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A GC-CONE PENETROMETER FOR GEOENVIRONMENTAL SITE CHARACTERIZATION

by

Yuk Ming Lam

B.Sc., M.Phil.

A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfilment of
the requirements for the degree of

Master of Applied Science

Department of Civil and Environmental Engineering

The Master of Applied Science Program
in Civil and Environmental Engineering
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administered by The Ottawa-Carleton Institute for Civil Engineering

Carleton University
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**A GC-CONE PENETROMETER FOR
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submitted by

Yuk Ming Lam, B.Sc., M.Phil.

in partial fulfilment of the requirements for
the degree of Master of Applied Science

Chair, Department of Civil and Environmental Engineering

Professor K.T. Law, Thesis Supervisor

CARLETON UNIVERSITY

Abstract

A field device for rapid determination of the extent of gasoline-type contamination in the vadose zone has been developed in this research. The building of the field device is based on cone penetration technology and gas chromatography. The cone penetration test system has been modified to be battery-operated. A prototype of the future portable gas chromatographic system has been re-built with additional features from a laboratory system. Design of the proposed soil-gas sampler, the best choice of absorbent material and the form of support for soil-gas sampling were investigated. Calibrations and optimization of the proposed field device have also been carried out.

The laboratory modelling showed that the time for the identification and measurement of gasoline-type contaminants is approximately 8 minutes, with the use of condensed chromatograms. Results obtained from the field trials are in good agreement with those obtained from the verification soil samples.

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Chapter 1

Introduction

1.1 Background

Petroleum products, industrial wastes, solvents and chemicals are stored in underground storage systems. If these liquids are stored improperly, there is a high potential for them to leak and pollute the environment. For example, according to the U.S. EPA, 29% of the existing underground fuel tanks may leak their contents into the surrounding soil (Mapes et al. 1993). In Russia and other eastern European countries, the problem appears to be even worse (Marsh and Grossa 1996). As a result, the soil and the associated groundwater become contaminated. Furthermore, volatile substances from a spill may escape from subsurface environments to the atmosphere. Various levels of toxicity in the human body can cause minor illness, cancer or death. As the cleanup costs may amount to over a million dollars per incident, the social and economic impacts of leaking storage systems are grave. Figure 1.1 illustrates the multi-phase hydrocarbon distribution resulting from a leaking underground gasoline storage tank.

FIGURE 1.1 Illustration of multi-phase hydrocarbon distribution resulting from a leaking underground gasoline storage tank (after Anderson 1994).

The presence of soil-gas may also influence and alter the properties of the host soil. Consequently, misleading design parameters may be established, and in some cases, may even jeopardize the stability of the foundations of the structures. Since the 1960s, researchers have investigated the effects of soil-gas on soil properties of the Athabasca tar-sand in Canada (Carrigy 1967, Dusseault and Morgenstern 1978, Dusseault 1979 and 1980, Dusseault and van Domselaar 1982). These investigations revealed a reduction of soil strength due to the presence of soil-gas. Coleman et al. (1974), Whelan et al. (1975, 1977 and 1978) and Esrig and Kirby (1977) clearly demonstrated that the presence of soil-gas is one of the main causes of shear strength reduction and subsequent failure in soft marine clay deposits. Rad et al. (1994) also found that the presence of soil-gas may strongly influence the undrained shear strength of a fine river sand, Baskarp Sand. The extent of the effect is a function of the gas type and the amount of gas.

The risk of gas blowouts during drilling operations with its subsequent life and financial losses is another potential hazard of not correctly identifying and quantifying the soil-gas. Soil-gas investigations have been performed prior to the commencement of a number of construction projects in the Congo, Hong Kong and North Sea (Norwegian Geotechnical Institute 1987, 1988, 1989a, 1989b, 1990a, 1990b and 1990c, Premchitt et al. 1990). These initial investigations serve as a safeguard for further scheduled soil investigation programme.

It has been found that the majority of underground storage systems are located in the unsaturated zone (U.S. EPA 1988), hence, it is worthwhile to develop a reliable field device targeted for rapid detection of gasoline-type contaminant in unsaturated soils.

Gasoline consists of any combination of C_4 through C_{12} petroleum hydrocarbons in addition to various additives. Motor gasoline contains more than hundred of compounds in measurable amounts (Riser-Roberts 1998, Petro-Canada 1998). The most environmentally significant components of gasoline are the monoaromatic compounds benzene, toluene, ethylbenzene and xylene. The mobility of these four components of gasoline decreases in the order of benzene, toluene, ethylbenzene and xylene (Reisinger et al. 1989). With respect to the volatility, toxicity and water solubility, benzene is normally targeted as the individual gasoline constituent of greatest concern (Fitzgerald 1989).

The contaminants are readily exchanged between soil phases and tend to partition between phases according to the chemical potential gradients across the phase boundaries. Water and gas move relatively slowly through soil pores, allowing time for contaminants to partition between phases. The amount of contaminants sorbed to solids, dissolved in water, or in vapour form depends solely on the contaminant physical and chemical properties and the relative amounts of each of these phases in the particular soils. Graphical depictions of the volatilization process for aqueous and soil systems are presented in Figure 1.2 and Figure 1.3, respectively. "Henry's Law", an empirical relationship concerning the partitioning of volatile chemicals between aqueous and vapour phases. According to this relationship, at equilibrium, the concentration of gas/vapour dissolved in a liquid is directly proportional to the partial pressure of that gas/vapour above the liquid. The constant of proportionality is being the Henry's Law constant.

$$C_G = H_C C_L$$

where, H_C is the Henry's Law constant

C_G is the concentration of contaminant in gas phase

C_L is the concentration of contaminant in liquid phase

FIGURE 1.2 Volatilization process for aqueous system (after Fitzgerald 1989).

FIGURE 1.3 Contaminant partitioning and volatilization within an elemental soil block (after Fitzgerald 1989).

However, volatilization from a bulk soil matrix includes solid, liquid, and gaseous compartments (Figure 1.3) is considerably more complex than volatilization from an aqueous solution. Since gasoline is a mixture of many hydrocarbons, partitioning relationships between individual compounds would be difficult to predict.

Fitzgerald (1989) further suggested that the equilibrium state of contaminant partitioning within an elemental soil block may be expressed by the following equation:

$$C(t) = \gamma C_s + \theta C_w + n C_a$$

where, $C(t)$ is the total contaminant concentration

γ is soil bulk density

C_s is the contaminant sorbed onto soil

θ is the volumetric soil water content

C_w is the contaminant concentration in soil water

n is the volumetric soil air content

C_a is the contaminant concentration in soil air

Contaminants can be detected by: direct sampling and analysis of the soil-gas, groundwater and soil samples; aerial photography; surface geophysical surveying; and downhole geophysical surveying. However, a single method of detection may not be adequate for detecting all kinds of contaminants and the choice of method is highly dependent on the types of contaminants involved and the associated subsurface conditions.

An ideal field device for rapid determination of the extent and nature of contamination should provide continuous, accurate subsurface profile information. It should also be able to chemically characterize the subsurface features with a minimum disturbance to the surrounding environment.

Over the years, numerous sensors, such as the resistivity/conductivity probe, fluorescence spectrometry, Raman spectrometry and absorption spectrometry, have been developed and successfully applied to geotechnical field devices for geoenvironmental investigations. These sensors are expensive and chemical specific. Their accuracy can be affected by the soil mineralogy (Bowders and Daniel 1994). Among the commonly available identification techniques, soil-gas analysis using gas chromatography appears to be an appropriate solution for the determination of multiple constituent contaminants. Its accuracy is, however, independent upon the soil type (Bowders and Daniel 1994).

The building of the field device is based on combining two existing technologies: cone penetration technology and gas chromatography. The cone penetration device penetrates into the soil at a steady speed to provide information on the soil type, groundwater condition, soil permeability and other soil characteristics. Soil-gas samples at various depths in the soil are collected on the absorbent Tenax-TA via an attached sampling module on the cone penetration device. The absorbed substances are then thermally desorbed and passed onto a gas chromatographic system for identification of the contaminant type. Hence, the extent and nature of the contamination both in the vertical and horizontal directions can be identified. Lam et al. (1997) and Law et al. (1999)

suggested a simplified chromatographic technique that would further shorten the time required for a gas chromatographic analysis, thereby achieving a higher efficiency for rapid field application.

1.2 Aim of Research

The present research is an integral part of a major research activity to understand the mechanics of contaminant migration through unsaturated soils. The purpose of this research is to develop a device for the rapid determination of the extent of the most abundant petroleum contaminant, gasoline, in the vadose zone.

1.3 General Outline of Research

As there are many existing methods readily available for geoenvironmental subsurface characterization, a general survey of a number of commonly used field investigation methods for the determination of volatile organic contaminants in the subsurface is presented in Chapter 2. The survey has shown that direct soil-gas sampling followed by a gas chromatographic analysis appeared to be a promising technique for identifying the volatile organic contaminants qualitatively and quantitatively.

Background information and the strength and limitation of cone penetration technology and gas chromatography for geoenvironmental investigations of hydrocarbon contamination are discussed in Chapter 3 and Chapter 4, respectively. Considerations for developing the proposed field device are also discussed. Assessments on the choice of material and technique for sampling hydrocarbon contaminated soil-gas samples and soil samples are presented in Chapter 5.

Enhancement of the cone penetration system, the modification of the gas chromatographic system and the developed data recording systems are presented in Chapter 6. Moreover, measurements of tip resistance, sleeve resistance and pore water pressure on the cone penetration device have been calibrated against dedicated loading systems. Optimum experimental conditions for the gas chromatographic system have been characterized against purchased BTEX standards. Optimum soil-gas sampling conditions have been characterized against laboratory prepared gasoline-contaminated soil samples with different contamination levels. Laboratory modelling in accordance with the Ontario soil cleanup criteria for potable groundwater situation (Ministry of Environment and Energy 1996) has also been carried out.

The final stage of the development is the integration of the complete soil-gas sampling system together with the piezocone penetrometer. A number of field trials at a selected location have been carried out for verifying the usefulness of the developed field device.

Chapter 2

Commonly Used Geoenvironmental Field Investigation Methods

Field investigation methods can generally be broken down into two major groups, Nonintrusive and Intrusive Methods (Byrnes 1994, Benson and Yuhr 1995). Examples of both of these methods are as follows:

Nonintrusive Methods:

- aerial photography, and
- surface geophysical surveying.

Intrusive Methods:

- soil-gas surveying
- downhole geophysical surveying, and
- shallow and deep soil sampling.

2.1 Nonintrusive Methods

As the title implies, nonintrusive methods do not require physical penetration of the ground surface. Prior to collecting samples of environmental media for on-site or laboratory analysis, one or more nonintrusive characterization surveys can be carried out to assist the positioning of the intrusive sampling points. The most commonly used nonintrusive methods for non-radiological contamination investigations are aerial photography and surface geophysical surveying (Byrnes 1994, Benson and Yuhr 1995).

2.1.1 Aerial Photography

Aerial photographs can be used to identify the potential surface contaminant migration pathways. In some cases, contaminant source areas can also be identified through careful evaluation of historic and/or recent aerial photographs (ASTM D-5518, ASTM D-5730). Fill area boundaries can sometimes be defined by identifying unnatural changes in topographic relief, or by identifying unnatural changes in vegetation patterns. The effectiveness of aerial photography as a site characterization tool is however, very much dependent on the quality and scale of the available photographs and the interpretation from experienced photointerpreters (Preslo et al. 1989).

2.1.2 Surface Geophysical Surveying

Surface geophysical methods can often provide useful data to assist in the identification of buried drums and tanks, boundaries of fill areas and in some cases, the boundaries of a contamination plume. Electromagnetic, ground penetrating radar, electrical resistivity and magnetic measurements are commonly used for measuring lateral changes. Seismic methods are often employed for measuring depth and thickness of geologic strata (Technos 1992a, ASTM D-5730, ASTM D-5777).

Greenhouse et al. (1993) successfully detected and mapped the floating hydrocarbons in the depth range from 0.3 to 9m using the ground penetrating radar technique. They reported however, that thin layers of product are detected by radar only under ideal conditions. Silty and clayey soils or an elevated total dissolved solids count in the pore fluid can also limit the radar penetration to a metre or less.

Benson et al. (1985 and 1986) employed the electrical resistivity method for mapping the lateral extent of inorganic contaminants. Unfortunately, they reported that the electrical resistivity method is not adequate for detecting contaminants at low concentrations. Furthermore, electromagnetic measurements can not be made along a railway track, since the railway tracks completely dominate the measurement (Benson and Yuhr 1995).

Benson and Yuhr (1995) also demonstrated the successful application of seismic techniques in revealing the geologic pathway for contaminant migration, a buried channel, within the bedrock surface. They also demonstrated the usefulness of magnetic surveys to map buried ferrous and non-ferrous metals in an open field.

In general, surface geophysical measurements are made on a station by station basis along the profile lines. The lateral resolution of surface geophysical methods is a function of the spacing between measurements. The vertical resolution of the surface geophysical methods however, decreases with an increase in depth (Benson and Yuhr 1995). Preslo et al. (1989) reported that they only detect anomalies that are approximately 3m thick. ASTM D-5370 also pointed out that all surface geophysical methods might be subjected to interference at a site, such as metal fences, powerlines, FM radio transmission, or ground vibrations. The depth of penetration and the interference effects are highly site specific.

In most situations, surface geophysical measurements alone cannot resolve all ambiguities and some additional source of geologic information is required. ASTM D-5370 stated that interpretation of surface geophysical surveys should be verified by borings or test excavations or confirmed by different types of geophysical measurements. Due to this inherent limitation, a single geophysical method can never be considered a complete assessment of subsurface characterization.

2.2 Intrusive Methods

Intrusive methods differ from nonintrusive methods in that they require the penetration of the ground surface. Examples of these methods include soil-gas surveying, downhole geophysical surveying and the sampling of shallow and deep soil.

2.2.1 Soil-Gas Surveying

Soil-gas surveying is one investigative technique that is commonly used where the contaminants of concern include volatile organic compounds. Once in the soil-gas, these volatile organic compounds diffuse vertically and horizontally through the soil to the ground surface, where they dissipate into the atmosphere. The most commonly used soil-gas surveying techniques include the Portable Volatile Organic Compound (VOC) Analyzer Method, Microseeps Method, Mobile Gas Chromatograph Method, and Petrex Method (Byrnes 1994).

Preslo et al. (1989), U.S.EPA (1990), Byrnes (1994) and Liikala and Evans (1997) utilized the portable flame ionization detector or photoionization detector along with a hand-driven stainless steel hollow sampling rod to measure the concentration of organic vapours at shallow depths. It is important to note that these portable detectors cannot provide results for identifying specific analytical compound of the soil-gas samples. Hence, it is commonly limited to serving as a qualitative method of identifying areas

where organic contamination is concentrated. Furthermore, a relatively large amount of soil-gas is required to fill up the dead volume of the sampling probe.

Wyatt et al. (1992) employed the Microseeps Method (Microseeps 1992) to sample soil-gas from shallow boreholes in defining the boundaries of a contaminant plume. The major drawback of this method is the possible loss of volatile organics during the removal of the drive rod and prior to the insertion of the probe sampler.

Clement et al. (1992) and Golding and Wichman (1993) analyzed soil-gas samples in the field using Mobile Gas Chromatograph Method immediately following sample collection. The usefulness of this method is restricted to areas that can be accessed by the mobile laboratory and the need for an uninterrupted supply of consumable accessories.

Byrnes (1990), Gomes et al. (1994), Liikala and Evans (1997) and Anderson and Church (1998) employed the Petrex Sampling Tube Method for collecting the contaminants of concern. The disadvantage of this passive soil-gas sampling method is that the results are not quantitative, but rather reflect relative variations in soil-gas content and concentrations. A second disadvantage is that it commonly takes several weeks to obtain preliminary analytical results.

2.2.2 Downhole Geophysical Surveying

Similar to the surface geophysical methods, downhole geophysical methods can be used to assist in defining a number of formation properties along the length of the borehole.

The most commonly used downhole geophysical logging techniques in the environmental industry include electromagnetic, borehole ground penetrating radar, electrical resistivity, borehole seismic, and video (Technos 1992b, ASTM D-5370, ASTM D-5753).

Keys (1990), Weemees (1990), Campanella and Weemees (1990) and Okoye et al. (1995) employed the electrical resistivity method in delineating hydrocarbon compounds in the subsurface. Weemees (1990) and Campanella and Weemees (1990) reported that difficulties in differentiating the high resistivity values above the groundwater table from the high resistivity values of the free petroleum product that encountered. Okoye et al (1995) also found that the applicability of the electrical resistivity method is highly dependent on the relative resistivity between the contaminants of interest and the local background measurements.

Huang et al. (1995) employed electromagnetic methods to detect and monitor diesel fuel contamination in the subsurface. They found that the applied electromagnetic energy must be well predetermined prior to the investigation. Variations caused by geological or hydrogeological conditions can significantly affect the subsurface current flow and alter the electric potential patterns.

Downhole ground penetrating radar can be used to locate anomalies and map stratigraphy units. It overcomes the limitation of surface ground penetrating radar. It extends the detection range in uncased hole or nonconductive casing (Tayler et al. 1989, Darr et al. 1990, Bratton et al. 1995). Bevan (1995) and Lane et al. (1996) successfully deployed ground penetrating radar with designed applied electromagnetic energy for rapid tomography surveys. They detect a given target type preferentially.

Although downhole geophysical methods can maintain their resolution independent of depth, a number of limitations that are found in surface geophysical methods remain unresolved. Many of the geophysical measurements are limited to a radius of only 150 to 300mm from the borehole. Drilling and construction aspects may also dominate the geophysical measurements from a cased well, as the borehole diameter becomes larger (Benson and Yuhr 1995).

2.2.3 Shallow and Deep Soil Sampling

Verification soil samples are commonly collected at close proximity to the test location for geotechnical testing and/or chemical analysis. Soil samples collected from a depth of 1.5m or less are generally referred to as shallow. The most commonly used shallow soil sampling methods include the Scoop (ASTM D-5633), Hand Auger (ASTM D-1452), Slide-Hammer (ASTM D-4700), Open-Tube (ASTM D-5451), Split-Tube or Solid-Tube (ASTM D-1586), and Thin-Walled Tube (ASTM D-1587, ASTM D-3550). Driving a

Split-Tube or Solid-Tube sampler most commonly collects deep soil samples. Hydraulically pushing a Thin-Walled tube into the ground with the assistance of an auger drill rig can retrieve high quality samples.

Byrnes (1994), ASTM D-4547 and ASTM D-4700 recommended that Slide-Hammer and Split-Tube or Solid-Tube are most effective in collecting shallow soil samples for volatile organics analysis. For deep soil sampling, the Split-Tube or Solid-Tube can be a more appropriate selection in collecting soil samples for volatile organics and all other chemical analysis. Scoop is considered acceptable when collecting shallow soil samples for this analysis. Hand Auger is not recommended to collect samples where the contaminants of concern at a site are volatile organics, since the augering motion facilitates volatilization. ASTM D-1587 also recommended that the Thin-Walled Tube is the most effective for collecting geotechnical samples.

2.3 Discussions

In this review, it has been found that nonintrusive methods can only provide qualitative information about the site being investigated. Together with the limitations and inaccuracy on the application of the surface geophysical methods, nonintrusive investigation techniques were not considered in the development of the proposed field device for geoenvironmental characterization of the subsurface. Similarly, downhole

geophysical methods could not eliminate the influences affecting the surface geophysical methods. They were also excluded for the same reason.

Among the intrusive methods, soil-gas surveying equipped with a mobile gas chromatograph appears to be an appropriate solution for the rapid determination of multiple constituent contaminant type, qualitatively and quantitatively. Its accuracy is independent of the soil types. In order to enhance the mobility of the gas chromatograph and the efficiency of the soil-gas analysis, modification and/or enhancement of the conventional gas chromatographic system would be included in this research. Owing to the disadvantages of the reviewed soil-gas surveying techniques, a more reliable and efficient soil-gas sampling system would be developed and incorporates into the cone penetration device for obtaining geotechnical and environmental data of the test locations.

Chapter 3

Cone Penetration Technology

3.1 Introduction

Cone penetration technology and other drive/push technologies are being used increasingly for the environmental field investigations to depths of 30 to 100m, depending on geology and the push capacity of the system (ASTM D-3441). The primary advantage of using cone penetration technology and drive/push technologies at contaminated sites include no cutting, increased worker safety, very little investigation-derived waste is generated with the procedure and the procedure produces little disturbance to the surrounding environment.

The cone penetration technology consists of pushing a series of cylindrical rods with a cone at the base into the soil at a constant rate, and measuring continuously or at selected depth intervals the penetration resistance of the cone and the friction resistance on a friction sleeve. In addition, the pore water pressure generated in the soil near the penetrometer tip can be measured during penetration by means of a pore pressure sensor

in the penetrometer tip. The ideal use of the cone penetration technology is in areas of known geology with soils that are gravelly sands or finer. A Hogentogler electronic 10-ton piezocone penetrometer is being employed as the field penetration device throughout this research (Figure 3.1).

FIGURE 3.1 Photograph of Hogentogler electronic 10-ton piezocone penetrometer.

3.2 Description of Equipment

3.2.1 Penetrometer

A penetrometer is a device made of a series of push rods screwed together, with a terminal body called a penetrometer tip. Figure 3.1 shows the penetrometer that is being used in this research. The penetrometer tip is made of the active elements that sense the

soil resistance: the cone, the friction sleeve and the porous filter. The cone is the cone-shaped end piece of the penetrometer tip on which the end bearing is developed (Figure 3.2). The friction sleeve is the section of the penetrometer tip where the local side friction resistance to be measured is developed (Figure 3.3). In order to measure the pore water pressure, the penetrometer tip can be equipped with a porous filter which can be made of porous plastic, sintered stainless steel or ceramic. The filter has been placed either at the tip or at mid-height of the cone or immediately behind the cone neck on the cylindrical part or behind the friction sleeve. To date, the position of the porous filter has not been standardized. However, ISSMFE (1988) proposed to locate the porous filter immediately behind the cone neck (Figure 3.3, Figure 3.4).

FIGURE 3.2 Photograph of cone tip and porous filter.

FIGURE 3.3 Photograph of friction sleeve.

FIGURE 3.4 Location of porous filter.

3.2.2 Pushing Equipment

In order to push the penetrometer into the soil, the use of a hydraulic jacking system is required. Usually, the thrust capacity needed for cone testing varies between 5 tons (soft soils) and 20 tons (maximum capacity of the push rods). The hydraulic rig pushes the rods at a constant rate of penetration of 20mm/sec. (ASTM D-3441). The push rods are used for advancing the penetrometer tip to the required test depth. They are made of high strength steel. The standard rods are one meter long with tapered threads and have the same diameter as the base of the tip and sleeve. Their maximum capacity is usually 20 tons. They are screwed together by hand and there must be no protruding edge at the screw connection between the rods. The depth of penetration can be increased by the use of a friction reducer. A depth encoder (Figure 3.5) measures the depth of penetration.

3.2.3 Recorder

During a cone sounding, the strain gauges built in the penetrometer give out electronic analogic signals continuously while the depth encoder outputs digital pulse signals. The recorder receives the analogue signals of the tip resistance, sleeve friction and pore water pressure from the electronic penetrometer and the pulse signals from the depth encoder. The collected data is stored for future analysis. A detailed description of the developed portable recording system is presented in Chapter 6.

FIGURE 3.5 Photograph of depth encoder.

3.3 Method of Interpretation

The friction ratio can be obtained directly from the ratio of the sleeve friction to the tip resistance at the same depth. Lithologic characterization and strength parameters can also be obtained from the correlation of the cone penetration test results to the published literatures.

Soil classification can be obtained from charts based on the cone penetration test or piezocone penetration test data (Douglas and Olsen 1981, Douglas 1984, Robertson and Champanella 1988). The in situ horizontal stress at rest can be estimated by correlating

the sleeve friction, the overconsolidation ratio and the vertical effective stress with the available chart (Masood 1988). The in-situ density can also be estimated by correlating the tip resistance and vertical effective stress with available charts (Baldi et al. 1981, Douglas and Olsen 1981, Villet and Mitchell 1981, Jamiolkowski et al. 1985, Schmertmann 1988).

The peak friction angle can be estimated from the correlation with the tip resistance (Robertson and Campanella 1983). The constrained modulus for clays can be obtained from the correlation with the tip resistance and the α values suggested by Sanglerat (1972) (Mitchell and Gardner 1975). The drained secant moduli at 25% and 50% of the failure deviator stress level, for different levels of vertical effective stress can be obtained from the correlation with the tip resistance (Robertson and Campanella 1983). Robertson and Campanella (1988) further correlated the estimated shear strength and the estimated overconsolidation ratio with the undrained Young's modulus at different stress level that based on Ladd et al. (1977). The maximum shear modulus can be estimated from the tip resistance, the vertical effective stress and the SPT value (Imai and Tonouchi 1982, Robertson and Campanella 1983). The sensitivity can be obtained by relating the sleeve friction to the remoulded shear strength (Robertson and Campanella 1988, Schmertmann 1988). The undrained shear strength can be correlated with the excess pore pressure measured during continuous penetration (Campanella et al. 1985, Konrad and Law 1987). The coefficient of consolidation can be derived from the in-situ measurement of the dissipation test (Levadoux and Baligh 1986).

3.4 Experience of Incorporating Cone Penetration Technology for Geoenvironmental Investigation of Hydrocarbon Contamination

A variety of laser-induced fluorescence (LIF) sensor probes have been developed and integrated into the cone penetrometer for subsurface detection of petroleum hydrocarbons. Basic fiber-optic-based LIF sensors have been developed by Inman et al. (1990), Lieberman et al. (1990 and 1991), Bratton et al. (1993), Lambson and Jacobs (1995), Shinn and Bratton (1995) and Davis et al. (1997). These basic LIF sensors have a detection limit of 100ppm of total petroleum hydrocarbons and their sensitivity decreases with an increase of penetration depth. This is due to the fiber-transmission losses and fiber-generated interference.

Modified LIF sensors have been developed by Germain et al. (1993), Gillispie et al. (1993), Lin et al. (1994 and 1996), Germain and Gillispie (1995), Gillispie and Germain (1995), Kenny and Henderson-Kinney (1995), Nau et al. (1995), Hart et al. (1996), Bloch et al. (1998) and Mosier-Boss and Lieberman (1998). With the presence of mixed type contaminants at the test location, misinterpretation of results has been reported in using these sensors.

An electrical resistivity module has also been integrated into the cone penetrometer for the determination of hydrocarbon contamination (Weemees 1990, Campanella and Weemees 1990 and Okoye et al. 1995). It has however, been reported that the applicability of this module for delineating the light non-aqueous-phase liquid (LNAPL)

hydrocarbons can be limited due to the high resistivity values in the vadose zone. The effectiveness of the resistivity delineation is subject to the degree of saturation of the underlying soils. Similarly, difficulty may also be encountered when such contaminant is the only source of contamination and is present in a very small quantity.

3.5 Discussions

For geotechnical applications, soil strength, deformation and dynamic properties remain the agenda. For geoenvironmental projects, chemical data and hydraulic properties of the subsurface strata are typically the focus.

From the experience of the other researchers, the cone penetrometer is a good device for geotechnical characterization of the subsurface. It can be easily enhanced to carry additional sensing devices to the subsurface. It has also been found that advanced sensors, such as resistivity/conductivity probe, fluorescence spectrometry and absorption spectrometry, are chemical specific and their accuracy can be affected by the soil mineralogy. In the present research, therefore, a proposed soil-gas sampling device will be developed and carried by the cone penetrometer to the desired location for collecting soil-gas samples for analysis.

During a cone penetration test programme, setting up the test station and moving it around the site can be a tedious pursuit. It is therefore inevitable that a battery-operated cone penetrometer together with a portable recording system will become more beneficial. The present research is therefore, geared towards developing a true portable cone penetration test system that can be mounted onto a drill rig for immediate operation in a short period of time.

Chapter 4

Gas Chromatography

4.1 Introduction

Gas chromatography has been widely used for identifying contaminants in soil (Poole and Poole 1991, Kolla 1994 and Scott 1995). The characteristic of gas chromatography is that the mobile phase of the column is an inert carrier gas and the stationary phase is a high molecular weight liquid that is deposited either on a packed column or on the wall of a capillary column. The sample is fully vapourized in the injection system and then passed onto the column for separation. Gas chromatography is advantageous for analysing gasoline vapour from the soil due to the low viscosity of the mobile phase; hence, longer columns may enhance the separation power for an analysis. Figure 4.1 shows the Varian 1440 Gas Chromatograph that is being used throughout this research.

FIGURE 4.1 Photograph of Varian 1440 Gas Chromatograph.

4.2 Description of Equipment

A gas chromatographic system consists of four major components: injection system, column, detector and recorder. The sample is introduced into the gas chromatographic system via the injection system and separation of individual components takes place in the column. The detector detects the separated components and gives a readout of characteristic voltage output signals. The recorder records the output signals for online visual display and permanent storage or further analysis. Figure 4.2 shows the basic components of a gas chromatographic system.

FIGURE 4.2 Block diagram of the basic components of a gas chromatographic system.

4.2.1 Injection System

The task of the injection system in a gas chromatographic system is to heat the sample to a certain temperature and then introduce the gaseous sample onto the column in a reproducible manner. The ideal sample introduction must be rapid and reproducible without adversely affecting the efficiency of the column. Improper choice, or use, of an injection system reduces the overall system performance and quality of data and can even prevent important sample components from reaching the column. Grob (1995) has discussed the strengths and weaknesses among various injection systems that included packed-column direct injection, split and splitless injection, cool on-column injection and programmable temperature vapourizer injection systems. In order to accommodate a load of large sample volume and very low concentrations on a capillary column, a 6-port valve injector with an external focusing tube is preferred. Figure 4.3 shows the 6-port valve injector being used in this research. Detailed description of the modified injection system is presented in Chapter 6.

FIGURE 4.3 Photograph of 6-port valve injector mounted on Varian 1440 Gas Chromatograph

4.2.2 Column

Columns may be divided into two categories: packed column and capillary column. A packed column is one in which the stationary phase (a liquid) is deposited on solid particles and packed in a tubular column. A capillary column is one in which the stationary phase is deposited onto the interior wall of the column. In both types of columns, the sample is introduced onto the head of the column and carried through the column by the carrier gas. Barry (1995) has discussed the performance and practical considerations of using packed columns and capillary columns. In order to achieve a non-polar response for our initial investigation on gasoline vapour, a 15m x 0.8mm Ultra

Alloy-1 capillary column coated with a 2-micron layer of 100% dimethylsilicone is employed.

For the multiple component mixtures such as gasoline, the separation of the components under a low isothermal column temperature may take hours to complete. At high isothermal column temperature, the low boiling point components will elute so quickly that the solute peaks may merge together and thus be difficult to identify. Deploying a temperature program not only improves the separation of the components but a linear increase of the column temperature with time can reduce the elution time of the high boiling point components. Consequently, it reduces the overall run time and allows a more rapid test programme. The optimized temperature program being employed in this research is described in Chapter 6.

4.2.3 Detector

Commonly used detectors for hydrocarbons analyses are flame ionization detector (FID), electron capture detector (ECD), photoionization detector (PID), thermal conductivity detector (TCD) and mass spectrometer (MS). The output voltages during a test are then passed onto the recorder and presented as a chromatogram. Poole and Poole (1991) and O'Brien (1985) have discussed the performance and practical considerations of using these detectors. It was found that the flame ionization detector has nearly universal response with approximately the same sensitivity to all organic compounds. O'Brien

(1985) and Scott (1995) also reported that most of their petroleum compounds tested could be measured at a very low level with the flame ionization detector. A SRI flame ionization detector with detectability of 100ppb is therefore, chosen for the present research.

For operating the flame ionization detector, the use of high purity gases that do not contain any hydrocarbon is required. From the economical point of view, purified nitrogen has been chosen as the principal and secondary carrier gases throughout the sample desorption stage and each chromatographic analysis. Ultra high purity hydrogen and zero air have been chosen to produce the hydrogen flame. Optimization of the deployed flame ionization detector is presented in Chapter 6.

4.2.4 Recorder

The recorder receives the characteristic voltage output signals of the detected components of the sample from the detector. It also provides the online visual display of a plot of the voltage output against time, called a chromatogram. The collected data is stored for future analysis. A detailed description of the developed recording system is presented in Chapter 6.

4.3 Method of Interpretation

A chromatogram is a plot of detector response against time, which represents the mass or concentration profile of the components of the sample. A typical chromatogram of gasoline showing each individual component is shown in Figure 4.4. Basically, two parameters from the chromatogram of a sample are taken for qualitative and quantitative analysis. These are the retention time and the size of the peaks. The retention time of a component in the sample is defined as the time between the injection and the maximum peak of that particular component when it passes through the detector. This retention time is a constant for a particular component under the fixed chromatographic conditions.

FIGURE 4.4 Typical chromatogram of gasoline showing each individual component

4.3.1 Qualitative Analysis

Qualitative analysis is a sample identification technique based on the comparison of the retention time. For a defined system with fixed conditions, an unknown component can be identified by comparison with retention time of a known sample. There are two methods in identifying the components in a sample qualitatively and they are component analysis and fingerprint analysis (Grob 1995).

Component analysis identifies the individual components of a sample from the individual peaks on the chromatogram. The result is used to interpret the presence of the contaminants of interest. The essential condition for the success of component analysis is the adequate separation of the components. Separation of all components in the sample is, however, not an easy task.

In fingerprint analysis, comparing the overall pattern of the chromatogram identifies the sample. The overall pattern obtained is compared to chromatograms of possible sources of contaminants tested under similar experimental conditions. This technique is particularly useful for the identification of the very complex mixtures, such as petroleum hydrocarbons. In addition, Lam et al. (1997) and Law et al. (1999) successfully demonstrated that the use of a condensed chromatogram could greatly reduce the time of a test, in which the condensed chromatogram also considers the overall matrix of the gasoline. A typical chromatogram of gasoline for fingerprint analysis and a typical

condensed chromatogram of gasoline are shown in Figure 4.4 and Figure 4.5, respectively.

FIGURE 4.5 Typical condensed chromatogram of gasoline vapour

4.3.2 Quantitative Analysis

Quantitative analysis is the process by which concentration levels of the components in the injected sample are quantified. The size of the component peak can be measured by either the height of the peak or by the area under the peak.

Peak height measurements are suitable for the determination of rapidly eluted components, which produce high and narrow peaks. Peak area measurements are useful

when there is a detectable amount of contaminant in the sample injected. In this research, the area under the condensed chromatogram, for a fixed time window, has been chosen for quantifying the detected contaminant.

In the standardization process, the detector response is related to the actual quantity of an introduced sample (Poole and Poole 1991). Since the external standard method chromatographed the known quantity of standard under a separate run, this method has been chosen for analysing the complex soil-gas samples. Calibration curves of the known standard could then be drawn. The area and the retention time of the analyte are compared to those obtained from the standard.

4.4 Experience of Using Gas Chromatography for the Determination of Hydrocarbon Contamination

Mathews et al. (1979 and 1980) and Lubeck (1987) have successfully employed programmable temperature-controlled gas chromatographic systems fitted with a flame ionization detector for analyzing hydrocarbon samples. Rygle (1987), Potter (1989), Van Delft et al. (1994) and Robbins et al. (1995) also successfully employed programmable temperature-controlled gas chromatographic systems for fingerprinting the gasoline-type contamination from its leaking source.

Moreover, Robbins et al. (1993) pointed out that there exists the potential for the false identification of the BTEX compounds using the gas chromatographic system equipped with a photoionization detector on properties containing condensate. It is due to the fact that the photoionization detector has enhanced sensitivity to the aromatic compounds and also detects aliphatic hydrocarbons.

Aelion et al. (1996) also employed a programmable temperature-controlled gas chromatographic system fitted with a flame ionization detector as the control device for verifying their proposed portable meter for monitoring the BTEX compounds in petroleum contaminated groundwater and soil vapour.

Djozan and Assadi (1997), Nilsson et al. (1998) interfaced the solid-phase microextraction (SPME) technique with the gas chromatography for the determination of BTEX compounds in groundwater and soil-gas. The use of SPME is however, not considered on this research due to the lengthy period for collecting representative sample for the quantitative analysis.

4.5 Discussions

From the experience of the other researchers, it has been found that a gas chromatograph equipped with a flame ionization detector performed the best for analyzing petroleum

hydrocarbon contaminants. In convention, a gas chromatographic analysis for gasoline may take up to 2 to 3 hours for a complete analysis in identifying each individual component of the tested sample. By adopting the condensed chromatogram type of analysis (Lam et al. 1997 and Law et al. 1999), the time required for a gas chromatographic analysis would be greatly reduced. As gasoline is a multiple component mixture, the external standard method is considered the most suitable standardization method for quantitative and qualitative analysis. Therefore, a series of laboratory prepared gasoline vapour from the mixtures of soil and gasoline with different concentrations will be run under exactly the same experimental conditions as the analyte, but under a separate chromatographic run. Calibration curves could then be drawn.

In consideration of the future development of a portable unit for the field applications, modifications on the laboratory gas chromatograph are geared towards developing a prototype for this purpose. By considering an ideal sample introduction for rapidity and reproducibility without adversely affecting the efficiency of the column, a 6-port valve injector was chosen. Furthermore, in order to accommodate the large loads of very low concentration moist samples onto a capillary column, it was decided that a focusing tube, filled with absorbent material, is to be superimposed onto the 6-port valve injector.

Chapter 5

Sampling Techniques for the Determination of Hydrocarbon Contamination in Soils

5.1 Introduction

Reliable qualitative and quantitative information on hydrocarbon contaminants in soils is essential to determine the need for cleanup programmes. Laboratory and field tests both involve sampling and subsequent qualitative and quantitative analysis on the contaminants of interest. The reliability of the test results is highly dependent on the sampling methods and, therefore, proper sampling and adequate protection for the collected samples, which take into account the possible losses, has to be adopted. This chapter discusses the commonly used techniques for collecting soil-gas samples and soil samples for the determination of subsurface hydrocarbon contamination. The strengths and limitations of these techniques are included. In addition, remediation and desirable improvement to the deficiencies of the existing methods are discussed.

5.2 Soil-Gas Sampling

As previously described in Chapter 2, soil-gas surveying is suitable for volatile hydrocarbon contaminants in soils, such as gasoline. It is particularly useful in isolating the area of highest level of contamination, and subsequently, identifying the source of release. The results from the soil-gas survey are frequently plotted as contour maps for representing the vapour plume. A rough estimate on the cost of soil-gas analysis compared to soil sample analysis for the identification of volatile organic substances in a site in Arizona is 1:7.5 (Rosenbloom and Carlson 1988).

Soil-gas samples can be obtained passively by placing a collection device in the soil and allowing the atmosphere within the device to come into compositional equilibrium with the soil atmosphere (Byrnes 1990, Gomes et al. 1994, Liikala and Evans 1997, Anderson and Church 1998, Ball et al. 1994). Soil-gas samples collected by active sampling are drawn from the sampling horizon to the surface through a transfer line by positioning a sampling device in the subsurface, such as a combination of the soil-gas probe with a hand pump (Preslo et al. 1989, U.S.EPA 1990, Byrnes 1994, Liikala and Evans 1997). A soil-gas sampling device can be pushed or driven to the sampling horizon from the surface, moreover, it can also be lowered into pre-drilled holes (U.S.EPA 1990).

For in-situ active soil-gas sampling, the transfer lines must be inert to the analytes being transported and flexible for storage and handling. Commonly used transfer lines are

made of stainless steel, nickel, aluminium and various grades of Teflon. Doskey et al. (1996) found that Type 316 stainless steel is superior to the other types of materials for quantitative volatile organic compound transport at ambient temperature (25°C). Transfer efficiency through stainless steel at various humidities (0-50%) is nearly 100%.

Collected soil-gas samples can be stored in special containers, such as stainless steel canisters, Tedlar bags and glass vials with a Teflon-lined septum cap. They can also be concentrated onto sorbent materials (Fitzgerald 1989, U.S.EPA 1990, Environment Canada 1997). Jones (1987) suggested that light-sensitive hydrocarbons could be stored in glass vials for several months without any serious degradation or loss of contaminants.

The collected samples are then analyzed in the field or in the laboratory by various methods depending on the purpose of the investigation and the required accuracy. Soil-gas samples concentrated onto sorbent material are employed in this research. Detailed description of the use of the sorbent material is presented in Chapter 6.

5.2.1 Soil-Gas Collection using Sorbent Materials

The sorbent material selected for the sampling or analysis is one that efficiently retains the analytes of interest as the vapour sample passes through it. Commonly used sorbent materials can be found in liquid and solid form. In order to minimize the generation of liquid waste and to avoid the difficulty of sample enrichment by evaporation of the

solvent under vacuum during a field operation, liquid absorbents were not considered in the present study.

Popular solid sorbents for the collection of organic compounds include charcoal, alumina, silica gel, Tenax, Porapak Chromosorbs, XAD, polyurethane foam and liquid stationary phases coated onto a support phase (Douglas 1991, Gomes et al. 1994, Liikala and Evans 1997, Anderson and Church 1998). Any sorbent material can retain only a finite amount of an analyte. Once the sorbent material exceeds its capacity, the sorbent material will no longer adsorb further analyte (EPA Method 5041, SIS 1997). Consideration must also be given to the other components of the sample matrix and their effect on analyte retention. High levels of water or other organic compounds can saturate and reduce the efficiency of some sorbent materials (Loeper 1995).

Sorbent materials can be prepared in tubes, cassettes and coated onto solid supports such as papers, filters and fibres for active and passive sampling applications (Douglas 1991, Rastyannikov and Drugov 1993, Brown and Wright 1994, Eriksson et al. 1994, Gomes et al. 1994, Levin and Lindahl 1994, Van Delft et al. 1994, ASTM D3868, EPA Method 5041, Djozan and Assadi 1997, SIS 1997, Liikala and Evans 1997, Anderson and Church 1998, Nilsson et al. 1998). To date, sorbent tubes are more widely used in active soil-gas sampling, while the other forms are frequently employed in passive sampling. The disadvantages of using the sorbent tubes are discussed in later sections.

5.2.2 Sample Preparation

Analytes adsorbed onto sorbent materials can be extracted either by thermal desorption or by replacement with a solvent such as carbondisulphide (Kolb 1976, EPA Method 5041, AEC Method 17070, Yang and Lo 1997). The volatility of the analytes collected on the sorbent will dictate the technique that can be employed for their extraction or removal.

Compounds extracted from soil samples by solvent extraction techniques are extracted from sorbents by the same process. It is thus assumed that the sorbent will not dissolve or degrade upon exposure to the solvent/temperature conditions for the extraction. The advantage of this solvent extraction method is that only an aliquot of the extract is analyzed, therefore, this makes replication possible. The principal disadvantage of the solvent extraction method is that higher levels for detection and quantitation can be the result unless a large volume of sample is analyzed.

Thermal desorption allows the concentration of the desorbed analytes and provides lower detection limits. Volatile analytes can also be thermally desorbed directly into the gas chromatographic column where they can be cryogenically focussed or trapped at the front of the column. The advantage of the thermal desorption method over the solvent extraction method is that the recovery of analytes from a sorbent occurs with the absence of sample dilution. If replicates are needed this can however, be a disadvantage.

5.2.3 Experience of Soil-Gas Sampling in Geoenvironmental Investigation

Nadeau and Lafornera (1985), Rad et al. (1988), Rosenbloom and Carlson (1988), Spittler et al. (1988), Golding and Wichman (1993), Mushrush et al. (1994), Rad and Lunne (1994) and Aelion et al. (1996) employed the active soil-gas sampling technique to collect soil-gas samples for subsequent analysis for the determination of subsurface hydrocarbon contamination. The effectiveness of the active sampling method will be limited by the ability of grain size of the soil around the sampling location to prevent plugging of the sampling tube. Furthermore, a pre-determined sampling depth is also required. It was also been noticed that if an auger method was used the removal of auger could encourage soil-gas venting and lowers sample representativeness. Furthermore, the insertion of the sampling device into the augered hole might cause additional venting of soil-gas as the sampling device displaces the atmosphere in the hole upon insertion. In this case, the use of a direct-push sampling device can be an advantage.

Byrnes (1990), Gomes et al. (1994), Liikala and Evans (1997) and Anderson and Church (1998) employed the Petrex method for passive sampling of soil-gas. As previously discussed in Chapter 2, the disadvantage of this passive soil-gas sampling method is that the results are not quantitative but rather, reflect relative variations in soil-gas content and concentrations. A second disadvantage is that it commonly takes several weeks to obtain preliminary analytical results. Furthermore, deep subsurface soil-gas sampling will be

difficult where deep excavation can introduce soil-gas venting and lower the sample representativeness.

Kerfoot (1991), Aldstadt et al. (1995), Myers et al. (1995 and 1998) and Davis et al. (1998) developed various in-situ purge-and-trap devices for use with a cone penetrometer for collecting hydrocarbon contaminants in the vadose zone. The disadvantage of this method is that cross-contamination may easily result since it requires the carrier gas to sweep through the soil matrix. Hence, soil-gas directly drawn from the soil matrix is preferred. Furthermore, the proposed systems might introduce a large amount of water vapour into the detection system. Subsequently, serious degradation of the analytical column can lead to a shorter life of the detection system.

5.3 Soil Sampling

As described in Chapter 2, surface soil samples can be collected using a hand auger, scoops or gloved hands and subsurface soil samples can be collected using Split-Tube or Solid-Tube samplers. In order to prevent the loss of volatile substance, the sample should be gathered from freshly exposed soil and preserved as soon after the excavation as possible (Environment Canada 1997). Clean stainless steel or Teflon is preferred for all sampling equipment. The same set of equipment should not be used twice unless proper cleaning has been ensured.

The collected soil samples are immediately placed in the sample container, such as a Mason jar or a glass vial. It is recommended that the containers should be rinsed with a spectrographic grade solvent and dried in an oven at 105°C (I.T. Corporation). It is best for BTEX and gasoline-contaminated soil samples to be kept cool, at 4°C, and in the dark during transportation to the laboratory (Siegrist and Jenssen 1990, Hewitt 1994). Ice packs are commonly used for this purpose. The properly preserved BTEX and gasoline-contaminated soil samples can be stored for 14 days without any serious degradation or loss of contaminants (Environment Canada 1997). Trip blanks are also placed with the collected samples during transportation and storage. Analysis of the trip blank can give information on the occurrence of cross contamination of the collected soil samples with foreign substances during transportation and storage (Parr et al. 1991).

5.3.1 Sample Preparation

The extraction of the components of interest from the collected soil samples is often necessary prior to the introduction to an analyser. The extraction of the volatile organic substances from a solid matrix is much more difficult than from a gas or liquid. Even though several methods have been proposed for extracting different volatile organic substances from the collected soil samples for analysis, there is no unique approach yet available in literature (Amaral et al. 1994). The commonly used methods include Headspace Analysis, Purge-and-trap, Solvent Extraction, Soxhlet Extraction, Ultrasonic Extraction, Supercritical Fluid Extraction and Microwave Extraction.

5.4 Discussions

Although passive sampling provides a simpler method when compared to active sampling for the collection of soil-gas, it requires long sampling periods due to the low uptake rates. Another disadvantage is that unstable flowrates may occur during the sampling period, when compared to the withdrawal of a defined volume of soil-gas sample at a specifically controlled flowrate in active sampling. In order to achieve a rapid in-situ soil-gas collection operation, the active sampling method is preferred over the passive sampling method for the present research.

Active soil-gas sampling devices are often pushed or driven to the sampling horizon from surface or lowered into pre-drilled holes. For the case of lowering the sampling device into pre-drilled holes, the removal of the hole-making device encourages soil-gas venting and lowers the sample representativeness. The subsequent insertion of a sampling device into the hole may cause additional venting of soil-gas as the sampling device displaces the atmosphere in the hole upon insertion. A sampling device positioned by means of pushing or driving is, therefore, preferred. From past experience, the cone penetrometer appears to be the most suitable field penetration device for the present application. The cone penetrometer is not only a good device for geotechnical characterization of the subsurface, it can also be adopted for carrying the soil-gas sampling device to the subsurface with minimum disturbance to the surrounding soils.

Furthermore, active soil-gas sampling by means of pushing from the surface is also superior to the current use of permanent monitoring wells. As the plume moves, the soil-gas trapped inside the installed monitoring wells or monitoring tubes may not be able to move along with the advancement of the plume. As a result, erratic measurements might be recorded during a long-term monitoring programme unless serious purging of the monitoring wells prior to each soil-gas sample extraction interval is made. However, purging alone has difficulty removing the memory effect on the monitoring wells if high concentration of moist soil-gas is trapped inside the wells for days at low soil temperatures. On the other hand, it might take hours to days to allow the soil-gas to diffuse back into the monitoring wells after the wells are cleaned. It is highly dependent on the volume of the monitoring wells and the soil properties. Changes in ground condition might also cause the subsequent change in soil properties hence, the pattern of the contaminant migration will be altered and additional monitoring wells will be required to cover the unexpected changes.

During the penetration process, the material of the sampling device must be able to withstand environmental conditions that are not intended for typical field instruments. These conditions include rough handling by operators, severe vertical and horizontal stresses during pushes, high humidity and high levels of silts and fines. Researchers have proposed various forms of sampling devices. It has been found that a sampling module with a sampling port opened on the side appeared to be the most straight forward and cost effective. In order to accommodate the previously described unfavourable environmental conditions during the penetration process, Type 316 stainless steel has been chosen as the

material for developing the sampling device. Type 316 stainless steel material can also be advantageous for efficient soil-gas sample transportation.

In order to achieve an efficient field operation, peculiar design considerations are confronted when interfacing a soil-gas sampling device to a cone penetration test rig. Not only should the material of the sampling device be able to withstand the possible unfavourable environmental conditions which arise during the penetration process, the design of the sampling device should overcome the constraint of the relatively narrow inner diameter of the push rods. The inner diameter of the most commonly used push rods is 25mm. The transfer lines must be narrow enough to allow threading through the push rods together with the presence of the cable for carrying the measuring signals of the cone penetrometer to the surface. From a practical point of view, the transfer line is suggested to be 50% longer than the depth of penetration in order to allow enough slack for easier handling at the surface.

The purge volume for removing ambient air prior to actual soil-gas collection is dependent on the volume of the sampling system. Although stainless steel tubing has a higher efficiency in transporting volatile organic compounds at ambient temperature (Doskey et al. 1996), it is equally important that the internal volume of the sampling system be kept to a minimum. U.S.EPA (1990) suggested that a purge volume of 1 to 5 times the casing volume is sufficient to exchange 98-100% of the air within the sampling system, while Doskey et al. (1996) reported that 2 times the casing volume is adequate. By considering these factors, therefore, a Type 316 stainless steel tubing of 1.59mm outer

diameter and 1.02mm internal diameter has been deployed in the present research. A 25 μ m Type 316 stainless steel frit was also placed on the surface of the sampling port to prevent clogging of the transfer line during active sampling.

In addition, an add-on split-tube type sampling module was proposed in this research. An advantage of the split-tube type sampling module is that it can be placed virtually at any intersection along the series of push rods where necessary. Hence, additional sampling modules can be added to the cone penetration test rig without interruption of an on-going operation. It is not uncommon that an additional round of soil-gas sampling at the shallow location is desired as the cone penetrometer advances to further depth for geotechnical characterization. Its usefulness will be more marked if a replacement sampling module or a transfer line is required to replace the damaged sampling module or flooded transfer line without retracting the cone penetrometer during a sounding.

As previously described, there are a wide variety of methods that can be used for storing the collected soil-gas samples. The major disadvantage of using containers for soil-gas collection is due to the extensive cleaning and testing of the containers between use. It tends to detract from the routine application of the method. Although soil-gas sampling into containers is the simplest sampling technique that allows the direct analysis of collected soil-gas, there is a possibility of chemical reactions occurring in the container during sample storage. It will be more marked in the presence of soil-gas containing moisture and oxygen, which are commonly found in partially-saturated subsurface

environments (Berezkin and Drugov 1991). Furthermore, sample pre-enrichment is required for analyzing a large volume of a very low concentration soil-gas sample.

Commonly used sorbent materials include various types of collection solvents and solid sorbents. ASTM D-3686 however, pointed out that water mist and vapour could interfere with the collection of organic compound vapours. Humidity greater than 60% can reduce the sorption capacity of activated charcoal to 50% for some analytes. Clements and Lewis (1988) also found that the irreversible sorption of some organics to activated charcoal and the potential reactions promoted by the high surface area of this sorbent might also cause problems.

Porous polymer absorbents, such as Tenax, Porapaks, Chromosorbs, XAD, and polyurethane foam are relatively chemical inert and hydrophobic. Due to their low affinity for water, they are ideal for the sampling of moist soil-gas. Of these porous polymer absorbents, Tenax is generally preferred because it can efficiently absorb organic compounds with a wide range of boiling temperatures, has a lower retention rate of water, has a greater chemical purity, and permits the use of high temperatures for rapid desorption (Schlitt et al. 1980, NIOSH 1984, Sturges and Elkins 1993, Ventura et al. 1993, Peters and Bakkeren 1994, Helmig and Vierling 1995, Baya and Siskos 1996, Yang and Lo 1997). Tenax also produces relatively little chromatographic background at high desorption temperatures and the thermal limit of Tenax is 350°C. High sorption efficiency for analytes of interest also permits a lower detection limit, providing that the

soil-gas samples are enriched on Tenax. Therefore, various forms of Tenax have been employed in this research.

Sorbent materials prepared in tubes can produce significant backpressure and decrease the sampling efficiency when collecting a soil-gas sample. EPA Method 5041 however, pointed out that back diffusion of the absorbed substance might occur when a high backpressure is developed during sampling. This is due to a large pressure drop after the cut off of the applied vacuum source. The applied flowrate for sample collection is another major factor that will affect the sampling efficiency of a chosen sorbent material. Winberry et al. (1990) and Manura (1997) recommended that the maximum linear velocity through the sorbent material should not exceed 500 cm/min. If the velocity is greater than 500 cm/min, the analytes of interest will pass through the sorbent material too quickly to permit efficient trapping on the sorbent material. In order to overcome these problems, a Tenax-coated filter absorbent 25mm in diameter was developed for active soil-gas sampling in this research. Optimum sampling flowrate was carefully characterized and applied throughout the research. Conventionally, it has been a disadvantage of thermal desorption if replicates are needed. Owing to this limitation, attempts have been made to determine the feasibility of obtaining a subsample within the same filter absorbent for replicates of thermal desorption and subsequent gas chromatographic analysis.

Cryogenic concentration followed by thermal desorption and gas chromatographic analysis can eliminate the generation of a large quantity of liquid waste in the field. The

typical cryogenic focusing unit, however, consumes a large amount of liquid cryogen, such as nitrogen or carbon dioxide, to cool the sample collection trap and this result in a higher operating cost and additional safety precautions. The nonliquid cryogenic concentration devices based on the Peltier effect may not be suitable for field applications. The operations of these thermoelectric cooling devices relied on a heavy supply of dc potential. Moreover, if insufficient water has been removed from the sample during cryogenic focusing, ice crystals can form and block the gas chromatographic column. As a result, the transfer efficiency of the analytes was lowered. Subsequently, water collected on the trap will be transferred to the gas chromatographic column when the trap is heated.

Instead of using the drying agent before the cryogenic trap for removing the excessive water vapour, an additional focusing tube filled with sorbent material with a lower affinity for water, has been employed in conjunction with thermal desorption and sample introduction for gas chromatographic analysis in this research. Analytes trapped inside the focusing tube are thermally desorbed at the same flowrate as the gas chromatograph. It minimizes any dilution of the desorbed analytes and entails sharp peaks without any cryotrapping. The effectiveness of the focusing tube deployment can be more marked if the optimum compatibility of the internal diameter between the focusing tube and the gas chromatographic column is achieved. Furthermore, the focusing tube has a shorter heating and cooling cycle due to its compact size. Compressed air is cheap, readily available, less combustible and less hazardous during handling thus it makes an attractive alternative for rapid cooling. The success of the attempt in replacing the use of liquid

cryogen and thermoelectric cooling devices by compressed air in this research could form a good foundation to the future development of a compact portable gas chromatographic system based on vortex tube (Ranque 1933, Hilsch 1947) for rapid field operations.

Although the collection of soil samples is not the primary objective of the present research, verification samples were collected for verifying the usefulness and effectiveness of the proposed field device. With reference to the local experience, a modified ultrasonic extraction method suggested by the Centre for Analytical/Environmental Chemistry of Carleton University for extracting gasoline range contaminants has been employed in this research.

Chapter 6

Instrument Development

6.1 Introduction

As discussed in Chapter 3, numerous sensors have been developed by other researchers and adapted onto existing geotechnical field devices for geoenvironmental characterization of the subsurface. It has however, been found that most of the proposed sensors are chemical specific and their accuracy can be affected by the soil mineralogy. As discussed in Chapter 2, soil-gas surveying with active soil-gas sampling followed by gas chromatographic analysis appeared to be a promising technique for the determination of multiple constituent contaminant type. Hence, it leads to the objective of the present instrument development.

6.2 Methodology

The building of the field device is based on combining two existing technologies: cone penetration technology and gas chromatography. The cone penetrometer penetrates into the soil at a steady speed to provide information on the soil type, groundwater condition, soil permeability and other soil characteristics. The attached split-tube type soil-gas sampling module permits active soil-gas sampling at various depths in the soil and passes the contaminants of concern onto a Tenax-coated glass fiber filter absorbent. The retained contaminants are then thermally desorbed and pass onto a gas chromatographic system for analysis. Hence, the extent and nature of the contamination both in the vertical and horizontal directions can be identified. A block diagram of the system components is shown in Figure 6.1.

FIGURE 6.1 Block diagram of system components.

6.3 Enhancement of the Cone Penetration Test System

6.3.1 Battery Operation

In order to minimize the demand for AC power in the field, the conventional AC operated power supplies for operating the cone penetrometer and the depth encoder have been replaced by the proposed battery-operated power supply. A DATEL 8-11 Watts, 2"x1"x0.375", triple output DC/DC converter has been employed in this research. This inverter has the capability of supplying multiple concurrent DC output voltages and it is placed inside a compact, water-resistance junction box. All the necessary input and output connections are made available on the cover of the junction box. A 12-Volt DC, 7.2 Ah rechargeable sealed gel cell power pack has been employed as the power source for the field device. The supplied 12-Volt DC has been converted into three independent power outputs of 15-Volt DC, -15-Volt DC and 5-Volt DC for operating the cone penetrometer and the depth encoder, respectively.

Furthermore, the enhanced battery-operating test system will also eliminate the necessity of additional protection for the testing equipment from the power surges that arise from the commonly used power generator. Figure 6.2 shows the junction box, the depth encoder and the PC-Card type data acquisition board together with their wiring configuration.

6.3.2 Data Recording System

In order to form a good foundation for the future development of advanced geotechnical field testing techniques it has been decided to develop the in-house data recording system in this research. The proposed data recording system for the cone penetration test system consists of an IBM notebook personal computer and a National Instrument DAQCard-700 PC-Card type data acquisition board. The strain gauge type sensors built in the cone penetrometer send out continuous electronic analogic signals to the data acquisition board, which converts the collected signals into a digital display in engineering units. The depth of penetration is closely monitored by the pulse signal transmitted from the depth encoder. The recording interval of the measured tip resistance, sleeve friction and pore water pressure is triggered by a predetermined penetration interval of 2mm during a cone penetration sounding. The recorded measurements are then passed onto the personal computer for permanent storage and/or further analysis. Figure 6.3 shows the IBM notebook personal computer equipped with a National Instrument DAQCard-700 data acquisition card.

FIGURE 6.2 Photograph of junction box.

FIGURE 6.3 Photograph of data recording system.

6.3.3 Data Acquisition Software

The computer program is written in QuickBasic language, a convenient low-level programming language for development purpose. The computer program is able to transmit the system control commands, FUNCTION command, and receive data signals to and from the data acquisition board. A flow diagram for the main program loop is given in Figure 6.4. After the initialization of the data acquisition board, the program performs a continuous scanning of all the output signals from the cone penetrometer and the depth encoder. All measurements are converted into a digital display in engineering units. The program then reports the status of the system setup that facilitates monitoring and inspection of the system prior to a piezocone sounding. The program is written in module form and allows the user to access a number of option subroutines built into the program through an option menu. A list of various options common for each test is as follows:

- [1] Enter the experimental conditions
- [2] Re-Zero
- [3] Enter the valves to be added after zeroing
- [4] Start the test
- [5] Adding push rod/collecting soil-gas sample
- [6] End the test
- [7] Clear all input data
- [8] Change title and filename
- [E] Exit menu

FIGURE 6.4 Flow diagram of main program loop (for CPT system).

The whole recording system is reset to zero after the cone penetrometer has been lowered to the ground and before the penetration has commenced. The required offset or initial datum can be added onto the measurement of the selected sensors. This option is particular useful if a cone penetration sounding is interrupted due to unexpected subsurface conditions or the replacement of damaged push rods. The data collection sequence can be halted for the addition of push rods or the collection of soil-gas samples. This option is also useful for performing a consolidation test at the location of interest. The exit menu provides an alternative means for switching the working environment between the data acquisition software and the computer operating system platform. If the system is equipped with wireless modems, data transmission back to the office is also possible from the test site.

6.3.4 Calibration

A number of notebook personal computers have been calibrated against the generated noise signals with the installed PC-Card type data acquisition board. Continuous measurement of a clean DC supply voltage has been conducted for 3 hours. This 3-hour duration is sufficient for warming up the internal circuits of all electronic equipment and for detecting the generated noise signals. It has been found that the IBM and Toshiba notebook personal computers have the best performance among the other tested machines. The observed noise level is maintained well below the resolution of the data acquisition board of 2.4mV. This discrepancy is due to the interference arisen from the

improperly shielded internal circuit of the tested computer. The data acquisition board is then calibrated with an IBM notebook personal computer for its linearity prior to use.

Since the measurements of both of the tip resistance, q_c , and the sleeve friction, f_s , are by means of load cells built into the penetrometer tip, the load cells are calibrated against the applied load provided by an MTS loading system at a constant temperature. Special base plates for calibrating tip resistance and sleeve friction are shown in Figure 6.5 and Figure 6.6. The pore water pressure measurements, u , are calibrated against the applied pressure in a sealed chamber at constant temperature (Figure 6.7). The sensors built in the cone penetrometer are calibrated separately. Each sensor is loaded twenty times to its full capacity or maximum applied pressure before calibration. After taking the initial output voltage from the sensor at zero load condition, the cone penetrometer is loaded progressively and the value of the output voltage corresponding to each applied load is recorded. The cone penetrometer is then progressively unloaded and records of output voltage corresponding to each applied load are obtained. Calibration curves of the sensors are presented in Figure 6.8 to Figure 6.10. Calibrated constants for tip resistance and sleeve resistance are 13.33 MPa/Volt and 133.33 kPa/Volt, respectively. The bi-linear response of the pore water pressure yields a constant of 1333.33 kPa/Volt for pressures below 100kPa and a second constant of 462.53 kPa/Volt for the pressure range of 100kPa to 600kPa. The shape of the calibration curves do change during the lifetime of the penetrometer tip, therefore, before each sounding an inspection should be made for wear on the cone, the friction sleeve and the shaft of the penetration tip. In addition, the seals between the different elements of a penetrometer tip should be inspected to determine

their condition. If the zero load error exceeds 1% of the full scale output or the calibration error exceeds 2 to 3% of the original calibration values, the penetrometer should be checked, cleaned and re-calibrated. The depth encoder transmits digital pulse signals at a resolution of 600 cycles per turn of the shaft. By using a 95.5mm diameter friction roller on the shaft of the depth encoder, the travel distance per cycle is then equivalent to 1mm.

FIGURE 6.5 Photograph of calibration device for calibrating tip resistance.

FIGURE 6.6 Photograph of calibration device for calibrating sleeve friction.

FIGURE 6.7 Photograph of calibration device for calibrating pore water pressure.

FIGURE 6.8 Calibration curve for tip resistance.

FIGURE 6.9 Calibration curve for sleeve resistance.

FIGURE 6.10 Calibration curve for pore water pressure.

6.4 Modification of the Gas Chromatographic System

A Varian 1440 Gas Chromatograph is re-assembled with purchased parts. It allows the use of a home-made focusing tube mounted on the 6-port valve for ideal sample introduction and for concentrating a load of large sample volume at a very low concentration prior to an analysis. The original packed column has been replaced by a 0.8mm internal diameter, 15m long, Ultra Alloy-1 capillary column coated with 2-micron film thickness of 100% dimethylsilicone for achieving a better separation of the introduced sample. A SRI flame ionization detector with detectability of 100ppb, has

been deployed in this research. The modified gas chromatographic system is then characterized for optimum experimental conditions. The condensed chromatogram technique proposed by Lam et al. (1997) and Law et al. (1999) has been chosen for analyzing the gasoline type contaminants throughout the research. Recording systems similar to the one for the cone penetration test system have also been developed.

6.4.1 Injection System

In order to accommodate a load of large sample volume at very low concentration on a capillary column, a 6-port valve injector with a focusing tube (Figure 6.11) has been deployed together with the self-sealing rubber septum injection port. Since the focusing tube on the 6-port valve injector fixes the volume of sample, the same volume of sample is introduced onto the column rapidly and consistently each time. The temperature of the 6-port valve injector is provided by an embedded 25.4mm long Chromalox cartridge heater, monitored by a type K thermocouple, and controlled by an Omega CN370 temperature controller via a Crydom solid-state relay unit (Figure 6.12). All transfer lines use Type 316 stainless steel tubing of 1.59mm outer diameter and 1.02mm internal diameter. The exposed sections of the tubing connected to the 6-port valve injector are insulated with glass wool. An aluminium block fitted with a 25.4mm long Chromalox cartridge heater (Figure 6.13) provides the required elevated temperature for desorbing the sorbed substance from the focusing tube. The temperature of the heating block is also monitored by a type K thermocouple and controlled by the second Omega CN370

temperature controller via a Crydom solid-state relay unit. A continuous supply of compressed air regulated at 207kPa is applied for cooling the focusing tubing to 20°C during the concentrating of the contaminants of interest. The design of the focusing tube is based on the Ontario soil cleanup criteria for potable groundwater situation (Ministry of Environment and Energy 1996). The focusing tube is designed to cope with soil-gas collected from the gasoline-contaminated soil with contamination level ranging from 1 to 100ppm. The advantage of using the sorbent material, Tenax, has been discussed in Chapter 5. The low affinity of Tenax-GR for water vapour further ensures the life cycle of the capillary column will not be jeopardized by repeatedly introducing moist soil-gas samples for analysis. Since stainless steel material is particularly efficient for heat transfer during the blast heating and rapid cool down, Type 316 stainless steel tubing of 1.59mm outer diameter and 1.02mm internal diameter has been chosen as the material of the focusing tube. With reference to Sugawara (1998), a 127mm long focusing tube filled with approximately 22mg of sorbent material Tenax-GR of mesh size 80/100 is sufficient for concentrating low to medium level gasoline type contaminants.

FIGURE 6.11 Photograph of focusing tube mounted on the 6-port valve.

FIGURE 6.12 Photograph of Omega CN370 temperature controller and Crydom solid-state relay unit.

FIGURE 6.13 Photograph of heating block for focusing tube.

6.4.2 Data Recording System

Two similar recording systems have been developed for use with the gas chromatographic system in this research. The first recording system has been developed under the same principle as the one for the cone penetration test system, and is aimed for field operations. It utilized an IBM notebook personal computer and a National Instrument DAQCard-700 PC-Card type data acquisition board. The recording system is then transferred onto a desktop personal computer installed with a National Instrument LAB-PC+ data acquisition board for laboratory usage. Calibration against the generated noise signals for the desktop computer installed with the data acquisition board has also been performed. A similar calibration procedure used for the cone penetration test

system for a continuous measurement of a clean DC supply voltage has been conducted for 3 hours. Excessive noise signals have been observed from the laboratory use recording system. This is due to the interference arising from the power supply of the desktop computer. Changing to a properly shielded power supply on the desktop computer has solved this problem. Linearity of the data acquisition board has also been calibrated prior to use. Characteristic voltage output signals of the detected components of a sample from the flame ionization detector are transmitted to the data recording system and recorded at a rate of 10 readings/second. A Gould OS4100 digital storage oscilloscope also receives the characteristic voltage output signals and are plotted as voltage output against time for online visual monitoring. Figure 6.14 shows the data recording system for laboratory usage.

FIGURE 6.14 Photograph of recording system for laboratory usage.

FIGURE 6.15 Flow diagram of main program loop (for GC system).

6.4.3 Data Acquisition Software

Computer programs written in the same structure as the one for the cone penetration test system have been developed. Since both data acquisition boards being used belong to the same product family, they share the same group of system control commands. The computer programs for the control of the test can therefore, be easily transferred between the two computer systems with a minor modification on the configuration parameters. A flow diagram for the main program loop is given in Figure 6.15. After the initialization of the data acquisition board the program performs a continuous scanning of the detector voltage output and reports the status of the system setup prior to a gas chromatographic analysis. A list of various options commonly used is as follows:

- [1] Enter the experimental conditions
- [2] Re-Zero
- [3] Start the test
- [4] End the test
- [5] Clear all input data
- [6] Change title and filename
- [E] Exit menu

The data recording sequence is triggered manually immediately after the sample has been introduced onto the capillary column for analysis. The time lag of this operation is normally within a fraction of second. The characteristic voltage output signals from the flame ionization detector are recorded at a rate of 10 readings/second.

6.4.4 Experimental Conditions

The accuracy of the chromatographic analysis is highly dependent on the apparatus used and the experimental conditions. The temperature programming technique has been employed in this research. The rate of increase of temperature has been optimized for the reasonable separation of the components of interest. The initial column temperature is kept at 40°C for one minute so that low-boiling components can be eluted separately enough to observe component peaks. The column temperature is then linearly increased at a rate of 20°C/min to a final temperature of 200°C to elute the high-boiling point components towards the end of the analysis. The temperature of the 6-port valve injector is kept at 160°C to maintain an efficient transfer of the desorbed substance being transported onto the capillary column for subsequent analysis.

With reference to Sugawara (1998), the carrier flowrate of 6 mL/min yields the best performance without reaching the breakthrough of the retained substances within the focusing tube. Therefore, principal and secondary carrier flowrates of 6 mL/min have been employed throughout the research.

High purity gases that do not contain any hydrocarbon have been employed for operating the flame ionization detector. They are Ultra High Purity Hydrogen and Zero Air that were purchased from BOC Canada. With reference to the recommendations given in the flame ionization detector instruction manual, optimization for the performance of the

flame ionization detector has been started with a hydrogen flowrate of 18 mL/min and an air flowrate of 250 mL/min. The detector temperature has also been maintained at 200°C to prevent condensation of impurities at the jet assembly. It has been found that there was no significant change in the sensitivity of the obtained chromatograms with minor variations of the hydrogen and air flowrates. Therefore, the recommended hydrogen and air flowrates are used for the subsequent analysis.

The total time for completing a gas chromatographic analysis under these experimental conditions is approximately 8 minutes. Reasonable separation of the components of interest has been observed in the obtained condensed chromatogram.

6.4.5 Calibration

The reliability and absorption efficiency of the focusing tube have been calibrated against benzene, toluene, ethylbenzene, and xylenes (BTEX) standards purchased from Supelco. Working standards are prepared by mixing BTEX standards of 5000 µg/mL together and diluting to 500µg/mL, 100 µg/mL, and 10 µg/mL in purge-and-trap grade methanol purchased from Fisher Scientific. In addition, a 1000 µg/mL benzene standard has been prepared for testing the capability of withholding benzene, the lowest-boiling point component among the standards, in a separate run.

A sample of 0.5 μL of 1000 $\mu\text{g/mL}$ benzene standard has been passed onto the focusing tube through the hot self-sealed septum injection port. The temperature of the self-sealed septum injection port is maintained at 200°C for ensuring complete vapourization of the injected liquid sample prior to passing it onto the capillary column for analysis. The temperature of the focusing tube is maintained at 20°C by continuously blowing compressed air directly onto the surface of the focusing tube. The obtained chromatogram shows that a large portion of the solvent can be removed in approximately 4 minutes (Figure 6.16), this is due to the low affinity for methanol with Tenax-GR. Furthermore, no breakthrough of the injected benzene standard is observed after a purge time of 7 minutes (Figure 6.16). A 4-minute purge cycle has therefore, been chosen for the subsequent calibration tests for the BTEX standards.

The trapped analytes are then desorbed at 200°C by putting the aluminium heating block directly onto the focusing tube and backflushed onto the capillary at 6 mL/min for analysis. The obtained chromatogram confirms the success of removing a large portion of the solvent during the purge cycle and yields a better separation of the analytes without changing the experimental conditions for the subsequent analysis (Figure 6.17).

A series of control tests has been performed by injecting 0.5 μL of each of the working standard directly onto the gas chromatographic system for analysis. The obtained chromatograms are compared to those obtained in the second test series of using the

focusing tube for characterizing the percentage recovery of the analytes trapped onto the focusing tube.

Prior to each run of the second test series, the focusing tube is rapidly cooled down to 20°C by continuously blowing compressed air directly onto the surface of the focusing tube. The analytes are passed onto the focusing tube by injecting the working standards through the hot self-sealed septum injection port and purged for 4 minutes. The trapped analytes are desorbed at 200°C by putting the aluminium heating block directly onto the focusing tube. By switching the flow path on the 6-port valve injector, the desorbed analytes are then introduced into the capillary column by a secondary carrier gas. Both the principal and secondary carrier flowrates are maintained at 6 mL/min throughout the tests. At this stage, the conventional backflushing technique for sample introduction has not been employed. Instead, the desorbed analytes travel through the focusing tube in the same flow direction as for the purge cycle. In this case, the focusing tube also serves as a miniature packed column for early separation of the low-boiling point components before passing them onto the capillary column for analysis. Hence, better separation of the more complex introduced samples can be achieved without a reduction of the carrier flowrate.

Typical chromatograms of the test series are shown in Figure 6.18 and Figure 6.19. Calibration curves of the working standards for direct injection and using the focusing tube are shown in Figure 6.20 and Figure 6.21, respectively. It has been found that the averaged percentage of recovery of the samples injected onto the focusing tube can be as

high as 100% when compared to the control tests using direct injection. The average percentages of recovery for individual standards are summarized in Table 6.1. It has been confirmed that the focusing tube is reliable and efficient for trapping BTEX range analytes under the present experimental conditions.

Concentration of Standard ($\mu\text{g/mL}$)	Benzene	Toluene	Ethylbenzene	m,p-Xylene	o-Xylene	BTEX
500	108.2	107.7	94.4	109.6	107.4	106.7
100	102.3	107.1	100.0	103.2	103.6	103.1
10	100.0	105.0	107.7	108.3	106.7	102.3

TABLE 6.1 Percentage recovery of BTEX standards.

FIGURE 6.16 Chromatogram of purging the 1000 $\mu\text{g/mL}$ benzene standard.

FIGURE 6.17 Chromatogram of analyzing the 1000 $\mu\text{g/mL}$ benzene standard.

FIGURE 6.18 Typical chromatogram of 100 $\mu\text{g/mL}$ BTEX standards (Direct Injection).

FIGURE 6.19 Typical chromatogram of 100 µg/mL BTEX standards (Focusing Tube).

FIGURE 6.20 Calibration curves of BTEX standards (Direct Injection).

FIGURE 6.21 Calibration curves of BTEX standards (Focusing Tube).

6.5 Development of the Soil-Gas Sampler

6.5.1 Sampling Module

As previously described in Chapter 5, Type 316 stainless steel material is not affected by the unfavourable working environment during the penetration process. Therefore, the soil-gas sampler made of Type 316 stainless steel has been developed for in-situ active soil-gas sampling. In addition, an add-on split-tube type sampling module has also been proposed in this research.

The soil-gas sampler consists of a 35.5mm outer diameter, 10mm thickness and 70mm long male-male threaded split-tube type sampling module (Figure 6.22), a 25µm Type 316 stainless steel frit is embedded on the surface of the sampling port located at the middle height of the sampling module (Figure 6.23), and 6m of 1.59mm outer diameter, 1.02mm internal diameter stainless steel tubing. In addition, a 35.5mm outer diameter, 10mm thick and 170mm long female-female threaded extension rod has also been prepared. The extension rod is being used for raising the sampling module well above the cable connector of the cone penetrometer to provide sufficient space for threading the data cable through the sampling module.

All tubing connections are connected and sealed by using Swagelok stainless steel tube fittings. The transfer line is end capped with a Swagelok stainless steel female quick-connector. It is particularly useful in sealing the transfer line between the collection of different soil-gas samples, and ensures the transfer line remains sealed when left in the push rod as it goes along with the cone penetrometer to greater depths during the subsequent geotechnical investigation. With the complete outfits incorporated onto the cone penetrometer, the soil-gas sampling point is located at 680mm when measured from the penetrometer tip. Figure 6.24 shows the complete outfits incorporated onto the cone penetrometer.

As there is no available literature for ensuring the complete purging of the deployed soil-gas sampling device before use, the required purge volume for the deployed transfer line

shall be used for calibration. Furthermore, the possibility of developed backpressure during active soil-gas sampling shall also be determined in order to avoid the possibility of back-diffusion of the sorbed substance from the sorbent material.

6.5.2 Calibration

Although clean sand is the commonly used backfill material around the underground storage tanks, in some cases, sand with some fines may be used and that depends on the availability of materials from the borrowed areas. Therefore, a series of tests on the possible developed backpressure has been performed on various combinations of soil mixtures of commonly used backfill materials. Different soil mixtures of silica 70 and kaolinite are mixed in an ODJOB o-ring sealed high-density polyethylene mixer. For the consistent control of the prepared soil mixtures, clean silica 70, kaolinite and gravelly sand oven dried at 105°C for 16 hours have been used.

The sampling module is pushed into the middle height of a 5-gallon pail filled with different tested soil mixtures. Soil-gas is withdrawn through the transfer line at different sampling rates by using a 100mL gastight syringe. The corresponding developed backpressure is measured by using a diaphragm type dual-scale low-vacuum gauge of 0 to -7.5 kPa purchased from Cole-Parmer Instrument Company. Figure 6.25 shows the dummy cone tip and the dual-scale low-vacuum gauge incorporated onto the soil-gas sampler for measuring the developed backpressure. Measurements of backpressure at

different applied sampling rates are listed in Table 6.2. It has been found that the maximum recorded backpressure is 5.5 kPa at a sampling rate of 60 mL/min. and the induced backpressure immediately returns to zero at the termination of the applied vacuum source. For the application of a sampling rate of 20 mL/min, the measured backpressure from the tested soil mixtures is approximately 2 kPa. It can be concluded that the backpressure developed under this sampling rate is not sustained at the end of soil-gas sample collection and thus vacuum desorption of the trapped analytes from Tenax will not occur.

The required purge volume of the deployed transfer line has been determined by connecting a 9m long transfer line directly onto the injection port and the flame ionization detector of the gas chromatograph. The transfer line is initially saturated by passing a volume of 10 mL of pure phase gasoline vapour through the tubing. The transfer line is then purged with nitrogen at a flowrate of 20 mL/min and the detector response is recorded (Figure 6.26). It has been found that the introduced gasoline vapour can be removed from the transfer line in approximately 100 seconds, which corresponds to a purge volume of 33 mL. By considering the actual application of a 6m long transfer line for the in-situ active soil-gas sampling, a purge volume of 30 mL, equivalent to 6 casing volumes of the transfer line, is adequate to remove the ambient air or residual soil-gas from the previous sampling location.

Soil Type	Moisture Content (%)	Applied Sampling Rate (mL/min)	Measured Backpressure (kPa)	Bulk Density (in loose state) (Mg/m ³)
100% Silica 70	0	12	1.3	1.419
		20	2.2	
		30	3.1	
		60	3.9	
	5	12	1.6	1.150
		20	2.0	
		30	2.6	
		60	4.2	
	10	12	1.6	1.197
		20	1.8	
		30	2.9	
		60	4.5	
90% Silica 70 10% Kaolinite	5	12	1.7	1.103
		20	1.8	
		30	2.4	
		60	3.9	
80% Silica 70 20% Kaolinite	5	12	1.5	1.036
		20	1.6	
		30	2.2	
		60	3.2	
Gravelly Sand	5	12	1.8	1.309
		20	2.2	
		30	2.7	
		60	5.5	

TABLE 6.2 Measured backpressure at different applied sampling rates.

FIGURE 6.22 Photograph of stainless steel sampling module.

FIGURE 6.23 Photograph of 25µm frit embedded on sampling module.

FIGURE 6.24 Photograph of complete outfits incorporated onto the cone penetrometer.

FIGURE 6.25 Photograph of attachments for measuring the developed backpressure.

FIGURE 6.26 FID response for purge volume.

6.6 Development of Tenax-Coated Glass Fibre Filter Absorbent

In order to avoid the difficulties previously discussed in Chapter 5 for using sorbent tubes for in-situ active soil-gas sampling, a Tenax-coated filter of 25mm in diameter has been used in this research for collecting soil-gas samples. Furthermore, in order to avoid passing large loads of very low concentration samples onto the capillary column, it has been decided that the analytes desorbed from the filter absorbent are re-concentrated onto the focusing tube prior to passing them onto the capillary column for analysis. The conventional method suggested by Winberry et al. (1990) for estimating the maximum flowrate and maximum sample volume for sorbent tubes may not be valid for the proposed Tenax-coated filter absorbent. Therefore, the optimum sampling flowrate and the maximum sample volume must be carefully characterized and applied throughout the research. The choice of filter for coating the sorbent material, Tenax, has also been examined.

6.6.1 Selection of Filter

Hardened ashless filter paper, glass microfibre filter, PTFE membrane filter, nylon membrane filter, cellulose acetate membrane filter and cellulose nitrate membrane filter are tested for their integrity against chloroform, the solvent for Tenax, and against a temperature of 200°C. It has been found that PTFE membrane filter and cellulose acetate membrane filter can not resist the solvent for Tenax and dissolved in the chloroform. On

the other hand, the nylon membrane filter and the cellulose nitrate membrane filter are damaged at high temperature. As a result, hardened ashless filter paper and glass microfibre filter are the only tested materials that perform satisfactorily under the integrity tests. Whatman 541 hardened ashless filter paper, Whatman 934AH glass microfibre filter, Whatman GF/B glass microfibre filter and Whatman GF/D glass microfibre filter have been chosen for the subsequent characterization on their performance.

6.6.2 Tenax Coating

In accordance with the manufacturer specifications for Tenax, chloroform is rated excellent among the suggested organic solvents for dissolving Tenax powder. For the compatibility of using the 22mg of Tenax-GR packed in the focusing tube, a similar quantity of Tenax is going to be coated onto the effective area of the filter. In order to avoid the necessity of extracting the Tenax component from Tenax-GR, Tenax-TA of mesh size 60/80 is used. Various concentrations of Tenax solution are prepared by dissolving a known amount of Tenax-TA powder into chloroform and stirred by a vibrating stirrer for 10 minutes. Selected filters of 47mm in diameter are immersed in the Tenax solution for a few seconds and then allowed to dry in a vacuum-sealed dessicator overnight. It has been observed that Whatman GF/B glass microfibre filter and Whatman GF/D glass microfibre filter shrink towards their centre without control as they absorb the Tenax solution. Therefore, the final choice of filter for developing the proposed filter-

supported absorbent is determined by the mass of Tenax that can be coated on the Whatman 541 hardened ashless filter paper, and that can be coated on the Whatman 934AH glass microfibre filter.

A specially designed filter cutter (Figure 6.27) extracts coated filters at 25mm in diameter. The mass of Tenax coated on each 25mm diameter filter is then obtained. By varying the concentration of the Tenax solution, it has been found that the difference in mass of Tenax coated on these two filters is at a ratio of two. From the economic point of view, Whatman 934AH glass microfibre filter has been chosen as the final choice of the filter support. In order to yield a mass of the coating of approximately 22mg of Tenax on the effective area of the filter, a Tenax solution of a concentration of 100 mg/mL has been revealed. The averaged net mass of Tenax coated on the filter is approximately 30mg. By using the filter holders of a filtration area of 346.4mm², the calculated effective mass of the coating on a filter is approximately 21mg.

With reference to the conventional procedures for preparing the sorbent tubes to the working condition, Tenax-coated glass fibre filter absorbents are then conditioned at 300°C in the desorption module under a constant nitrogen flow of 50 mL/min for 3 hours prior to use. Conditioned filters are kept in glass vials and stored in the freezer.

From a separate series of tests, the exit end of the desorption module is connected directly onto the flame ionization detector. Analytes eluted from the desorption module are

monitored as the coated filter is being conditioned. It has been found that the time required for conditioning the coated filters can be greatly reduced. The majority of impurities on the filter have been removed within three minutes. Efficiency and absorption capacity of the conditioned filters have also been verified using the BTEX standards. It has been found that coated filters conditioned for longer than 15 minutes are sufficient for trapping the analytes of interest. The measured percentages of recovery of the BTEX standards retained on these filters are identical. To be conservative, a period of 30 minutes was chosen as the standard conditioning time for the future preparation of the Tenax-coated filter absorbents.

FIGURE 6.27 Photograph of 25mm diameter filter cutter.

6.6.3 Filter Holders

Two types of Millipore Type 316 stainless steel 25mm filter holder have been employed in this research. A modified microsyringe 25mm filter holder is used for the collection of soil-gas samples. The front end of the filter holder has been modified to accommodate a Swagelok Type 316 stainless steel quick-connect male connector to provide rapid connection and removal of the Type 316 stainless steel transfer line (Figure 6.28). The luer-lock rear end allows the use of syringes as the applied vacuum source during soil-gas sampling. The modified gas line 25mm filter holder is used for desorbing the trapped analytes. Both ends of the gas line filter holder are connected with Type 316 stainless steel tubing to allow nitrogen to pass through the heated filter absorbent and carry the desorbed analytes to the focusing tube (Figure 6.29). To ensure complete desorption of the sorbed substance from the filter absorbent without obstruction, both of the filter holders employed in this research have the same filtration area of 346.4mm².

6.6.4 Desorption Module

The desorption module consists of a modified Millipore Type 316 stainless steel gas line 25mm filter holder and an aluminium heating block fitted with a 63.5mm long Chromalox cartridge heater. The heating block provides the required elevated temperature for desorbing the sorbed substance from the filter absorbent. The temperature of the heating block is monitored by a type K thermocouple, and controlled

by an Omega CN370 temperature controller via a Crydom solid-state relay unit. Figure 6.30 shows the aluminium heating block milled in shape to accommodate the gas line filter holder. A continuous supply of compressed air regulated at 207kPa is applied onto the surface of the gas line filter holder for cooling it down to 20°C prior to loading the filter absorbent. All transfer lines are using Type 316 stainless steel tubing of 1.59mm outer diameter and 1.02mm internal diameter. The exposed tubing connected to the 6-port valve injector is insulated with glass wool. A load of large sample volume of the desorbed analytes at diluted concentration is then passed onto the focusing tube and re-concentrated prior to analysis.

FIGURE 6.28 Photograph of modified microsyringe filter holder with Swagelok quick-connect male connector.

FIGURE 6.29 Photograph of modified gas line filter holder.

FIGURE 6.30 Photograph of heating block for modified gas line filter holder.

6.6.5 Calibration

The reliability and absorption efficiency of the Tenax-coated filter absorbent have been calibrated against benzene, toluene, ethylbenzene, and xylenes (BTEX) standards purchased from Supelco. Working standards are prepared in the same manner as those prepared for calibrating the focusing tube.

The total desorption time required to desorb the sorbed substance from the filter absorbent is estimated by introducing 0.5 μL of 500 $\mu\text{g/mL}$ working standard onto the filter absorbent through the hot self-sealed septum injection port under a carrier gas flowrate of 6 mL/min. The trapped analytes are then desorbed at 200°C and passed directly onto the flame ionization detector. Figure 6.31 shows that the total time required for completely desorbing the trapped analytes from the filter absorbent is approximately 5 minutes. By varying the total purge time across the focusing tube, it has been found that a total purge time of 6 minutes yields the best response for analyzing the BTEX standards together with the removal of the solvent peak (Figure 6.32). Therefore, a 6-minute purge cycle has been chosen for the subsequent calibration tests.

A series of tests has been performed by passing 0.5 μL of each of the working standard onto the filter absorbent. The temperature of the self-sealed septum injection port is maintained at 200°C to ensure complete vapourization of the injected liquid sample prior to passing it onto the filter absorbent. Prior to each run of the test series, the focusing

tube and the filter holder are rapidly cooled down to 20°C by continuously blowing compressed air directly onto the surface of the focusing tube and the filter holder.

The analytes are then passed onto the filter absorbent by injecting the working standards through the hot self-sealed septum injection port under a nitrogen flowrate of 20 mL/min.

The filter absorbent is then transferred onto the desorption module and the analytes are desorbed at 200°C by putting the filter holder directly onto the aluminium heating block. The analytes are re-concentrated onto the focusing tube under a nitrogen flowrate of 6 mL/min for a 6-minute purge cycle. The re-concentrated analytes are then desorbed and introduced into the capillary column for analysis. The obtained chromatograms are compared to those obtained in the control test series for characterizing the percentage recovery of the analytes trapped onto the filter absorbent.

A typical chromatogram of the test series is shown in Figure 6.32. Calibration curves of the standards for using the filter absorbent are shown in Figure 6.33. It has been found that the average percentage of recovery of the samples introduced to the filter absorbent can be as high as 100% when compared to the direct injection control tests. Percentages of recovery for individual standards are summarized in Table 6.3. It has been confirmed that the filter absorbent is reliable and efficient for trapping BTEX range analytes under the present experimental conditions.

FIGURE 6.31 Total desorption time of 500 µg/mL BTEX standard.

FIGURE 6.32 Typical chromatogram of 100 µg/mL BTEX standards (Filter Absorbent).

FIGURE 6.33 Calibration curves of BTEX standards (Filter Absorbent).

Concentration of Standard ($\mu\text{g/mL}$)	Benzene	Toluene	Ethylbenzene	m,p-Xylene	o-Xylene	BTEX
500	103.4	109.0	101.7	110.3	108.1	106.8
100	100.9	103.6	98.2	103.2	103.7	102.1
10	100.0	108.0	107.7	112.5	108.3	103.9

TABLE 6.3 Percentage recovery of BTEX standards.

The developed filter absorbent application is extended for collecting soil-gas from gasoline-contaminated soils. Gasoline-contaminated soil mixtures with contamination levels of $1\mu\text{g/g}$ to $5000\mu\text{g/g}$ are prepared by mixing a known quantity of soil with a predetermined volume of liquid gasoline in a 500 mL amber wide mouth jar sealed with

Teflon septum screw cap. The selected soil materials for the laboratory tests are clean oven-dried silica 70 and kaolinite. Soils mixed at different mixing ratios and at different moisture contents are contaminated with various quantities of regular unleaded gasoline purchased from Esso, Imperial Oil. Regular unleaded gasoline has a density of 0.73 g/cc at 15°C, which is equivalent to approximately 0.726 g/cc at room temperature.

Soil samples prepared with fresh liquid gasoline are used for characterizing the maximum capacity of the filter absorbent against the collected soil-gas from gasoline-contaminated soil samples. Soils samples prepared with weathered liquid gasoline are used for characterizing the optimum efficiency of the filter absorbent against the collected soil-gas from the simulated field soils.

In accordance with the Environment Canada technical assistance bulletins for contaminated sites, a sample bottle half-filled with soil can yield the best result without sample dilution. Therefore, a fixed quantity of 400g of soil has been taken as the standard mass of soil for each bottle of laboratory prepared gasoline-contaminated soil mixture. Soil mixtures and liquid gasoline are mixed by vigorously shaking the jar for 30 seconds until well mixed. A developing time of three hours at 25°C based on Sugawara (1998) is employed for allowing sufficient time for the gasoline vapour in the headspace to reach equilibrium. Prior to the soil-gas sampling, the jar is vigorously shaken for another 30 seconds. The required amount of soil-gas is then extracted from the headspace by pinching through the Teflon septum screw cap. Each soil sample is used once and

then discarded. The volume of liquid gasoline mixed with a standard mass of 400g of silica 70 together with the corresponding contamination levels are listed in Table 6.4.

Contamination Level ($\mu\text{g/g}$)	Volume of Gasoline Added to Soil Mixture (μL)
1	0.56
10	5.50
50	27.60
100	55.10
500	275.50
1000	551.00
3000	1653.00
5000	2755.00

TABLE 6.4 Volume of liquid gasoline added to soils for different contamination levels.

The total desorption time required to desorb the sorbed gasoline vapour from filter absorbent is estimated by collecting 5mL of the laboratory prepared gasoline-contaminated soil-gas with a contamination level of 100 $\mu\text{g/g}$ onto the filter absorbent. A mass of 400g of oven-dried silica 70 is mixed with 55.1 μL of fresh liquid gasoline. The trapped analytes are then desorbed at 200°C and passed directly onto the flame ionization detector. Figure 6.34 shows the total time required for complete desorption of the trapped analytes from the filter absorbent. It has been found that the trapped analytes can be desorbed from the filter absorbent in approximately 6 minutes. To be conservative, an 8-minute purge cycle was chosen for the subsequent calibration tests for gasoline-contaminated soil-gas.

FIGURE 6.34 Total desorption time of 5mL of gasoline vapour.

The optimum sampling rate, the maximum sample volume and the highest allowable contamination level of gasoline-contaminated soil-gas that the filter absorbent can accommodate was characterized by iteration. In order to include the BTEX components within gasoline for the estimation of the total petroleum hydrocarbons of the tested soil sample, the window for area calculations was chosen to be from 200 to 400 seconds. It should be noted that soil-gas higher than $10\mu\text{g/g}$ level must be diluted prior to analysis. Figure 6.35 shows the typical chromatogram of the gasoline-contaminated soil-gas at $10\mu\text{g/g}$ level.

From Figure 6.36, it has been observed that non-linear gas chromatographic response is occurred beyond the $500\mu\text{g/g}$ level. This contamination level also reflects the highest allowable contamination level that the filter absorbent can accommodate. The determined

optimum sampling rate lies between 12 mL/min and 20 mL/min (Figure 6.37), and the maximum deviation of the trapping efficiency at 60 mL/min is approximately 15%. By considering the aim of developing a rapid in-situ sampling procedure, a sampling rate of 20 mL/min has been chosen. Figure 6.38 shows that the filter absorbent can efficiently collect 5 mL of soil-gas without losing the major constituents of gasoline. In order to minimize the required amount of soil-gas to be collected and maintain a good gas chromatographic response, a sample volume of 3 mL has been chosen. By doing so, replicates of soil-gas samples at the same location will be possible. Furthermore, a repeated round of soil-gas samples can be collected, at minor deviation, as the penetration process continues to the greater depths.

FIGURE 6.35 Typical chromatogram of 10 μ g/g gasoline-contaminated soil-gas.

FIGURE 6.36 Calibration curve for different contamination levels.

FIGURE 6.37 Calibration curve for different sampling rates.

FIGURE 6.38 Calibration curve for different sampling volumes.

Uniformity of the trapped analytes on the filter absorbent has also been examined. Two 3-mL samples of gasoline-contaminated soil-gas of contamination level of $10\mu\text{g/g}$ are collected onto two separate filter absorbents. Trapped analytes on the first filter absorbent serves as the control sample and are completely desorbed onto the gas chromatographic system for analysis. Three identical filter pieces of 8mm in diameter are extracted at 180° apart from the second filter absorbent using a specially designed filter cutter (Figure 6.39). Trapped analytes on each of the 8mm diameter filter absorbent are then loaded onto the desorption module and supported by a Type 316 stainless steel holding plate (Figure 6.40).

The chromatograms obtained for each of the 8mm diameter filter absorbent are compared among themselves and to the control sample. It has been found that the percentage

difference of the chromatograms obtained for the 8mm diameter filter absorbent is less than 3%. Therefore, it is concluded that the sorbed analytes can be evenly distributed on the filter absorbent. Furthermore, the ratio of the recovered analytes on the 8mm diameter filter absorbents to the control filter absorbent is approximately 1 to 6.9. It is in good agreement with the area ratio of the 8mm diameter filter absorbent and the effective area of the 25mm diameter filter absorbent. It further proved that the filter absorbent not only provides a reliable and efficient means for collecting soil-gas samples, it also has the ability of producing replicates for thermal desorption type of analysis when subsamples are required.

FIGURE 6.39 Photograph of 8mm diameter filter cutter.

FIGURE 6.40 Photograph of 8mm diameter filter holding plate.

6.6.6 Laboratory Modelling

Five types of soil mixtures have been mixed with weathered liquid gasoline at different contamination levels for simulating the field soils. They are 100% of silica 70 at 5% moisture content, 100% of silica 70 at 10% moisture, 90% of silica 70 and 10% of kaolinite at 5% moisture content, 80% of silica 70 and 20% of kaolinite at 5% moisture content, and 100% of gravelly sand at 5% moisture content. In accordance with the Ontario soil cleanup criteria for potable groundwater situation (Ministry of Environment and Energy 1996), the maximum allowable contamination level for gasoline-contaminated soils is 100 $\mu\text{g/g}$. Therefore, gasoline-contaminated soil samples have been prepared at contamination levels of 100 $\mu\text{g/g}$, 10 $\mu\text{g/g}$ and 1 $\mu\text{g/g}$ for tests. A 3 mL soil-

gas sample is extracted from each soil sample at a sampling rate of 20 mL/min and trapped onto the filter absorbent. The sorbed analytes are then thermally desorbed at 200°C and passed onto the gas chromatographic system for analysis. It has been found that the test results exhibit a linear behaviour within the same type of soil mixture. There is a tendency of decrease in gas chromatographic response as the moisture content increases. Increase in clay content and impurities also reduce the gas chromatographic response. These may be due to the solubility of low-boiling point analytes, such as benzene, in water. The increase in moisture content will increase the capacity of the soil to retain benzene in the solution phase, hence, reducing the quantity available for vapour phase diffusion. Kaolinite can also act as a dual absorbent in retaining water and organic vapour, and the organic matter in gravelly sand can provide a larger surface area upon which physical adsorption can occur. Therefore, volatilization can be retarded in these types of soils. Figure 6.41 shows the gas chromatographic response with respect to different type of soil mixtures.

FIGURE 6.41 Gas chromatographic response for different soil mixtures.

6.7 Discussions

Through this research, it has been successfully demonstrated that the use of the battery-operating cone penetration test system enhances the mobility and efficiency of a cone penetration test programme. This achievement also forms the foundation for enhancing the other commonly used field testing methods. Subsequently, more accurate results and lower operating cost for these frequently employed field test programmes, such as the standard penetration test, can be achieved.

Although powerful, personal computers are commonly available at a low cost nowadays, careful calibrations should be carried out prior to their usage for data collection. This is to ensure that the accuracy and reliability of the recorded measurements are not affected by unreliable hardware being employed.

The development of the in-house data acquisition software is advantageous over using purchased third-party software. The use of the low-level programming language is particularly important in gaining direct control over the system at the development stage. It also allows a better understanding of the whole development. This can also form a good foundation for future development of a more complex fully automated system.

Since soil-gas sampling is always quicker than its subsequent analysis, it is worthwhile to develop two separated portable systems for performing these tasks. Hence, it will not interrupt the cone penetration advancement due to a relatively longer period for gas chromatographic analysis at the selected location. This can prevent the possibility that soil setup occurs where clay layers are situated. The developed soil-gas sampling module can also be extended in its usage for collecting groundwater samples during a penetration push. Alternatively, a number of sampling modules can be stacked together to form a multilevel monitoring well.

From the calibration test of the developed sampling module, it has been found that the required purge volume has exceeded the suggested purge volumes of 1-5 casing volume (U.S.EPA 1990, Doskey et al. 1996). Therefore, the suggested purge volume can not be

taken as the standard and applied to all soil-gas sampling devices. Purge volume for different soil-gas sampling devices should be calibrated independently.

The successful attempt in replacing the use of liquid cryogen and thermoelectric cooling devices by compressed air in this research forms a good foundation to the future development of a compact portable gas chromatographic system that is based on the Ranque-Hilsch vortex tube (Ranque 1933, Hilsch 1947). The use of the vortex tube can also replace the demand for electric heaters for blast heating during the gas chromatographic analysis.

Furthermore, it can eliminate the radio frequency noise and magnetic field interference generated from electric cooling and heating devices. Since the focusing tube can efficiently trap the analytes of interest at 20°C, the required inlet pressure for operating the vortex tube to maintain the required temperature can be greatly reduced. Hence, it lowers the consumption of the supplied compressed air and extends the usage of the refilled gas cylinders during the field operations. It is advantageous, especially, for working at remote sites.

Impurities detected during the desorption of the sorbent substance from the filter absorbent at high temperature is mainly due to the viton o-ring seal of the gas line filter holder which becomes unstable as it approaches its maximum operating temperature of 177°C. However, a replacement silicone o-ring seal does not resolve this problem when

it is used for conditioning the filter absorbent at 300°C. In order to solve this problem, a Kalrez Compound 4079 o-ring seal has been taken in place. No bleeding of the Kalrez Compound 4079 o-ring seal is observed from the continuous monitoring of the flame ionization detector response at an operating temperature of 300°C. Therefore, the Kalrez Compound 4079 o-ring seal has been employed for conditioning the freshly prepared filter absorbent at the temperature of 300°C and the routine desorption of the sorbed substance at 200°C, throughout this research.

The use of filter absorbent allows the use of a higher sampling rate compared to the sorbent tubes that contained the same amount of Tenax. If a higher sampling rate is desirable when using the sorbent tubes, longer tubes packed with more sorbent materials are required to permit efficient trapping of the analytes of interest. However, a higher induced backpressure will result. Furthermore, a longer purge time is required for removing the water vapour of the collected moist soil-gas sample. Subsequently, a longer desorption time will be expected for ensuring the complete desorption of the trapped analytes. Moreover, it leads to the demand for a higher capability heating and cooling system for the operation.

The induced backpressure across the filter absorbent will be much smaller when compared to that which occurs in the sorbent tube under the same sampling rate. The pressure difference between the inlet face and the outlet face of the filter absorbent will be minimal. This is due to the small thickness of the filter absorbent compared to the

length of the packed materials in the sorbent tube. The filter absorbent also has a shorter desorption time due to its small thickness. In addition, the filter absorbent is easier to prepare together with a shorter required conditioning time when compared to the sorbent tubes. This great reduction in conditioning time makes possible the preparation of a large number of Tenax-coated filter absorbents for field applications on short notice.

From the uniformity test of the trapped analytes on the filter absorbent, it has been shown that reliable replicates can be obtained from the filter absorbent for thermally desorbed gas chromatographic analysis. This is another advantage over the use of sorbent tubes during the field operations.

In principle, the solid-phase microextraction technique (SPME) employed by Djozan and Assadi (1997), Nilsson et al. (1998) and Mindrup (1998) can be extended in its usage to active in-situ soil-gas sampling. However, due to the size of the coated micro-fibre, a significant induced backpressure will be encountered unless a very low sampling rate is being used. By doing so, a dedicated device has to be incorporated in the field to achieve the required sampling rate for efficiently trapping of the analytes of interest. Furthermore, the operation of the cone penetration advancement will also be seriously interrupted. Therefore, the use of filter absorbent is superior to SPME for active in-situ soil-gas sampling.

By using a time window of 200 to 400 seconds on the condensed chromatogram for quantitative analysis, the background noise arising from organic substances that are

commonly found in clean subsurface environments can be eliminated. False identification of a hydrocarbon-contaminated subsurface that is caused by mis-interpretation of the methane gas measurement is a typical example. As shown in Figure 6.32 that the major components, BTEX, of the gasoline range organics are situated well within the selected time window for the quantitative determination of the total petroleum hydrocarbons of the tested sample. Therefore, more accurate and reliable quantitative analysis can be achieved.

Relationship between the vapour content and the mass content of gasoline-contaminated soils at different contamination levels can be established from the laboratory modelling, from which the upper bound of the gas chromatographic response for each tested soil type has been revealed.

It has been found that there is a tendency of decrease in gas chromatographic response as the soil moisture content increases. This may be due to the solubility of low-boiling point analytes, such as benzene, in water. Moreover, the displacement of residual water from the surface of soil particles into the pore space by gasoline may create a gasoline-wet scenario. The water is covering the gasoline-wet soils and increases the soil sorption capacity. Furthermore, soil moisture is an essential factor for the organic activity in soils. More organisms are able to grow and reproduce at higher soil moisture content. Hence, it increases the soil sorption capacity and the sorption speed (Riser-Roberts 1992). However, there is a controversy on the effects of soil moisture content on the headspace development. For instance, Arvid et al. (1996) reported a positive effect of water

addition for the extraction of BTEX compounds from soils. On the contrary, Bryan et al. (1988) reported no effect of soil moisture content on toluene recovery from the Athabasca oil sands. Although an increase in soil moisture content may enrich the headspace concentration for some specific components of gasoline, the reduction in response due to the previously described reasons may be larger than the enrichment effect for a given soil.

Decrease in gas chromatographic response was also observed at the increase in clay content and impurities. Kaolinite can act as a dual absorbent in retaining water and organic vapour. Clay surfaces have excess negative charge and thus clay has an ability to absorb positively charged molecules. Due to the particle size of clay, it has a large surface area per unit mass and has a high water holding capacity. Moreover, the organic matter in gravelly sand can provide a larger surface area upon which physical adsorption can occur. These characteristics further contribute to the sorption capacity. Therefore, volatilization can be retarded in these types of soils (Riser-Roberts 1992).

On the other hand, the test results exhibit a linear behaviour within the same type of soil mixture. Therefore, it confirms that the filter absorbent works satisfactorily for collecting the gasoline-contaminated soil-gas. The gas chromatographic response obtained from the laboratory modelling can serve as the upper bound of the tested soil type. It is particularly useful for extrapolating the revealed vapour content to mass content correlation to the future measurements of the collected soil-gas samples from the similar soil type. More accurate co-relation between the vapour content and the mass content for the study area can be obtained through a small-scale local calibration by analyzing a small

number of verification soil samples collected adjacent to the selected soil-gas sampling location.

Chapter 7

Field Trials

7.1 Introduction

A number of field trials at a selected site have been carried out for the performance verification of the developed field device. A site located on Uplands Drive in the municipality of Ottawa-Carleton has reported significant hydrocarbon impact and exceeds the Ontario soil cleanup criteria (Van Geel 1999). From the regional geological information, sands and sandy materials dominate the site. In order to make use of the obtained laboratory calibration curves (as presented in Chapter 6), it is more favourable to choose a test site where the soil types are similar to those that have been investigated in the laboratory modelling. This allows immediate projection to the expected results within the similar types of soils. Therefore, this particular site was chosen for the trial operations.

Since hydrocarbon contaminants are a multiple constituent contaminant type, the gas chromatographic analysis was chosen for analyzing all the collected soil-gas samples and

verification soil samples. Soil-gas samples were analyzed using the modified gas chromatographic system developed in this research. Verification soil samples were extracted and analyzed at the Centre for Analytical/Environmental Chemistry (CAEC) of Carleton University.

Evaluation on a qualitative and quantitative performance of the developed field device was made. A pilot test using a manually driven vapour probe was carried out to obtain background contamination information for the selected test hole locations. Consequently, a qualitative performance of the developed Tenax-coated glass fibre filter absorbent could also be determined. Field trials using the developed field device have been carried out at close proximity to the pilot test locations. Recovery of verification soil samples occurred immediately adjacent to the field trial location. The stratigraphic profile of the test hole locations together with the performance of the developed field device will be presented in this chapter.

7.2 Site Description

The location of the study area (Tank Farm, Canadian Forces Base Ottawa) and the neighbouring lands are presented in Figure 7.1. The Tank Farm area is approximately 4.5 hectares and lies within the Department of National Defence lands. The site fronts onto Uplands Drive in the municipality of Ottawa-Carleton, and is approximately 600 metres

north of the Airport Parkway. The site has been operated as a fuel storage and handling facility. At the time of the fieldwork, the study area was vacant. The terrain is relatively flat. All major facilities within the study area, including four above ground storage tanks, each capable of containing 864,000 litres, have been removed. However, it has been reported that the selected site had been significantly impacted with petroleum hydrocarbon, possibly jet fuel. The total petroleum hydrocarbon levels exceed the Ontario soil cleanup criteria.

In accordance with the regional published data, the geological conditions in the general area of the study area consist of a glacial till ridge that is oriented from southwest to northwest across the area. The till is a silty sand containing some gravel and boulders, and is present near the surface in the general area. Sands and gravels are deposited on either side of this till. Uniform sands are deposited in either a fluvial or near-shore environment. Sands and sandy till deposits comprise a regionally significant watertable. The depth to the watertable is greatest along the topographically high areas. There is a regional watertable divide that is generally coincident with the height of land and till ridge.

The Tank Farm area is located several hundred metres east of the height of land and the regional groundwater divide. This location is east of the till ridge and uniform sands and/or some fine gravel are expected to underlie the Tank Farm. The regional groundwater flow is in an easterly direction with the depth to the watertable at approximately 1.2 metres below ground surface.

FIGURE 7.1 Location of study area.

All of the drainage around the Tank Farm area flows east to Sawmill Creek. From the Tank Farm, there is surface drainage north of the site, to the east across the Airport Parkway to Sawmill Creek. Similarly, south of the Tank Farm, drainage is to another ditch that also drains to the east, and then to the southeast across the Airport Parkway to the Macdonald-Cartier International stormwater pond, that drains to Sawmill Creek.

7.3 Test Programme

At that time of the fieldwork, a total number of 5 test hole locations have been chosen around the removed above-ground storage tanks at the Tank Farm. The test hole locations are shown in Figure 7.2. A pilot test using a manually driven vapour probe was advanced to a depth of 0.9 metres for a preliminary soil-gas survey. For the purpose of enabling a comparison of the soil-gas response using different soil-gas sampling devices, a 14-day waiting period was given prior to the subsequent investigation at the same test hole locations using the developed field device. This is longer than the recommended 2-day waiting period (Environment Canada 1998) to allow the tested locations to re-establish an equilibrium state. Piezocone soundings were advanced to depths ranging from 1.3 and 2.1 metres below existing ground surface and located at close proximity to the pilot test locations. Along the piezocone soundings, soil-gas sampling using the developed soil-gas sampling device was carried out at the same depth as for the pilot test. Verification soil samples were recovered immediately adjacent to the piezocone

sounding locations for analytical testing. All collected soil-gas samples and extracts obtained from verification soil samples were analyzed using gas chromatography for qualitative and/or quantitative identification of hydrocarbon contamination. The conditioned Tenax-coated glass fibre filter absorbents for the collection of soil-gas samples were stored in glass vials and kept at 4°C in a cooler prior to use.

FIGURE 7.2 Test holes location plan.

7.3.1 Pilot Test Using Manually Driven Vapour Probe

A pilot test using a manually driven vapour probe was conducted at the selected locations at the Tank Farm (Figure 7.2). This test series goal was to test the performance of the developed Tenax-coated glass fibre filter absorbent for qualitative determination of the hydrocarbon contamination under the actual field conditions. The manually driven vapour probe consists of a retractable stainless alloy tip, vent holes with stainless steel screens, and an up-and-down hammer attachment. Based on the regional hydrogeological information, the depth to the groundwater table is approximately 1.2 metres below ground surface. Therefore, soil-gas sampling depth was limited to a depth of 0.9 metre. At each test hole location, a 100mL soil-gas sample of approximately 5 times the casing volume was drawn through the Teflon vapour tube using a gastight syringe. It was to ensure that all ambient air was removed from the sampling system. In accordance with the optimum sampling conditions obtained in Chapter 6, soil-gas samples of 3mL were then collected at a rate of 20mL/min. at ambient temperature for each test hole location. The absorbent trapped with soil-gas sample was then stored in glass vials and kept at 4°C in a cooler. All collected soil-gas samples were then transported to the laboratory for subsequent gas chromatographic analysis. Trip blanks were also obtained and tested for ensuring the quality of the collected samples.

7.3.2 Field Trials Using Developed Field Device

Following the pilot test, field trials were carried out to verify the performance of the developed field device. The test holes were put down using a truck-mounted power auger drill rig, operated by a crew of two. The test procedure consisted of pushing the piezocone penetrometer, integrated with the developed add-on soil-gas sampling device, at a rate of 20mm/sec. Soil-gas samples were collected within the vadose zone and guided by the measurements of the pore water pressure sensor in the penetrometer tip. Attempts were made in collecting soil-gas samples from the depth of 0.9 metre below ground surface and beyond at a regular interval until the groundwater table was reached. Prior to each soil-gas sampling, a 30mL sample of soil-gas was drawn through the transfer line to ensure the complete removal of ambient air and residual soil-gas along the borehole. A series of four 3mL soil-gas samples at different dilutions was then collected at a rate of 20mL/min at each sampling depth. The collected soil-gas was trapped onto the conditioned Tenax-coated glass fibre filter absorbents at ambient temperature. One 3mL soil-gas sample would be trapped directly onto the absorbent without dilution and served as the benchmark for that series. One 3mL soil-gas sample would be collected at a dilution of 10 times from a gas-tight syringe. One 3mL soil-gas sample would be collected at a dilution of 100 times from a gas-tight syringe. A 30mL soil-gas sample would also be trapped directly onto a developed Tenax-coated glass fibre filter absorbent. Trip blanks and dummy samples between test holes were also obtained. All collected

soil-gas samples were thermally desorbed and analyzed in the laboratory using the modified gas chromatographic system described in Chapter 6.

7.3.3 Soil Sampling

Verification soil samples were recovered from boreholes immediately adjacent to the piezocone test locations using a 50mm diameter split-spoon sampler. Soil samples were taken at the corresponding depths to the soil-gas samples. The collected soil samples were immediately placed in 500mL amber wide mouth glass jars fitted with Teflon caps, and stored at 4°C in a cooler. In order to minimize the potential for cross-contamination between boreholes and samples, all split-spoon samplers were cleaned with a wire brush and rinsed in water between samples. All augers were also cleaned with water between boreholes.

Extraction and analysis of the hydrocarbon contaminants from soils has been carried out at the Centre for Analytical/Environmental Chemistry (CAEC) of Carleton University. A modified ultrasonic extraction method was employed in according to the local expertise. A known weight of collected soil sample was mixed with a fixed volume of extraction solvent, n-Pentane, in an ultrasonic device for 20 minutes. The extracts were then passed onto the gas chromatographic system for subsequent analysis.

A Varian 3300 gas chromatographic system fitted with a 30m x 0.25mm narrow bore DB-5 capillary column, programmable temperature control and a flame ionization detector was employed in this research. The column temperature is kept at 45°C for 1.5 minutes and then linearly increased at a rate of 10°C/min. to a final temperature of 300°C. The total run time is approximately 32 minutes. Calibration curves for gasoline-range organics were also obtained from this gas chromatographic system. The presence of the contaminant of interest was then identified qualitatively and quantitatively with reference to the obtained calibration curves.

7.4 Interpretation of Results

7.4.1 Stratigraphic profile

The stratigraphic profiles of the test locations consist mainly of fill material over loose to compact gravelly sand and/or silty sand. The data interpretation is based on the measurements of tip resistance, sleeve friction and pore water pressure recorded during the penetration process. The profiles of tip resistance, sleeve friction, pore water pressure and friction ratio are shown in Figure 7.3 to Figure 7.7.

Since the friction ratio is the ratio of the sleeve friction to the tip resistance at the same depth, this ratio will increase with the increasing coefficient of earth pressure at rest and

increasing fines content. In sand deposits where the coefficient of earth pressure is constant, the friction ratio could be used to note the increases in fines content. Particularly, the friction ratio obtained for CPT-3 shows a strong indication of the presence of the silty material at shallow depths. The state of compactness of the soil layers could also be determined by the tip resistance measurements using available charts. The classifications of soil types based on the piezocone soundings are also in accordance with the collected verification soil samples.

Groundwater levels at the test locations were determined by the measurements of the pore water sensor in the cone penetrometer tip. At the time of the fieldwork, the measured groundwater levels varied between 0.97 and 1.52 metres below existing ground surface. These groundwater level measurements also served as the guideline on the termination depth for the soil-gas sampling operations.

7.4.2 Pilot Test Using Manually Driven Vapour Probe

Moist soil-gas has been collected in the soils at a depth of 0.9 metre using a manually driven vapour probe. Soil-gas samples of 3mL were trapped onto the developed filter absorbent at ambient temperature under the field conditions. The performances of the filter absorbent as well as the proposed soil-gas sampling procedure were then investigated.

The data interpretation for qualitative analysis is based on the comparison of the overall pattern of the chromatograms and the retention time of the peaks for the contaminants of interest to those obtained from the calibration standards (Figure 6.32 and Figure 6.35). From the overall pattern of the obtained chromatograms, positive indication of gasoline-type contamination was found at test hole locations CPT-4 and CPT-5. A successful identification was made indicating that the contaminants on the test site consisted of the gasoline-range organics. It was also demonstrated that the developed filter absorbent could successfully recover the gasoline-range organics from the moist soil-gas in the field.

However, very low chromatographic responses were obtained on soil-gas samples recovered from test hole locations CPT-1 to CPT-3. This was possibly due to a low level of contamination having taken place in these locations. The actual levels of contamination in soils at the test hole locations were verified by the soil analysis in this test programme. The results of the soil analysis show an accordance with the general trend of the pilot test.

By comparing the chromatograms of the soil-gas sample recovered at test hole location CPT-5 (Figure 7.8 and Figure 7.9), it was observed that there was a significant loss in the heavier hydrocarbon components (after 300 seconds) in the collected soil-gas sample using the manually driven vapour probe. This significant loss in the heavier hydrocarbon components might be due to the large purge volume employed prior to soil-gas sampling using the manually driven vapour probe. Subsequently, a large quantity of vapour phase

heavier hydrocarbon components was removed and the sampling location cannot immediately return to its equilibrium state. As a result, the tested samples yielded a response mainly on the more volatile hydrocarbon components. From this observation, it is suggested that the manually driven vapour probe is not favourable for active soil-gas sampling, unless a large quantity of soil-gas at the same concentration is available at the test location. No attempts at quantitative analysis were made for the pilot test.

FIGURE 7.3 Stratigraphic profile of test location CPT-1.

FIGURE 7.4 Stratigraphic profile of test location CPT-2.

FIGURE 7.5 Stratigraphic profile of test location CPT-3.

FIGURE 7.6 Stratigraphic profile of test location CPT-4.

FIGURE 7.7 Stratigraphic profile of test location CPT-5.

FIGURE 7.8 Chromatogram of 3mL soil-gas sample recovered at CPT-5 (Manually Driven Vapour Probe).

7.4.3 Investigation Using Developed Field Device

Following the pilot test, soil-gas sampling with the guidance of the piezocone penetrometer was conducted within the vadose zone at the selected test hole locations. Similar to the analysis for the pilot test, the data interpretation for qualitative analysis is based on the comparison of the overall pattern of the chromatograms and the retention time of the peaks for the contaminants of interest to those obtained from the calibration standards (Figure 6.32 and Figure 6.35). Multilevel soil-gas sampling was conducted at test hole location CPT-4. Soil-gas samples were recovered at the depths of 0.9 metre and 1.5 metres. The capability of the developed field device for multilevel soil-gas sampling was successfully demonstrated.

It was found that the trapping efficiency using the developed field device is superior to the manually driven vapour probe. It was mainly due to the great reduction of the required purge volume. The significant loss in heavier hydrocarbon contaminants in the soil-gas sample was eliminated. From Figure 7.9, it was observed from the overall pattern of the obtained chromatograms that a better-matched pattern to the response of the gasoline-range organic contaminants (Figure 6.35) has been obtained. Therefore, the use of the developed field device could minimize the disturbance to the subsurface conditions prior to soil-gas sampling. It was also demonstrated that the developed field device could successfully recover the gasoline-range organics from the moist soil-gas at ambient temperature with confidence.

FIGURE 7.9 Chromatogram of 3mL soil-gas sample recovered at CPT-5 (Developed Field Device).

The quantitative analysis is based on the area under the chromatographic curve. A total number of 4 soil-gas samples were collected at each sampling location. As shown in Chapter 6, for analyzing a given type of gasoline-contaminated soil at different contamination levels, the gas chromatographic response should yield a linear response. Hence, the following interpretations can be deduced:

- If a 3mL soil-gas sample reports a very low gas chromatographic response, the level of contamination of the tested sample might fall below the range of 1-10 $\mu\text{g/g}$. Furthermore, if the gas chromatographic response for the 30mL soil-gas sample persisted at a low level, it can be concluded that the level of contamination of the tested sample is lower than 0.1-1 $\mu\text{g/g}$.
- If a 3mL soil-gas sample yields a similar response to those obtained from the laboratory calibration curves (Figure 6.41); the level of contamination of the tested sample might fall in the range of 1-10 $\mu\text{g/g}$. One may confirm this finding by a comparison of the result to those obtained from the 3mL soil-gas sample at a dilution of 10 times. A linear response must be achieved in order to obtain a positive confirmation. Otherwise, the filter absorbent could be overloaded. Hence, the level of contamination of the tested sample would be higher than the range of 10-100 $\mu\text{g/g}$.
- If a 3mL soil-gas sample at a dilution of 100 times gives a non-linear response to the soil-gas sample at a dilution of 10 times, this would confirm that the filter absorbent

has been overloaded. Hence, the level of contamination of the tested sample should be higher than 100 $\mu\text{g/g}$.

Low chromatographic responses for contamination at locations CPT-1 to CPT-3 were also detected from the collected soil-gas samples using the developed field device. From the results of the 30mL soil-gas sample, these 3 test hole locations were identified as zero to low impact of gasoline-type contamination. Nominal amounts of gasoline-range organics were detected at location CPT-1. Chromatograms of the 30mL soil-gas samples recovered at test hole locations CPT-1 is shown in Figure 7.10. It was found that effluents of heavier gasoline-range organics were detected approximately after 300 seconds. Signs of gasoline-type contamination were not detected at locations CPT-2 and CPT-3.

FIGURE 7.10 Chromatogram of 30mL soil-gas sample recovered at CPT-1.

With reference to the laboratory calibration curves presented in Figure 6.41, the estimated concentration of the tested sample recovered from test hole location CPT-1 falls into the range of 0.1-1 $\mu\text{g/g}$. A summary of the detected concentration levels at the test hole locations is listed in Table 7.1.

Strong indications of gasoline-type contamination have been detected at test hole locations CPT-4 and CPT-5. However, non-linear responses were obtained by a comparison to the results of the 3mL diluted soil-gas samples. It has therefore been determined that the filter absorbents were overloaded during soil-gas sampling. Hence, the level of contamination of these test hole locations should be higher than 100 $\mu\text{g/g}$. Chromatograms of the soil-gas samples recovered at test hole locations CPT-4 and CPT-5 are shown in Figure 7.11, Figure 7.12 and Figure 7.9.

FIGURE 7.11 Chromatogram of 3mL soil-gas sample recovered at CPT-4 (0.9m).

FIGURE 7.12 Chromatogram of 3mL soil-gas sample recovered at CPT-4 (1.5m).

Location	Estimated Range of Contamination Level ($\mu\text{g/g}$)
CPT-1	0.1-1
CPT-2	Lower than 0.1-1
CPT-3	Lower than 0.1-1
CPT-4 (0.9m)	Higher than 100
CPT-4 (1.5m)	Higher than 100
CPT-5	Higher than 100

Table 7.1 Summary of detected concentration levels at test hole locations (Developed Field Device).

From Figure 7.11 and Figure 7.12, it was observed that stronger gas chromatographic response was detected with an increase in depth. It indicates that a significant impact of contamination might have occurred in the groundwater. By the nature of the gasoline-type contaminants, they would be concentrated on the top of the groundwater table.

7.4.4 Analysis of Verification Soil Samples

Analysis of the verification soil samples was carried out at the Centre for Analytical/Environmental Chemistry (CAEC) of Carleton University. The data interpretation for qualitative and quantitative analysis is based on the retention time of the peaks and the area under the chromatographic curve. By the inspection of the chromatograms obtained for the calibration of the gasoline standards, the window for area calculations was chosen from 0.6 to 20 minutes. This should cover the chromatographic response of the gasoline-range organics within a tested sample.

From the overall pattern of the obtained chromatograms, it was clearly identified that the contamination on the test site consisted mainly of gasoline-range organics. It further confirmed that the developed field device provided a positive identification on the contaminants of interest. From the area calculations, the quantities of the contaminants at the test hole locations were also revealed. Lower levels of contamination were detected on soil samples recovered from locations CPT-1 to CPT-3. The detected concentration levels ranged from 9.9 to 18 $\mu\text{g/g}$. These estimated concentration levels are dominated

by the heavier hydrocarbons of the gasoline-range organics presented in the collected samples. The correlation of the results obtained from the verification soil samples to the soil-gas measurements using the developed field device is approximately two orders of magnitude.

On the other hand, high levels of contamination were encountered at locations CPT-4 and CPT-5. At these locations, the detected concentration level ranged from 1980 to 8221 $\mu\text{g/g}$. It is more than one order of magnitude greater than the Ontario soil cleanup criteria of 100 $\mu\text{g/g}$. A summary of the detected concentration levels at the test hole locations is listed in Table 7.2.

The results of the verification soil samples show that they are in accordance with the general trend obtained from the investigation using the developed field device. Hence, a local correlation between the soil-gas response and level of contamination in the soil matrix can be made. This correlation is particularly useful in projecting an estimate on the level of contamination in the soils based on the soil-gas analysis at different locations across the test site.

Location	Contamination Level in Soil ($\mu\text{g/g}$)
CPT-1	18
CPT-2	12
CPT-3	9.9
CPT-4 (0.9m)	1980
CPT-4 (1.5m)	2040
CPT-5	8221

Table 7.2 Summary of detected concentration levels at test hole locations (Verification Soil Samples).

7.5 Discussions

By itself, the developed field device is a valuable tool in contamination site investigations. Besides providing information on the extent of contaminant of interest, the piezocone penetrometer may also be used for the determination of stratigraphic profiles, geotechnical parameters and hydrogeological properties. The pore water sensor in the penetrometer tip can quickly determine steady state pore water pressure in drained soils. In sandy soils, equilibrium can be reached almost instantaneously. Hence, the location of the groundwater table that indicates the boundary between the vadose zone and the saturated zone can be revealed. This measurement can serve as the guideline on the termination depth for the soil-gas sampling operations. The hydraulic conductivity for fine-grained soils can be determined by pore pressure dissipation measurements. This

is particularly important for the subsequent analysis of contamination migration. Furthermore, any potential pathways for the contaminant movements can also be revealed from the stratigraphic profiles.

It is also important to clearly identify the type of petroleum contaminants detected in a contamination site. One should be aware of the risk level difference between the gasoline-range organics and the diesel-range organics at the same level of contamination. Positive identification of the gasoline-type contamination in the test site has been made in the field trials. Hence, this could assist the engineers to arrive at the most efficient and economical remediation solution.

Rapid assessment of the three dimensional extent of the contamination can be made after a series of penetration soundings using the developed field device. Typically, this can be done to delineate the boundaries of a contaminant plume. Furthermore, by comparing the gas chromatographic response at certain test locations to the contaminant concentrations determined from the laboratory modelling, the gas chromatographic results may be used semi-quantitatively to give an indication of the concentrations of contamination at other test locations. A correlation of 1 to 100 could be applied to the conducted field trials. As discussed in Chapter 6, a lower gas chromatographic response can be obtained from the collected soil-gas samples and it is highly dependent on the amount of fines content and organic matter present in the soils.

On the basis of any initial investigation with the use of the developed field device, planning for other forms of investigation such as the installation of piezometers and monitoring wells can be made accordingly. The developed field device can also be used for periodic monitoring of a site to note the advance of any contaminants and/or the efficiency of any on-going remediation works. Furthermore, any subsequent changes in soil parameters due to the remediation works can be immediately revealed.

Chapter 8

Conclusions and Future Recommendations

8.1 Conclusions

This experimental investigation shows that the piezocone can be developed to yield results on the gasoline-type contamination in the vadose zone.

A battery-operating cone penetration test system has been developed in this research. The conventional demand of AC power source has been replaced by a rechargeable sealed gel cell power pack. A fully recharged power pack is able to provide steady and continuous operation of the piezocone for a minimum of 24 hours without interruption.

The conventional data recording system for the cone penetration test has been enhanced to a compact portable system. It has been found that the IBM and Toshiba notebook personal computers have the best performance among the tested machines. Excessive noise signals have been recorded from the other tested notebook personal computer

installed with the PC-Card type data acquisition board. An IBM notebook personal computer has been chosen in this research.

Excessive noise signals have also been recorded from the desktop computer of the laboratory use data recording system of the gas chromatographic system. A properly shielded replacement power supply has resolved this problem.

The modified gas chromatographic system has been successful in recovering and identifying the gasoline-type contaminants. The time required for a gas chromatographic analysis using the condensed chromatogram is approximately 8 minutes. The condensed chromatogram type of analysis yields a higher efficiency when compared to the conventional component analysis of requiring 2 to 3 hours of time. Optimum experimental conditions have also been established for the development of the future portable gas chromatographic unit for field operation.

False identification of hydrocarbon-contaminated subsurface due to the mis-interpretation of background organics measurements has been eliminated by choosing a time window of 200 to 400 seconds for the condensed chromatogram type of analysis.

The developed add-on split-tube type sampling module can be placed virtually at any intersection along the series of push rods. A number of sampling modules can also be stacked together for simultaneous multilevel soil-gas sampling.

The calibration of the developed sampling module has determined a required purge volume of 30mL and it exceeds the purge volumes of 1-5 casing volume suggested by U.S.EPA (1990) and Doskey et al. (1996). This indicated that the suggested purge volume can not be taken as the standard and applied to all soil-gas sampling devices. Purge volumes for different soil-gas sampling device must be calibrated independently. The optimum sampling rate has also been characterized against the backpressure developed during sampling.

The Whatman 934AH glass microfibre filter performs the best under the integrity test and yields the most Tenax coating compared to the other tested filters. A Tenax solution of a concentration of 100mg/mL yields an average of approximately 21mg of Tenax coating on the filtration area of a 25mm diameter filter absorbent. A special filter cutter has been made for consistently extracting the coated filter absorbents at 25mm in diameter.

It was found that coated filters conditioned for longer than 15 minutes are sufficient for trapping the gasoline-type contaminants. The majority of the impurity on the freshly coated filter absorbent can be removed within 3 minutes. To be conservative, a period of 30 minutes has been chosen as the standard conditioning time for all the coated filter absorbent prior to use.

The successful attempt in replacing the use of liquid cryogen and thermoelectric cooling devices by using compressed air forms a good foundation to the future development of a

compact portable gas chromatographic system that is based on the Ranque-Hilsch vortex tube.

The ability of a subsample within the same filter absorbent to be used for replication of thermal desorption and subsequently gas chromatographic analysis has also been confirmed. The percentage difference of the results obtained from replicates is less than 3%. The ratio of the recovered analytes on the replicates to that on the whole control filter absorbent is approximately 1 to 6.9. It is in accordance with the area ratio of the size of the replicates and the effective area of the control filter absorbent.

Relationship between the vapour content and the mass content of gasoline-contaminated soils at different contamination levels has been established from the laboratory modelling. The test results exhibit a linear behaviour within the same type of soil mixture. The gas chromatographic response obtained from the laboratory modelling can serve as the upper bound of the tested soil type. It has also been found that there is a tendency for decrease in gas chromatographic response as the soil moisture content increases. Decrease in gas chromatographic response has also been observed with increase in clay content and impurities.

Low chromatographic responses for contamination have been detected from soil-gas samples collected at locations CPT-1 to CPT-3. The estimated concentration falls into the range of 0.1-1 µg/g or below. Strong indications of gasoline-type contamination have

been found at locations CPT-4 and CPT-5. Stronger response has also been observed at location CPT-4 as the sampling depth increases.

The obtained non-linear responses among the collected soil-gas samples indicated the filter absorbents have been overloaded during soil-gas sampling. The level of contamination at these locations are therefore, determined to be higher than $100\mu\text{g/g}$. The results obtained from the verification soil sample are in accordance with the general trend of the soil-gas samples. A correlation of 1 to 100 can be applied to the conducted field trials.

8.2 Future Recommendations

Further fieldwork is required to further correlate the vapour content of the contaminated field soils to their mass content. The possible effect on the amount of organic matter present in the contaminated soil is also desirable to investigate and for possible improvement of the correlation.

Further development of a much simplified, more economical and much more compact portable system with respect to the modified gas chromatographic system developed in this research would then be undertaken. Replacement of the conventional heating elements by vortex tubes is also recommended. A database for component identification

can also be incorporated into the portable recording system. A more comprehensive laboratory-modelling programme is therefore, recommended.

Effects on the heavier Tenax coating of the filter absorbent and the length of the focusing tube for accommodating contaminants at the higher contamination levels are worthwhile to study. Further investigation on the feasibility of incorporating the developed filter absorbent inside the sampling module for simplified active sampling is also recommended. The suggested simplified active sampler could further eliminate any possible disturbance to the subsurface condition prior to soil-gas collection.

By doing so, a series of the suggested add-on type simplified active samplers can be stacked together for simultaneous multilevel and multidirectional soil-gas sampling. It would further reduce the time required for a soil-gas sampling operation. The applicability of the developed field device for groundwater investigation may also be studied. Hence, rapid assessment of the three dimensional extent of the contamination can be made after a series of penetration soundings using the developed field device. The developed field device can also be used for periodic monitoring of a site to note the advance of any contaminants and/or the efficiency of any on-going remediation works. Consequently, any changes in soil strength parameters can also be determined.

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Appendix A Summary table of Ontario soil cleanup criteria

Groundwater Situation	Contaminant	Cleanup Criteria	
		Residential	Industrial
Potable	Total Petroleum Hydrocarbons (Gasoline/Diesel)	100 ppm	100 ppm
	Benzene	0.24 ppm	0.24 ppm
	Toluene	2.1 ppm	2.1 ppm
	Ethylbenzene	0.28 ppm	0.28 ppm
	Xylene	25 ppm	25 ppm
Nonpotable	Total Petroleum Hydrocarbons (Gasoline/Diesel)	5000 ppm	5000 ppm (10000 ppm)
	Benzene	63 ppm	89 ppm (230 ppm)
	Toluene	510 ppm (1000 ppm)	510 ppm (2500 ppm)
	Ethylbenzene	1000 ppm	2500 ppm
	Xylene	460 ppm (1000 ppm)	460 ppm (2500 ppm)

() Criterion value in brackets applies to medium and fine textured soils.

Appendix B Summary table of The United States of America soil cleanup criteria

State	Contaminant	Cleanup Criteria
Arizona	Total Petroleum Hydrocarbons (Gasoline)	100 ppm
	Benzene	0.13 ppm
	Toluene	200 ppm
	Ethylbenzene	68 ppm
	Xylene	44 ppm
California	Total Petroleum Hydrocarbons (Gasoline)	10-1000 ppm
	Benzene	0.3-1 ppm
	Toluene	0.3-50 ppm
	Ethylbenzene	1-50 ppm
	Xylene	1-50 ppm
Connecticut	Total Petroleum Hydrocarbons	50 ppm
Florida	Total Petroleum Hydrocarbons	5 ppm
	BTEX	0.1 ppm
Illinois	Benzene	0.005 ppm
	Toluene	2 ppm
	Ethylbenzene	13.6 ppm
	Xylene	0.44 ppm
Indiana	Total Petroleum Hydrocarbons	100 ppm
Maine	Total Petroleum Hydrocarbons	20-50 ppm
Massachusetts	Total Petroleum Hydrocarbons	100 ppm
	Benzene	10 ppm
Minnesota	Total Petroleum Hydrocarbons	1 ppm
Mississippi	BTEX	100 ppm
New Hampshire	Total Petroleum Hydrocarbons	10 ppm
	BTEX	1 ppm
New Jersey	Total Petroleum Hydrocarbons	100 ppm

Oklahoma	Benzene	0.2 ppm
Rhode Island	Total Petroleum Hydrocarbons	50-100 ppm
Tennessee	Total Petroleum Hydrocarbons Gasoline	100 ppm 10 ppm
Vermont	Total Petroleum Hydrocarbons	10 ppm
Washington	Total Petroleum Hydrocarbons	200 ppm
Wisconsin	Total Petroleum Hydrocarbons	10 ppm
Wyoming	Total Petroleum Hydrocarbons (where groundwater < 50 ft)	10 ppm
	Total Petroleum Hydrocarbons (where groundwater > 50 ft)	100 ppm