attributes and data needs in IMS detection of environmental contaminants such as low molecular weight chlorocarbon and aromatic compounds. Qualitative experiments were conducted to simulate detection of single compounds and mixtures present at a hazardous waste site in Nevada. Results of these studies contributed to a decision by the U. S. EPA to **proceed** with a laboratory demonstration of IMS under the Superfund Innovative Technology Evaluation (SITE) Program. Many other references also document the history of IMS (Karasek, 1970; Cohen and Karasek, 1970; Hill et al., 1990; Karasek et al., 1970; Karasek, 1974; Karasek et al., 1977; Bain and Hill, 1982, Spangler and &T&J 1983; Bain et al., 1982, Bain et al., 1983; Leasure et al., 1986).

6.1.2 Theory of Operation

The principles of IMS involve the ionization of molecules and the analysis of subsequent ions by using ionic mobilities. Characterization through IMS is based on ion separations due to ionic mobilities rather than masses; this distinguishes IMS from mass spectrometry. An IMS is operated at atmospheric pressure, a characteristic that leads to practical advantages including size, power, weight, and simplicity.

Ambient air is usually pumped into the IMS through semipermeable membranes. (One model also uses an adjunct carrier gas.) Ions are formed from air or carrier gas molecules by using an ionization source such as Nickel 63. These ions then react with analyte molecules to form ion clusters which are subject to atmospheric pressure "time of flight" measurements. The ions are allowed to enter a drift region where they move under the influence of an applied field to a collector electrode. The electrode current is monitored continuously, thus allowing a mobility spectrum to be measured. Ionization preferences of analytes and mobility differences of the ion clusters impart specificity. Separations are a function of ion size.

Selectivity of IMS for different analytes is based on the atmospheric pressure ionization events (which relate to the proton and electron affinities of the analytes), the polarity of the products (i.e., positive versus negative ions), and the mobility of the ions. Target analytes with electron or proton affinities higher than those of other chemicals in the ambient environment can be differentiated and detected readily. Analytes with low affinities can be measured as long as chemicals with strong affinities are absent.

6.1.3 Methodology

Self-contained IMSs are commercially available. The smallest unit weighs approximately 2 kg and is easily used in the field. It is a hand-held unit which is designed for use by unskilled operators, although servicing of the instrument requires a trained technician. More complex instruments are available, but the weight and required number of components increase with the degree of sophistication. For example, a currently marketed package contains two basic parts, a controller and a recirculating gas supply. However, the system also requires a 12-volt battery pack and a portable computer. **In** addition to size and weight constraints, these more sophisticated units also require users to have a basic knowledge of chemistry.

The IMS units are preprogrammed and are capable of monitoring one or a number of chemicals in a defined situation. They operate in either negative or positive ion modes. Hand-held units can be preprogrammed into these modes for specific analytes (i.e., a maximum of 5 analytes in the positive mode and 3 in the negative mode). These hand-held units use a liquid crystal display of bars that relate to preprogrammed concentration levels. The more sophisticated packages enable the operator to reprogram the instrument. They also provide more capability in terms of quantitative measurements and compound identification. To advance IMS technology in the identification of mixtures while maintaining cost and size efficiency, gas chromatography is being combined with TMS (Meuzelaar et al., 1990).

6.1.4 Application to WHPA Monitoring

Although most IMS research emphasizes vapor sampling and monitoring, ongoing work is relevant to WHPA monitoring strategies. For example, the analysis of water samples for several organic compounds is being performed in a laboratory demonstration of IMS under the U. S. EPA SITE Program (Koglin and Poziomek, 19%). The results will indicate how well some of the existing commercial IMS instruments can detect selected organic compounds in water. Additionally, New Mexico State University, under the sponsorship of the U. S. EPA Office of Exploratory Research, is examining IMS as a rapid, inexpensive field screening method for organic contaminants in water. Though preliminary findings seem promising, there are still uncertainties, including the predictive/interpretive capabilities that are governed by the ionization chemistry and the suitability of the IMS interface with aqueous samples. *In situ* monitoring of water has also been proposed with a submersible IMS that could fit into monitoring wells.

The sensitivity of the IMS is generally in the low ppm to low ppb range with the possibility of parts-per-trillion (ppt), depending on the analyte and instrument parameters.

6.1.5 Limitations/Performance

There is still much to learn about IMS applications. For example, several fundamental issues need to be resolved concerning the handling of complex mixtures. Compounds can be measured independently but not always simultaneously. The response of a particular analyte may be influenced by the presence. of other chemicals. The many ions that might form in a complicated mixture of compounds would undoubtedly interact with each other. Such interactions need to be understood to take full advantage of IMS capabilities.

The development of ***in*** situ monitors also presents challenges. For example, monitors must be developed to fit into confined places such as monitoring wells. Generally, miniaturization of monitors results in the loss of sensitivity. Researchers must also design interfaces that allow a vapor sampler to be operated with aqueous samples and develop an IMS probe that can tolerate high humidities over a sustained period.

6.1.6 Summary

IMS is emerging as a technique for the detection and characterization of organic compounds as vapors at the ppb level in air. More attention is being paid to exploit IMS for environmental applications. There are still issues to be resolved, especially the handling of complex mixtures without sacrificing cost and equipment compactness. There is also a need to extend the concentration range for quantitative determinations.

Current research targets the use of IMS to characterize water samples. A proposal has also been made to develop a prototype IMS that could be submersed in water. Though IMS has not been used as a wellhead monitoring technique, the state of the research warrants the development of IMS monitoring devices for use in WHPAS.

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6.2 MOLECULAR OPTICAL SPECTROSCOPIC METHODS

6.2.1 Introduction

Molecular spectroscopic techniques potentially offer advantages over conventional techniques for ground-water monitoring, screening, or analysis associated with wellhead protection (Eastwood et al., 1989). These techniques provide information often not obtainable with other analytical techniques. For example, depending on the technique, one may obtain information about the composition of some non-volatile compounds, detect very low concentrations of some chemicals, or determine structural information about a broad range of organic and inorganic chemical classes. By incorporating fiber optics or flow-through systems, some of these methods can also be used to make remote, nondestructive measurements.

When properly used, molecular spectroscopic techniques may be moderately to highly sensitive and highly selective. These techniques, which use portable, field-deployable or transportable instrumentation, make it possible to rapidly screen, characterize, and prioritize large numbers of samples on site. Results are cost-effective because detailed analyses can be limited to a few samples containing contaminants in detectable concentrations.

Spectroscopic methods discussed here include ultraviolet-visible absorption, ultraviolet-visible luminescence, infrared (IR) absorption, and Raman scattering techniques.

6.2.2 Theory of Operation

Electronic spectroscopic techniques can be used to measure absorption or emission processes (luminescence) in the near ultraviolet-visible-near-IR spectral range (wavelengths in the range from 200 to 2,800 nm). Vibrational spectroscopic techniques are used to measure the absorption of energy corresponding to the vibrations of the molecule. These absorptions occur in the near or mid-TR spectral range (4,000 cm^{-1} to 500 cm^{-1}). Indirect measurements of vibrational shifts by inelastic Raman scattering spectroscopy occur in the visible or near-IR spectral region. The major regions of the electromagnetic spectrum are illustrated in Figure 6-l.

Absorption and Inelastic Scattering Techniques--Electronic absorption spectroscopy measures processes that occur when molecules absorb photons in the near ultraviolet or visible spectral (UV-vis) region corresponding to changes in electronic states of the molecules (Burgess and Knowles, 1981; Murrell, 1985).

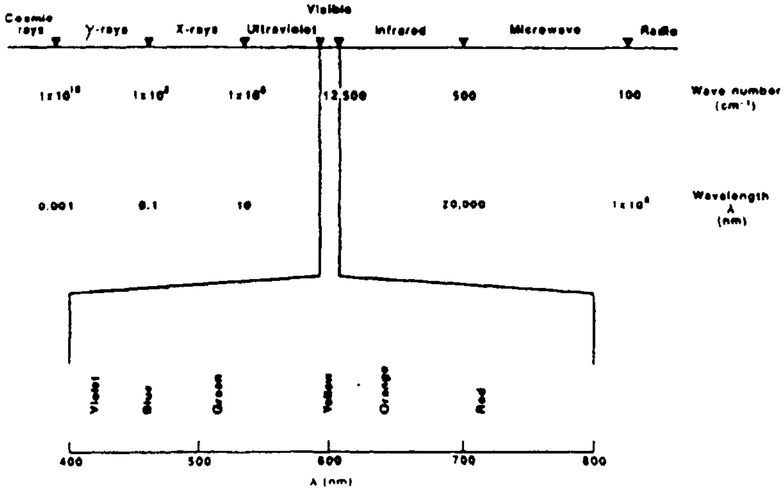

Figure 6-l. Major regions of the electromagnetic spectra.

Absorption occurs when a molecule is raised to a higher energy state (electronic or vibrational). This higher energy state is achieved when a molecule of the sample absorbs a photon of energy. In the simplest case (sometimes called the Beer-Lambert Law), a parallel beam of light, perpendicularly incident on a sample, can he absorbed or transmitted. The logarithm of the ratio of the incident light to the transmitted light, usually called absorbance or optical density, is directly proportional to the concentration of the analyte.

IR absorption spectroscopy is used to measure absorption in the near- to mid-IR spectral range (Colthup et al., 1964, Griffiths and DeHaseth, 1986). In the mid-IR region, peaks are often sharp, and individual peaks can be correlated to specific chemical group stretches or deformations. This feature makes the mid-IR region very useful for chemical classification or identification. Spectra in the near-IR range are broader, vibrational peaks overlap, and combinations of vibrational frequencies are observed. Therefore, spectral &convolution and pattern recognition procedures are necessary for signal discrimination before identification of specific chemical constituents is possible.

An inelastic scattering process (Raman scattering) is normally used to measure in the visible or near-IR spectral range (Colthup et al., 1964, Vo-Dinh, 1989, Long, 1977). Laser Raman spectroscopy is a technique that complements IR spectroscopy because the two techniques provide different kinds of information **about** vibrational transitions and related chemical groups. Characteristic frequency shifts associated with vibrational transitions and changes of electrical polarizability (or distortion of the electron cloud) associated with a molecule are measured with this technique, thus allowing identification of specific analytes of interest.

Emission or Luminescence Techniques

Luminescence (UV-vis photoluminescence) is a technique that is highly sensitive to certain classes of chemicals such as polyaromatic hydrocarbons. Luminescence, which is the emission of a photon, occurs after a photon is absorbed by an atom or molecule and is due to the transition of an excited electron from a higher to a lower energy state after exposure to an exciting light (Parker, 1968, Becker, 1969; Schulman, 1985,1988; Miller, 1981).

Luminescence can involve either fluorescence or phosphorescence. The difference depends on the lifetime of the excited state: typically less than 50 nanoseconds for fluorescence and from a few microseconds to several seconds for phosphorescence. Phosphorescence arises from a different type of excited state and occurs at longer wavelengths than fluorescence.

Most fluorescence methods measure emitted light as a function of wavelength, while exciting at a fixed wavelength. Alternate methods such as synchronous fluorescence are being developed (VoDinh, 1981). Synchronous fluorescence simultaneously scans both the excitation and emission wavelengths with a constant offset wavelength. This method sharpens and simplifies the observed spectra often to a single peak per compound, thus separating the spectra of compounds such as polyaromatic hydrocarbons (PAHs) with different numbers of fused rings where the emission spectra overlap.

Room temperature phosphorescence is another method being developed (Vo-Dinh, 1984; Perry et al., 1989). It can be observed at ambient room temperature **by** using a rigid substrate such as filter paper to provide a suitable environment to protect excited molecules from deactivation. Room-temperature phosphorescence enables analysts to detect and analyze halogenated compounds like polychlorinated biphenyls (PCBs) that phosphoresce more intensely than they fluorescence.

Fiber Optic Chemical Sensors

FOCS provide a tool for use in obtaining *in situ* spectroscopic information in monitoring wells and at other sites where access is limited (Klainer et al., 1990; Wolfbeis, 1988, Seitz, 1985). An optical fiber is used to transmit light to a chemical-sensing element attached to the distal end of the fiber. Energy with known spectral characteristics transmitted down the fiber induces absorption or luminescence in the sensing element which is modified if a contaminant is present. Luminescent or reflected light, which is measured by analyzing spectral characteristics of light returned through the optical fiber, is used for detection of specific substances (Figure 6-2).

Calorimetric or fluorometric reagents attached to the end of the fiber enhance sensor selectivity and sensitivity to specific analytes and minimize interferences. Reagents attached to the end of the fiber also alter the system*s spectral response and allow the use of inexpensive fibers for transmitting in the visible region of the electromagnetic spectrum. Other optical properties (e.g., changes in refractive index caused by absorption of analytes with the swelling of cladding) have also been used with FOCS.

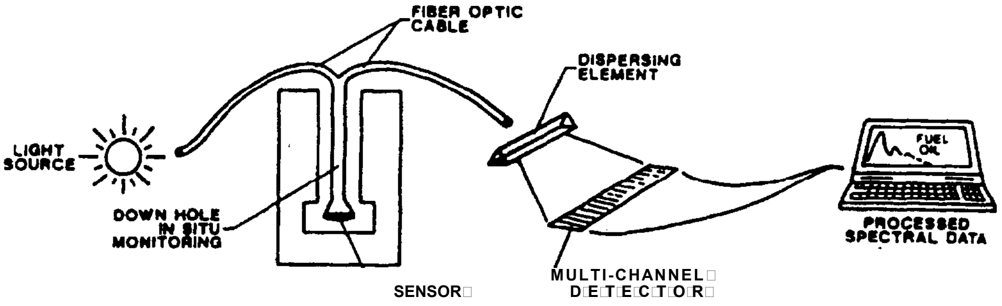

Figure 6-2. Fiber optic chemical analysis system.

6.2.3 Methodology

UV-vis absorption spectroscopy is often used for quantification or identification. The technique can be applied directly or after chemical reaction with a reagent to produce a highly colored product in the visible spectrum (Jungreis, 1985). It is also used in conjunction with liquid chromatography. Field deployable and hand-held instruments are available for measurements in the visible region.

Field-deployable instruments and methods have been used in mobile laboratories to make UV-vis luminescence measurements (Montgomery et al., 1985; Remeta and Gruenfeld, 1987). Portable instruments are under development. Several American Society for Testing and Materials (ASTM) standard methods are available for luminescence analysis of oils and creosotes, fluorescent aromatics, substituted aromatics, and PAHs (ASTM, l!%&, b). Other methods are being developed for phenols, PCBs, fluorescent pesticides, other fluorescent heterocycles, and uranium.

Dispersive IR spectrophotometers and Fourier Transform IR spectrophotometers (FTIRs) are available as field-deployable instruments for identification, classification, and quantification of total oil and grease. They are also used to identify volatile organic chemicals (Grant and Eastwood, 1983). Long-path length FTIRs are used for air monitoring; portable gas-cell dispersive IR instruments are used for industrial hygiene monitoring applications (Small et al., 1988). FTIRs are frequently used as detectors with 00 (Griffiths and Henry, 1986, Gurka, in press).

A number of pattern recognition techniques and expert systems have been developed to aid in the classification or identification of petroleum oils or other complex PAH mixtures. For example, methods have been developed for mid-IR and fluorescence spectra (Puskar et al., 1986; Sogliero et al., 1985). Different approaches are required for the two techniques because room temperature fluorescence spectra have fewer and broader peaks than mid-IR spectra.

FOCS will be useful for ***in*** situ monitoring activities. They are used with a variety of spectroscopic techniques. Instrumentation is available to support FOCS systems. The major obstacle is the development of analyte-specific coatings to selectively monitor individual compounds.

6.2.4 Application to WHPA Monitoring

Molecular spectroscopic methods provide WHPA monitoring activities with techniques that are mature and proven. Techniques that are in the development stage also have the potential to impact monitoring activities. Many such methods are simple and cost-effective. Field-deployable and portable instruments are available, along with methods that cover the analysis of organic and inorganic compounds (Table 6-l).

Absorption methods are especially useful for detection of PA.% or calorimetric reaction products that absorb energy in the visible region where only a limited number of contaminant compounds absorb. UV-vis absorption spectroscopy, without derivatization, is used to quantify content of relatively simple mixtures, often after separation by liquid chromatography (Ekambaram and Burch, 1988). Examples of these mixtures include aromatics (1 ppm detection limit), PAHs, total oil or grease content, dyes, or calorimetric reaction products that absorb strongly in the visible region (Duquette et al., 1988; Hanby, 1988, Woolerton et al:, 1988). It is possible to use UV-vis absorption with derivatization for the analysis of metals and some anions in concentrations below the ppm range.

Portable filter calorimeters are available as hand-held instruments for analyzing chemicals. UV-vis measurements are relatively simple and inexpensive; however, the operator must have some knowledge of chemistry and must be familiar with the kinds of interferences frequently encountered.

Fluorescence is especially useful for detecting, identifying, classifying, and quantifying polyaromatic compounds such as substituted and unsubstituted aromatics and PAHs (heterocyclic compounds), pesticides, PCBs, dyes, uranium, petroleum oils (both fuel and crude), creosotes, and complex PAH mixtures (Berlman, 1971; Eastwood, 1981). Fluorescence is often also used after separation of mixtures by thin layer chromatography or by liquid chromatography with multichannel analyzers (Ekambarum and Burch, 1988; Hurtubise, 1989). Room-temperature phosphorescence is especially useful for detection and classification of polyhalogenated polyaromatics such as biphenyls, dibenzofurans, dibenzodioxins, and phenols (Purcell et al., 1985). Luminescence can be used for a few inorganic constituents such as rare earths and uranium (Femandez-Gutierrez and Munoz de la Pena, 1985; Kaminski et al., 1981; Bushaw, 1983). Fluorometric methods after chemical derivatisation allow a broad range of organic& metals, and anions to be measured, often to ppb (McKinney et al., 1972). Sensitivities for luminescence may range from ppm to ppt, depending on the instrumentation and the chemical being detected. Laser excitation may permit even lower detection limits if desired.

IR spectroscopy is frequently used to identify or classify organic and some inorganic chemicals. It is also used to quantify chemicals such as oils and greases. IR absorption spectroscopy is widely applicable for organic analysis and is increasingly used for volatile and semivolatile organics as a detector for gas chromatography (Grant and Eastwood, 1983; Griffiths and Henry, 1986, Gurka, in press; Stout and Mamantov, 1989).

Raman spectroscopy may have potential future applications for WI-IPA monitoring because water and glass do not interfere with measurements, but considerable improvements are needed to make the instruments simpler, more rugged, and more compact. A prototype, portable, Raman instrument is being developed. It will use surface-enhanced Raman to detect rocket fuels such as hydrazine.

TABLE 6-1. APPLICATION OF SPECTROSCOPIC TECHNIQUES TO MAJOR CHEMICAL GROUPS

MAJOR CHEMICAL GROUPS	UV-VIS ABSORPTION		UV-VIS LUMINESCENCE		MID-INFRARED ABSORPTION	NORMAL RAMAN[a]
		COLORIMETRIC		FLUOROMETRIC		
			INORGANICS			
CATIONS		* SUB-ppm		ppm-ppb		
RARE EARTHS			ppm-ppb			
URANIUM			ppTr			
ANIONS		ppm		* ppm-ppb		
CYANIDE				* ppm-ppb		100 ppm
			ORGANICS			
AROMATICS/SUBSTITUED AROMATICS	≥1 ppm		ppb		low ppm	100 ppm
PHENOLS			ppb			100 ppm
POLYAROMATIC COMPOUNDS	≥1 ppm		ppm-ppt		low ppm	100 ppm
PAH[1]	low-ppm		ppb			100 ppm
COMPLEX PAH MIXTURE	low-ppm		ppb		ppm-ppb	
PETROLEUM OILS/GREASES	low-ppm		ppb			
CREOSOTES	low-ppm		@ ppb			
HETEROCYCLES	ppm		@ ppm-ppb		low-ppm	100-10 ppm
PYRIDINE						10 ppm
HYDRAZINE						100 ppm
PCBs[2]	ppm		ppm-ppb		100-10 ppm	100 ppm
PESTICIDES			@ ppb		100-10 ppm	100 ppm
DYES	ppm		@ ppm-ppt		100-10 ppm	100 ppm
OTHER ORGANICS			not detected	@ ppm	100 ppm	100 ppm

' NEAR INFRARED DETECTED DOWN TO PARTS PER THOUSAND

[a] SURFACE-ENHANCED RAMAN HAS MUCH LOWER DETECTION LIMITS FOR SOME COMPOUNDS

@ NOT ALL COMPOUNDS WITHIN CLASS DETECTED

ppm PART PER MILLION

[1] POLYNUCLEAR AROMATIC HYDROCARBONS

[2] POLYCHLORINATED BIPHENYLS

* WITH DERIVATIZATION

ppt PART PER TRILLION

Analyte-specific FOCS are available for *in situ* applications using UV-vis absorption and emission spectroscopic techniques (Klainer et al., 1988; Murphy and Hostetler, 1989, Olsen et al., 1988; Zhang and Seitz, 1989). FOCS provide a technique for detection of substances in monitoring wells and other inaccessible places; however, only a few rugged, durable sensors suitable for field use are available, and adequate field tests and calibration procedures are not yet developed. Several commercially available fluorometers with fiber optic attachments are available for use with these sensors.

6.2.5 Limitations/Performance

The UV-vis absorption method is relatively insensitive and subject to chemical interferences; therefore, it is most useful for situations in which alternative techniques do not exist.

Near IR spectroscopy is being developed to identify and quantify major constituents of simple mixtures (Kelly et. al., 1989). This technique only has the capability of detecting substances with concentrations in the parts per hundred (pph) or parts per thousand (ppth) range. At least one portable near-IR instrument has been developed for use with a fiber optic sensor to measure octane numbers of gasolines. Low sensitivity and lack of advanced knowledge of constituents likely in mixtures of environmental pollutants has reduced the utility of near-IR techniques for WHPA applications; however, special applications may exist.

Raman instrumentation, relatively complex and usually not rugged enough for field use, is available for laboratory research applications with visible and near-IR laser sources (Angel and Myrick, 1989 Pemberton et al., 1989; Williamson et al., 1989, chase and Parkinson, 1988). The technique can be used to detect analytes with concentrations that are on the order of 100 ppm (Table 6-l). The sensitivity of Raman measurements can be enhanced several orders of magnitude by using roughened metal surfaces like silver, copper, or gold to selectively adsorb some contaminants such as pyridine and PAHs (surface-enhanced Raman) or by excitation with an ultraviolet laser (resonance Raman) (Carrabba et al., 1987, Christesen, 1988, Gerrard and Bowley, 1989; Terpinski, 1987; Marley et al., 1985). Surface-enhanced Raman is being developed and may provide increased detection sensitivities for some chemical substances that cannot be easily detected with luminescence, presently the most sensitive spectroscopic technique.

Methods utilizing bare fibers for UV-vis absorption or laser-excited fluorescence are also available; however, interferences are a problem at low signal levels. Optical fibers used for these measurements are expensive if transmission in the ***W*** is desired; the fibers are subject to photodegradation if high powered UV lasers are used. Better sensing elements, calibration techniques, and standardized procedures must be developed. A greater selection of analyte-specific sensors needs to be developed before FOGS become a mature analytical technique.

Advantages and disadvantages of the various spectroscopic methods are summarized in Table 6-2.

TABLE 6-2. ADVANTAGES AND LIMITATIONS OF VARIOUS SPECTROSCOPIC METHODS

ADVANTAGES	LIMITATIONS
UV-VIS ABSORPTION	
MATURE TECHNIQUE	EXTENSIVE SAMPLE PREPARATION
INSTRUMENTATION READILY AVAILABLE	UNSPECIFIC (COMPARED TO IR AND LUMINESCENCE)
GOOD QUANTITATIVE ACCURACY FOR SINGLE COMPOUNDS AND SIMPLE MIXTURES	MODERATE SENSITIVITY
SPECTRAL DATA AVAILABLE	QUANTITATION MAY BE AFFECTED BY SOLVENT, POLARITY OF MEDIUM, CHEMICAL COMPLEXES
UV-VIS LUMINESCENCE (FLUORESCENCE AND PHOSPHORESCENCE)	
MOST SENSITIVE METHOD FOR TRACE AND ULTRATRACE ANALYSIS WHEN APPLICABLE	LIMITED TO COMPOUNDS WITH FAIRLY HIGH LUMINESCENCE YIELDS (USUALLY PACs, UNLESS DERIVATIZED)
INSTRUMENTATION READILY AVAILABLE	RELATIVELY UNSPECIFIC FOR STRUCTURAL INFORMATION (COMPARED TO IR)
NO INTERFERENCE BY WATER	QUANTITATION COMPLICATED BY DIFFERENCES IN QUANTUM YIELDS, QUENCHING, MICROENVIRONMENTS
FEW INTERFERENCES BY NONAROMATICS	
SOME STRUCTURAL SPECIFICITY - ENHANCED BY SPECIAL TECHNIQUES	LIMITED REFERENCE SPECTRA AVAILABLE
VERY SELECTIVE - ENHANCED BY TIME AND WAVELENGTH VARIABILITY	
INFRARED (DISPERSIVE AND FOURIER TRANSFORM	
HIGHLY SPECIFIC STRUCTURAL DATA ON FUNCTIONAL GROUPS FOR CLASSIFYING ORGANICS	MID/LOW SENSITIVITY (LESS SENSITIVE THAN LUMINESCENCE)
MATURE TECHNIQUE	WATER IS INTERFERENT (1-10 ppTHOUSAND DETECTION WITH SAMPLE CELL)
INSTRUMENTATION WIDELY AVAILABLE	FTIR CAN TOLERATE SOME WATER (BACKGROUND SUBTRACTION)
REAL-TIME FLOW-THROUGH VAPOR APPLICATIONS - GC-FTIR	REQUIRES SPECIAL OPTICS/SOLVENTS
SPECTRAL LIBRARIES AVAILABLE	QUANTITATION DIFFICULTIES
	WEAK OPTICAL SOURCES AND DETECTORS
NEAR INFRARED	
SOURCES AND OPTICAL MATERIALS BETTER THAN MID-IR	LESS SPCTRAL STRUCTURE THAN MID-IR
OPTICALLY GOOD SENSOR MATERIALS	- OVERTONE OVERLAP -LESS SPECIFICITY -INTERPRETATION COMPLICATED
CAN DISTINGUISH MAJOR COMPONENTS OF SIMPLE MIXTURES	NOT USEFUL FOR COMPLEX MATRICES
FEWER INTERFERENCES THAN MID-IR	SIGNAL PROCESSING AND PATTERN RECOGNITION REQUIRED

(Continued)

TABLE 6-2. Continued

ADVANTAGES	LIMITATIONS
NORMAL RAMAN SPECTROSCOPY (NRS)	
SPECIFIC AS IR FOR STRUCTURAL INFORMATION	RELATIVELY LOW SENSITIVITY (100 ppm)
DIFFERENT SELECTION RULES - COMPLEMENTS IR	FLUORESCENCE INTERFERENCE IN UV-VIS
FEWER INTERFERENCES THAN IR IN VIS OR NEAR-IR REGIONS	REQUIRES LASER SOURCE
WATER AND GLASS NOT INTERFERENCES	RELATIVELY COMPLEX INSTRUMENTATION
GOOD OPTICS AND SOLVENTS AVAILABLE	REQUIRES SKILLED OPERATOR
CAN HANDLE UNUSUAL SAMPLE SHAPES/SIZES	NOT AS MATURE AS IR
SURFACE-ENHANCED RAMAN SPECTROSCOPY (SERS)	
SPECIFIC IN STRUCTURAL INFORMATION	RELATIVELY NEW TECHNOLOGY
MORE SENSITIVE THAN NORMAL RAMAN	SURFACE/SUBSTRATE MATERIAL DEPENDENT
AS SENSITIVE AS LUMINESCENCE IN FAVORABLE CASES	REPRODUCIBILITY NOT ESTABLISHED
NO INTERFERENCE BY WATER	REQUIRES LASER AND SPECIAL SUBSTRATE
(SEE ALSO NRS)	NOT ALL ANALYTES ENHANCED EQUALLY
	FEW SPECTRAL LIBRARIES
	(SEE ALSO NRS)

6.2.6 Summary

Molecular spectroscopic techniques have the potential to rapidly screen, characterize, or quantitate samples in the field or laboratory. With continued development, spectroscopic techniques could be applied to WHPA monitoring activities.

UV-vis absorption spectroscopy is a mature technique for quantification. Because of interference in the *W* region, it is primarily of interest for use in the visible region after chemical derivatisation (calorimetry). ***W-vis*** luminescence has the advantage of potentially high sensitivity for certain classes of pollutants. These include polyaromatic and aromatic compounds such as PAHs, PCBs, phenols, and pesticides as well as uranium and fluorometric reaction products for anions and cations. This method is used for identification, classification, and quantification (especially for petroleum oils and other PAH mixtures). Field applications of this technique are rapidly increasing with recent improvements in instrumentation. Infrared spectroscopy (using both dispersive and FTIR instruments), although only moderately sensitive, is a mature technique widely applicable for analysis of organics. It is used in the field especially for vapor measurements, monitoring for industrial hygiene, and as a detector for gas chromatography.

Raman spectroscopy remains a laboratory research technique because of its relatively complex instrumentation and low sensitivity. Recent advances in surface-enhanced Raman indicate that sensitivities can be increased for at least some classes of analytes adsorbed on special substrates. This provides a possible future application for WHPA monitoring activities after more research.

FOCS, especially colorimetric and fluorometric sensors, in addition to other chemical sensors such as electrochemical, conductivity, or mass sensors, have potential for remote in situ monitoring, Several techniques, including laser-excited luminescence, laser-excited surface-enhanced Raman, and FOCS merit further research and development to explore possibilities of improved WHPA monitoring applications.

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6.3 EXTRACTION MEMBRANES

6.3.1 Introduction

A variety of information is available on the use of solid-phase extraction. For example, one application bibliography lists over 500 articles to assist practitioners in choosing procedures for the extraction and purification of a wide variety of chemical compounds (Analytichem International). Most manufacturers of solid-phase extraction products also provide simple guides for sample preparation and choice of sorbents. Applications are not limited to environmental contaminants.

Several references provide insight on the potential application of extraction membrane methodology to WHPAs. The use of solid-phase membranes in the form of 25- or 47- mm disks for the extraction of pesticides, PCBs, and phthalates at the microgram per liter range is described in Hagen et al. (1990). Standard filtration equipment (a suction flask) was utilized. Ground water, surface water, and laboratory tap water samples were used for pesticide, PCB, and phthalate analysis, respectively. The membranes were obtained from Analytichem International with a typical composition of 90% (by weight) of octyl (C8)- or octadecyl (C18)- bonded silica particles and 10% fibrillated polytetrafluorethylene. Recoveries exceeding 80 to 90% were obtained for the classes of compounds examined. This work demonstrates the utility of such membranes for preconcentration purposes.

Recent research addresses the potential of utilizing solid phase extraction membranes as part of a field screening method (Poziomek et al., 1991). The research involves using commercially available extraction membranes to preconcentrate contaminants onto the membranes by sorption from aqueous solution followed by nondestructive spectroscopic measurements in the field. Depending on the analytes being measured and the system parameter, the measurements could involve UV-vis luminescence directly, colorimetry/fluorometry with appropriate reagents, XRF analysis, and radioactivity measurements.

6.3.2 Theory of Operation

The basic concept involves the use of commercially available soil-phase extraction membranes as sensors. These membranes normally serve as alternatives to column chromatography in preconcentrating analytes from dilute solution and would be examined in the field using appropriate portable instruments.

The use of solid-phase extraction techniques to replace conventional liquid-liquid extraction for isolating analytes has gained in popularity (Figure 6-3). Two reviews on water analysis cite various examples (Mac&thy et al., 1987, and MacCarthy et al., 1989). The usual approach is to use short columns or cartridges containing various solid sorbents. Such columns are prepacked and readily available from a number of manufacturers. The use of solid-phase extraction membranes for preconcentrating analytes is also gaining popularity. The type of sorbent used to concentrate trace materials can vary widely depending on the analyte and the medium. The absorption theory behind the process relates to removal of components from both gases and liquids.

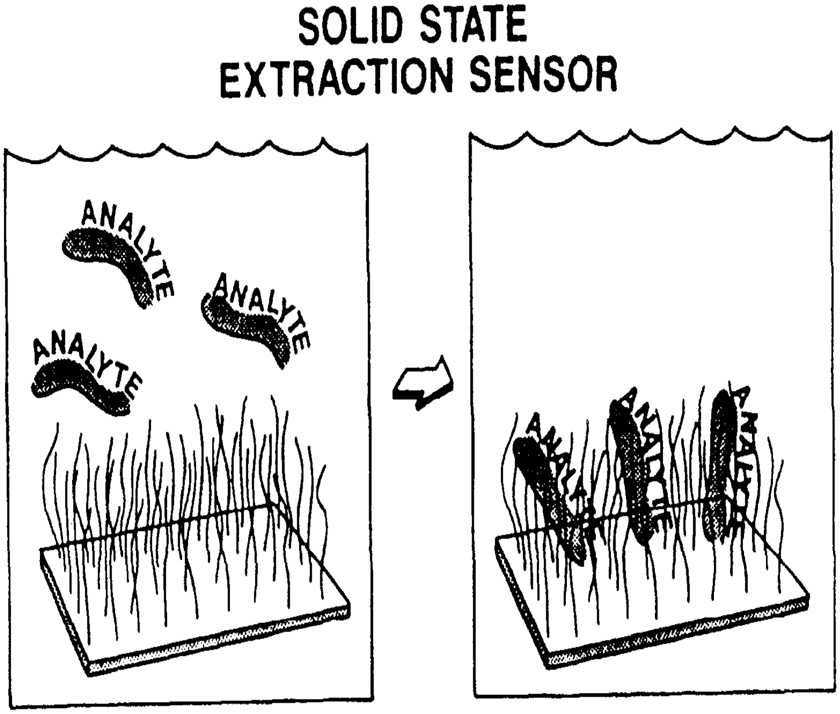

Figure 6-3. Schematic diagram showing extraction disk concentrating the analyte of interest.

References to a variety of materials that have been examined for solid-phase extraction applications can be found in a paper by Carr and Harris (1988). These include cellulose, carbon, fiberglass, zeolites, Chelex 100, XAD, Tenex, and glass or silica gel derivatized with alkyl chains. Analytes can be sorbed either directly onto the surface or through specific chemical interactions.

Organic analytes preconcentrated on the support are usually extracted with an appropriate solvent. The extract is then analyzed using an appropriate laboratory method such as GC, GUMS, or liquid chromatography-mass spectroscopy (LC-MS). The WHPA field screening application would involve examining the extraction membrane directly. Laboratory analysis would be an option after field screening.

63.3 Methodology

C18 Empore membrane disks for adsorption of Anthracene from water were analyzed nondestructively by solid-state fluorescence spectroscopy (Poziomek et al., 1931). These experiments simulated dip-stick or water-well insertion modes. Tabs were cut from the membrane disks and suspended without stirring in aqueous solutions containing ppb concentrations of anthracene at room temperature. The tabs were exposed to the solutions for given time intervals at different concentrations of anthracene. The tabs were then withdrawn, allowed to dry in air, and examined using fluorescence spectroscopy. Various relationships were found (e.g., linear increase in fluorescence intensity for 10 **ppb** anthracene versus time [minutes to days]). The results reported are preliminary, but very promising.

Carr and Harris (1988) concentrated pyrene from methanol-water solutions onto a C-18 derivatized porous silica column. They examined the column fluorescence as the pyrene was being sorbed and later allowed to desorb. The C18 silica was packed into a custom, fabricated, quartz tube (43 mm long, 3.2 mm outside diameter, and 0.96 mm inside diameter). The tube was held in place by a brass cuvette. It represented a flow cell arrangement so that the sorption/desorption of the pyrene could be followed in real time by measuring the column fluorescence. Membrane technology was not used in this case. Nevertheless, the reported results add support to the possibility of monitoring the sorption of pollutants onto membrane tabs in real time. It would be difficult to adapt a column flow cell to field operations. However, the use of membrane tabs in a dipstick mode or in wells with fiber optic spectroscopy seems attractive to pursue (Poziomek et al., 1991).

Wyzgol et al. (1990) have proposed the use of a combination of membrane extraction and attenuated total reflection IR spectroscopy for continuous measurements of waste water and air in industrial plants and during remedial actions. Th? extraction and spectroscopic procedures are combined to give real-time measurements of various organic compounds. The limits of detection have been estimated to be from 0.3-60 mg/L depending on the compound.

Leyden and Luttrell(1975) immobilized metal-ion chelating functional groups by reacting silica gel with various silylating reagents. They concluded that these materials have potential as preconcentration aids for X-ray analysis. This work is cited to indicate the potential scope of combining solid-phase extraction with various spectroscopic techniques in field screening of not only organic compounds but also metal ions.

Taguchi et al. (1985) preconcentrated phosphorus as phosphomolybdenum blue on nitrocellulose or acetylcellulose membranes in the presence of n-dodecyltrimethylammonium bromide. The membrane was dissolved in dimethylsulfozide and the absorbance of the solution was measured. An alternative field method would be to measure the color of the filter directly using a portable visible absorbance photometer.

6.3.4 Application to WHPA Monitoring

The application of extraction membranes to WHPA field screening is new, but promising. The scientific concepts involve both solid-phase extraction and solid-surface spectroscopy. Each has a strong scientific basis and does not need extensive development.

The simplest method is to utilize tabs of an extraction membrane in a dip stick configuration. In a typical scenario, the dipstick would be placed in a water sample for a specified period of time. The dipstick would then be removed and placed in the appropriate field spectrometer for analyte measurements. Semiquantitative results should be possible. Another method would be to filter water sample through the membrane. Conceivably, a series of different membranes could be used in tandem to allow neutral and charged organic compounds and metal ions to be preconcentrated in one operation, Another application would be to lower the membrane tabs into a well for longer periods of time. Tabs could be positioned at various distances from each other in the same well, thus giving a profile of contamination zones.

These applications require preconcentration of the analytes, a step that is followed by spectroscopic measurements. Systems could be designed in which the tabs are monitored remotely; however, this would result in greater development costs.

Applications to WI-WA monitoring can be designed to take advantage of commercially available solid-phase extraction membranes and field spectrometers. The use of extraction membranes in the field applications described above is nondestructive. One can discard the membranes, save them, or send them to the laboratory for more detailed analysis.

6.3.5 Limitations/Performance

Performance data from the use of solid-phase extraction membranes for preconcentration of pollutants from water is starting to emerge in the scientific literature (Hagen et al., 1990). The use of solid-surface spectrometry for analytical applications (e.g., using luminescence) is well known (Taguchi et al., 1985). However, the combination of using solid-phase extraction membranes together with solid-surface spectrometry for ground-water monitoring and measurement applications is new (Poziomek et al., 1991). The idea of using commercially available extraction membranes as dipsticks in sorbing analytes from aqueous solution is also new.

The combination of extraction and analysis using the same medium in a nondestructive manner in the field has not been examined sufficiently to allow limitations to be defined. The

6.3.6 Summary

The use of solid-phase extraction membranes to preconcentrate pollutants onto the membranes by sorption from aqueous solution followed by nondestructive spectroscopic measurement has potential as a field screening method for WHPA monitoring. Attractive features involve the use of commercially available extraction membranes and portable field instrumentation. The concept allows flexibility in choosing configurations for use in WHPA monitoring (e.g., dipsticks, standard filtration, or placement into wells at various positions to profile contamination zones). These applications are in the initial stages of development and require validation studies.

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6.4 SURFACE ACOUSTIC WAVE PROBES AND QUARTZ-CRYSTAL MICROBALANCES

6.4.1 Introduction

Surface acoustic wave (SAW) probes and quartz-crystal microbalances (QCMs) represent a class of chemical microsensors that measure changes in mass when analytes sorb and/or react with the device coatings. Such mass measurement devices are conceptually simple, rugged, and low cost. They have attracted many investigators to pursue sensor applications. For example, Ring (1964) reported the potential of piezoelectric sorption detectors. Most of the subsequent applications have been for detecting vapors (Katritzky and Offerman, 1989; Mierzwinski and Witkiewicz, 1989, Ballantine and Wohltjen, 1989 Guilbault and Jordan, 1988). However, some research has been conducted on applying SAW and QCM devices for solution analysis (Ward and Buttry, 1990; Janata and Bezegh, 1988, Janata, 1990). SAW or QCM devices for vapor or aqueous solution monitoring could be applied to WHPA monitoring activities. These microsensors can achieve sensitivities at the ppb level.

6.4.2 Theory of Operation

The SAW and QCM microsensors are oonaptually similar. A chemically selective coating (which could be chemical or biochemical in nature) is coupled to a physical probe (SAW or QCM) that acts as a signal transducer. The analyte sorbs onto or into the chemically selective coating, reversibly or irreversibly, through molecular association effects and/or chemical reactions. The physical probe “senses” these interactions and produces signals which are then measured by any one of several means, depending on the transducer.

The SAW and QCM devices are based on piezoelectric substrates. Though both respond to mass changes of coatings deposited on the device surfaces, the SAW microsensors possess several distinct advantages over the QCM microsensors. The advantages of SAW devices include higher sensitivity (due to higher operating frequencies), smaller size, greater ease of coating, and increased ruggedness (Ballantine et al., 1986). QCM devices, on the other hand, are more readily adaptable to use in solutions with the current state of the technology. Both QCM and SAW microsensors are mass-to-frequency transducers. A typical output would be changes in device frequency over time.

6.4.3 Methodology

SAW vapor sensors and their necessary support electronics can be miniaturized. A demonstration unit was configured so that the entire instrument fit within a 43/4” x 8” x 3” enclosure, a size that allowed room for pumps, valves, and vapor transfer lines (Jarvis et al., 1991).

Early reports on the use of QCMs to perform analysis in solutions such as ammonia and hydrogen sulfide involved protecting the sensor coatings from the liquids by using gas-permeable membranes (Webber and Guilbault, 1977). As another example of solution methodology, QCM piezoelectric crystals with silver-plated gold electrodes were used to determine cyanide in solution (Nomura and Hattori, 1980). The crystal was immersed in the test liquid, then removed, washed, and dried before the new frequency was determined. Though enthusiasm has been expressed for SAW and QCM device applications in gas phase and solution analyses, work is still needed to realize the full potential of the technology.

6.44 Application to WHPA Monitoring

The application of SAW and QCM technology to WHPA monitoring seems promising for both vapor and aqueous solution monitoring because of the variety of compounds which might be sensed. Organic chemical vapor sensing applications probably have a better chance of success because more is known about this application than solution monitoring. The design of probes should include membranes to protect their sensor coatings when immersed in solution. The QCM probes would have a greater chance of success as *in situ* water monitors than the SAW devices because more is known about their use in solution. The QCM and SAW technologies are still developing and have not been applied routinely to ground-water monitoring.

6.45 Limitations/Performance

The major technology barrier to the development of mass sensitive and other chemical sensors is the proper selection of the sensor coating materials. A comprehensive review on the research and development of sensor coatings is available (Poziomek, 1989). Several problems persist, impeding rapid development of the technology. For example, no information base on chemical reactions and molecular association effects in vapor-solid and liquid-solid phases exists to draw on for the development of chemical sensor coatings. In addition, few guidelines describe the selection of solid phase coatings for use in conjunction with chemical sensors, and standard methods for screening and evaluating candidate solid phase coatings in sensor applications are not readily available (Poziomek and Engelmann, 1990). Most likely, an array of QCM and/or SAW microsensors would be necessary to increase selectivity. Single sensors that are specific to a particular pollutant or a class of chemicals are conceivable; however, a sensor array would broaden the utility of the technologies.

6.4.6 Summary

SAW and QCM microsensors measure changes in maw when analytes sorb and/or react with the device coatings. Such devices have attracted the attention of the sensor community because of their simplicity, ruggedness, and low cost. The major applications to date have been for organic chemical vapor sensing, but the use of the devices, especially QCMs in solution, is beginning to emerge. Specific application to WHPAs seems promising. However, the major technology barrier toward exploiting the potential of SAW and QCM microsensors is proper selection of the sensor coatings. Guidelines need to be established to help practitioners choose coatings.

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6.5 SPECTROELECTROCHEMISTRY

6.5.1 Introduction

Spectroelectrochemistry combines spectroscopy and electrochemistry to study redox chemistry. Early work involved the use of an optically transparent electrode for the spectral observation of an electro-generated product (Kuwana et al., 1964). In spectroelectrochemistry, spectroscopy is used as an *in situ* technique to identify electrochemistry products in real time. The approach has been proven effective, elucidating the redox chemistry of a variety of inorganic, organic, and biological molecules. It represents a mechanism to obtain both spectra and redox potentials and to observe subsequent chemical reactions of species that are generated electrochemically.

Two early reviews give an appreciation of the principles of spectroelectrochemistry and the progress made during the first decade since its discovery (Kuwana and Heineman, 1976; Heineman, 1978). A recent review on the application of spectroelectrochemistry in analytical chemistry provides 62 references (Widring et al., 1990).

6.5.2 Theory of Operation

Electroactive species change at an electrode by the addition or removal of electrons. In spectroelectrochemistry, spectral measurements are made on the solution adjacent to the electrodes as the electrochemical process proceeds. In some cases, the surface itself is examined. Thus, spectroscopy is used as a probe to observe the consequences of an electrochemical process. A typical output would be several spectra of a particular substance obtained for a series of potentials. However, one is not limited to the use of transmission spectroscopy. Specular reflectance and internal reflectance spectroscopy have been used as well. Since its inception in 1%4, the “spectra” part of spectroelectrochemistry has been expanded to include electron spin and nuclear magnetic resonance as well as luminescence and scattering spectroscopies. Ultraviolet and visible spectroelectrochemistry are now quite commonly used to identify electrode reaction products and intermediates. Several improvements have been made, including the use of fiber optics for the propagation to and subsequent illumination and detection of light at electrode surfaces. Infrared and Raman spectroscopy are also being applied more frequently to electrochemical problems. Several sources delineate theory and provide specific examples of the different types of spectroscopy that have been used (Heineman et al., 1984; Gale, 1988; McCreery, 1986, Sharpe et al., 1990).

6.5.3 Methodology

Through spectroelectrochemistry, it is theoretically possible to determine the composition of solutions and electrode adsorbed species. The technology allows elucidation of reactants, intermediates, and products.

Recent developments in methodologies include: (1) an IR thin layer cell with a gold or platinum working electrode that serves as a minor for the light beam, (2) mercury/solution interfaces for study of absorbtions, (3) angle-resolved IR spectroelectrochemistry for *in situ* depth profiling of electrode/electrolyte interfaces, (4) surface-enhanced Raman spectroscopy (SERS) for studying adsorption and electroreduction at silver electrodes, (5) surface-enhanced resonance Raman spectroscopy for monitoring electrode surface reactions of biological molecules, (6) improvements in cell geometries and novel applications of UV-vis spectroelectrochemistry, (7) the use of fiber-optic absorbance probes in conjunction with a bulk electrochemical cell, (8) improvements in optically transparent spectroelectrochemical cells, including the fabrication of high surface area working electrodes, (9) improvements on long optical path length cells for simultaneous electron spin resonance - electrochemical investigations, and (10) extended X-ray adsorption fine structure spectroelectrochemistry (Widring et al., 1990).

The use of spectroelectrochemistry has elucidated the basic chemistry that occurs on the surface of an electrode. Examples of compounds and ions studied recently using any one of a variety of spectroelectrochemistry techniques include ethanol, carbon monoxide, methanol, sulfate, formaldehyde, tetraphenylporphyrin-metal complexes, benzoic acid, benzoate, cyanate., ferrocyanide, dioxouranium (VI), hexakis (arylisocyanide) chromium (III), polythiophene, dopamine, pyrrole, phenaxine, nitrobenzene, hydroquinone, ethylene, bipyridine, hydrogen, ferrocene, diaminobenzene, polyaniline, iodide, and copper (Widring et al., 1990). Though the above list gives an idea of current research, many other examples and considerable data are available. One possibility is to combine photochemistry with spectroelectrochemistry. For example, the use of light may serve to selectively increase the electroreactivity of certain analytes. Other options are also available (Weber and Long, 1988).

6.5.4 Application to WHPA Monitoring

The use of a microelectrode as a transducer in combination with spectroscopy (involving the use of fiber optics) is attractive to consider as an *in situ* monitoring and measurement method in aqueous media. It is potentially an important technique for WHPAs. However, applications of spectroelectrochemistry for environmental monitoring have not yet emerged. A scan of the literature shows that the emphasis has been on elucidating basic chemistry rather than on application. The use of microelectrodes in combination with spectroscopy in an integrated sensor approach would appear to offer the potential for high sensitivity and selectivity; however, this potential has not been exploited.

Researchers have proposed the use of spectroelectrochemical sensing of chlorinated hydrocarbon solvents for field screening and *in situ* monitoring applications using fiber optic probes (Carraba et al., 1991). The procedure is based on a photon-induced electrochemical reaction which is detected by SERS on electrodes. This appears to be a variation of combining photochemistry with spectroelectrochemistry. The work is still in the preliminary stages, but provides an example of how spectroelectrochemistry might be applied to WHPA monitoring.

6.5.5 Limitations/Performance

Though spectroelectrochemistry has been utilized for almost three decades, the work has been very basic in nature. A thorough examination of the spcctroelcctrochemistry literature is nccdcd to establish the feasibility of the technology for use in wellhead monitoring. Assessments should target particular problems such as how spectroelectrochemistty might handle a mixture of contaminants.

6.5.6 Summary

Spectroelectrochemistry represents the combination of electrochemistry and spectroscopy to study redox chemistry. The work to date has been very basic in nature; however, researchers are starting to focus on applications, including WHPA applications. A thorough review of the literature should be performed before establishing strategies for WHPA development work.

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6.6 BIOSENSORS

6.6.1 Introduction

First reported by Clark in 1962, biosensors are relatively immature tools of analytical chemistry and are regarded by some as emerging technology. For the purposes of this report, a biosensor is defined as an analytical device that incorporates a biologically active material in intimate contact with an appropriate transduction element in order to detect (reversibly and selectively) the concentration or activity of chemical species in any type of sample (Arnold and Meyerhoff, 1988). This definition relates to the type of (bio) chemical reaction that provides the analytical output (usually electrical).

6.6.2 **Theory of Operation**

Biosensors are classified into two operational types: biocatalytic and receptor biosensors.

1. Biocatalytic biosensors - the sensing tip of the detection probe contains a very small amount of immobilized biocatalyst which communicates between the analyte and the detector element. As analytes move from the sample medium into the biocatalytic area at some diffusion-controlled rate, they are converted into a form that is measurable by the detector. At the same time, the converted form of analyte (product) diffuses out into the sample medium at some rate. At steady-state conditions, the signal at the detector relates to the concentration of the analyte in the sample.

2. Receptor biosensors - molecules in the detector tip are selective from the shape of their functional, reactive groups. As specific analyte molecules move toward the receptor molecule, they can dock, or link-up, to form a stable receptor-ligand complex The strength of this stable complex is related to the size and shape of the ligand and the receptor molecule. The lack of reversibility makes receptor-type biosensors inadequate for monitoring ground water around WHPAs.

The most common biocatalytic-based biosensors use enzymes (Figure 6-4). The sensor response is proportional to the rate of analyte-enzyme product arrival at the sensor or detector element. As a result, analyte movement (mass transport) into the biocatalytic zone and the formation rate of analyte-enzyme product control the overall rare at the sample/sensor interface (Albery et al., 19%). Relatively high enzyme levels within the biocatalytic layer produce faster response, greater selectivity, and longer sensor lifetime.

6.6.3 Methodology

The methodology of biosensors is one of the* areas in greatest ne-ed of development. Nevertheless, the literature provides a few preliminary guidelines for this analytical technique.

1. Artificial enzymes should be used in field testing of any prototype (or commercial) biosensor because they have better performance ratings. Isolated natural enzymes generally perform in biosensors for about one week Artificial enzymes, on the other hand, can perform for more than six months. The first biosensor with artificial enzymes was used in the analysis of acetoacetic acid (Ho and Rechnitz, 1987).

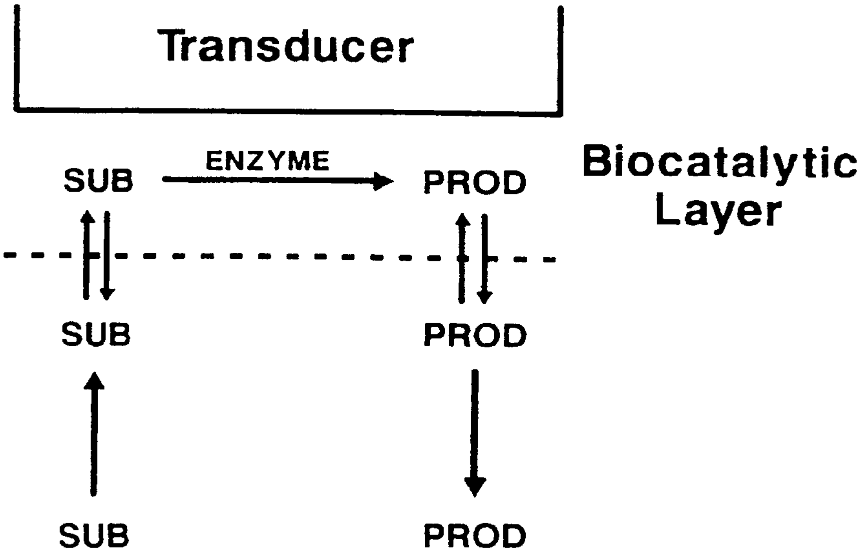

Figure 6-4. Schematic diagram of a biocatalytic-based biosensor (after Arnold and Meyerhoff, 1983).

2. Multiple enzyme systems promise synergistic benefits. Their combination can be used to form new biosensors, to increase sensor selectivity, and to amplify chemically the sensor response (Arnold and Meyerhoff, 1988).

3. Fiber optic biocatalytic biosensors use the immobilization of an enzyme at the tip of an optical fiber, and detection is through opto-electronic means. Other biosensors use electrochemical means to send their signal through shielded, metallic conductors to the analytical instrument. An advantage of fiber optic devices over electrochemical devices is their capability to use a single fiber for monitoring multiple wavelengths. A disadvantage is that fiber optic cables are usually made of quartz, making them considerably more expensive and less durable than electrical conductors.

6.6.4 Application to WHPA Monitoring

The number of available ground-water monitoring biosensors, even in concept or prototype form, is currently very limited. Biosensors for the detection of sulfate anions (Kobos, 1986) and ammonium ions (Reidel et al., 1985) have been described.

6.6.5 Limitations/Performance

High enzyme levels in the detector **produce** faster biocatalytic reactions, but the sensor response is limited by diffusion. Low enzyme levels in the detector produce slower biocatalysis, and sensor performance depends on reaction rats. The current list of analytes that are detectable through fiber optic biocatalytic biosensors contains little of interest to WHPA monitoring (Arnold and Meyerhoff, 1988).

Biosensors generally have two main components: (1) a molecular recognition, or biological entity, and (2) a signal-producing entity, or the component connected to the analytical instrumentation. Biosensor research and development requires a large measure of creativity to gain an optimal union between these two components. As biosensors are further developed and improved through innovative technology, applications can be expected in medicine, agriculture, biotechnology, military applications, and environmental studies such as ground-water monitoring for WHPAs.

6.6.6 Summary

Few analytes can be monitored with biosensors; nevertheless, the technique is worthy of continued research. The medium of conveying the signal from biosensor to analyzing instrument for ground-water monitoring for WHPAs should be based on electrically-conducting cable in which ruggedness and cost are controlling considerations. The literature reports many biosensors, but this research focuses mainly on biomedical monitoring of analytes not expected to be found in ground water. Biosensors have been &scribed that can monitor sulfate ions and ammonium ions.

6.6.7 References

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SECTION 7

CASE STUDIES

This section describes two case studies that exemplify innovative applications of monitoring technologies for drinking water. The first case study is the Orange County Water District, (0CWD) located in Southern California. The OCWP is monitoring ground water using “Multiport Wells” equipped to continuously measure temperature and water level. This data is linked to a centralized computer and water management data base system. The second case study is the State of Florida*s Ground Water Quality Monitoring Network and related applications of continuous remote monitoring station that utilize telemetry.

7.1 ORANGE COUNTY (CALIFORNIA) WATER DISTRICT: INNOVATIVE APPROACH TO GROUND-WATER MONITORING USING AN IN-SITU, MULTI-LEVEL, CONTINUOUS GROUND-WATER DATA ACQUISITION SYSTEM

The OCWD manages a large alluvial ground-water basin in the coastal plain of southern California (Figure 7-la). Today the OCWD supplies more than 65 percent of the total water demand of the 1.8 million people within the District.

The portion of the basin managed by OCWD covers an area of about 300 square miles and has a useable storage of approximately 1.5 million acre-feet. Though the fresh water aquifers extend to depths up to 4,000 feet, at this time, most production occurs above a depth of 1,500 feet (Figure 7-lb).

Prior to OCWD implementing recharge activities, the natural safe yield of the basin was about 60,000 acre-feet per year. With a ground-water demand of more than 250,000 acre-feet per year, the District must artificially recharge the basin and control sea water intrusion. The recharge facilities, located on more than 1,600 acres of land along the Santa Ana River, consist of about 1,000 wetted acres of in-river and shallow and deep spreading basins. Water is diverted into these facilities from storm and base flows of the Santa Ana River and from the California and Colorado River Aqueducts. As much as 350,000 acre-feet per year can be recharged in these facilities, depending on the availability of water from local and imported sources.

In addition, sea water intrusion caused by the large pumping depressions in the central part of the basin poses a potential problem in certain areas near the coast. The District controls this problem by injecting imported water and reclaimed wastewater into coastal aquifer zones. The District also monitors ground-water contamination problems in the basin and is active in District-financed remedial investigations and clean ups.

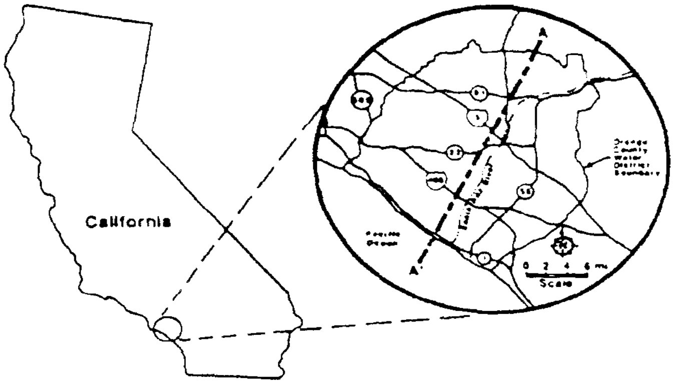


Figure 7-1a. Location map.

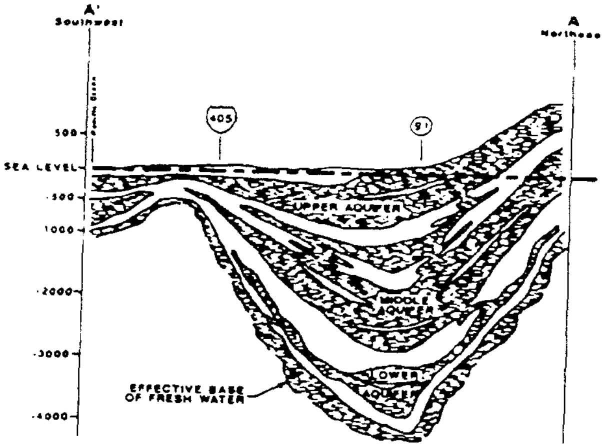


Figure 7-1b. Idealized hydrogeologic cross section.

This multifaceted program requires a comprehensive monitoring system to provide the data for management decisions. The District has begun a lo-year program to install up to 150 deep and shallow, multi-level monitoring wells throughout the basin. The objective of these wells is to provide an areal as well as vertical understanding of the basin hydrogeology. Typically, these wells are about 1,500 feet in depth, but range from 300 to 2,000 feet. After investigating and experimenting with several construction methods, including nested, cluster, and single standpipe wells (Figure 7-2), the District selected the MP system (Westbay Instruments Inc.), which consists of a single standpipe with multiple screens. A comparison of the alternate methods is given by Black et al. (1988). The monitoring wells are constructed of 4-inch in diameter, mild steel casings and screens. Screens are isolated in the annulus with a mixture of bentonite chips and coarse-grained sand that is placed by pumping through a tremie pipe (Figure 7-3). The MP System isolates the screens on the interior of the casing with water-inflated packers. This system allows the District to isolate, monitor, and sample any or all aquifers penetrated by any given well for both piezometric pressure and water quality. These wells have been useful in locating contaminants, determining hydraulic characteristics of individual aquifers, and identifying flow pathways as water moves from the recharge areas of the basin toward the points of extraction.

The District has installed more than 20 deep and 50 shallow monitoring wells, which provide more than 300 monitoring points for collecting samples and obtaining water pressure measurements. A water quality sample is taken from each point in each well once per quarter for the first year and twice per year thereafter. Pressure measurements are carried out every month. However, as the number of monitoring wells increases, the manpower required to conduct the monitoring and sampling increases to a point that would eventually be economically unacceptable to the District. Recognizing this dilemma, the District decided to participate in a research and development project with Westbay to find a more efficient method of conducting the needed monitoring. Several wells are currently fitted with this down-hole monitoring equipment to evaluate its effectiveness.

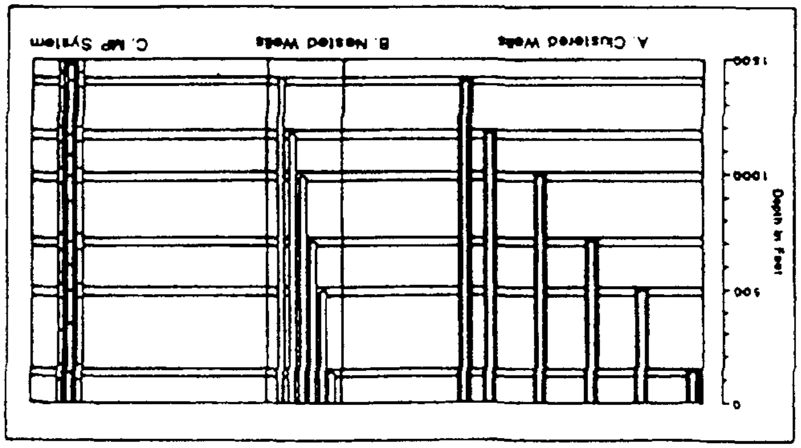


Figure 7-2. Comparison of methods for monitoring ten levels between 0 and 1,500 ft.

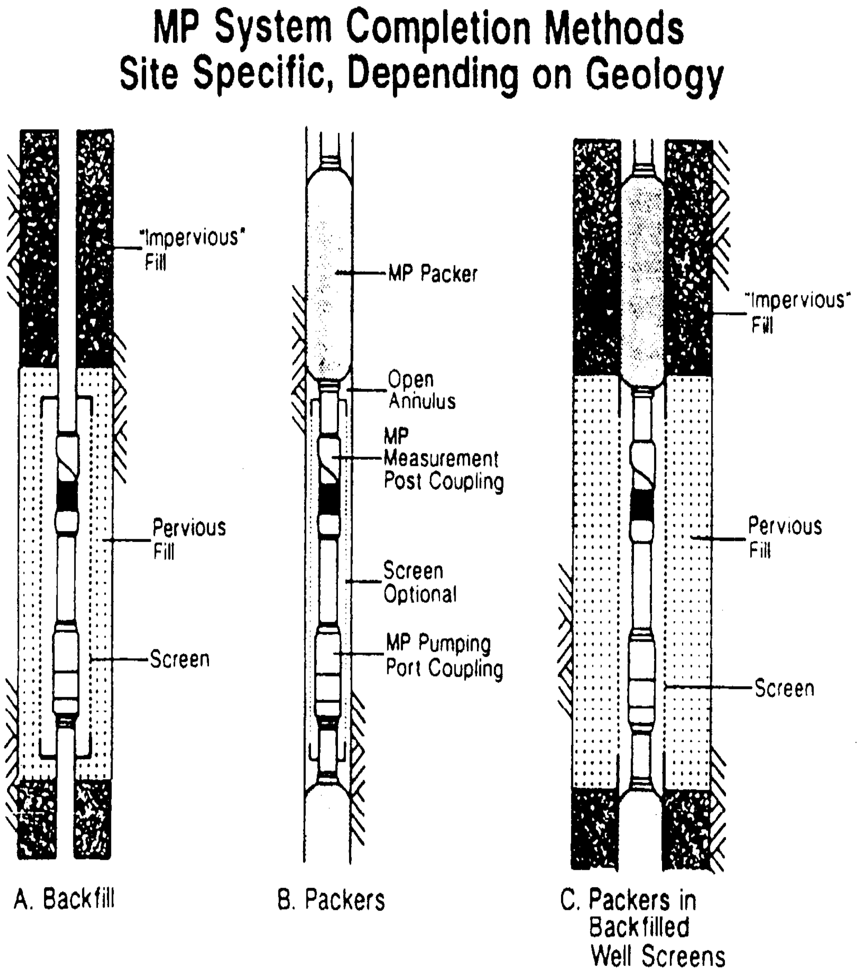


Figure 7-3. Schematic diagram showing various multiport well construction techniques used for site specific applications.

Westbay is currently developing a multi-point monitoring system called MOSDAX . In January 1990, a prototype system was shipped to OCWD for field testing. The plan was to conduct the testing in two phases. The first phase consisted of a pump test using two pumping wells and a single District-owned MP-equipped monitoring well. The second phase is designed to evaluate the long-term, multi-level, multi-well application with a telemetry interface. The first phase of testing has been completed and the second phase of testing is now underway and is expected to be completed by mid-1991. Ultimately, all data from the system will be telemetered to the District*s Water Resources Management System (WRMS), which contains the water resources data base. In the future, therefore, District manpower levels should remain stable, allowing personnel to analyze rather than just collect data.

THE MOSDAX SYSTEM

The MOSDAX System is a multi-level, continuous, ground-water pressure monitoring system for use with MP System monitoring wells. MOSDAX consists of a series of probes with pressure transducers (pressure probes), which are located at selected measurement ports in the MP monitoring well, and a surface module which is placed at the wellhead (Figure 7-4). Data are collected from each of the probes based on user-selected criteria and are transmitted to the surface module for storage or passed on to a host computer using telemetry techniques (dedicated telephone line, cellular phone, or radio).

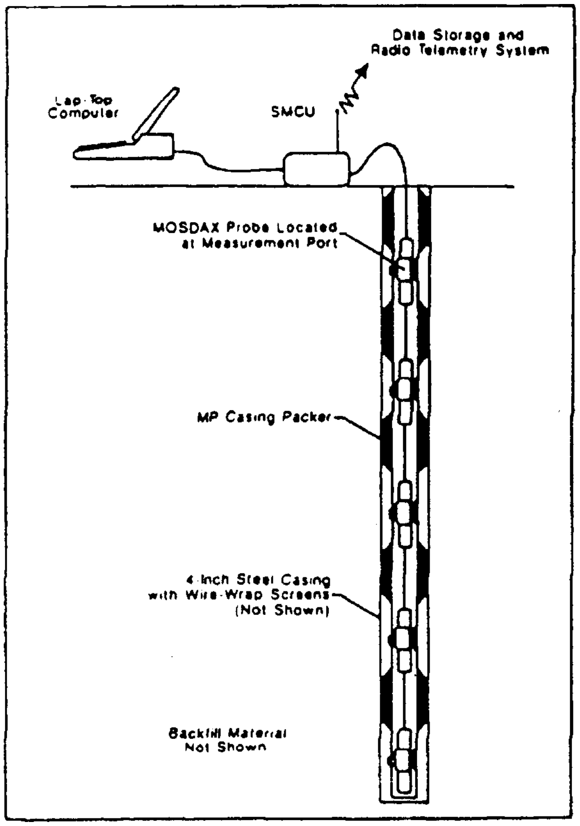


Figure 7-4. Schematic illustration of MOSDAX System monitoring fluid pressure at multiple levels in an MP System well.

MOSDAX Pressure Probes

Each MOSDAX pressure probe is functionally similar to a standard Westbay pressure probe, but takes advantage of recent advances in electronics technology. The main functional units of the pressure probe are the micro-computer module, the pressure sensor, the activation motor assembly, and the stainless steel pressure housing. As with the standard Westbay pressure probe, the MOSDAX probes are lowered to the selected measurement port and activated. The activation motor causes the probe to seal against, and open the measurement port valve and read fluid pressures in the monitoring zone on the outside of the MP casing. A discussion of the operation of the MP System is given by Black et al. (1986).

A single preassembled high strength wire connects the probes to each other and to the surface module. The surface module communicates with the probes via digital, “multidrop” communications techniques which allow complex instructions to be sent quickly and accurately to a large number of probes on a single pair of conductors. Each probe has a unique serial number stored in its memory so it can identify and distinguish messages. The surface module can query each of the probes for diagnostic information as well as pressure and temperature sensor information.

Each probe is capable of obtaining approximately seven pressure readings each second. This data collection rate can be maintained with approximately 15 probes connected to the surface module. When additional probes are connected to the surface module, the data collection rate is reduced slightly. For special applications, the probes contain a memory buffer which can temporarily store readings for transmission to the surface as time permits.

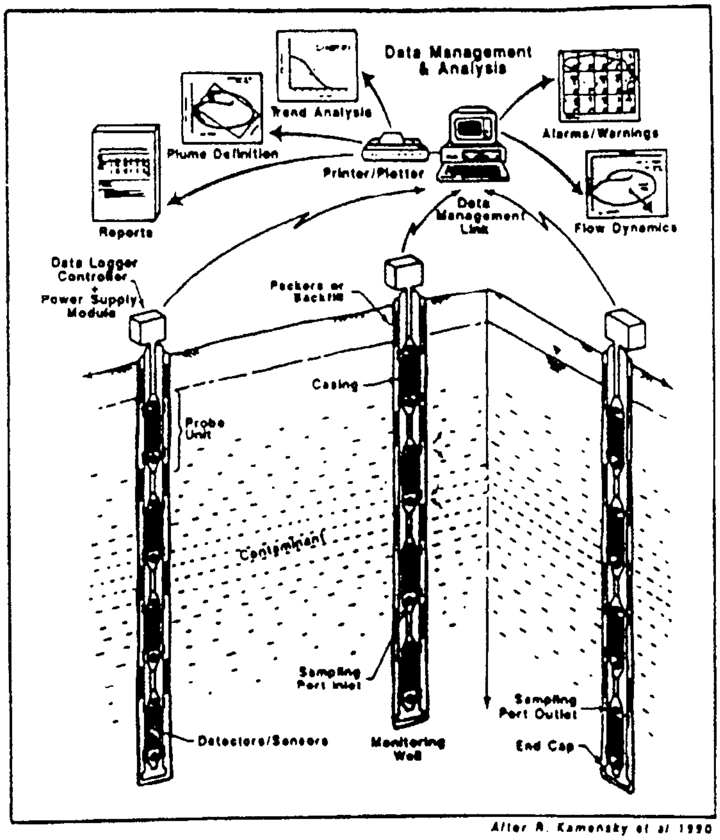
Surface Module

The surface module can take several forms, depending on the application, The module used for the field test was a self contained data logger called a surface memory and control unit (SMCU). The SMCU is designed for long-term, stand-alone operation. It contains a microcomputer with up to 1 Mbyte of memory, an internal battery, and a barometric pressure sensor, all housed in a water tight enclosure. As with the MOSDAX probes, low power consumption was a design priority. Depending on the data collection rate, unattended data logging for periods of months is possible.

The SMCU is configured by the use of a lap-top computer. Once the parameters for data logging have been entered into the SMCU, the lap-top is disconnected and removed. The collected readings are stored in the SMCU and can be transferred to the lap-top computer when the site is visited. The collected data are taken to the office for conversion to popular formats such as LOTUS 123®. Modifications to the SMCU, which are currently being tested in the Phase II field trials, permit the SMCU to transmit data to the district*s central water resources data base (Figure 7-5).

Quality Assurance Considerations

A major concern in any downhole equipment is verifying the output of the various sensors. When the MOSDAX System is used with the MP System, formation fluid pressures can be corroborated and verified. The pressures can be verified by checking the operation of the pressure response trends in adjacent monitoring zones or against a known pressure. This is done in the field by using the fluid pressure resulting from the column of water inside the MP system casing (which is



After R. Kamensky et al 1990

Figure 7-5. Cartoon schematic showing idealized ground-water monitoring system.

distinct from the fluid outside the casing). The procedure requires deactivating each probe so that it reads the pressure inside the MP casing. Following the performance check, the probes can be reactivated to continue monitoring formation fluid pressures. Using this technique, the sensor drift can be checked. It is possible to carry out this check remotely through the telemetry system. The communications protocol between the probes and the surface module contains error checking routines to detect errors in the transmission. If an error is detected, the SMCU can request a retransmission.

Data are stored in the surface module in a memory-efficient form that is not readable without special conversion routines. Manipulating or altering the raw data is difficult. In addition, each of the raw data files contains a header which includes information from the originating probe, such as serial number, sensor calibration constants to be used, and date and file tracing information.

Innovative Monitoring of Recharged Groundwater

The OCWD operates an extensive recharge facility, known as the Forebay, along the Santa Ana River, in Anaheim, California. Because the Orange County ground-water basin is located at the end of the Santa Ana River watershed, it is the recipient of often poor-quality waters generated primarily from three sources. The first, and foremost, is the high-nitrate tertiary treated waste water discharged to the Santa Ana River by upstream municipal sewage treatment plants. The second is agricultural and dairy wastes runoff entering the Santa Ana River, which contributes high nitrates and salt loads. The third is the imported Colorado River water which, although vitally necessary as the primary water supply to the upper basin and Orange County area, contributes high salt concentrations and indirectly contributes to salt concentrations in waste waters discharged to the river. The incorporation of large quantities of waste water (which make up the base flow of the Santa Ana River) for ground-water replenishment has generated significant concerns pertaining to health effects associated with municipal ground-water usage. Recently, the State Department of Health Services and the Regional Water Quality Control Board have recommended that the OCWD document the changes in ground-water quality (waste-water related) in the forebay area, with particular emphasis on the purification benefits derived from soil filtration. In the next three to four years, OCWD plans to complete a Health Effects Study that will also include toxicological studies at three to four sites. Preliminary studies show that water entering the Forebay Recharge Facilities contains average nitrate ($N0_3$-N) concentrations of 7.0 mg/L. Analysis of samples collected from deep, multipoint, monitoring wells located adjacent the Santa Ana River channel indicate that significant biodegradation occurs vertically and laterally through the soil. Comparing nitrate concentrations from Forebay surface waters to underlying ground-water indicates that nitrate removal may lx as high as 50%. The shallow, unconfined aquifer systems of the Forebay contain average nitrate concentrations of 3.0 mg/L. Downgradient from the Forebay, in the confined aquifer systems, nitrate concentrations generally drop below detection limits.

Innovative Monitoring for Delineating the Vertical Distribution of TCE and TDS

Ground-water quality in the Irvine area has been impacted by elevated concentrations of trichloroethylene (TCE) and total dissolved solids (IDS) due to industrial and agricultural land uses, respectively. The heterogeneity of the fluvial- and estuarine-derived sediments has imposed vertical hydraulic constraints which have created a “stratified” water-quality profile.

The OCWD installed and sampled a series of single and multiscreened monitoring wells to delineate the extent of a ground-water TCE plume. Vertical and lateral variations in TCE, nitrates, TDS, and piezometric heads were used to identify at least two distinct aquifer zones. The shallow aquifer zone, from zero to 200 feet below ground surface (bgs), is generally characterized by IDS >2,000 mg/L and elevated NO_3 concentrations and low to non-detectible TCE concentrations; the deeper aquifer (from 200 to 500 feet bgs) contains relatively low salts (<l,000 mg/L) and TCE concentrations from zero to 50 : g/L.

Measured vertical piezometric head differences of up to 40 feet within a single multiscreened well coincide with variations in water-quality data, indicating hydraulic separation of the shallow and deep aquifers. Vertical changes in water quality and piezometric levels become less apparent in the southeastern portion of the study area, indicating potential vertical hydraulic connection between shallow and deeper aquifers in this vicinity. Depth-specific, water-quality data collected from the monitoring wells were used to design and construct a 1,000-gpm extraction well screened specifically in the TCE-impacted aquifer zones.

Innovative Monitoring Strategies Using Soil Gas Surveying to Evaluate a Groundwater VOC Plume

In January 1987, a City of Orange production well was shut down due to the detection of chlorinated VOCs above state drinking-water standards. OCWD determined the extent of VOC contamination of the shallow ground water in the vicinity of the contaminated well through the use of soil-gas surveys to identify potential source areas, and the construction of ten 100- to 200-foot deep monitoring wells to delineate the lateral extent. In addition, three existing 1,500- to 2,000-foot deep multiscreen monitoring wells were sampled to evaluate the vertical extent migration potential of the plume. Although only the western edge of the plume has been defined to date, a ground-water extraction and treatment system is being installed to minimize further VOC migration. Additional wells will be constructed to delineate the full extent of the plume for future remedial planning and source identification.

SUMMARY

OCWD plans to continue with a program of installing monitoring wells and collecting ground-water pressure and chemical data as required to meet the needs of the ground-water producers in the basin, Accurate and timely data will be provided by a data collection network which will rely on automatic data collection and telemetry techniques to transfer the data directly to a central location. To efficiently store and retrieve a large amount of project data, OCWD is developing their WRMS. The WRMS program will be a network data base which will store data, from virtually every aspect of the ground-water resource. The information includes well design information, lithologic logs, geophysical testing results, geochemical data, and water-level data. The data base will be linked to graphic and modeling tools to facilitate evaluation. Generation of contour maps and cross-sections based on the information contained in the data base or developed from models will become easy and routine. This program, coupled with the data continuously generated from the MOSDAX-equipped MP monitoring wells, will help OCWD meet its mission and responsibilities well into the twenty-first century.

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7.2 FLORIDA*S GROUND-WATER QUALITY MONITORING NETWORK

More than 90 percent of Florida*s 11.5 million population depends on ground water for drinking water supplies (USGS, 1987). Florida has three major aquifer systems. (Southeastern Geological Society 1986). In ascending order (deepest to shallowest), the three major systems are the Floridan aquifer system, the intermediate aquifer system or intermediate confining unit, and the surficial aquifer system (Figure 7-6).

The rocks that make up the Floridan system are easily dissolved by acidic rain water, and portions of rocks making up the aquifer already have been dissolved. This has resulted in the development of karst features such as large cave systems and sinkholes beneath most of Florida.

In many areas of the state, the Floridan becomes highly mineralized with depth. South of Lake Okeechobee, the water within the aquifer is of poor quality and is not used for drinking. However, throughout most of the rest of the state, the quality of water in the upper portion of the aquifer is excellent. This makes the Floridan aquifer the states single most important source of water.

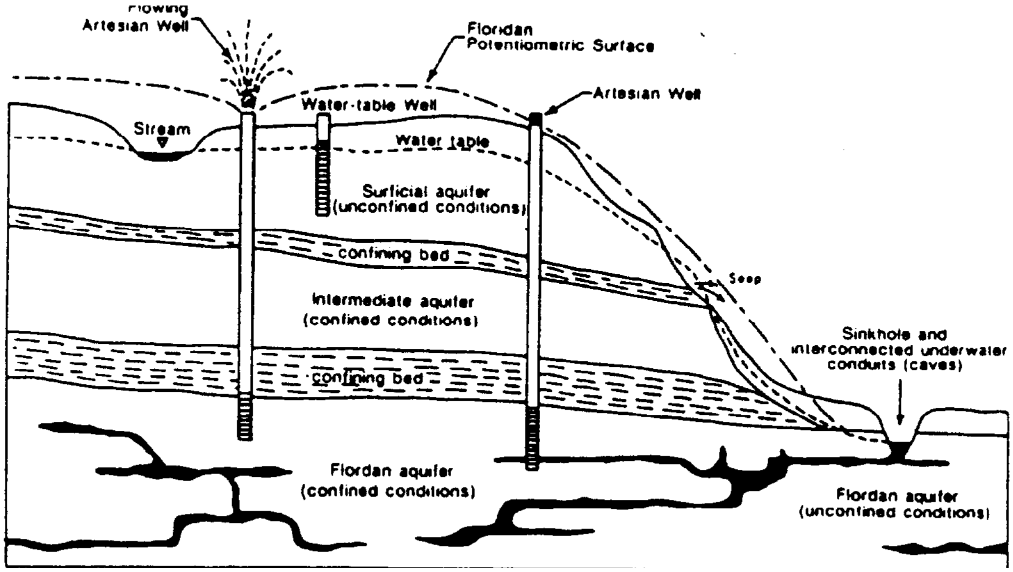

Figure 7-6. Idealized cross-section showing aquifers and confining beds of Florida.

The Floridan aquifer is underlain by a confining bed and is overlain, throughout most of the state, by the intermediate aquifer system (or intermediate confining unit). However, in some areas, the Floridan is found exposed at or near land surface (Figure 7-7).

In 1983, the Florida Legislature passed the Water Quality Assurance Act, a portion of which required the Department of Environmental Regulation to "establish a ground water quality monitoring network designed **to** detect or **predict** contamination of the state*s ground water resources" (Florida Statutes, Chapter 403.063). To facilitate this effort, the act requires that the Department work cooperatively with other federal and state agencies, including the five water management districts (Figure 7-8) and other government agencies in the establishment of the network.

The three basic goals of the Ground Water Quality Monitoring Program are:

- To establish the baseline water quality of major aquifer systems in the state.
- To detect and predict changes in ground-water quality resulting from the effects of various land use activities and potential sources of contamination.
- To disseminate water quality data to local governments and the public.

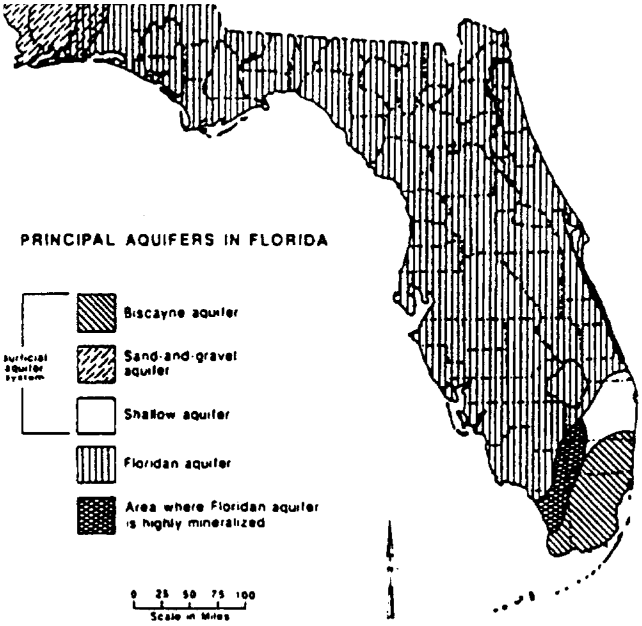

Figure 7-7. Principal aquifers within Florida.

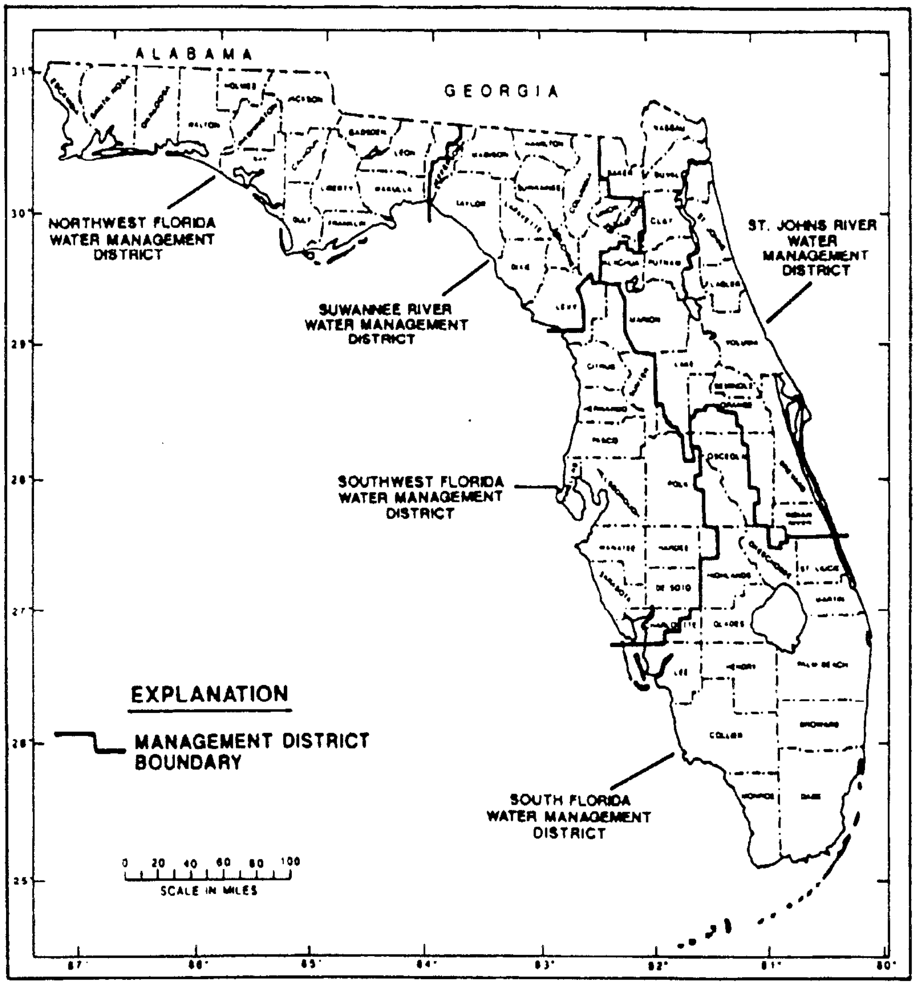

Figure 7-8. The five water management districts in Florida (from Leach, 1978).

OBJECTIVES

ORGANIZATION AND ESTABLISHMENT OF THE NETWORK

The Department of Environmental Regulations is the lead agency in the network determining goals and strategies, setting priorities and coordinating the effort. Contracts were developed with the five water management districts and other government agencies to carry out most of the necessary field work

The network consist of two major subnetworks and one survey, each of which has unique monitoring priorities and goals. These are:

- Background Network, designed to help define background water quality through a network of approximately 1700 wells that tap all major potable aquifers within the state.
- The Very Intense Study Area (VISA) Network, designed to monitor the effects of various land uses on ground-water quality within aquifers in selected areas.
- Private Well Survey, designed to analyze ground-water quality from 50 private drinking water wells in each of Florida*s 67 counties. This data will supplement the Background Network by providing additional sampling points, while indicating the general quality of water consumed by private well owners. This survey is a joint effort between the Florida Department of Health and Rehabilitative Services and the Department of Environmental Regulations.

BACKGROUND NETWORK

Before changes in ground-water quality can be detected, baseline water quality must be determined. The term baseline differs from background in that it refers to current regional groundwater quality. This may or may not be synonymous with background, or pristine, ground-water quality that existed before measurable human impact on the aquifer. A well in the Background Network is designed to monitor an area of the aquifer that is representative of the general ground-water quality of the region. It is not designed to be associated with degradation from contamination sources.

The first sampling of each well in the network involves the measurement of a comprehensive set of field, chemical, microbiological, and naturally occurring radioactive parameters (Table 7-l). These analyses, combined with historical data, can be used to estimate baseline ground-water quality. This process of establishing current baseline helps to delineate areas where ground-water quality has degraded. Once this baseline has been determined, data from future monitoring of the network will be continually evaluated to determine changes in water quality over time.

After the initial samples are collected and analyzed, background monitoring wells are periodically sampled for a small group of indicator parameters, in an attempt to detect the onset of degradation or contamination.

Among the indicator parameters selected, the analysis for VOCs is used as a way to detect the presence of organic chemicals in the samples. If a sample is found to contain significant concentrations of VOCS, further analyses for specific organic parameters arc conducted.

Development of the Background Network occurred in the following phases:

- Phase I: Data collection, compilation, and location of existing wells which could be incorporated into the network
- Phase II: Selection and drilling of initial monitoring wells.
- Phase III: Initial sampling of the Background Network to determine ground-water quality trends and define baseline.
- Phase IV: x of wells found to contain significant concentrations of one or more parameters.

TABLE 7-1. BACKGROUND NETWORK MONITORING PARAMETERS

Parameter	Standard Method [1,2]	Parameter	Standard Method [1,2]
	Major Ions		Field Measurements
Bicarbonate	406	Conductivity	205
Carbonate	406	pH	423
Chloride	407A, 407B, or 407D	Temperature	212
Cyanide	412B, 412C, or 412D		Microbiological
Fluoride	413A, 413B, 413C, or 413E	Fecal Coliform	908C or 909C
Nitrate	418C or 418F	Total Coliform	908A or 909A
Phosphate	424F or 424G		Organics
Sulfate	426 or 426C	Total Organic Carbon (TOC)	505
	Metals	Volatile Organic Compound (VOC)	EPA 602 and 602 or EPA 624
Arsenic	303E	*** If VOC is found to be significant, the well will be resampled. If high VOC is confirmed, a standard pesticide scan may be performed, along with analyses for any other suspected pesticides or volatile organics as determined by the Department of Environmental Regulations.	
Barium	303C		
Cadmium	303A or 303B		
Calcium	303A or 311C		Radiometric (if suspected)
Chromium	303A or 303B	Gross Alpha	703
Copper	303A	Gross Beta	703
Iron	303A or 315B		Other
Lead	303A or 303B	Total Dissolved Solids (TDS)	209B
Magnesium	303A or 319B		
Manganese	303A or 319B		
Mercury	303F		
Nickel	303A or 322B		
Potassium	303A or 322B		
Selenium	303E		
Silver	303A or 303B		
Sodium	303A or 325B		
Zinc	303a or 303B		

[1] Methods are from Standard Methods for the Examination of Water and Wastewater, 15th edition (American Public Health Association, 1980) or from the Florida Department of Environmental Regulation's Supplement "A" to Standard Operating Procedures and Quality Assurance Manual.

[2] Other approved methods with the same or better minimum detection limits, accuracy, and precision are also acceptable.

- Phase V: Refinement of the network through removal of redundant wells and affected wells and drilling of additional wells where needed.
- Phase VI: Ongoing periodic x to define variations in ground-water quality over time.

VISA NETWORK

The VISA Network monitors specific areas of the state that are believed to be highly susceptible to ground-water contamination, based on predominant land use and hydrogeology. A VISA well is designed to monitor the effects of multiple sources of contamination on water quality within a segment of the aquifer.

Development of the VISA Network is broken down into the following phases:

- Phase I: Evaluation of data to determine areas of predominant land use (Table 7-2).
- Phase II: Determination of relative susceptibility to contamination of each potable aquifer.
- Phase III: Determination of percentage use of each aquifer as a source of potable water.
- Phase Iv: Selection of VISAS based on above data.
- Phase V: Data collection, compilation, and selection of suitable existing wells within each VISA
- Phase VI: Drill additional wells as needed.
- Phase VII: Sample VISA wells.

Areas of predominant land use were located using the Florida Summary Mapping System, a microcomputer geographic information system developed at the University of Florida. The system contains land use data derived from ad valorem tax information for each of Florida*s 67 counties. This data has been summarized to each square mile section of the state based on the Public Land Survey System (section, township, and range).

Aquifer vulnerability was determined using DRASTIC, a mapping system developed jointly by the U.S. EPA and the National Water Well Association. DRASTIC is an acronym representing the seven hydrogeological parameters considered most indicative of relative pollution potential. These are:

D - Depth to water
R - Net recharge
A - Aquifer media
S - Soil media
T - Topography
I - Impact of the vadose zone
C - Hydraulic conductivity

Each of these parameters is mapped separately, and numerical scores are assigned to each map polygon. The seven parameter maps form overlays which are combined to create a composite DRASTIC aquifer vulnerability map. The score for each Polygon in each overlay is multiplied by a weighting factor, and the weighted scores are summed to produce a DRASTIC index for each polygon on the composite map. Higher scores indicate higher relative pollution potential. Statewide

TABLE 7-2. PREDOMINANT LAND USE CATEGORIES - VISA NETWORK

I. URBAN OR BUILT-UP LANDS

- A) *Urban Areas:*
  - Regional Shopping Centers
  - Multi-Story Office Buildings
  - Professional Services Buildings
  - Financial Institutions
  - Insurance Company Offices
  - Hospitals
- B) Suburban Areas:
  - Single Family
  - Mobile Homes
  - Multi-Family: 10 or more units
  - Condominiums
  - Cooperatives
  - Retirement Homes
  - Miscellaneous Residential
  - Multi-Family: 10 units or less
  - Hotels, Motels

II. INDUSTRIAL LANDS:

- C) Light Industrial Areas:
  - Repair Service Shops (excluding Automotive)
  - Light Manufacturing, Small Machine Shops, etc.
  - Fruit, Vegetable, & Meat Packing Plants
  - Canneries & Distilleries
  - Other Food Processing
- D) Heavy Industrial Areas:
  - Heavy Manufacturing
  - Lumber Yards, Sawmills, Planing Mills
  - Warehousing, Distribution Terminals
  - Open Storage, Junkyards
- E) Utility & Transportation Areas:
  - Airport, Maine Terminals, Piers, & Marinas
  - Service Stations
  - Automotive Repair
  - Race Tracks
  - Utilities: Gas, Electric, Railroads, Pipelines
  - Rights-of-Way: Roads, Irrigation Channels, etc.

III. AGRICULTURAL & SILVICULTURAL LANDS

- F) Cropland Agricultural Lands:
  - Improved Agriculture
  - Cropland Soil Capability Classes I-III
- G) Silvicultural Lands:
  - Timberland: Site Index 50-90 and above
  - Governmental Forests & Parks
- H) Grazing & Pasture Lands:
  - Grazing Land Soil Capability Classes I-VI
- I) Orchards, Groves, & Ornamental Horticulture:
  - Florist, Greenhouses
  - Orchards, Groves, Citrus
  - Ornamentals, Shrubs, Ferns, etc.
- J) Confined Feeding Operations:
  - Poultry, Apiaries, Tropical Fish, Rabbits, etc.
  - Dairies and Feed Lots

IV. OTHER LANDS

- K) Mining & Mineral Processing Lands:
  - Mineral Processing Plants
  - Mining & Petroleum Lands
  - Subsurface Rights
- L) Military Lands:
  - Military Reservations
- M) Wetlands:
  - Rivers, Lakes, Submerged Lands
- N) Wastelands:
  - Sewage Disposal, Solid Waste, Borrow Pits, etc.

• For a more complete explanation and listing of the above land use codes, see Miller et al. (1986).

DRASTIC mapping is scheduled to be completed in the summer of 1990, for the Surficial and Floridan aquifer systems. At that time, maps for each county will be published.

All wells in the VISA Network will be sampled for a standard list of parameters. Additional parameters which are not in the standard list, but are suspected to occur based on land use, also will be included. For example, in industrial areas, products used or produced by facilities within the VISA will be included in the parameters to be sampled. Likewise, in agricultural and urban areas, substances typically produced as byproducts of these land uses will be determined and monitored.

Data from VISA wells will be statistically compared to like parameters sampled from Background Network wells representing the same aquifer segment, to determine the effects of land use and site hydrogeology upon ground-water quality. By analyzing this data, reasonable predictions can be made on the effects of siting similar land uses in hydrogeologically similar areas of the state.

PRIVATE WELL SURVEY

The Florida Department of Health and Rehabilitative Services is conducting a survey of private drinking water systems to determine the general water quality of these wells. The two departments have entered into a cooperative agreement to select up to 70 wells per county (50 primary, 20 backup) for the study, using the same criteria developed to select existing Background and VISA wells. The Department of Health and Rehabilitative Services is sampling these wells for approximately 180 parameters and these analyses will supplement data generated by the Ground Water Quality Monitoring network

Automated Remote Monitoring System

To meet their monitoring requirements, several of the agencies have installed computerized automated remote monitoring and transmitting systems called Supervisor Control and Data Acquisition (SCADA) systems.

The SCADA system links a computer, located at a centralized site, to remote field monitoring and structure control stations using a two-way radio transmitter link.

The field monitoring stations measure hydrological data including ground-water level using floats with encoders, transducers, or sonic devices and selected water quality parameters using available sensors such as DO, electrical conductance, or pH.

The stations are also used to monitor hydrographic **data** such as reservoir and canal levels, inflow and outflow, and water control structures. Additionally, meteorologic parameters are measured including air temperature, wind-speed, wind-direction, evapotranspiration, rainfall, barometric pressure, and relative humidity.

These monitoring stations can be equipped with radio-transmitter/receiver terminals placed in remote locations and powered by solar cells. The remote radio terminals are capable of automatic event reporting. The data is generally recorded hourly and radio interrogated four-times daily. The system uses radio repeater stations to relay the data transmissions from the remote field sites to the central control center although data transmission can be accomplished using microwave, satellite systems, infrared telephone, meteor burst, or hardwire options. The data is stored and analyzed using a computer system equipped with data acquisition software at the control center (Figure 7-9). The two-way communication enables interactive data collection and structure control from the control center. Also, data access and control can be performed using remote computer terminals or fieldportable computers. The system allows personnel working in the field to use a portable computer and a cellular telephone to monitor and manipulate the communications network

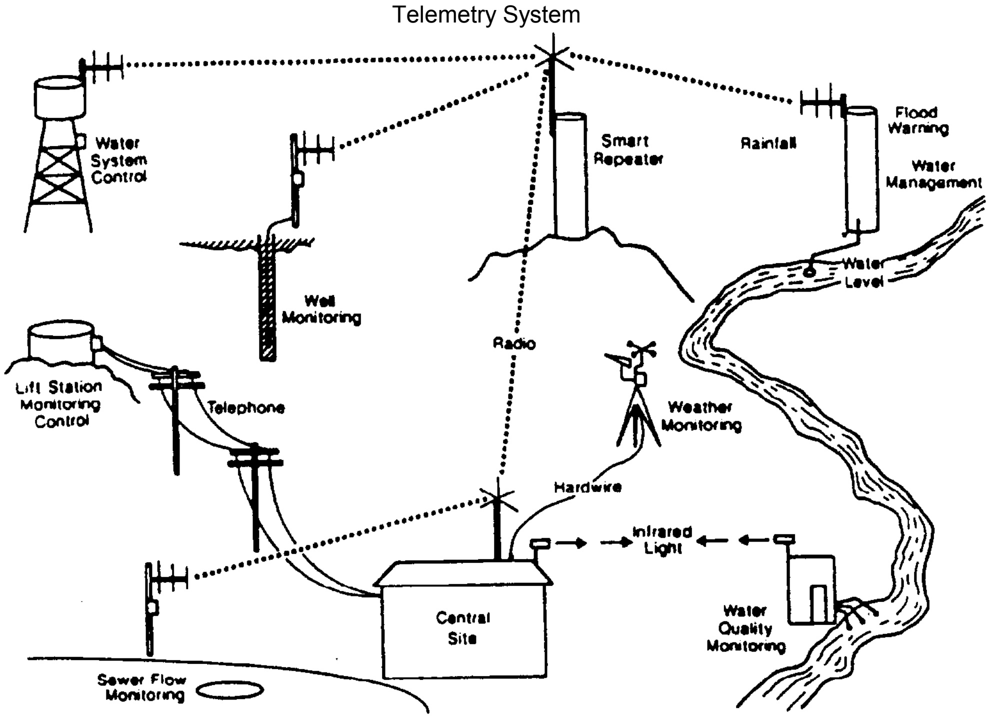

Figure 7-9. Schematic illustration showing generalized SCADA concepts (from Sierra-Misco, Inc.).

SUMMARY

The sampling frequency and chemical parameters to be monitored at each site are based on several factors, including Network well classification (Background, VISA, HRS), land use activity, hydrogeologic sensitivity of the site, and available funding. Wells near suspected sources of contamination will be sampled more frequently than wells in undeveloped or background areas.

Data generated by the Ground Water Quality Monitoring network will be statistically analyzed to:

- Establish baseline and background water quality. This will allow estimation of groundwater quality by aquifer anywhere in the state.
- Determine current ground-water quality statewide and predict future changes to it as a result of anthropogenic activities.
- Determine the degree of degradation of water quality in VISAS.
- Refine the network where needed to maximize information generated at a minimum cost.

The hydrogeological data collected through this monitoring program will be used to map in detail the extent and thickness of the major potable aquifers of Florida. Local mapping will be conducted to more thoroughly define individual water-bearing zones within each aquifer system. Additionally, water level data will be collected from each well. This information, along with similar data generated by other governmental agencies and the private sector, will be used to delineate physical ground-water divides. This will aid in determining the boundaries of ground-water basins.

When ground-water basins for each monitored aquifer have been determined, chemical data from the Network will be used to establish the baseline water quality of smaller aquifer segments within each basin. These chemically similar aquifer segments will be subdivided using statistical techniques. Definition of these aquifer segments will be based on concentrations of parameters present in the aquifer. Therefore, aquifer segments may differ in extent and thickness for each parameter or group of chemically related parameters tested. It is from these data that water quality maps will be produced for each sampled parameter.

Data generated by the Ground Water Quality Monitoring program will provide information for preparation of numerous water quality maps. It will also help with future land use planning, zoning decisions, and the development of more effective Local Government Comprehensive Plans. The raw data, screened for accuracy through various statistical analyses and field checking, is available to the public. Data from the network will help state and local governments evaluate the effects of land use and changes in ground-water quality through time. Information regarding this program may be obtained from:

Ground Water Quality Monitoring Program
Department of Environmental Regulations
Bureau of Drinking Water & Ground Water Resources
2600 Blair Stone Road
Tallahassee, Florida 32399-2400
Tel: (904) 488-3601