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Implementation of a Fully Automated Process Purge-and-Trap Gas Chromatograph at an Environmental Remediation Site.

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Abstract

The AQUASCAN, a commercially available, fully automated purge-and-trap gas chromatograph from Sentex Systems Inc. (Ridgefield, N.J), was implemented and evaluated as an in-field, automated monitoring system of contaminated groundwater at an active DOE remediation site in Pinellas, FL. Though the AQUASCAN is designed as a stand alone process analytical unit, implementation at this site required additional hardware. The hardware included a sample dilution system and a method for delivering standard solution to the gas chromatograph for automated calibration. As a result of the evaluation the system was determined to be a reliable and accurate instrument. The AQUASCAN reported concentration values for methylene chloride, trichloroethylene, and toluene in the Pinellas ground water were within 20% of reference laboratory values.

Introduction

The Pinellas Plant, located in Largo, FL, occupies approximately 100 acres. It is owned by the United States Department of Energy (DOE) but is managed and operated by Lockheed Martin Specialty Components, Inc. Since the late 1950s, the facility has been used to manufacture weapons components for the DOE. From the manufacturing operations, 15 sites at the Pinellas Plant have been identified as having experienced environmental contamination.

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There are a number of active remediation sites currently present at the plant. One, an area of approximately 4 acres and located at the northeast corner of the property, is officially referred to as the Northeast Site. In the past this area has been used as a waste solvent staging and storage area as well as a disposal area for drums of waste and construction debris. A surficial ground water aquifer, approximately 9 m deep and

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underlain by a 23 m thick clay layer, exists at this site. It has been determined that between two and three acres of the aquifer at the Northeast Site have been contaminated by chlorinated volatile organic compounds at total concentrations ranging from 30-1000 ppm. These contaminants are predominately methylene chloride, trichloroethylene, dichloroethylene, toluene, and vinyl chloride. To continuously monitor the concentration of analytes in the ground water during remediation activities, a fully automated purge-and-trap gas chromatograph, the AQUASCAN from Sentex Systems Inc. (Ridgefield, N.J), was obtained and deployed at the site. This report summarizes the performance of that instrument for an evaluation period from November 21 to December 12, 1995.

Analytical System Hardware

The AQUASCAN purge-and-trap gas chromatograph (GC) is intended to be a completely automated system that can perform an entire water analysis for VOCs from the low ppb to ppm concentrations without the need for additional equipment. It is designed to automatically collect calibration or process samples and perform analyses at predefined intervals. This includes: purge-and-trap the sample, thermally desorb and subsequently inject sample trapped on sorbent material, perform chromatographic separation and identification, identify and integrate chromatographic peaks, and display chromatograms, retention times, concentration levels and operating conditions for data analysis. The GC system deployed at the Northeast Site is fully enclosed in a steel instrument rack with a full length back door, a shorter front door that provides access to the lower portion of the rack and a Plexiglas window in the upper portion of the rack that allows viewing of the computer monitor. All openings are fitted with silicone type gasket seals to ensure adequate protection from the ambient environment. The system was physically located under a temporary shelter that provided some protection from weather conditions. The system was plumbed into a shallow ground water recovery well located approximately 45 m from the unit.

Though the AQUASCAN is designed as a stand alone unit, implementation at the Northeast Site required additional hardware. Analysis of the Pinellas ground water indicates high concentrations, in the 10-1000 ppm range, of methylene chloride, trichloroethylene, dichloroethylene, toluene, and vinyl chloride. A dilution system was deemed necessary to minimize system contamination with high levels of organic contaminants and to reduce the cleaning cycle of the detector system. Therefore, a custom, though simple, dilution system was obtained from Sentex Systems. It consists of a high flow pump (0-2000 ml/min, Fluid Metering Inc., pump model QD), a low flow pump (0-12 ml/min, Fluid Metering Inc., pump model QG-20) and calibrated flowmeters. Contaminated ground water is pumped by the low flow pump through 1/16"-tubing. Dilution water, from the municipal water system, is pumped by the high flow pump through 1/2"-tubing. Adjustment of the dilution ratio is accomplished by changing the flow rates of the pumps through adjustments of the flow control valves associated with each pump. The contaminated ground water and dilution water combine at a tee joint downstream from the pumps and are then mixed by turbulent action in 3 m of 1/8"-tubing prior to introduction into the AQUASCAN system sampling port. Power to the dilution system pumps is controlled by the AQUASCAN. When automated GC sampling is triggered by the computer, voltage is applied to the dilution system pumps to power them. Both the dilution system and the AQUASCAN operate on standard 120 VAC.

A useful feature of the AQUASCAN system is its ability to run automatic calibrations on a predetermined schedule. However, for remote operations this requires that a stable source of calibration solution be available to the system. Therefore, a facility for refrigeration, storage, and delivery of the calibration solution was designed, built, and implemented on site for this purpose. The calibration solution is contained in a non-reactive Tedlar bag placed inside a small refrigerator maintained at 6°C to minimize loss of volatile compounds in the solution. The calibration solution is directly connected to the GC using tubing attached to a plumbing fitting in the Tedlar bag and exiting the refrigerator through a hole drilled in the side of the unit. This is then connected to a coil of stainless steel tubing that is used to warm the sample to ambient conditions prior to injection into the AQUASCAN calibration port.

Ground water or calibration samples are drawn into the system and a 10 ml Plexiglas purge cell at approximately 100 ml/min through 1/16"-tubing using a Fluid Metering Inc. pump model QG-150. The purge cell fill time can be varied but the liquid flow rate remains constant allowing multiple volumes to wash through the liquid lines and purge cell. There are six 1/4"-Swagelock inlet ports for the system; 4 sample ports, 1 clean water port, and 1 calibration port. Tubing internal to the system, between inlets, valves, and pumps is 1/4"-Teflon. A cylinder of ultra high purity argon (99.999%) gas is plumbed to the system. It is used as purge gas, carrier gas, and is an integral part of the detector system.

During the purging cycle two types of sample preparation are available with the AQUASCAN system. At low ppb analyte concentrations a carboxen trap (2.22 cm by 0.32 cm diameter) is used to collect the volatile components in the purging sample. The purge time is dependent on the analyte volatility and concentration but for trichloroethylene at 5 ppb a typical purge time is 30 sec. At higher analyte concentrations preconcentration of the volatile compounds by trapping them on a sorbent material is not necessary. The sorbent tube is physically bypassed and sample is collected in a 1/32"-Teflon tube loop approximately 6 cm long. The purge time required is shorter, i.e. for trichloroethylene at 5 ppm a 10 sec purge is typically used. An electrical connection must be physically changed to switch between sample collection modes. Therefore, it is not possible to automatically switch between sampling modes during remote operations.

After collection the sample is injected onto a 30 m Restek MXT-VOL capillary GC column that is located inside a temperature controlled oven. Oven temperature can be increased linearly or maintained under isothermal conditions. Argon carrier gas, at 10 psi, flows through the column at all times. Samples are introduced onto the column by either rapidly heating the sorbent tube to approximately 700°C by means of a platinum filament wound around the tube or by diverting carrier gas through the sampling loop.

The detector used on this system is an Argon Ionization Detector (AID). Suitable for most organic compounds, including halomethanes and haloethanes, it can be considered a simpler and more rugged detector for field use than most other GC detectors. It operates on the principle that argon atoms can be energized by tritium to an excited state with which organic molecules collide and subsequently react. The resultant excited atoms undergo ionization, resulting in a positive ion and an electron. High voltage, applied at the detector, produces a current that is amplified and measured. The detector response recorded as a function of time results in the chromatogram. Tritium in the detector is present in a solid form as titanium tritide. It has a reported activity level of 150 millicuries and therefore paperwork, documentation and procedures must be in order for the transportation and receipt of the system.

Data Retrieval

During this evaluation, the AQUASCAN was set up to run at the Northeast Site remotely and continuously for three weeks. At the end of each week, data was downloaded to an Albuquerque, NM site. Remote communications for operations and data retrieval with the AQUASCAN is handled by a Norton-Lambert commercial software package Close-Up (version 6.0). The AQUASCAN's computer system stores the raw chromatogram data in an ASCII data file, which are then downloaded for data reduction. All data processing was performed using Grams/386 (Galactic Industries Corporation). The AQUASCAN software does allow data review. However, it was necessary to export the data and use a more flexible software package for detailed examination of the data.

Operating Parameters

During the three week instrument evaluation, the following parameters were used. Laboratory analysis of the ground water indicated that five organic analytes are present in the ppm range. These analytes are methylene chloride, trichloroethylene, dichloroethylene, toluene, and vinyl chloride. It was decided that analyzing for three of these analytes would be sufficient to determine progress of the remediation activity. Therefore, methylene chloride, trichloroethylene, and toluene were monitored. Due to the relatively high concentration of these analytes the dilution system was operated at a dilution ratio of 22:1. Three of the system's four sampling ports, labeled as ports 2,3, and 4, were connected to the diluted ground water. Port 1 was connected to the municipal water supply to routinely rinse the system with clean water and examine sample carry over. Sample fill time was 60 sec. The GC oven was operated isothermally at 70°C, argon purge time 10 sec, and chart duration (chromatogram run time) 5 min. Total sample cycle time took approximately 30 min due to backflushing and system rinsing. A schematic of the Pinellas experimental set-up is shown in Figure 1.

Results of Groundwater Analysis

A calibration solution containing 10 ppm of methylene chloride, 6 ppm of trichloroethylene (TCE), and 5 ppm of toluene used for routine calibration of the AQUASCAN was prepared volumetrically, fed into the Tedlar bag, placed in the refrigerator, and plumbed into the manifold system of the GC. For the time period from November 27 to December 5, the GC system was programmed to take calibration samples after every 40 samples, resulting in a total of seventeen calibration samples for this time period. A calibration chromatogram, Figure 2, is shown as detector intensity versus retention time. The three analytes in the calibration solution are readily apparent and have retention times of 89, 187, and 287 sec for methylene chloride, trichloroethylene, and toluene, respectively. The integrated area for the GC peaks associated with the three analytes of concern for the seventeen calibrations are plotted versus time of collection in Figure 3. The percent standard deviations of the integrated areas of the three analytes, methylene chloride, toluene, and trichloroethylene, were 10%, 13%, and 8%, respectively. Though some scatter can be observed in the data, it appears that a periodic function is superimposed on the scatter. This cyclic pattern correlates with relative changes in the ambient temperature. This could be due to inconsistent heating of the sample in the warming coil effecting partitioning during sparging of sample.

A typical chromatogram of the diluted ground water being analyzed is shown in Figure 4. As can be seen, the retention times for the three analytes in the sample agree with retention times in the calibration solution. However, an additional peak, at 126 sec can be observed. This is cis-1,2 dichloroethene which is also present in the groundwater. It was observed that the retention times for all of the analytes varied. Whereas the software program allows you to define a time window associated with every analyte retention time, for subsequent integration and concentration determination a concern was present that if the time window was too broad, the GC peak of an unknown analyte could appear within that window, resulting in an incorrect concentration determination for a given analyte. Therefore, the cause for the retention time variation was investigated. Plotting analyte retention time and ambient temperature versus time of collection for all three analytes, Figure 5, it was determined that ambient temperature conditions were affecting the GC retention times. This is probably due to oven temperature correlations with ambient temperature, possibly due to an inaccurately referenced thermocouple. Carry over of the volatile compounds from the ground water samples to the clean water sample analyses was observed. The amount varied from run to run and is therefore difficult to quantitate. However, apparent shifts in the chromatographic peak retention time for methylene chloride, shown as lower retention time spikes in Figure 5, are due to difficulty in assigning peak maximums of these low concentration chromatograms. Trichloroethylene and toluene peaks were of sufficient magnitude to provide reliable estimation of the peak maximum.

The total integrated areas for the three analytes monitored versus time of collection are shown in Figure 6. Breaks in the data can be observed. Some are due to times when data was being downloaded. However, on close inspection of the data it was observed that intermittent periods of unexplainable lapses in data collection were present.

A steady downward trend can be observed for all analytes with the largest decrease occurring for toluene. This is consistent with what would be expected from an active pump-and-treat remediation site. Furthermore, the low intensity data spikes, which occur for all compounds simultaneously, could be due to intermittent pumping that occurs to maintain ground water depth levels. When the integrated areas are converted to concentration values based on the on-going calibrations, Figure 7, steps in the concentration data can be seen. This is due to the error associated with the calibration measurement. Direct comparison between the AQUASCAN reported concentrations and concentrations obtained from a reference laboratory is difficult due to the sparsity of reference concentrations. However, comparing the average concentration taken on the first day, sample A, with the sample sent to the reference laboratory, sample B, and the average concentration for 12/9/95, the last day of the AQUASCAN operation, sample C, with the reference concentration for the sample collected on 12/11/95, sample D, provides encouraging results. As can be seen in Table 1, the AQUASCAN and the reference laboratory reported concentrations agree to within 20%.

Conclusions

The AQUASCAN fully automated purge-and-trap gas chromatograph, in general, was shown to be a reliable system for on-line monitoring of groundwater at an active remediation site. The concentration values for the analytes of concern that were reported by the instrument were within 20% of reference laboratory values. However, an ambient temperature correlation was observed that shifted the analyte retention times. The software allowed remote access to the instrument for downloading data and to change instrument parameters. The system enclosure protected the instrument from environmental conditions in Florida.

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Table 1

Comparison of automated GC system with field samples sent to laboratory

Analyte	Lab Results (ppm) Sample B	AQUA-SCAN (ppm) Sample A	Relative Percent Difference of A and B	Lab Results (ppm) Sample D	AQUA-SCAN (ppm) Sample C	Relative Percent Difference of C and D
methylene chloride	5.7	5.9	3	4.2	4.2	0
toluene	1.3	1.4	9	1.1	0.9	18
TCE	0.6	0.6	0	.6	0.4	20

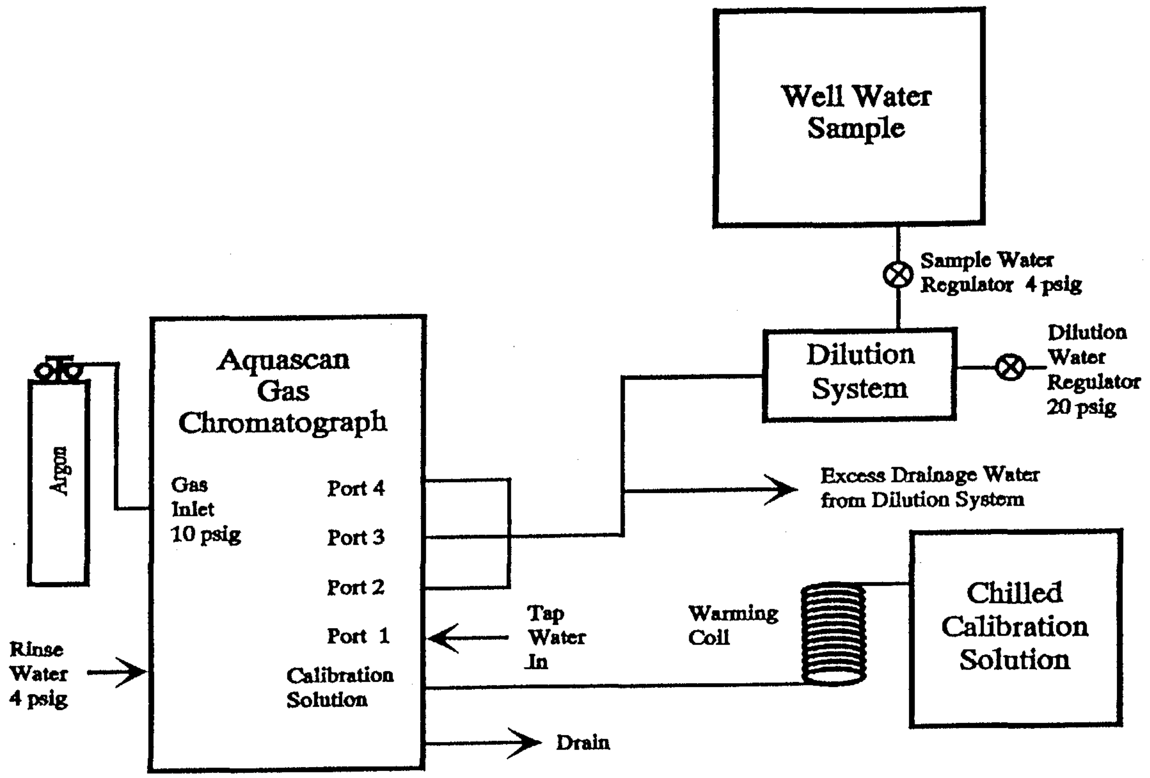

Figure 1. Schematic of system hardware installed at Pinellas Plant in Largo, Florida.

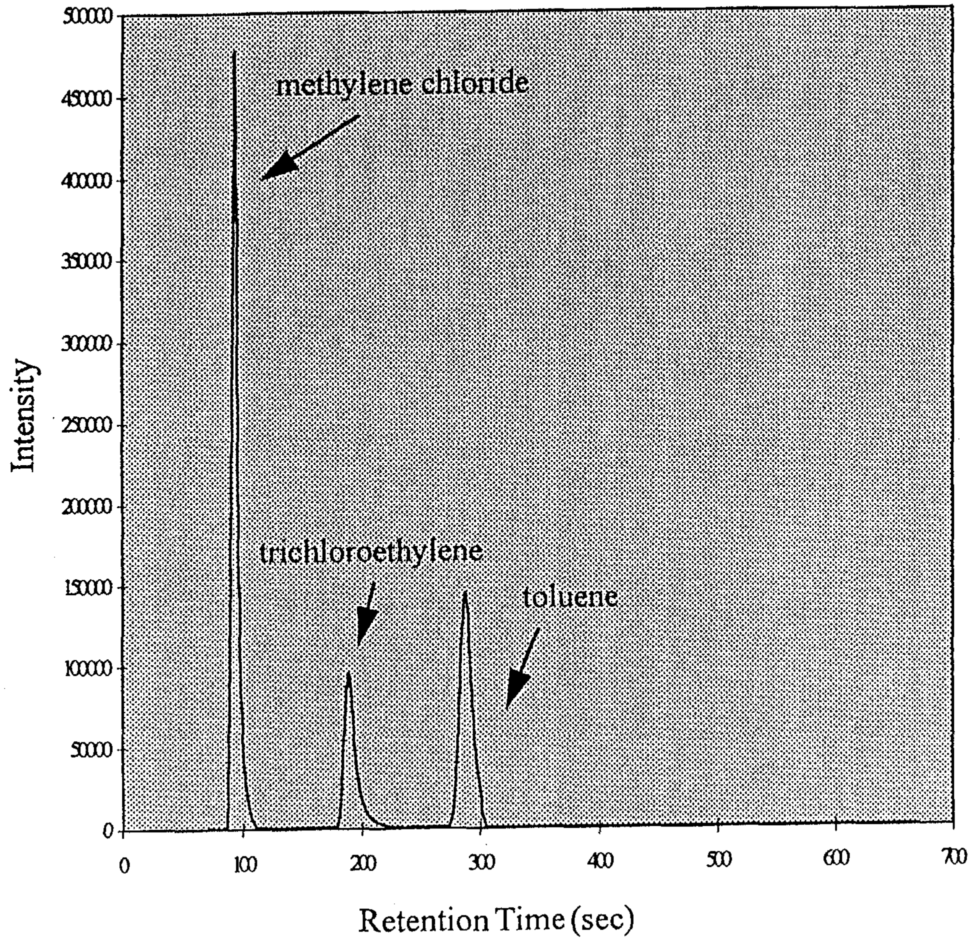

Figure 2. Chromatogram of calibration solution taken on Nov. 29,1995.

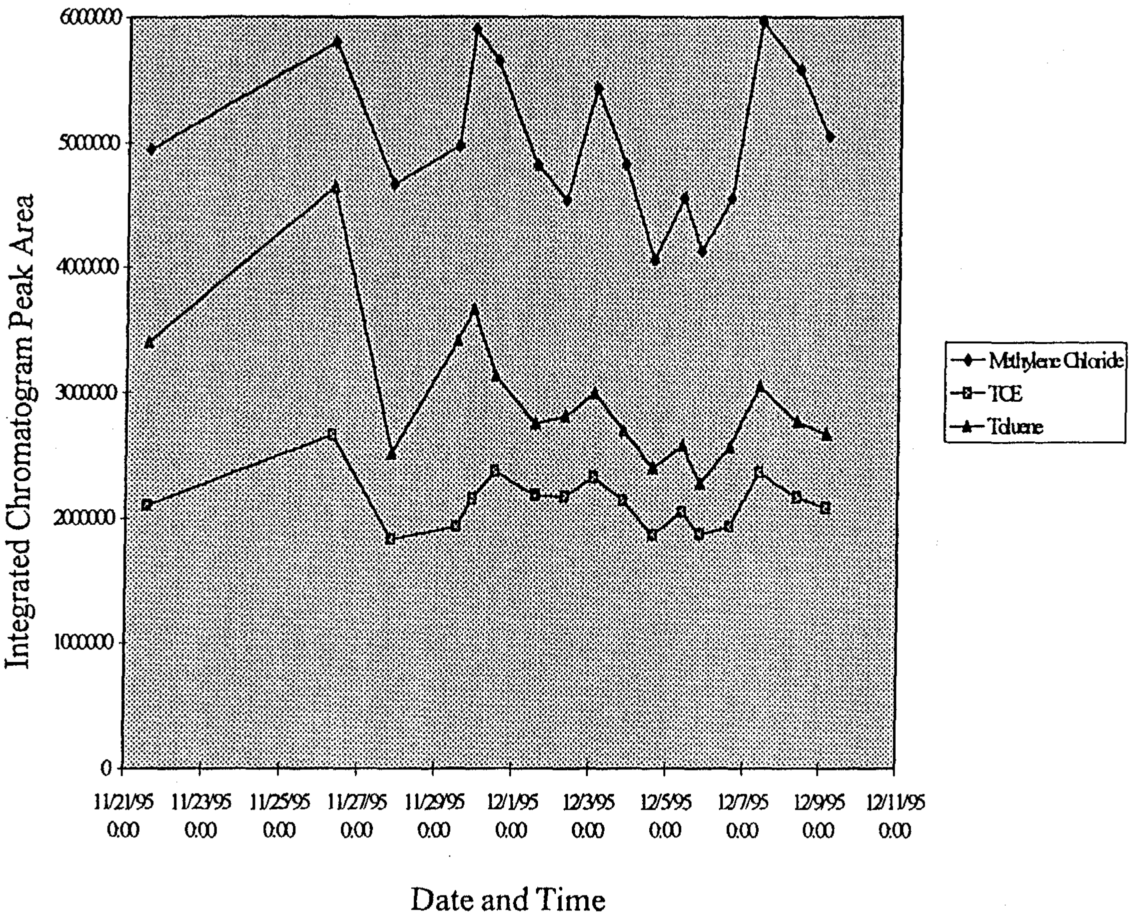

Figure 3. Integrated area versus collection time for calibration solution.

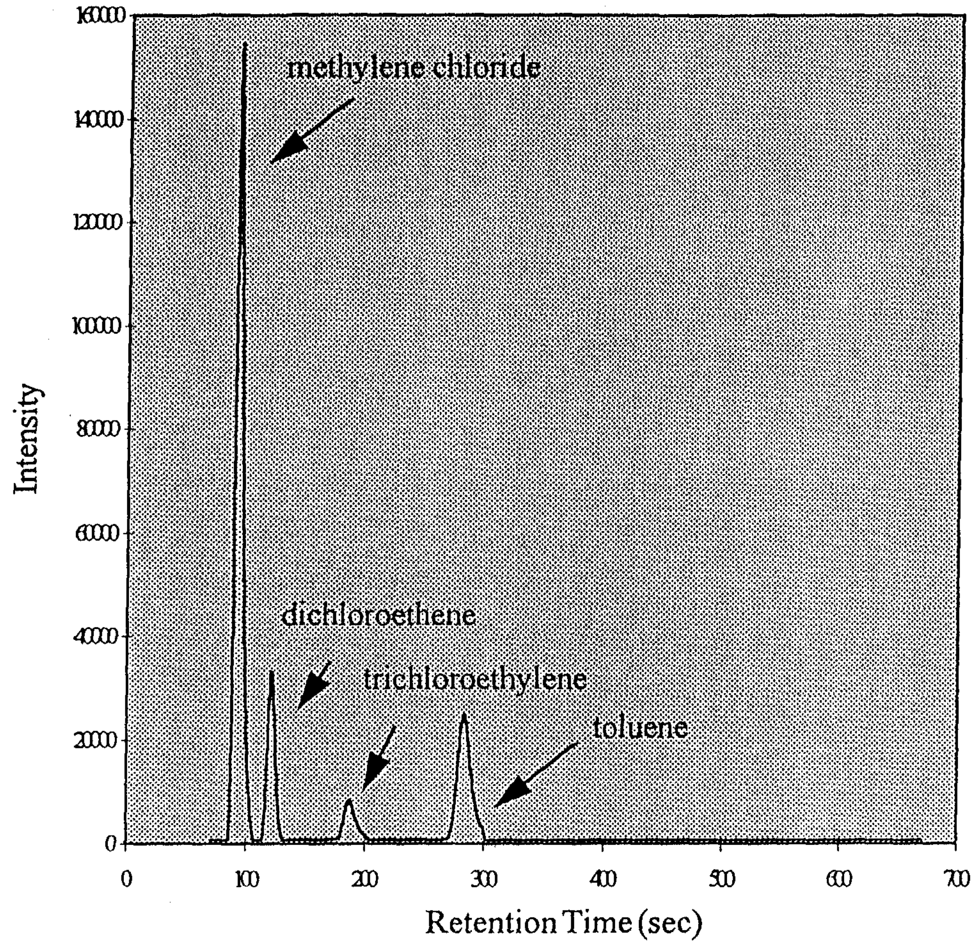

Figure 4. Chromatogram of Pinellas ground water sample taken Nov. 28, 1995.

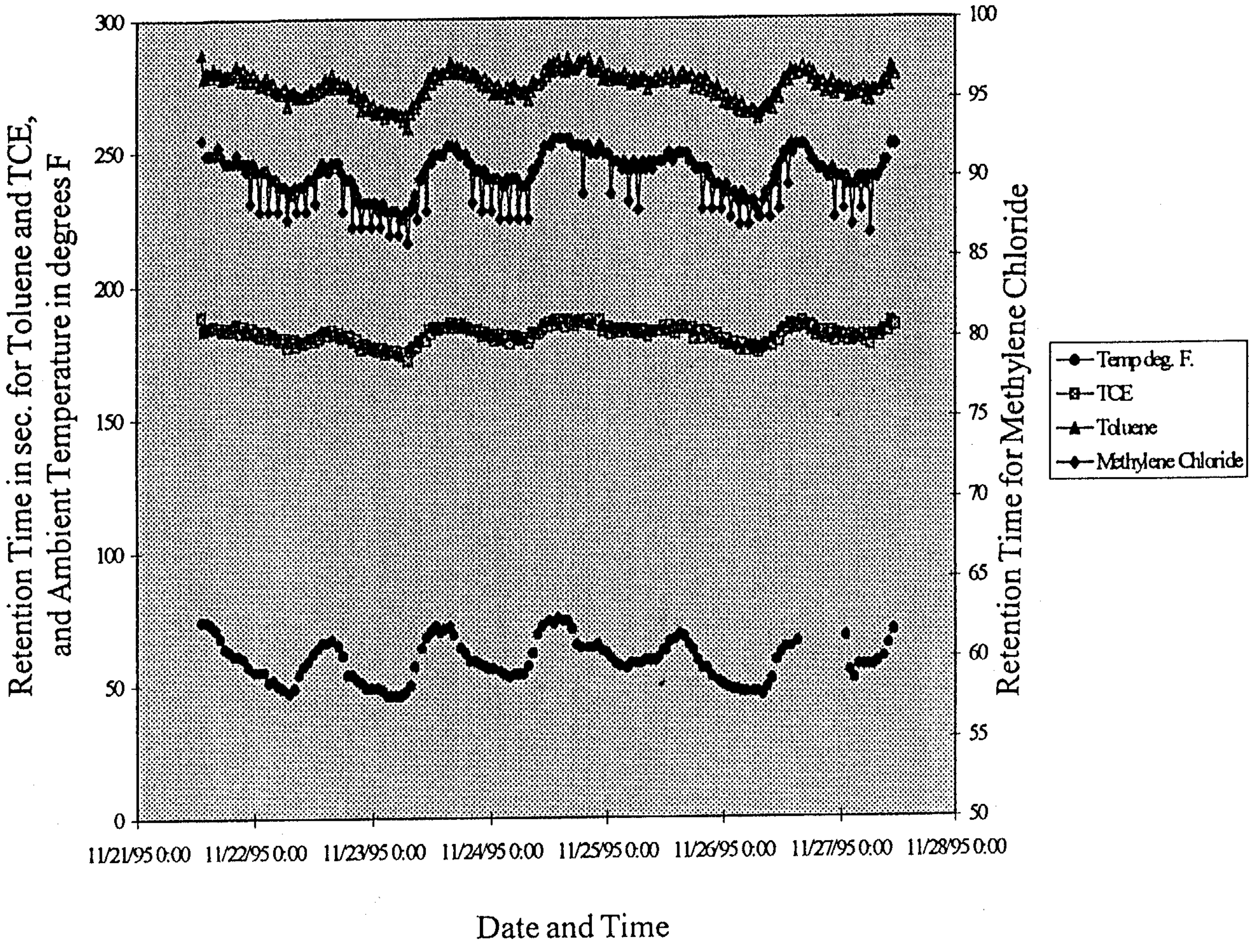

Figure 5. Retention time for all analyzed samples and ambient temperature as a function of time of sample collection.

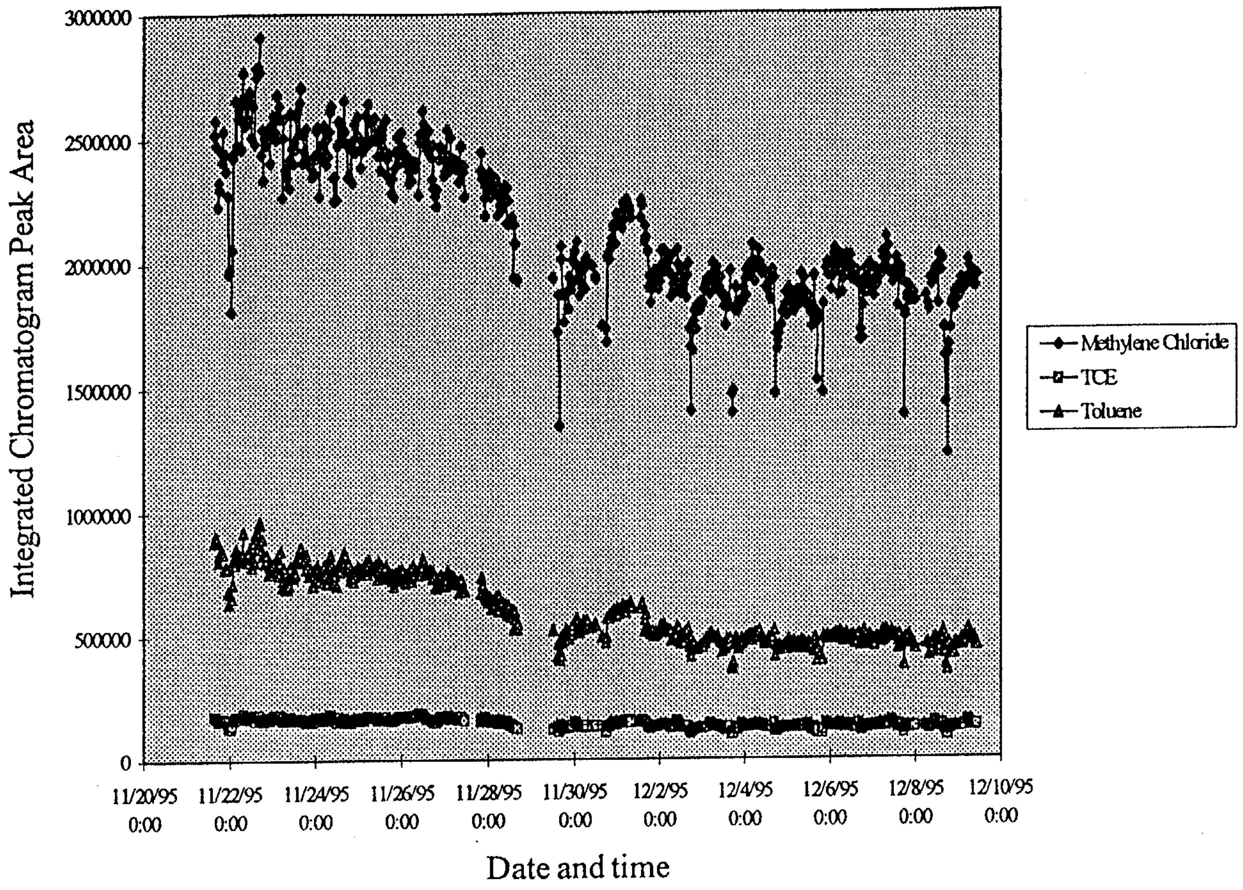

Figure 6. Integrated area versus time of collection for ground water samples.

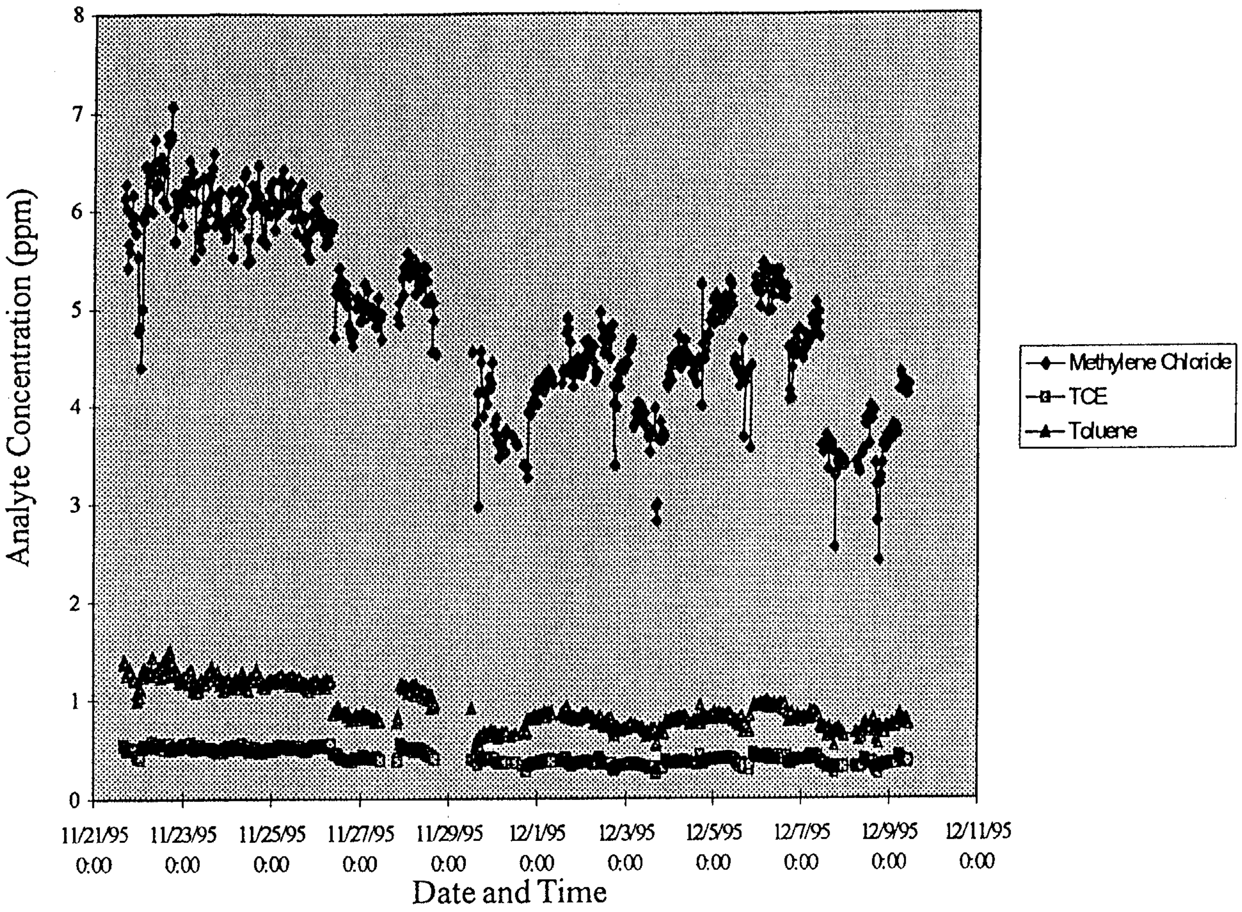

Figure 7. Sample concentration versus time of collection for ground water samples.