A review of Environmental Cone Penetration Probes

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Linköping in October 1996
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by

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June 1996
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Summary

This report presents the results of a literature study conducted by the Swedish Geotechnical Institute to identify environmental cone penetrometer (ECPT) probes being manufactured or developed world-wide.

The conventional practice of environmental site investigation and its inherent disadvantages has led to the development of ECPT probes. Overall characteristics of ECPT probes, their advantages, and limitations are presented in Chapter 1.

Chapter 2 explains the methodology of the research study which eventually contacted 32 sources to identify the 28 probes presented in the report.

A brief review of chemical compounds and transport principles for readers who do not have a background in the environmental engineering field is presented in Chapter 3. Factors affecting contaminant migration potential are also discussed.

The ECPT probes identified in the study are presented in Chapter 4. The measurement theory and compounds which could be detected or analyzed are presented preceding each class if applicable. Information specific to unique probes including specific measurement principles and capabilities, development status, and operational comments is also addressed in the chapter.

Chapter 5 gives an overview of the probe classes to aid the reader in identifying the ideal probe class for a specific environmental investigation. The general class properties include developmental availability, analysis capabilities, and general probe costs. Advantages and disadvantages of each probe class are also discussed.

Conclusions of the report are discussed in Chapter 6. A complete reference list including published and unpublished material is found in Chapter 7.
Chapter 1

Introduction

The field of cone penetrometer testing (CPT) for geotechnical site investigations is a well known and developed technology. Geotechnical cone penetration testing was developed to provide more detail of the subsurface stratigraphy at a lower cost compared to the conventional site investigation method of collecting soil samples and bringing them to the surface for identification and/or laboratory testing. Some soil parameters and their variation with depth may be estimated using geotechnical CPT, thereby avoiding costly continuous sampling and laboratory testing.

The conventional practice today for environmental sampling is to collect soil or ground water samples in the same manner as was done in geotechnical soil sampling before the development of geotechnical cone penetrometer testing. A standard drill rig is used to reach the sampling interval using such techniques as rotary drilling and augering, both of which are very time consuming. The sample is collected in a collection device and brought to the surface whereby it is placed into a sampling container. After shipment of the sample to the laboratory, the results are typically received after two to three weeks, however for some analyses the results may not be received until several months afterwards. In the case of ground water sampling, monitoring wells are usually used to collect water samples from discrete intervals. Therefore, several monitoring wells may be required to sample the full depth of the aquifer at each location. Each of the wells may need to be purged and developed prior to sampling.

There are many disadvantages associated with the conventional practice of environmental sampling. Overall, it is a costly, time consuming process which may still produce samples whose integrity has been compromised during the entire process. The high costs are due to the time consuming drilling method, the use of laboratories to perform the analyses, and the uncertainty inherent to the sampling method. This uncertainty is a function of the limited amount of data which is collected at the site and when the results are received in relation to other site activities. Continuous or small sampling intervals are prohibitively expensive and therefore there is uncertainty between the widely spaced sampling intervals. Also, the placement of monitoring wells, remediation equipment or the collection of additional samples may not be influenced by recently collected samples since the results of the analyses are not known until more than two weeks afterwards. The less information known during these activities causes them to be collected or placed in the wrong locations, or at the least, the decrease in information adds uncertainty to the project implementation and design, and ultimately higher costs. Additionally, costs may be higher because the conventional methods for the collection of soil and ground water samples generate soil cuttings and water which must be disposed. The fees for these disposal costs are usually very high.

The types of environmental site investigation analyses can be divided into two classifications: qualitative, and quantitative. Qualitative analyses are used to identify the presence of contaminants, but are not capable of identifying specific quantities. Certain types of qualitative data have the ability to identifying the presence of different
contaminates in a matrix of several contaminants, e.g. benzene. The second type of analysis, quantitative analysis, is capable of identifying not only the presence but also the quantity of a specific contaminant, e.g. 101.3 ug/L of benzene. Quantitative data is not required in the initial stages of most site investigations when the contaminant plume is being defined. Instead, qualitative data may be used in these cases and followed by the collection of more costly qualitative and quantitative data when more knowledge about the plume is required. Throughout the conventional process, there are many possibilities when the integrity of the sample may be compromised, including the sampling process and placement into shipping containers. Additionally, the integrity of the samples is unknown once they reach the laboratory which is typically a separate company and therefore direct control of the sample integrity is not possible.

In recent years, on-site analysis has become more common. The loss of sample integrity during shipping and off-site analysis is removed in this method, but the same costly, time consuming sampling method is typically used. In addition, this method is usually only able to produce qualitative data.

Due to the limitations of the conventional sampling method, environmental cone penetrometer (ECPT) probes and samplers have been developed to produce more cost effective and time oriented analyses. The development of these devices was based on the technology of geotechnical cone penetrometer testing probes, using the same probe diameters and push installation systems.

ECPT's may be divided into two groups: probes and samplers. ECPT probes generally perform the analysis in-situ and only require the probe to be brought to the surface after reaching the final testing depth in that borehole. On the other hand, ECPT samplers collect soil or ground water samples and are subsequently extracted to the surface in between sampling intervals to collect the samples for analysis. Similar to the conventional techniques, the samples are then placed in shipping containers and sent to the laboratory. The disadvantages of this method have already been presented. In-situ environmental analyses are never possible with ECPT samplers. Although these types of samplers may be more cost effective than installing permanent monitoring wells or use of larger diameter sampling equipment, they do not allow for continuous testing.

There are several common characteristics of ECPT probes, some of which have been previously mentioned:

- Most of the probes are attached above a conventional geotechnical CPT probe so that geotechnical parameters such as cone resistance, sleeve friction, and pore pressure can be measured concurrently. From these geotechnical parameters, other geotechnical and hydrogeological parameters are often computed including: relative density, deformation modulii, strength parameters (friction angle and undrained shear strength) and even liquefaction susceptibility. A complete discussion of geotechnical CPT testing and its evaluation may be found in Larsson, 1995 and Robertson and Campanella, 1988.

- The probes typically perform their analyses in-situ in the unsaturated and saturated zones.
The probe is not removed between measurement intervals.

The probes are typically installed at a rate of 2 cm/s.

The data is typically qualitative.

The data is transmitted to the surface by a cable which runs through the inside of the drilling rods. Some geotechnical CPT probes transmit data by vibrating the rods, negating the use of an awkward cable, but this technology has not been used for ECPT probes.

Some of the advantages of ECPT probes over the conventional sampling method have already been presented and include:

• More detailed vertical definition.

• Decreased time at each borehole because the probe is not removed between sampling interval.

• More exact depth determination than auger sampling in certain soils.

• No soil cuttings or water is generated during the installation of the probe, lessening exposure of workers to hazardous substances and negating costly disposal fees.

• Fewer costly laboratory analyses (typically used for calibration of probe).

• Concurrent collection of geotechnical cone data.

• Real time or instantaneous on-site results which can be immediately used for the placement of additional investigative probings or installation of monitoring wells or remediation equipment.

• Lower data collection costs allow for greater definition of the contaminant plume and a less conservative remediation design.

• Collection of environmental data in some difficult drilling conditions, e.g. running sands.

As with any investigative method, there are some limitations of ECPT probes:

• The probes may not be able to penetrate dense soil deposits such as gravels, dense sands, moraines, or fills or they may not be able to penetrate to great depths.

• Calibration of the probe may be required prior their use at each borehole, but is not needed between sampling intervals.

• Interpretation of the data requires an understanding of the soil stratigraphy since changes in density, material type, and saturation can affect the results. It is therefore recommended that geotechnical CPT data always be collected concurrently.
Because the data is typically qualitative, some regulatory agencies may be resistive to its use even for initial site investigations. This trend is changing though because of the realization that qualitative data can be used to gather more accurate quantitative data. Regulatory acceptance is also increasing because many ECPT probe developers are now submitting developmental test results to regulatory agencies during the design process to increase the prospect of acceptance. If the regulatory agencies are included in the design process, its acceptance is then much more likely.

No physical soil sample is produced.

The popularity of ECPT probes is steadily growing and therefore a research study has been conducted by the Swedish Geotechnical Institute (SGI) to identify ECPT probes being manufactured or developed world-wide. The results of this study are presented in this report including a review of some basic environmental principles for those readers who do not have a background in the environmental field. Additionally, the theory of each probe's analysis method is presented when applicable. It should be emphasized, that only ECPT probes and not ECPT samplers were identified in the study.
Chapter 2

Research Study Methodology

2.1 INTRODUCTION

The following chapter presents the methodology of the research study conducted over a four month period from February to May 1996. The research study was conducted in three phases which included:

• a review of literature sources,
• contact letters to research and developmental sources with more specific information requests, and
• receipt of information and additional contacts for more information.

2.2 METHODOLOGY

Literature sources were identified in two media: written and computer based. The written study began by reviewing two conference proceedings, "CPT'95", (1995) and "The Summary Report of the Workshop on Advancing Technology for Cone Penetration Testing For Geotechnical and Geoenvironmental Site Characterization", (Bowders and Daniel, 1994). These two sources contained a wealth of information on the subject of ECPT probes from which additional sources were identified. Additional written media were subsequently reviewed as the study progressed.

Throughout the study, the Internet was an excellent source of information, and the author would like to emphasize its use in subsequent investigations. Most of the initial written literature consulted contained only brief accounts of new probes being developed and seldom contained information which would allow the reader to contact these sources directly. Addresses, fax numbers, etc. of these sources could often be found on the internet through use of browsing software, e.g. Netscape® and Mosaic®. Much of this information has been placed on the Internet by research sources in the United States associated with governmental agencies. These agencies have embraced the Internet as a medium to publicize their research in summary articles, and in some cases, they also described additional sources to contact.

Contact letters were written to 32 of the sources identified as being connected with ECPT probe research or commercial development. The letters stated explained that a literature review was being conducted by SGI and asked the recipients to review an attached data survey containing detailed requests for information such as detection limits, accuracy, calibration techniques, etc.

Within the next four months, information was received from the contact sources, mostly those associated with development of probes. Follow-up contacts were made by telephone, email, and fax to encourage the contact sources to submit information to the study. In all, some type of contact was made with 28 or the 34 sources. Relevant information was received from 19 sources, and 7 sources were found to be not applicable
to the study. These 7 sources had either not yet developed their probes to the minimum requirement of initial field testing or no subsequent improvements had been made to their probes after problems during initial testing. No contact was ever made with the remaining 4 sources, whose information was deemed supplementary to the study prior to the initial contact or time constraints hastened contact.

Unfortunately, many sources did not provide detailed information regarding the capabilities of their probes. Developers were understandably hesitant to reveal specific product capabilities prior to having a manufactured product. Similarly, many of the manufacturers only provided sales brochures which were vague in the capabilities of the probes. Overall though, information received and utilized in this study included published and non published material, Sales brochures, letters, email, and verbal communications were considered unpublished material.
Chapter 3

Introduction to Chemical Compounds and Transport Principles

3.1 INTRODUCTION

A simple understanding of contaminate compounds and where they may be found is necessary before presenting the probes identified in the study. This chapter begins by presenting a brief review of the different types of contaminate and is followed by discussing different contaminate transport characteristics and phases they may be present in subsurface environments. This chapter is intended for the use of those readers who do not have a background in the environmental engineering field. Those readers who are familiar with this topic may skip to Chapter 4 where the probes are presented.

3.2 CHEMICAL COMPOUNDS

Several million compounds exist and have been divided into two main groups: organic and inorganic. Organic compounds are classically defined by the presence of carbon in their molecular structure, however there are some notable exceptions such as carbon dioxide, CO$_2$. Carbon is singled out because of the ability of carbon to form strong covalent bonds with one another. Some of the most common contaminates present in the subsurface are organic compounds and include:

• crude oil and petroleum products,
• poly-aromatic hydrocarbons (PAHs) (the majority of creosote),
• polychlorophenols including pentachlorinated phenols,
• many solvents including chlorinated aliphatics such as trichloroethene (TCE) and tetrachloroethylene (PCE), and
• pesticides.

All other substances which are not organic are considered inorganic substances and include metals and inorganic metal compounds, and inorganic salts. For a more complete discussion of the compound classification, the reader is encouraged to consult Petrucci (1985) or Schwarzenbach et al., (1993).

3.3 CONTAMINATE TRANSPORT AND PHASES

The subsurface stratigraphy is divided into two zones: saturated and unsaturated (see Figure 3.1). The saturated zone is located below the ground water table where the pores of the soil are saturated with water and the pore water pressure is greater than atmospheric. The unsaturated zone, or the aerated zone, is located above the ground water table and characteristically has a pore water pressure less than atmospheric, and is not fully saturated. The unsaturated zone is also divided into three zones (Figure 3.1): the capillary fringe, the intermediate zone, and the soil-water zone. The capillary fringe...
is located immediately above the ground water table. Depending on the soil type and relative density, water may be pulled into the pores of this layer by the effects of capillary tension between soil particles. The pores of the intermediate zone are filled with both air and water or may be described as an "incomplete saturation". The top layer, the soil-water zone, is directly affected by evaporation and precipitation. During periods of intense precipitation the soil pores may be completely saturated and conversely during dry periods they may be completely dry.

Figure 3.1. Division of Subsurface Stratigraphy. (Bear, 1979)

Physical and chemical properties of the contaminants affect their migration potential. These properties govern the behaviour in the unsaturated and saturated zones and include the:
- density,
- sorption coefficient for soils,
- solubility in water,
- solubility in various solvents,
- octanol-water partition coefficient, and
- volatilization from water and soil.

Some of the most important properties will be examined in more detail.

Density

The density of a substance is its mass per unit volume, and directly determines where the substance will be found in an environment. For example, compounds may either float or sink in water depending on their density relative to water (1.0 kg/l at 15.5°C); compounds having densities less than 1.0 kg/l float to the top of the liquid and those with densities greater than 1.0 kg/l sink. The same principle also holds true for compounds in the gaseous phase in a volume of air, e.g. an empty room. Many classes of compounds have similar densities which may facilitate or hinder their cleanup in aquifers. Petroleum compounds typically float on top of the ground water table due to their low density (<
1.0 kg/l) while chlorinated compounds usually sink to the bottom of the aquifer making their cleanup more difficult.

**Solubility in Water**

The *solubility in water* is a measure of the degree to which a contaminant will dissolve in water. It is a function of the temperature, the presence of dissolved salts and minerals in the water, and can also be affected by the presence of naturally occurring dissolved organic material (Baker and Herson, 1994). Those compounds with a high solubility in water will easily dissolve in water and are termed "aqueous-phase liquids" or APLs. Compounds having a low solubility in water include many organic liquids (e.g. most petroleum products, and chlorinated solvents) will remain in their pure product (free phase). Compounds which remain in their free phase are often termed "non-aqueous phase liquids" or NAPL's.

The density and solubility properties of many compounds are similar which has facilitated the description of their migratory behaviour. NAPL's which have a density less than that of the ground water will float on the top of the saturated zone, acting more or less as a continuous layer. These are termed "light non-aqueous phase liquids" or LNAPL's. Petroleum compounds are common LNAPL's. On the other hand, NAPL's which have a density greater than that of the ground water sink to the bottom of the aquifer until they encounter a barrier such as a clay layer. These type of compounds are termed "dense non-aqueous phase liquids" or DNAPL's and include chlorinated solvents and creosote. These terms will be used later in the report.

Contaminants may be present in many phases in both the unsaturated and saturated zones. Within the unsaturated zone where the pores space contains water and air, product may be in both the gaseous or liquid phases depending on the volatilization properties of the contaminant and the moisture content (Figure 3.2). Liquid product which is trapped between soil particles and exists in globular form is called ganglia and may exist in both the saturated and unsaturated zones. In the saturated zone, contaminates may be present in both the free and dissolved phases. They may also be present in an "intermediate" phase termed colloids. Colloids in liquids such as ground water may have atoms which are hydrophobic as well as hydrophilic and therefore they only partially dissolve. Mixed phases may even occur for contaminates which have a low solubility. They may dissolve during the migration of the contaminant, e.g. DNAPL sinking to the bottom of an aquifer, or by repeated contact with water (Figure 3.2).
Although the physical properties of a compound may be known, it may still be difficult to predict its exact location due to complicated transport processes and heterogeneous properties of the subsurface which can affect its movement. There are two main transportation forces which move the contaminant in the subsurface: the gravitational force and the capillary force. Processes such as ground water flow or gradient (shown in Figure 3.3) and lateral spreading of free product due to the weight of more product are due to the gravitational force. The properties of the subsurface which affect contaminant migration include: particle size, porosity, humic or organic content, moisture content, and stratigraphy. As mentioned earlier, the presence of low permeability layers may stop the downward flow of contaminants, e.g. DNAPL's. However, discontinuous layers or cracks in the layers may redirect the downward migration, see Figure 3.4.
Figure 3.4. Affect of low permeable layers on downward contaminate migration. (Testa and Winegardner, 1991).
Chapter 4

ECPT Probes

4.1 INTRODUCTION

The literature study identified 28 ECPT probes with differing measurement capabilities and principles, and differing stages of development. Common measurement principles and thus common contaminants detected was the first criteria for grouping followed by the development stages. Based on this methodology, the probes were placed into six groups of ECPT probes:

- Resistivity/Conductivity
- PRT
- Fluorescence
- Developing
- Hydrogeology, and
- Surface Analysis.

The following chapter presents the results of the literature study pertaining to each of the six probe classes. The measurement theory and compounds which may be detected are presented preceding each class if applicable. Information specific to unique probes including specific measurement principles and capabilities, development status, and operational comments will be addressed when presenting each probe in a probe class. After presenting each probe, the reference information used to formulate the description is shown. If more complete descriptions of the reference information is required, Chapter 7 should be consulted. Sales brochures and general communications are not specifically identified and are grouped with the reference for the commercial or developmental source. Probes are presented in each class by alphabetical order by owner.

Throughout the description of the ECPT probes, unless otherwise noted, the terms "geotechnical parameters" and "geotechnical cone" imply the combined measurement of tip resistance, sleeve friction, and pore pressure common to geotechnical cones.

4.2 RESISTIVITY/CONDUCTIVITY PROBES

Of all the probes identified, resistivity/conductivity (RC) probes have one of the simplest measurement principles. In addition, resistivity principles had been used in other fields for over 50 years and their transition to ECPT probes involved transferring the technology onto an ECPT probe. This section will present the:

- basics of resistivity/conductivity theory,
- applicable compounds for detection and/or measurement by RC probes,
- RC probes identified in the study.
4.2.1 Resistivity/Conductivity Theory

The conductance of a substance is a measure of its capacity in conducting or passing electrical current. The resistance is simply the inverse of the conductance or the capacity in not conducting electric current. The resistance of a soil may be determined by measuring the voltage drop between two electrodes at a constant current by Ohm's law or:

\[ R = \frac{E}{I} \]

4.1

where \( R \) is resistance of the conductor in ohms (\( \Omega \)), \( I \) is current in amperes (A), and \( E \) is voltage drop in volts, (V). The resistance however is not a unique material property of the soil, but instead is a function of the cross-sectional area and the length of the conducting material being measured. Computation of the resistivity (\( \rho \)) negates this influence by:

\[ \rho = \frac{(A/L) \cdot R}{\Omega \cdot m} \]

4.2

where \( A \) (m\(^2\)) is the cross sectional area of the electrical conducting material being measured and \( L \) (m) is the distance between electrodes that the electrical current must pass through. The resistivity is measured in units of \( \Omega \cdot m \).

If it is assumed that the conductance media is homogeneous and isotropic, then the quantity \( (A/L) \) in Equation 4.2 may be represented by a calibration constant, \( K \), determined for each different electrode spacing. Computation of the resistivity may then be performed by:

\[ \rho = K \cdot R \]

4.3

The conductivity, \( C \), is merely the reciprocal of the resistivity and may be presented in units of mS/m (1000+p). The calibration constant can be determined by submerging the probe in a temperature compensated buffer solution of known resistivity or conductivity.

The resistivity computed by Equation 4.3 is the bulk resistivity, \( \rho_b \) which includes the resistivity of the pore water and the soil particles. The bulk resistivity is dominated by the conduction through the pore water and therefore it may be used to provide a qualitative assessment of the relative ground water resistivity.

In order to compute the pore water resistivity from the bulk resistivity, a formula developed by Archie, 1942 called Archie's formula (Equation 4.4) may be used. In the formula, the bulk resistivity is assumed to be directly related to the pore water resistivity and the geometry of the pore spaces. A formation factor is used to relate soil resistivity, pore fluid resistivity, and pore geometry by:

\[ F = \frac{\rho_b}{\rho_f} = a \cdot n \cdot m \]

4.4

where \( F \) is the formation factor, \( \rho_b \) is the bulk resistivity (\( \Omega \cdot m \)), \( \rho_f \) is the fluid resistivity (\( \Omega \cdot m \)), \( a \) and \( m \) are constants for a given soil, and \( n \) is porosity of the soil. For
unconsolidated soils \( a \) is approximately 1 and \( m \) is dependent on soil type. For sands, \( m \) is approximately 1.5, and for clays Jackson et al., (1978) found \( m = 1.8 \) to 3. According to Jackson et al., (1978), \( m \) is only a function of the grain shape. Once the formation factor is computed, the fluid resistivity may be computed by:

\[
\rho_f = \frac{\rho}{F}
\]

It is recognized that Equation 4.4 is an oversimplification of the relationship between the bulk and pore fluid resistivities. However, it is still valid under the conditions that the pore fluid resistivity is relatively low and there is only a small quantity of clay minerals present in the soil which may affect the bulk resistivity through surface conduction. The bulk resistivity can be a function of other factors as well. Therefore, the measured formation factor is referred to as the apparent formation factor.

A typical resistivity/conductivity probe is shown in Figure 4.1. The bottom of the probe is occupied by a standard geotechnical CPT probe which measures the common geotechnical parameters: cone resistance, sleeve friction, and pore pressure. The resistivity/conductivity probe is threaded to the top of the geotechnical CPT probe and the push rods are attached to the top of the resistivity/conductivity probe. A known current is passed through two of the four metal electrodes located in the middle of the module which are separated by either plastic or ceramic insulators, hashed areas shown in Figure 4.1. The two "current" metal bands are termed the current and ground electrodes respectively. The voltage drop is then measured by the other two electrodes and the resistance may then be easily computed.

The distance between electrodes affects the measurement length interval, the depth, and the accuracy of the measurements. Greater spacing between electrodes increases the depth of the radius of measurement while providing an average reading over a larger length interval. Smaller spacing between electrodes provides greater definition of thinner layers of contrasting resistivity. However, greater definition is accompanied by a decrease in the radius depth of measurement. If the electrodes are spaced too close, material outside the zone of compaction, created during the installation of the probe, may not be measured. The compacted material may affect the measurements. According to Christy et al., (1995), the Schlumberger array, where the distance between the outer electrodes is much larger than the distance between the inner electrodes, is effective when soil contact with the probe is not ideal. Lastly, a layer is not fully registered unless it is completely within the electrode spacing.

![Figure 4.1 Typical resistivity/conductivity probe. (Campanella and Weemes, 1990).](image-url)
As previously mentioned, the most important mechanism of conduction is the transfer of a charge through pore water by electrolytic conduction, i.e. the physical movement of ions in response to the application of an electric field, (Campanella and Weemes, 1990). In general, the more ions present in the pore fluid the greater the conductivity and the lower the resistivity. Dissolved solids in the aqueous phase add ions to the pore water and hence increase the conductivity. Conversely, non-aqueous phase contaminants typically act as insulators of an electrical current and result in the opposite effect; lowering the conductivity and increasing the resistivity.

Changes in temperature affect the viscosity of pore fluids. The viscosity intern affects the conductivity of ions in an electrolyte, thereby affecting the conductivity/resistivity measurements.

The most noticeable contrast in resistivity measurements is seen between the saturated and unsaturated zones. Unsaturated soils produce much higher resistivities since there is less pore water to conduct the current. A typical resistivity sounding is shown in Figure 4.2. Pore pressure measurements indicate that the ground water table is at 1.3 m. Above this depth, resistivity measurements are greater than 125 Ω·m. However once the ground water table is encountered, conduction begins to take place in the pore water and the resistivity decreases dramatically. Measurements from this zone are also very jagged although not shown in Figure 4.2.

Figure 4.2 Effect of ground water table on measurement of uncontaminated soil. (Campanella and Weemes, 1990)
Between two identical soil types, the differences in porosity may effect readings, i.e. larger porosities will allow more pore water and hence a greater capacity of conductance.

Changes in material composition have a definite effect on resistivity results. For example, clay layers typically exhibit lower resistivities due to their ionic composition which conducts current better.

Campanella and Weemes (1990) state that another important factor is the resistivity of the pore water, especially in the saturated zone. Surface conduction between soil particles becomes negligible when there is a low resistivity in the pore liquid, i.e. the electrolyte conduction chooses the path of least resistance through the pore water. An example shown in Figure 4.3 illustrates this fact. Surprisingly, the clayey silt layer at 11.8 m does not provide a considerable resistivity contrast with the sand bounding this layer. This is due to the fact that a much greater proportion of conduction in both soils takes place through the low resistivity pore water. The reverse effect holds true in cases where the pore water resistivity is high.

![Figure 4.3 Effect of pore water resistivity, (Campanella and Weemes, 1990)](image-url)
4.2.2 Applicable Compounds and Factors Affecting Measurements

RC probes can detect both organic and inorganic compounds in saturated and unsaturated zones if these compounds increase or decrease the resistivity (or conductivity) of the soil pore water. Examples of contaminants commonly detected by RC probes and their effects on resistivity and conductivity readings are shown in Table 4.1. The author would like to emphasize that Table 4.1 is by no means a complete listing of all substances which will affect the resistivity/conductivity of the pore water enough for their detection.

Table 4.1: Examples of Substances Detected by RC Probes

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Effect on Resistivity</th>
<th>Effect on Conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>inorganic salts</td>
<td>decrease</td>
<td>increase</td>
</tr>
<tr>
<td>acids</td>
<td>decrease</td>
<td>increase</td>
</tr>
<tr>
<td>bases</td>
<td>increase</td>
<td>decrease</td>
</tr>
<tr>
<td>petroleum hydrocarbons</td>
<td>increase</td>
<td>decrease</td>
</tr>
<tr>
<td>creosote</td>
<td>increase</td>
<td>decrease</td>
</tr>
</tbody>
</table>

A common identification technique is to measure the resistivity/conductivity versus depth in areas known to be free of contamination and compare these to measurements taken in contaminated areas. Concurrent collection of geotechnical parameters also allows identification of changes in soil type, density, and moisture content which may affect the readings as discussed in Section 4.2.1.

Several papers have been published regarding RC testing for various substances. Kokan (1990) reports on the successful delineation of a PAH substance. The detection of creosote contamination, a petroleum hydrocarbon, in saturated soils is described by Okoye et al., (1995). Mapping (or detection) of inorganic salts composed of sodium and calcium chlorides is reported by Tonks et al. (1993). Free phase petroleum hydrocarbon products, consisting primarily of aviation jet fuels, were detected with reasonable success by Strutynsky et al, (1991).

An example of the delineation of salt water infiltration by a RC probe is described by Campanella and Weemes (1990) and is shown in Figure 4.4. Three probings each separated by 50 m in a line perpendicular to the bank of a river are shown in the figure. The probing location closest to the river is shown to the left. A salt water infiltration situation exists which is complicated by seasonal fluctuations in the flow of the river which affect the ground water salinity near the river. Conditions of increased salinity decrease the resistivity (or increase the conductivity) of the pore water which is clearly shown in Figure 4.4 where a contour of 6 Ω·m has been drawn. Areas of salt water infiltration are indicated below the contour line. The resistivity readings decrease as the river is approached indicating that salt water infiltration is occurring. Below a depth of 11.0 m there is very little difference between resistivities of the three probings which indicates that there is very little ground water movement below this depth otherwise salt water infiltration would be evident.
It should be noted that insulating (highly resistive) contaminants normally must be in very high concentrations, e.g. free product in oil, for accurate detection in the unsaturated zone. Because background resistivity readings are normally high in the unsaturated zone, changes in the resistivity readings may not easily be detected. On the other hand, it is possible that conductive compounds may be detected at lower concentrations because they generate a higher contrast from the background resistivity readings.

According to Campanella and Weemes (1990), insulating contaminants which increase the resistivity may be detected when they are found in concentrations of 20,000 to 50,000 mg/l. They also stated that "the lower bound is more than adequate for the detection of dense NAPLs that pool on low-permeability layers". The range of 20,000 to 50,000 mg/l may be applicable to DNAPLs found in the saturated zone, however as stated above, the author feels that this range may not always be applicable in the unsaturated zone.

Some RC probes also measure moisture content by measuring the dielectric content, $K_d$, and computing the moisture content using Topp's equation, Topp et al., (1980). The dielectric constant is a proportionality constant related to the effect that the medium separating two charged objects has on the electromagnetic force existing between them. Measurements are made based on the significant contrast between the dielectric constants of soil ($K_s$ of dry soil is between 3 and 7) and fresh water ($K_s = 80.4$). According to Topp et al., (1980), dielectric constants are only weakly dependent on soil
type, soil density, soil temperature, and pore water conductivity. However, Knowlton et al., (1995) reports that "in reality, the relationship between actual and predicted moisture content has some uncertainty and does vary with soil type".

4.2.3 Resistivity/Conductivity Probes (RC Probes)

Seven RC probes were identified during the literature study and are shown in Table 4.2. All seven are either manufactured or can be contracted for hire. The measurement principle of each probe appears to be based on the theory presented in Section 4.2.1. The purchase prices range between 30 000 to 50 000 SEK based on information received from 4 of the 7 companies. Probes which measure the moisture content are also noted in Table 4.2.

RC probes allow the user to determine if an area is contaminated or not. They do not allow for the qualitative identification if more than one compound is present nor do they allow for quantitative measurement.

<table>
<thead>
<tr>
<th>Probe Name</th>
<th>Owner</th>
<th>Moisture</th>
</tr>
</thead>
<tbody>
<tr>
<td>The Conductivity Cone</td>
<td>A.P.vd. Berg</td>
<td>No</td>
</tr>
<tr>
<td>Soil Moisture/Resistivity Module</td>
<td>Applied Research Associates</td>
<td>Yes</td>
</tr>
<tr>
<td>HIM-Probe</td>
<td>Delft Geotechnics</td>
<td>Yes</td>
</tr>
<tr>
<td>S15-CFIE, Conductivity Cone</td>
<td>GeoMil Equipment B.V.</td>
<td>No</td>
</tr>
<tr>
<td>S15-CFIM, Soil Moisture/Resistivity</td>
<td>GeoMil Equipment B.V.</td>
<td>Yes</td>
</tr>
<tr>
<td>Soil Conductivity Probe</td>
<td>Geoprobe® Systems</td>
<td>No</td>
</tr>
<tr>
<td>Resistivity Probe</td>
<td>Hogentogler</td>
<td>No</td>
</tr>
</tbody>
</table>

The Conductivity Cone - A.P.vd. Berg

The Conductivity Cone computes the resistivity/conductivity by using the same 2 electrodes for the induction of the current and measurement of the voltage drop. The item is sold as a module and may be connected to the top of a "standard tip-friction cone", either 10 or 15 cm² in area. The manufacturer states that the cone is "usually pushed in saturated zones to get reliable results", however "in vadose zones the measurements could show aberrants".

Reference information: sales brochure and communications.


The SMR module measures resistivity/conductivity as well as soil moisture content. RC measurements appear to be made by the use of 2 electrodes on a module which is attached to the top of a geotechnical cone. The array operates at a frequency of 30-40 cycles per second (Hz) during resistivity measurements. The measurement of the dielectric constants for moisture content computation is performed through another two electrodes through which a 100 MHz excitation frequency is passed. According to
ARA, the SMR module is capable of measuring volumetric soil moisture contents between 0-100 % water. A software algorithm is used to compute the moisture contents by applying Topp's equation to the dielectric constant measurements. Calibration for moisture content measurement is performed in the field using predetermined mixtures of water and air.

Reference information: sales brochures

HIM-Probe - Delft Geotechnics

The HIM (High frequency Impedance Measuring probe) utilizes a different body design than the other RC probes to measure the electrical conductivity and soil moisture content of soils. The probe is pushed to the measurement depth in the closed position shown in Figure 4.5a. At measurement depth, the cone tip is unlocked and the outer casing of the probe is pushed downward. The entire probe assembly is then pushed downward and the soil sample comes into contact with a probe extending from the retracted tip, (Figure 4.5b). High frequency electromagnetic pulses, between 10-500 MHz, are applied to the sample volume which has entered the casing. The electrical conductivity and dielectric constant are measured and subsequently the moisture content can be computed. According to Olie (1996a), the accuracy of the electrical conductivity and dielectric constant can be measured to an accuracy of 5%. After measurement, the cone tip is retracted to the closed position, thereby removing the sample and cleaning the interior parts of the sample cup. The process is repeated at deeper probing depths. It is not possible to measure geotechnical parameters with this probe. A probe for the continuous measurement of electrical conductivity and dielectric constant is being developed.

Reference information: Olie and Viergever (1995) and communication with Olie (1996a).

Conductivity and Soil Moisture/Resistivity Cones - GeoMil Equipment B.V.

There are two probes sold by GeoMil which may be used for RC measurements: the S15-CFIE Conductivity Cone and the S15-CFIM Soil Moisture/Resistivity Cone. The probe casing of both cones appear to be identical and both probes have two electrodes. The differences are in the internal "sensors" used by the probes. According to communication with Pluimgraaff (1996), the cone may be used for the direct measurement of water content if a 100 MHz sensor is used although he reports that the conductivity is of less accuracy. If conductivity measurement is the more important parameter to the investigation then a three frequency sensor (10, 20, and 30 MHz) is used for direct conductivity measurements. Pluimgraaff reports that "the water content is computed from the obtained permittivity by using algorithms in combination with the friction ratio". The Soil Moisture Cone is also equipped with a temperature sensor which may be used to compensate soil moisture or conductivity readings, however the Conductivity Cone does not appear to include a temperature sensor.

Reference information: Sales brochures and communication with Pluimgraaff (1996).
Figure 4.5: HIM Probe, a) Closed position, b) Measurement position. (Olie and Viergever, 1995)

Soil Conductivity Probe - Geoprobe® Systems

Geoprobe® Systems manufactures soil probe equipment which is installed by a hydraulically driven percussion probing machine, typically attached to the rear of a truck or van. Percussion is applied to the top of the probing rods at a frequency of approximately 30 Hz. The probes are advanced at a variable rate depending on the strength of the soils and the friction of the rods, and typical rates vary from 0.6 to 7.6 meters per minute. No information has been found concerning a standard or recommended advancement rate.

The Soil Conductivity Probe has 4 electrodes which may be operated in either the Schlumberger or dipole arrays described in Section 4.2.1. Windows-based software for conductivity logging is available as well as a device for testing the electrical integrity (isolation and continuity) prior to use at each probing location. Vertical resolution is 0.02 m. No geotechnical parameters may be measured with the probe. Geoprobe® Systems sales literature markets their probe as a tool to classify soil types (e.g. clays usually exhibit higher resistivities than sands). However, it has been demonstrated at the Savannah River Demonstration Site in the United States and has been used for environmental applications in Europe.

Reference information: Sales brochures, and Internet.
Resistivity Probe - Hogentogler

The commercially available Hogentogler resistivity probe operates in a Schlumberger array and may be attached to the top of a geotechnical cone which includes the possibility of probe inclination measurements. Software for the plotting of conductivity measurements may also be purchased. SGI will be conducting laboratory and field testing using a Hogentogler Resistivity Probe.

Reference information: Communications and Laboratory testing

4.3 pH, REDOX AND TEMPERATURE PROBES (PRT PROBES)

The common measurement of three parameters: pH, redox potential, and temperature were used to define the PRT probes. No special measurement theory will be given for this probe class since most of the probes appear to utilize common commercially available sensors. Definitions of these three parameters and why their measurement is important will be presented in this section followed by a description of each probe.

4.3.1 Measurement Parameters

The pH, redox potential, and temperature are all important parameters in many aspects of the environmental field. Often, all three of the parameters are required for work in the following areas of concern:
- detection of leaching wastes,
- monitoring and selection of in-situ bioremediation,
- prediction of compound dissolution,
- differentiation between drilling fluids and acidic wastes,
- determination of contaminate reaction rates, and
- detection of dissolved metals and salts.

pH

The classical definition of pH is that it is the negative logarithmic of the hydrogen-ion concentration in a solution or -log [H⁺]. In real terms, it is a measure of the acidity of a solution, the lower the pH, the greater the acidity. A pH of 7.0 at 25°C denotes a solution which is equally acidic and basic.

Redox Potential

In addition to the hydrogen ion concentration, the direction, rate, and end products of organic and inorganic reactions are determined by the movement of electrons. The tendency of a substance to donate or accept electrons is given by its electron potential or redox potential, (Eₚ). Values of Eₚ have units of volts and can be measured between a reference junction and an inert platinum interface. In ground water, there are numerous reactions occurring simultaneously so the determination of the redox potential provides an indication of the amount of electron donors which may be present in a system.
Ideally, redox potential measurements should be corrected to a standard pH and therefore the measurement pH should be determined concurrently.

**Temperature**

Measurement of the temperature is important for many applications including the prediction and monitoring of in-situ chemical and biological reactions and the temperature dependent correction of other data such as resistivity/conductivity, pH, and redox potential measurements.

### 4.3.2 PRT Probes

Five PRT probes were identified during the literature study and are shown in Table 4.3. Unlike the RC probes, all the PRT probes are not fully developed for purchase. The developmental status of the PRT probes is also shown in Table 4.3. The material composition of the sensors relates to their durability. Some probes use glass sensors which may not be very durable although some owners are now beginning to incorporate more durable sensors. Based on information from 2 of the companies, the price range to purchase the probes is approximately 35 000 to 50 000 SEK.

Each of the probes allows the user to quantitatively determine the measured parameters, and in the case of site investigations, these values may then be used as indicators to identify areas of contamination versus non-contamination. If the effect of the contaminants on the parameters is known, PRT probes allow for the qualitative vertical and horizontal delineation of the contaminants.

<table>
<thead>
<tr>
<th>Probe Name</th>
<th>Company</th>
<th>Developmental Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Envirocone®</td>
<td>A.P.vd. Berg</td>
<td>Manufactured</td>
</tr>
<tr>
<td>ORP/pH Probe</td>
<td>Applied Research Associates</td>
<td>Manufactured</td>
</tr>
<tr>
<td>Alkatemp</td>
<td>Applied Research Associates</td>
<td>Manufactured</td>
</tr>
<tr>
<td>Chemoprobe</td>
<td>Delft Geotechnics</td>
<td>Manufactured with additional developed</td>
</tr>
</tbody>
</table>

**Envirocone® - A.P.vd. Berg**

The commercially available, Envirocone® measures the pH, redox potential and temperature. A.P.vd Berg recommends that the cone only be used in the saturated zone and that "in the vadoze zone, measurements could show aberrants" (communication from Duyfjes, 1996). Buffer fluids are used to calibrate the cone every two tests and it is recommended that the cone be decontaminated with distilled water or a special solvent after every test. An adapter should be available soon to connect the cone to a standard geotechnical cone. It may also be possible to include the measurement of electrical conductivity in the cone. The penetration rate is 2 cm/s although it is recommended that the penetration be stopped regularly for more accurate readings.
The Envirocone® was reviewed by the Public Works Department Rotterdam, (communication from Duyfjes 1996), who made several recommendations including that the cone always be used with a pore water pressure sensor to definitively identify testing in the saturated zone. The report also concluded that:

- "measurements with the Envirocone® show a definitive picture as a function of depth for pH as well as for potential redox. The results are consistent with theoretical expectations",
- "values read directly while the cone is forced into the ground are not stable, but move slowly to a constant final value (dissipation)", and
- "stable results at a fixed depth were found after 450-1100 seconds (7-20 minutes)"

The report also stated that this long period is dependent upon the researched matrix, a dredged soil.

Reference information: Sales brochures and communication from Duyfjes, 1996.

BioProbe - Applied Research Associates and GeoMil Equipment B.V.

The BioProbe will allow for the measurement of pH, redox potential, and temperature when it is available in August or September of 1996. The probe is manufactured by ARA and will be sold in Europe by GeoMil under the name Bioprobe, S15-CFIPO.

Initial specifications indicate that the probe could be used with a geotechnical cone including inclination measurements, however, pore pressure measurements may not be possible.

Reference information: Sales brochures (GeoMil) and communications (ARA).

ORP/pH Probe - Applied Research Associates

Three measurement electrodes are located on the surface of the ORP/pH Probe for the determination of the pH, redox potential, and temperature in the capillary fringe and saturated zones. Redox potential and pH measurements are compensated for changes in temperature. A geotechnical cone may also be used concurrently. According to ARA, "measurements of pH have been observed to be exceptionally high in soils with a low plasticity" due to "a polarization of ions occurring when soil smears on the face of the probe". Further testing to correct this effect is being conducted.

Reference information: ARA research brochure

Alkatemp Probe - Applied Research Associates

The commercially available Alkatemp Probe is the only of the PRT probes which does not measure redox potential, although the probe does still measure the pH and temperature. It is capable of measuring pH between 2 and 10 to an accuracy of 0.25 pH units, and readings are corrected due to temperature variations. The module is attached directly to the top of a standard geotechnical cone.

Reference information: Sales brochures
Delft Geotechnics has developed the Chemoprobe for the detection of pH, redox potential, temperature, and electrical conductivity. The pH, redox potential, and electrical conductivity sensors are located in the interior of the probe and therefore the pore water must be brought to the sensors which differs from the other four PRT probes. During installation of the probe, the Chemoprobe is flushed by pressurized nitrogen gas from a cylinder. At the required depth, the gas pressure is reduced to the atmospheric pressure so that the ground water fills the probe. The inflow is detected by a pressure transducer which measures the increasing water head inside the probe. The rate of increase may be used as a rough indication of the hydraulic conductivity of the soil environment and the ground water filter through which the ground water sample passes. According to Olie et al., (1992), measurement readings typically reach steady values after one minute, and the measurements are considered valid if they are stable for 3 minutes. After each measurement interval, the probe is pressurized again by nitrogen gas to drive out the ground water.

Decontamination of the probe is conducted immediately after driving out the ground water and is done using demineralized water which is pushed from the surface through the probe filter and into the surrounding soil. Proper functioning and cleaning of the equipment are evaluated during the rinsing of the probe by monitoring changes in temperature, pressure, electrical conductivity and pH. Once the rinsing is completed, the nitrogen gas pressure is applied, and the probe may be driven to a new measurement interval. Olie et al., (1992), recommends a minimum of 0.5 m between intervals to assure geochemically undisturbed conditions since the introduction of the distilled water may affect the pH and electrical conductivity readings.

The Envirocone may be hired or purchased from Delft Geotechnics, but it is considered a productive prototype because the development of the probe is still in progress. No geotechnical parameters may be measured with the probe although the developer claims that the tip load can be computed from the trust needed to keep the penetration rate constant.


4.4 FLUORESCENCE PROBES

The introduction of fluorescence probes is an exciting development in ECPT technology which may lead to the quantitative detection of specific contaminants. Similar to other ECPT technologies, fluorescence technology was developed for other applications before being applied in the probe apparatus. This section will present an introduction to fluorescence theory, applicable contaminants for detection or measurement, factors which may affect the measurement results, and a presentation of the probes identified in the study.
4.4.1 Fluorescence Theory

Fluorescence is phenomena whereby substances emit light when subjected to an excitation source. This excitation source is usually a light source; either visible, ultraviolet (UV), or infrared light. When certain molecules are subjected to excitation sources of known wavelengths, the molecules absorb a photon and are excited to a higher energy level, Figure 4.6. This unstable, excited state cannot be maintained indefinitely so the molecule reverts to the lower energy level by emitting a photon. This emission is known as fluorescence and takes place at a specific wavelength depending on the fluoresced molecule.

Fluorescence Principle

The excitation light source may be located either on the ground surface or in the probe itself. In the case of surface sources, lasers are used whose light is transmitted to the probe by a fiber-optic cable. A typical laser induced fluorescence (LIF) probe is shown in Figure 4.7. The light may be refocused by optics located in the probe and is then redirected out the side of the probe by other optics or mirrors. A sapphire window is often used to shine the light through into the surrounding soil. Once the compounds are fluoresced, the emitted light shines back through the window and is collected by another fiber-optic cable which then transmits the emitted light to the surface. There, it is spectrally analyzed by an analogue system for intensity at either a single or a range of emitted wavelengths, e.g. 300 to 500 nanometer (nm). Probes which have light sources in the cone, typically a bulb, also analyze the emitted light at the surface and therefore also utilize: a window to pass light to and from the surrounding soil, a fiber-optic cable for the transmission of the emitted light, and an analogue system for spectral analysis.
It is important for the reader to note the distinction between the excitation and emission light sources because both of these are measured in wavelengths which may be confusing. For example, the excitation wavelength may be at 337 nm, but the emission wavelength being monitored by the spectral analyzer may be 400 nm because the contaminant of interest emits at this wavelength. Other key points of fluorescence include:

- There is an optimum excitation wavelength for each compound which will induce fluorescence. Wavelengths surrounding this optimum wavelength will induce fluorescence but usually to a much lesser degree.
- Of those excitation wavelengths which do cause some form of fluorescence, only one emission wavelength is generated which depends on the molecular make-up of the fluoresced compound.

Fluorescence results may be presented in many different forms depending on the type of excitation light source and the spectral analysis performed on the emitted light. A typical presentation format is the spectral intensity vs. depth which is monitored at a single emission wavelength as shown in Figure 4.8. In this case, the semi-quantitative magnitude of contamination, e.g. high vs. medium vs. low, may often be interpreted and at the very least areas of suspected contamination may be identified. For optimum results, the optimum excitation wavelength and the emission wavelength of the
contaminate of interest should be known prior to testing. Another presentation style is the fluorescence spectrum, shown in Figure 4.9, where a range of emitted wavelengths are monitored at a specific depth instead of only one wavelength in the former method. A fluorescence spectrum allows the wavelength of peak intensity to be determined which may allow "fingerprinting" or qualitative identification of contaminates. In Figure 4.9, three different contaminates are identified by their three different peak intensities measured at the three different depths. Other presentation styles, unique to the probes, will be discussed when presenting the probes in Section 4.4.3.

![Fluorescence Spectrum Diagram](image)

Figure 4.8: Fluorescence intensity vs. depth presentation format, (Jacobs et al., 1995).

There may be some concern about cross contamination of Fluorescence probes between probing intervals caused by smearing of the window on the side of the probe when sampling in "stickier"-compounds such as coal tars. According to Delft Geotechnics (1996), the probe window is cleaned during installation by the adjacent soil, thereby negating the need for decontamination between intervals. They do recommend that an effective minimum cleaning depth be considered for cleaning. However, the author knows of no data concerning the efficiency of removing "stickier" compounds which may be more resistant to removal and may continue to fluoresce at lower depths where no contamination is present. The effects of these compounds should be investigated further.
Fluorescence probes may displace the layer of a LNAPL-water interface which could affect the measurement results. According to communications with Olie (1996a and b), the probe "punches a hole in a plastic layer" (Figure 4.10) and may lower the depth of the LNAPL layer to be observed at a slightly lower elevation during fluorescence readings.

Figure 4.10: Disturbance of LNAPL-water interface during installation of a fluorescence probe. (Van Ree and Olie, 1993).
4.4.2 Applicable Compounds and Factors Affecting Measurements

Fluorescence probes allow for the detection of many petroleum hydrocarbon products and PAH compounds which fluoresce. These products are typically detected as a free phase and may be present in either the saturated or unsaturated zones. Common petroleum hydrocarbons capable of detection (depending on the excitation wavelength) include: ethylbenzene, toluene, xylene, naphthalene, gasolines, JP 4 and 5 jet fuels, diesel fuels, and tar wastes. Correlations between total class identifiers, e.g. TPH (total petroleum hydrocarbons), and fluorescence measurements have also been made for TPH, volatile petroleum hydrocarbons (VPH), and total BTEX.

As previously mentioned, the detection of compounds by fluorescence methods is dependent upon the molecular make-up of the compounds, the excitation wavelength of the light source, and the emitted spectral wavelengths being monitored. According to Lieberman et al. (1992), "longer emission wavelengths may be explained, in general, by changes in composition (i.e. number or aromatic rings) for the polycyclic aromatic hydrocarbons (PAHs) in different fuel products". In tests conducted by Lieberman et al. (1992) using a 337 nm excitation wavelength, jet fuel (JP5) whose PAH composition is limited primarily to two-ring aromatic hydrocarbons (naphthalene and naphthalene derivatives) exhibited a peak fluorescence intensity at approximately 403 nm. Diesel fuel marine (DFM) which contains two, three and some four ring PAHs showed a higher peak fluorescence intensity at approximately 417 nm. Burner oil, which is the heaviest compound tested, showed the longest wavelength emission. Similar trends, but with different excitation wavelengths, were reported by Jacobs et al. (1995). Emissions in the 260 to 300 nm range indicated single-ring aromatics such as the BTEX compounds. Emissions in the 300 to 350 nm range indicated two-ring aromatics such as a naphthalene and larger polycyclic aromatic hydrocarbons fluoresced at wavelengths longer than 350 nm.

The capability of Fluorescence probes for field screening is illustrated by an example shown in Figure 4.11 from ARA (1994). Three pushes were performed transecting a contaminate plume which was being remediated with air sparging wells located at the areas of highest contamination. The first push, Figure 4.11a, was expected to be in a clean area. However there was a slight increase in the fluorescent intensity near 8 feet. Subsequent confirmatory soil sampling taken adjacent to the push location showed a TPH concentration of 200 ppm. The second push location, Figure 4.11b, was located closer to the center of the plume and correspondingly the intensity and vertical delineation increased. A 12 foot deep air sparging well was placed at a location identified as previously having the highest level of hydrocarbon contamination. Use of the fluorescence probe at this location, Figure 4.11c, shows that the air sparging system had been effective in generating bioremediation at lower depths.

The in-situ fluorescence response of hydrocarbons to laser light sources is sensitive to variations in soil matrix including soil surface area, soil grain size, mineralogy, and moisture content. Each of these factors affects the relative amount of analyte that is adsorbed on or absorbed into the soil because only that part of the contaminate that is optically accessible at the window of the probe can contribute to the emitted fluorescence. Of the four factors listed, the dominant variable appears to be soil surface area (Apitz et al. 1992a). Sensitivity of LIF probes in detecting petroleum hydrocarbons
on soil has been shown to be inversely proportional to the available surface area of the soil substrate, (Apitz et al., 1992b). Sandy soils typically have a much lower total available surface area than clayey soils. Therefore hydrocarbon compounds in sandy soils generally yield a higher fluorescence intensity than they do in clayey soils. The moisture content of the soil matrix is also an influential factor. Higher soil moisture content generally increases the sensitivity of LIF probe measurements on petroleum hydrocarbons. However in some natural soils, the effect appears to be small, (USEPA, 1995a). The sensitivity of LIF measurements is also affected by soil grain size. The LIF sensitivity generally increases with increased grain size as reported by Apitz et al, (1992a) where the measured fluorescence was shown to be substantially greater in coarser soils.

![Graph](image_url)

**Figure 4.11:** Example of field screening capabilities of Fluorescence probes - fluorescent intensity vs. depth. a) Area thought to be clean, b) Near the center of the plume, c) Location of remediation by air sparging. (ARA, 1994)

It is important to remember that the UV excitation light may cause other substances besides hydrocarbons to fluoresce. The inability to discriminate between hydrocarbon fluorescence and non hydrocarbon fluorescence may lead to false positives for the detection of hydrocarbons. Non hydrocarbons may also mask the presence of hydrocarbon fluorescence, thereby leading reduced sensitivity or even worse, they may lead to false negatives for the detection of hydrocarbons. These non hydrocarbon substances may be man-made as well as naturally occurring. Man-made substances which are known to fluoresce strongly include: de-icing agents, antifreeze additives, and many detergent products. Naturally occurring substances include humus which is found in the organic component of soils. Humus is a residual of plant decay and often contains small amounts of fluorescent PAHs. However in at least one study conducted for one of
the LIF probes presented in this section, (Davey et al., 1994), the presence of humics did
not interfere with the detection of hydrocarbons in soils. The cause of this effect may be
because humic fluorescence is minimal at concentrations found in even the most organic­
rich soil, (USEPA, 1995a). The potential for the presence of non hydrocarbon
substances should always be considered when assessing the field screening data.
Spectral analysis of the emitted wavelength may allow for the detection of non
hydrocarbon fluorescent compounds since they usually have distinctive spectral shapes.

The qualitative and semi-quantitative measurements of contaminants is probe
dependent and will be addressed separately for each of the Fluorescence probes. Overall
though, qualitative identification of some compounds is possible and certainly
contaminated versus non contaminated areas may be identified. In most instances,
quantitative analysis is more accurately semi-quantitative since typically only levels of
contamination, e.g. high, medium, and low, can be accurately identified. However, for
initial site investigations this type of data is applicable.

There has been some evidence that the emission intensity, or number of photons
emitted, may be linearly proportional to analyte concentration at low concentrations as
shown in Figure 4.12 from laboratory tests conducted by ARA (1994). This principle
however does not appear to apply to all fluorescence compounds and requires that
calibrations of fluorescence intensity to analyte concentration be performed prior to
interpreting the results in this manner. If more defined, this type of analysis technique
may be useful in quantitating emitted substances.

![Figure 4.12: Laboratory fluorescent response for diesel fuel mixed with sand showing
linear relationship between fluorescence intensity and concentration. (ARA, 1994)](image)

4.4.3 Fluorescence Probes

Four Fluorescence probes were identified during the research study, utilizing both the
surface laser (LIF) and in-probe light sources discussed in Section 4.4.1. The probes,
developers, light sources, light source locations, and the excitation wavelengths are
shown in Table 4.4. All the probes may either be purchased or contracted for hire
depending on the developer.
The purchase price of Fluorescence probes is quite high, between 0.14 and 1.75 million SEK with the LIF probes being toward the higher prices in this range. Due to the high cost at least one of the probes may be hired at a daily rate which is still much more cost-effective than conventional soil sampling.

<table>
<thead>
<tr>
<th>Probe</th>
<th>Developer</th>
<th>Light Source</th>
<th>Light Source Location</th>
<th>Excitation Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FFD</td>
<td>Applied Research Associates</td>
<td>Mercury Bulb</td>
<td>Probe</td>
<td>254</td>
</tr>
<tr>
<td>Hydrocarbon Probe</td>
<td>Delft Geotechnics</td>
<td>Bulb</td>
<td>Probe</td>
<td>250</td>
</tr>
<tr>
<td>ROST™ Loral/Lockheed Martin</td>
<td>Tunable-Dye Laser</td>
<td>Surface</td>
<td>266 or 280 to 300</td>
<td></td>
</tr>
<tr>
<td>SCAPS-LIF</td>
<td>U.S. Navy RD Division</td>
<td>Laser</td>
<td>Surface</td>
<td>337</td>
</tr>
</tbody>
</table>

**FFD - Applied Research Associates**

The FFD (Fuel Fluorescence Detector) probe is commercially available from ARA and utilizes a 254 nm mercury vapor lamp which is located in the probe. The probe is driven at a rate of 2 cm/s. BTEX and Jet Fuels values have been measured using the FFD, but the probe appears to be mainly targeted toward the identification of gross contamination, or "field screening", through the identification of index parameters such as TPH.

Semi-quantitative analysis may be possible with the FFD probe. ARA recommends that a grab sample be collected prior to use of the probe in order to correlate fluorescent intensity readings to concentration levels. According to ARA, the probe has been used to detect TPH values as low as 80 parts per million (ppm or 80 mg/kg) in sands. Other contaminate levels may then be determined due to the linear correlation of fluorescence intensity to hydrocarbon contamination previously discussed in Section 4.4.2. This linearity may be site-specific and therefore should be determined at each site.

According to communication with Babineau (1996a), ARA feels that a low excitation wavelength of 254 nm is advantageous because there is less chance for "backhitting" during emission measurements. Backhitting is a term used to describe when the excitation wavelength is reflected back onto the window and is picked up by emission fiber-optic cable which is also monitoring at a similar wavelength. Since most compounds emit fluorescence at wavelengths greater than 254 nm, there is less chance for emission monitoring at that wavelength and hence less chance for backhitting.

Three-dimensional statistical models have been prepared by ARA on site by incorporating the data from the FFD probe in real-time. This data acquisition system may also be purchased from ARA. A standard geotechnical cone is also used with the FFD system.

Reference information: Sales brochure, communications including Babineau (1996).
The Hydrocarbon Probe - Delft Geotechnics

The second fluorescence probe having a light source located in the probe is the Hydrocarbon Probe, commercially available from Delft Geotechnics (Delft). The UV excitation lamp emits at a wavelength of 250 nm and fluorescent emissions are typically monitored at 390 nm. According to Delft, aromatics alone do not emit fluorescence at 390 nm, however, polycyclic aromatics (PCAs) found in many petroleum products do fluoresce at this wavelength and therefore they may be detected by the Hydrocarbon Probe. These compounds in the free phase located in both the saturated and unsaturated zones include: gasoline, diesel fuel, motor oil, coal tars. Peat does not appear to affect the measurements of the probe.

If calibrations are performed prior to use, Delft suggests that some quantitative analyses may be performed. These calibrations may be performed in one of two ways. Either soil samples may be collected subsequent to probings to quantify the measured fluorescent intensities or non-fluorescent solvents are used to make diluted samples of the products expected to be encountered. These samples are then measured by the Hydrocarbon Probe and curves of fluorescent intensity vs. dilution can then be prepared to predict in situ contaminant levels based on in situ fluorescent measurements. In one study to construct dilution curves for three petroleum products, Olie and Sellmeijer (1995), detection limits as low as 13 mg/kg dry weight for domestic fuel, 130 mg/kg for leaded gasoline, and 250 mg/kg for fufural-containing motor oil were measured. Upper signal saturation limits were also determined of 3,000 mg/kg, 16,000 mg/kg, and 30,000 mg/kg respectively. Delft has reported that normal detection limits are 50 mg/kg for "light NAPLs".

According to communications with Delft (1996), a minimum of 6 cm of penetration is recommended to consider the probe window cleaned by the adjacent soil. The type of contaminant or soil type to which this recommendation is applicable is not known by the author.

Of the geotechnical parameters, only the tip resistance may be measured with the Hydrocarbon Probe.

Reference information: Olie and Viergever (1995) and Olie and Sellmeijer (1995), sales brochures, and communications

ROST - Loral

The Rapid Optical Screening Tool (ROST™), developed by Loral, is an LIF probe which can be operated in the saturated and unsaturated zones. The surface mounted UV laser is different than the other three fluorescent probe because it can be operated over several excitation wavelength bands, either at 266 nm or between 280 to 300 nm. The chosen emission monitoring wavelength depends on the suspected contaminant and the mode of operation. The ROST™ system uses a Nd:YAG laser to produce a light at 532 nm at a frequency of 50 Hz. A dye laser and tuning mirror are then used to convert the fixed wavelength light of the Nd:YAG laser into wavelengths that can be optimized for the contaminant(s) of interest, hence the name "tunable-dye laser". The repetition of the
laser rate may be selected and the fluorescence responses to a prescribed number of laser pulses are averaged together. In several tests using the ROST™ system, the averaging of 50 pulses at a penetration rate between 1.5 and 2.5 cm/s yielded a spatial resolution of approximately 2 cm. The probe has been used in several cold weather applications, below -7°C, where it requires more time to warm the equipment up.

The probe may be operated in two modes, either statically or dynamically. In the dynamic mode, the probe monitors one emission wavelength and presents the data in the fluorescence vs. depth format discussed in Section 4.4.1. Due to the averaging of fluorescence responses, the results are actually the average fluorescence vs. depth. A probe which can simultaneously monitor four emission wavelengths is under development. When areas of significant contamination are encountered or when attaching more push rods, the probe may be operated in the static mode to produce 3-dimensional data representations, called wavelength-time-matrices (WTM). A WTM represents a plot of relative fluorescence intensity versus the length of time of fluorescence emission versus wavelength. Example WTMs are shown in Figure 4.13 for four common petroleum compounds. Generation of a WTM can allow for the semi-qualitative identification of compounds, similar to fingerprinting discussed in Section 4.4.1, and also their degree of weathering. The WTMs shown in Figure 4.13 exhibit differences in their wavelength contours which allow their identification. The WTMs shown are all for unweathered compounds and weathering is known to affect their shape. However in some cases, the delineation of weathered and unweathered product may be important, and a WTM collected on a site with only one fluorescent contaminant should show these states well.

Figure 4.13: Wavelength-time-matrices generated by the ROST™ probe. (USEPA, 1995b)
During WTM acquisition, either the excitation or fluorescence emission wavelength can be varied. Normally though, the excitation wavelength is held constant and the emission monitoring wavelength is varied. Similar to the static mode, the data from between 100 to 200 laser pulses are averaged at each of a series of return emission wavelengths separated by 10 nm, between 500 to 300 nm (Figure 4.13). The acquisition time for a WTM is reported to take about 5 minutes longer than the average time to add a push rod.

Prior to probing, the ROST™ probe is calibrated to a standardized reference solution. All data gathered is then reported as a percentage of the reference solution intensity. The operation of the system is also checked when using the reference solution and the data is normalized for variations in laser power, background noise, and other factors. The standardized reference solution was chosen since its fluorescent emission included the wavelength range of commonly occurring petroleum, oil and lubricants (POLs).

There are several papers and publications describing either case histories and evaluations of the ROST™ probe. The investigation of a site contaminated with diesel fuel was reported by Jacobs et al. (1995) along with ROST™ probing recommendations. In another paper by Jacobs et al. (1996), the determination of different levels and types of aromatic hydrocarbons was described. Soil sampling was conducted to calibrate fluorescence intensity readings to levels of BTEX and TPH contamination with promising quantitative results. Three different types of hydrocarbons were also identified using WTM. The most comprehensive known evaluation of the ROST™ system was conducted by the United States Environmental Protection Agency (USEPA) in 1994 as part of a technology demonstration program, (USEPA, 1995b). Data produced by the ROST™ system was qualitatively and quantitatively compared to data generated from conventional soil sampling and laboratory analysis. Overall, the demonstration found that the ROST™ technology produced "screening level data". The qualitative assessment showed that the "stratigraphic and chemical cross sections were comparable to the reference (conventional) methods". The quantitative assessment showed that during the 1994 demonstration, the ROST™ system "could not be used as a reliable predictor of actual contaminant concentration". According to comments made by Loral in the same report, improvements to the ROST™ system have been made.

The ROST™ probe can only be contracted for hire from several companies licensed by Loral including Fugro and Hogentogler. For future reference, Loral may soon change its name to Lockheed Martin who has recently acquired the company.


SCAPS-LIF - U.S. Navy RD Division

Three branches of the United States military teamed up to develop the Site Characterization and Analysis Penetrometer System or (SCAPS) to develop more effective site investigation techniques. As part of SCAPS an LIF probe (SCAPS-LIF) was developed for the detection of PAHs included in many common petroleum, oil and lubricants (POLs) both in the saturated and unsaturated zones. The probe uses a
nitrogen based laser to produce an excitation wavelength of 337 nm at a rate of 10 Hz.
The general hardware of the probe is similar to the ROSTT system in many respects, i.e.
sapphire window, fiber-optic cables, however, it does not produce WTM's like the ROST
system. The sapphire window is coated with an anti-reflective material to reduce 337 nm
backhitting light from entering the emission fiber-optic cable. Two personal computers
are required during operations, one for data acquisition and the other for post-acquisition
processing. Three dimensional plots may also be prepared with SCAPS software.

The SCAPS-LIF probe is normally used to collect data at a fixed, site-specific
wavelength and is presented in the fluorescence vs. depth format. It may however be
used to monitor a range of emission frequencies between 300 to 800 nm (Figure 4.9)
although it is usually not used in this manner. Monitoring a range of emission
frequencies may allow for the fingerprinting of contaminants based on the wavelengths of
peak emission. According to communication with Lieberman (1996a), the 337 nm
excitation wavelength will easily cause heavier fuels, e.g. diesel, to fluoresce, but it may
have difficulties causing fluorescence of lighter 2-ring compounds such as naphthalene.

There is a great deal of published material regarding the development and validation
of the SCAPS-LIF probe. A ten site validation study of the probe quantitatively and
qualitatively compared results directly with conventional laboratory based chemical
analyses for TPH and Total Recoverable Petroleum Hydrocarbons (TRPH) (Lieberman
et al., 1995a). The quantitative study compared the two methods on a "detect/non
detect" basis for 219 samples. Overall, the probe agreed with the conventional analytical
TRPH analyses 83% of the time and with TPH analyses 84% of the time. By
comparison, two laboratory analyses on splits of the same sample agreed with each other
using the same criteria 93% of the time. The qualitative analysis concluded that the
SCAPS-LIF probe could be used to identify the presence of more than one product as a
function of various depths. The fluorescence emissions over the spectral region of 350
to 720 nm. were recorded at various depths and then overlayed on top of each other to
look for the presence of different peak fluorescence intensities as shown in Figure 4.9.
The same method could also be used in the horizontal delineation of a product across a
site. The SCAPS-LIF probe was evaluated by the USEPA in same type of technology
demonstration program that was described for the ROSTT probe, (USEPA, 1995c). The
demonstration reached similar conclusions about the SCAPS-LIF probe, that the probe
produced "screening level data" and that a qualitative assessment showed that the
"stratigraphic and chemical cross sections were comparable to the reference
(conventional) methods". The quantitative assessment found that the SCAPS-LIF data
was "most closely correlated to the total petroleum hydrocarbons and volatile petroleum
hydrocarbons data".

The SCAPS-LIF probe is commercially available although the majority of probes
produced so far appear to have been for U.S. governmental agencies. An operations
manual has been produced for the SCAPS system by the Waterways Experiment Station
(WES).

Reference information: USEPA (1995c), Lieberman et al., (1995a), compilation of
papers received from Lieberman (1996) and communications including Lieberman
(1996a).
4.5 DEVELOPING PROBES

Developing probes represent the next generation of environmental probes which are currently being developed. In most cases, the probes have at least begun field testing. The seven probes include five different measurement principles and most of the probes are targeted to the identification of a specific classes of compounds, e.g. metals and chlorinated aliphatics. Because there are so many different measurement principles in this category, the measurement principle and targeted compounds for detection of each probe will be reported when describing each probe. The seven probes in the developing class are shown in Table 4.5 along with their measurement principle and targeted class of compounds.

Table 4.5: Developing Probes

<table>
<thead>
<tr>
<th>Probe</th>
<th>Developer</th>
<th>Measurement Principle</th>
<th>Target Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>VOC/SVOC Probe</td>
<td>Argonne National Laboratory</td>
<td>Unknown</td>
<td>VOCs and SVOCs</td>
</tr>
<tr>
<td>Raman-CPT Probe</td>
<td>EIC &amp; ARA</td>
<td>Raman spectroscopy</td>
<td>LNAPLs &amp; DNAPLs</td>
</tr>
<tr>
<td>In-Situ Sense</td>
<td>Geotech and FCI</td>
<td>Coated Sensor</td>
<td>TPH</td>
</tr>
<tr>
<td>LIBS Probe</td>
<td>NRaD</td>
<td>Laser induced breakdown spectroscopy</td>
<td>Metals</td>
</tr>
<tr>
<td>LIBS Probe</td>
<td>SAE</td>
<td>Laser induced breakdown spectroscopy</td>
<td>Metals</td>
</tr>
<tr>
<td>RCL Monitor</td>
<td>Transducer Research</td>
<td>Solid State Chemical Sensor</td>
<td>Chlorinated Compounds</td>
</tr>
<tr>
<td>Fiberoptic Raman</td>
<td>WES and NRaD</td>
<td>Raman spectroscopy</td>
<td>LNAPLs &amp; DNAPLs</td>
</tr>
</tbody>
</table>

VOC/SVOC Probe - Argonne National Laboratory

Argonne National Laboratory is being funded by the US Department of Energy (DOE) to developing a method, to be incorporated into an ECPT probe, for the near-real-time analysis of VOCs and SVOCs. The initial field test at the Savannah River Site, conducted in the Spring of 1996, identified a number of problems which have required some modifications to the probe. No information is known about the measurement principle of this probe.

Reference Information: Communications.

Raman-CPT Probe - EIC and Applied Research Associates

Raman spectroscopy is the measurement of the wavelength and intensity of scattered light from molecules. When electromagnetic radiation passes through matter, most of the radiation continues in its original direction but a small fraction is scattered in other directions. Light that is scattered due to molecular vibrations in molecules or optical
phonons in solids is called raman scattering. Raman scattered light occurs at wavelengths that are shifted by as much as 4000 cm\(^{-1}\) from the incident light. Similar to fluorescence measurements, a laser is used as a common light source. The scattered light may be very difficult to detect in some conditions and therefore improved detection equipment is a key focus of the technology development. Raman spectroscopy allows for the detection of LNAPLs and DNAPLs such as TCE and PCE which are common solvents and are found in many contaminated aquifers.

EIC Laboratories, Inc. has been developing a raman spectroscopy system and has been working with ARA to incorporate the system in an ECPT. The probe which may also measure geotechnical parameters has been used in several field evaluations including the Savannah River Site (SRS) in the United States where many new ECPT technologies have been demonstrated. It appears that this generation of raman technology will certainly offer qualitative and semi-quantitative determination. To date minimum detection concentrations for inorganic salts in aqueous solution and organic compounds in carbon tetrachloride have been in the range of 50-500 ppm and benzene is easily detected at near-saturation levels (approx. 1000 ppm). EIC is currently planning to conduct additional field testing for more evaluation of the probe.


In-Situ Sense System Probe - Geotech and FCI

The In-Situ Sense System probe being developed by Geotech Environmental Equipment, Inc. (Geotech) appears to incorporate a TPH sensor commercially available from FCI Environmental, Inc. (FCI). The fiber-optic tip of the sensor has a special coating that absorbs specific compounds. These coatings change the amount of light that can be refracted and are then able to determine the contaminant and amount in the saturated and vadose zones. If only one product is known to be present at a site, the sensor allows for quantitative measurement in the mid-ppb range for the BTEX compounds and also measures TCE and PCE to the low ppm range. According to Butler (1996), the TPH Coated Sensor Probe was being "field scale tested" in April 1996 and may be available by the summer of 1996. Geotechnical parameters may be measured with the probe.

Reference information: Butler (1996), communications with Geotech (concerning development of probe) and FCI (concerning capabilities of the sensor).

Laser Induced Breakdown Spectroscopy Probe- NRaD

Laser induced breakdown spectroscopy (LIBS) may be the first in-situ method to detect metals. The technology uses a high powered pulsed laser which is focused on a small spot and generates a high power density. In this region, the high power density results in the rapid heating, volatilization, and ionization of a small amount of material. Thus a laser induced plasma is formed which emits light that is collected, dispersed and analyzed to provide information about the plasma's elemental constituents. Similar to LIF probes, the LIBS technology uses a surface laser, fiber-optic cables for excitation transportation and emission measurement, and wavelength analysis equipment.
An LIBS probe is currently being developed by the United States Navy, Naval Command, Control and Ocean Surveillance Center (NRaD). A feasibility study was conducted to decide if LIBS was applicable to use in cone penetrometer probes. In this study, lead (Pb) was used as a representative metal sample in the laboratory tests with different concentrations of Pb mixed into sand. As shown in Figure 4.14, the Pb emission line at 405.78 is clearly discernible and emission intensity is proportional to the differing Pb concentrations which may eventually lead to the possibility of quantitative analysis. Another promising result was that the LIBS sensor was found to have a detection limit in the very low ppm range for Pb. Further testing is being conducted by NRaD to determine matrix effects of moisture on reduction of the laser power density. A prototype probe has been tested twice and another test is planned within the next several months, Lieberman (1996b).

Reference information: Lieberman et al, (1995b), Lieberman (1996b), and communications

![Figure 4.14: LIBS spectra of various concentrations of Pb on sand showing clear emission at 405.78 nm and emission intensity as a function of contamination. Data is background corrected. (Lieberman et al., 1995b).](image)

**Laser Induced Breakdown Spectroscopy Probe - Science and Engineering Associates, Inc.**

Another LIBS probe was recently identified and is being developed by Science and Engineering Associates, Inc. (SAE) for the U.S. Department of Energy. Saggese and Greenwell (1995) describe a feasibility evaluation study in which a LIB sensor was utilized to measure differing Pb concentrations. Similar results as those described for the NRaD probe were found except a higher detection limit range of 10-40 ppm for Pb was measured. It appears that SAE is currently proceeding further to design and evaluate an
optical fiber probe, however no direct contact with the company has been made to substantiate this.

Reference information: Saggese and Greenwell (1995)

**RCL Sensor - Transducer Research**

Transducer Research has developed the RCL sensor which may be used for the identification of chlorinated aliphatic compounds such as TCE, PCE, and vinyl chloride (VC). A hand held instrument, incorporating the RCL sensor, has been developed and is reported in Buttner et al. (1995). The sensor may only be used to detect vapors, and therefore samples taken below the ground water table will require separation. Chlorinated aliphatic compound levels have been determined between 0.2 and 500 ppm in gas within 90 seconds using the hand held instrument. Specific details of the sensor technology have not been released. According to a communication with Buttner (1996) a "highly successful demonstration" of the RCL sensor operating in a cone penetrometer (RCL Probe) was conducted in early 1996. During the demonstration, the RCL Probe was used at depths up to 36 meters and preliminary test results indicate that the probe provided at least semi-quantitative analysis results. There is some evidence that the RCL sensor can not be used to distinguish between different chlorinated aliphatic compounds. A paper describing the RCL probe field testing will be published in late 1996.


**Fiberoptic Raman - NRaD and Waterways Experiments Station (WES)**

A raman spectroscopy probe, the Fiberoptic Raman probe, has been co-operatively developed by the NRaD and the U.S. Army Waterways Experiments Station (WES). The probe appears to operate under the same measurement theory as the Raman-CPT probe. However, according to Lieberman (1996b), the measurements with the Fiberoptic Raman probe have produced poor sensitivity, almost requiring saturated compound for detection.

Reference information: research brochure and conversation with Lieberman (1996b).

### 4.6 HYDROGEOLOGY PROBES

Hydrogeology probes are a special class designation for probes which do not detect or measure the presence of contaminants, but instead allow for the determination of geohydrological and geotechnical parameters. Often, these parameters are important in designing remediation systems and predicting off-site boundaries or movement of contaminant plumes. Only one ECPT probe was considered to be a Hydrogeology probe during the study and is described below.

**In Situ Permeability (ISP) Probe - Delft Geotechnics**

The In Situ Permeability (ISP) Probe, commercially available from Delft Geotechnics allows for the in-situ determination of hydraulic conductivity and may be a cost effective
alternative to other hydraulic conductivity testing techniques such as pump testing. The ISP Probe computes the hydraulic conductivity by injecting water from the probe into the aquifer at a constant rate, shown in Figure 4.15. The pressure changes induced by the water are measured at two locations on the probe by piezo pressure transducers and are then used to compute the hydraulic conductivities in the range of $10^{-3}$ to $10^{-6}$ m/s. Vertical resolutions of less than one meter are possible. According to communications with Olie (1996a), the probe is not applicable for measurements in clays although it is not known why. The probe is not equipped with geotechnical parameters, however the piezo pressure transducers can be used to compute pore pressures. Validations of the ISP Probe compared to pump tests have been performed and a paper describing them will be forthcoming from Delft.

Reference information: Visser et al. (1993) and communications with Olie (1996).

![Figure 4.15: In Situ Permeability Probe. (Visser et al., 1993)](image)

4.7 SURFACE ANALYSIS PROBES

ECPT probes are defined as generally performing their analyses in-situ and the exception to this definition are Surface Analysis probes. As the name implies, this class of probes collects a water or gas sample at a probing interval carries it to the surface where the measurement analysis is subsequently performed. The analysis may be conducted on-site or may be sent to a laboratory however the advantage of real time data collection is lost in the former case. Either option though, still allows for quicker drilling time as compared to conventional sampling techniques because the probe is not removed between probing intervals. Another advantage of Surface Analysis probes, which may be applicable on sites where quantitative analysis is required at all probing locations and depths, is that conventional analysis methods, which typically have a higher degree of accuracy, are used with Surface Analysis probes. Other surface analysis devices, such as the BAT probe, were not investigated in the study because they are not based on the
technology of geotechnical cone penetrometer testing probes, e.g. using the same probe diameters.

Three Surface Analysis probes were identified during the study and are described in this section. The probes differ in the analysis possibilities and the method of bringing the sample to the surface. Two of the probes may be purchased or may be contracted for hire while the third probe is still being developed. The probes, developers, carrier methods which are dependent upon the desired sample, and the availability status are shown in Table 4.6. The capital cost for two of the probes is estimated to be between 70 000 and 700 000 SEK depending on the complexity of the sample extraction method.

<table>
<thead>
<tr>
<th>Probe</th>
<th>Developer</th>
<th>Sample: Carrier Method</th>
<th>Availability Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>ConeSipper®</td>
<td>Applied Research Associates</td>
<td>Water: gas</td>
<td>Commercial</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Gas: vacuum</td>
<td></td>
</tr>
<tr>
<td>Envirocone®</td>
<td>ISMES</td>
<td>Water: pump in probe</td>
<td>Contract hire, possible commercial</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Gas: vacuum</td>
<td></td>
</tr>
<tr>
<td>Thermal Desorption VOC Sampler</td>
<td>WES</td>
<td>Water: gas</td>
<td>Development</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Gas: vacuum</td>
<td></td>
</tr>
</tbody>
</table>

ConeSipper® - Applied Research Associates (ARA)

According to ARA, gas (vapor) and water samples may be analyzed at the surface by use of the commercially available ConeSipper®. Samples are collected in an 80 ml stainless steel sampling chamber located in a module which is attached to the top of a geotechnical cone. Water samples are drawn into the chamber under hydrostatic force (or a slight vacuum) through a one-way check valve which prevents back flow of water into the chamber. Once the chamber is full, inert gas pressure is applied down a tube from the surface and the water is forced to the surface. A check valve in the sample line prevents back flow into the chamber and therefore multiple samples may be collected without air entering the sample line. Gas samples are typically collected by applying a vacuum from the surface through the sample line, according to communication with Babineau (1996c).

In between sampling intervals, the chamber and sample line if required, are backflushed with water or gas for decontamination. The sample line is then closed and the pressure is increased to open a second check valve which allows clean water or gas to be flushed through the filter. The probe may then be pushed to the next sampling interval, although the recommended sampling interval to avoid contamination from previous backflushings was not described.

A two-stage stainless steel filter is used to filter out soil particles. The primary filter located on the outside of the probe keeps sand from entering the cone. A secondary filter behind the primary filter removes fine particles.
The only known testing of the ConeSipper® has taken place at the Savannah River Site (SRS) where water samples were collected from depths of over 55 meters. A study was conducted in which the chemical quality of water samples obtained using the ConeSipper® were compared to those obtained by conventional methods at SRS, however information from this study has not yet been released.

No specific information has been provided concerning analyses which may be performed using the probe, but since samples are brought to the surface, it appears that qualitative and quantitative surface analyses may be performed. These analyses could include, on-site gas chromatography for gas and water samples, on-site drager tubes for gas samples, and off-site laboratory analyses for both gas and water samples.

ARA is attempting to incorporate fiber-optic sensors in the probe and an additional system to monitor the rate of water inflow in order to calculate the hydraulic conductivity.

Reference information: Sales brochures and communication with Babineau (1996).

Envirocone® - ISMES

The Envirocone®, developed at ISMES, allows for the measurement of gas and water samples. The probe utilizes a modified bladder pump located in the probe to pump water samples to the surface for analysis. The maximum pumping rate of the pump is 60 ml/min. Gas samples may also be collected in the vadose zone by pulling a vacuum from the surface. The gas samples may then be analyzed in-line by gas chromatography, placed into sampling bags, e.g. Teflon, to be analysed on-site by gas chromatography or drager tubes. Samples collected in sampling bags may also be sent to an off-site laboratory.

Water samples may be analysed by one of two methods depending on the parameters of interest. In the first method, an in-line flow cell at the surface allows for the measurement of pH, electrical conductivity, dissolved oxygen, and redox potential. The flow rate and other parameters such as ammonia, total hydrocarbons, nitrates, and chlorinated hydrocarbons may also be measured after the in-line flow cell. In the second mode, the in-line sensors are bypassed and samples may be taken directly from the flow stream for analysis by a field portable gas chromatograph or off-site laboratory analysis. Temperature and sampling/flushing sensors are located in the probe and are available for measurements in either operating mode. Before collection of a sample, ISMES (Piccoli and Benoît, 1995) recommends that pumping be continued until electrical conductivity readings have remained constant to assure that "the system is saturated with ground water only". The probe is decontaminated by pumping pure water through the sampling lines at least one meter above the intended sampling interval.

Measurements are typically collected at discrete intervals although ISMES is developing probe sensors for continuous measurements. The use of an in-line gas chromatograph has not been fully developed and is awaiting field testing (communication with O'Neill, 1996). The in-line sensors for pH and dissolved oxygen are calibrated using buffer solutions, however the recommended frequency of calibration is unknown.
Only the tip resistance and pore pressure geotechnical parameters may be measured with the Envirocone®.

Both gas and water samples are pulled through a filter located on the outside of the probe. Depending on the expected soils to be encountered, different filters may be used. The sampling/flushing sensor is used to monitor clogging of the filter which can then be unlogged by backflushing water from the surface.

According to O'Neill (1996), sample collection times may be lengthy in clay deposits where low permeability soils hamper collection of water samples. Sampling rates as low as 5 ml/min have been measured. The combination of collecting the actual sample and purging of the sampling line from the probe to the surface for each sampling interval may be prohibitively long with sampling rates in this low range.

Several case histories using the Envirocone® have been documented and are described in Piccoli and Benoît, (1995) and O'Neill et al., (1995).

The probe may be contracted for hire from ISMES.


**Thermal Desorption VOC Sampler - U.S. Waterways Experiments Station (WES)**

The Thermal Desorption VOC Sampler (TDVS) being developed by the WES will allow for the detection of volatile solvent and hydrocarbon compounds in the vadose and saturated zones. The probe, shown in Figure 4.16, will heat soil which has been collected in a sampling chamber in order to purge volatile contamintes. These compounds are then transferred to the surface using a carrier gas and are analyzed on-site using a gas chromatograph and/or an ion trap mass spectrometer. The soil sample is then expelled and the probe is pushed to a new probing interval. In the vadose zone, a vacuum is applied to draw vapors to the surface.

According to communication with Robitaille (1996), the probe is in the demonstration/validation phase and will be tested in the summer of 1996 to foster regulatory acceptance. Operational status is expected in two years.

It appears that the main use of the probe will be in the unsaturated zone because according to communication with Cespedes (1996), "the deepest sample obtained to date has been to three feet below the ground water table. No operational problems were encountered at these depths. Deep penetration of the saturated zone would probably pose problems because of hydrostatic pressures forcing water up into the sampler."

Reference information: Informational brochure from SCAPS program and communications with Robitaille (1996) and Cespedes (1996).
Figure 4.16: Thermal Desorption VOC Sampler showing pushing and sampling configurations
Chapter 5

ECPT Class Properties

5.1 INTRODUCTION

If the data presented in this report is to be used for the selection of an ECPT probe for an environmental investigation, an optimum probe class must be identified. In order to aid the reader in this process, this chapter will briefly present general class properties which should aid in the selection process. After selection of the correct probe class for the intended use, Chapter 4 may then be consulted for specific information about the probes in the selected class.

5.2 GENERAL CLASS PROPERTIES

When identifying an ECPT probe class for an environmental investigation several questions must be answered prior to beginning the selection process and include:

• subsurface zones (saturated or unsaturated) to be investigated,
• compounds required for analysis, and
• precision amount of analysis required.

The maximum allowable cost must also be identified.

With these analysis and cost questions in mind, Table 5.1 was constructed to identify general class properties for each of the six ECPT classes identified in the study. The table can be used as a tool to select a probe class for further investigation. Besides the questions related to the analysis and cost, the developmental availability of the probe class must first be consistent with the time of intended use and is therefore presented initially in the table. As stated in Chapter 4, all the probes are generally available either for purchase or contract for use except those in the Developing class.

The subsurface zone in which the probe is intended for use is shown next; all the probe classes may be used in the saturated zone and half may also be utilized in the unsaturated zone.

At a minimum, most ECPT probes may be used for the delineation of contaminate plumes or identification of areas which are contaminated versus those which are not. As discussed in Chapter 1, these types of analyses are considered qualitative. The probe classes were evaluated for the possibility of detection on this basis for five major compound classes shown in Table 5.1. Compound classes marked with an "X" may be qualitatively detected, and all the probe classes except the Hydrogeology class are able to detect at least one of the five compound classes to this minimum level of detection. The symbol "*" next to an "X" indicates compounds which are more easily analyzed by a probe class.
### Table 5.1 Analysis capabilities and properties of ECPT probe classes

<table>
<thead>
<tr>
<th>Probe Class</th>
<th>Availability</th>
<th>Zone</th>
<th>Petroleum</th>
<th>PAH</th>
<th>Solvents</th>
<th>Acid/Base</th>
<th>Metals</th>
<th>Qualitative</th>
<th>Identify</th>
<th>Quantitative</th>
<th>Purchase Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Resistivity/Conductivity</strong></td>
<td>Com</td>
<td>Sat</td>
<td>X</td>
<td>X</td>
<td>X*</td>
<td>X</td>
<td>X</td>
<td>Y</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>RPT</td>
<td>Com</td>
<td>Sat</td>
<td>X</td>
<td>X</td>
<td>X*</td>
<td>X</td>
<td>X</td>
<td>Y</td>
<td>N</td>
<td>N</td>
<td>L</td>
</tr>
<tr>
<td>Fluorescence</td>
<td>Com/Cont</td>
<td>Both</td>
<td>X*</td>
<td>X</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Y</td>
<td>SEMI</td>
<td>SEMI</td>
<td>H</td>
</tr>
<tr>
<td>Developing</td>
<td>Dev</td>
<td>Both</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>-</td>
<td>X</td>
<td>Y</td>
<td>POSS</td>
<td>POSS</td>
<td>?</td>
</tr>
<tr>
<td>Geohydrology</td>
<td>Com</td>
<td>Sat</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>?</td>
</tr>
<tr>
<td>Surface Analysis</td>
<td>Com/Cont</td>
<td>Both(1)</td>
<td>X*</td>
<td>X*</td>
<td>X*</td>
<td>X*</td>
<td>X*</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>L-H</td>
</tr>
</tbody>
</table>

Notes:

- Com = commercially available
- Cont = contract hired for use
- Dev = developmental, commercial release unknown
- Sat = saturated zone
- Both = saturated and unsaturated zone
- Y or X = majority of probes in class are applicable
- N or - = majority of probes in class are not applicable
- SEMI = full qualitative identification not possible or semi-quantitative analysis only possible
- POSS = may be possible once probe is available
- ? = no data available
- NA = not applicable

(1) Analysis performed by gas sampling in the unsaturated zone and water sampling in the saturated zone.
Some probe classes may allow for higher levels of analyses, i.e. identification of specific contaminants when more than one compound is present in a contaminated matrix or semi-quantitative analysis, in addition to qualitative analysis. The abilities of the probe classes for these types of analyses are also shown in Table 5.1. The possibility of identifying specific contaminants is listed under the heading "Identify". The letter "Y" under one of the three analysis levels indicates that generally, the analysis level may be attained with the ECPT probe class. It should be noted that the symbol "SEMI" in the case of the Fluorescence class denotes that a full degree of analysis has not been fully realized to identify contaminants and for quantitative analyses. For example, the identification that different compounds are present in the matrix may be possible, but specific identification of the compounds may not be possible in the qualitative sense. Similarly, specific quantitative contaminate levels may not be possible, but differing "semi-qualitative" levels of contamination, e.g. high versus low, may be identified.

The general purchase cost of each probe class is the final category presented in Table 5.1. Only two levels are presented; either "L" denoting a lower capital cost category, and "H" denoting a higher capital cost category. Very general classifications were deliberately chosen in this category because the cost was known for only 40 percent of the probes identified in the study.

Properties of a probe class include general advantages and disadvantages which are inherent in the probe class and these are shown in Table 5.2 for each of the probe classes. General advantages and limitations of ECPT probes were presented in Chapter 1.
<table>
<thead>
<tr>
<th>Probe Class</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
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</table>
| Resistivity/Conductivity | • Simple to use and interpret  
                          • Low capital cost  
                          • Continuous Measurements | • Sensitive to soil type and other matrix properties |
| PRT                 | • Monitoring or applicability of bioremediation  
                          • Moderately simple to use | • Limited use for identification of contaminates  
                          • Redox potential difficult to measure accurately |
| Fluorescence        | • Measurements possible in both saturated and unsaturated zones  
                          • Possibility of qualitative identification and quantitative analyses of organics | • High capital cost  
                          • Complex technology  
                          • Possible matrix effects |
| Developing          | • Detection of new classes possible, e.g. metals and chlorinated solvents  
                          • Increased accuracy | • May not be available  
                          • Possibly expensive  
                          • Possible complex technology  
                          • May not be possible to combine with conventional CPT probes |
| Hydrogeology        | • Detection of hydrological properties important for contaminant transport | • No environmental analysis capabilities  
                          • Not applicable (or impractical) in low permeability soils |
| Surface Analysis    | • High degree of accuracy, qualitative identification and quantitative analysis possible  
                          • Knowledge of subsurface not required for interpretation | • Not continuous  
                          • Real-time often sacrificed for increased accuracy |
Environmental cone penetrometer probes produce more cost effective and real-time analyses compared to the conventional method of sampling for environmental investigations. There are some limitations of the technology which should be evaluated prior to use. Currently, there are six classes of ECPT probes:

- Resistivity/Conductivity
- PRT
- Fluorescence
- Developing
- Hydrogeology, and
- Surface Analysis.

The probe classes differ in their measurement possibilities and corresponding measurement techniques. Within each class there may be many different probe specific capabilities and measurement techniques for differing degrees of cost.

The author would like to emphasize again that the results of this study were evaluated based on published and unpublished data (e.g., sales brochures). The information for each of the probes presented in this report is by no means comprehensive, and therefore, manufacturers or development sources should be contacted directly for more detailed, up-to-date information.
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