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Abstract

A field portable GC fitted with a non-analyte specific surface acoustic wave detector (SAW) was used to monitor DNAPL plume migration at Lawrence Livermore Laboratories, Berkeley. CA. The instrument is capable of producing complex chromatograms in 10-60s which were used to measure both qualitatively and quantitatively the extent of contamination by using reference standards of known concentration.

Introduction

One of the more complex and teasing problems associated with hydrology and the impact of liquid contaminants on water quality is the prediction of migratory patterns of both light non-aqueous phase and dense non-aqueous liquid phases (LNAPL & DNAPL) in the environment¹. To some extent the LNAPL is made easier when contaminants are encountered at the vadose air-water interface although additional complexities are easily found which relate

	Target Analyte
1)	cis-dichloroethylene (cis-DCE)
2)	chloroform (CF)
3)	carbon tetrachloride (CT)
4)	trichloroethylene (TCE)
5)	tetrachloroethylene (PCE)
6)	1,1,2,2-tetrachloroethane (1,1,2,2 TCA)

Table 1: Typical volatile chlorinated hydrocarbon contaminants.

to solubility of contaminants not only with water but also between LNAPL & DNAPL components.

One of the most commonly encountered environmental contaminant groups is the volatile chlorinated hydrocarbon (v-CHC) group of compounds (see table 1), many of which are suspect carcinogens. Most members of this group are, to varying degrees, miscible with water and in this way are able to enter biological systems. These compounds have anthropogenic origins and are usually found related to some form of industrial activity where they were often used as metal degreasing agents during fabrication, machining or plating.



At the outset, and usually during the lifetime of environmental remediation projects, the

Figure 1:Ultra-rapid SAW/GC component schematic

extent of contamination and the speed of migration or infiltration of the contaminant plume must be ascertained. This process usually depends on a series of strategically placed wells, which when sampled, can provide information on the contaminant flux over a period of time². In this way the dynamics and concentration data in three dimensions may be ascertained and is often summed in the form of an isopleth contour plot which can be most usefully manipulated by computer.

Before detailed maps can be drawn, the collection of copious quantities of analytical chemistry data must be envisaged. Although the collection of some information, depending on the type of contaminants present, can be partially automated at the well-head by various sensing devices the v-CHC's are notably difficult to analyze due to their relative insensitivity as perceived by some of the more commonly available devices. Thus the analytical process and generation of analyte specific concentration data can often be time consuming and very expensive.

There is clearly a need for site methods which will quickly and economically emulate traditional analytical chemistry lab data with sufficient accuracy to both evaluate and map concentration gradients. The availability of ultra-rapid gas chromatographs³⁻⁶ fitted with non-analyte specific detectors, is clearly an advantage to mapping plume migration and to site survey in terms of environmental chemistry.

Body: Discussion

Instrumentation

A field-portable ultra-rapid GC utilizing a surface acoustic wave detector (SAW) has



Figure 2: Lab standard of TCE and PCE used for retention time calibration and quantitation

been routinely used in our laboratories and taken into the field in a variety of proving expeditions. The basic layout of the instrument is shown in figure 1.

For the detection of VOC's, sampled air is pumped through a Tenax packed trap for a pre-selected time. The trap is then fired electro-capacitativly and the desorbed vapors directed via a heat controlled rotary valve to a short GC column. The GC column may be thermally ramped and the effluent chromatographed vapors directed onto the surface of the SAW. The SAW is normally set to resonate close to 500Mhz and is highly sensitive to any impinging vapors. The corresponding diminution in frequency caused by surface loading of the SAW oscillator is recorded and displayed in the form of an integram in a Windows based proprietary software adapted to run on an associated lap-top PC. The computer simultaneously displays an evolving chromatogram produced from the differential of the integram. The differential mimics the form of a traditional chromatogram but will usually display a typical negative inflection following each chromatographic peak which is the normal result of differentiating a signal through a change in sign and describes the physical effect of adsorption followed by desorption of each analyte from the SAW's surface. A typical chromatogram registered by the SAW detector is shown in figure 2.

Field Application

The useful application,⁷ in the field of this instrument has been demonstrated during routine monitoring of a mature DNAPL plume at Lawrence Berkeley Laboratories. The plume has been migrating over a period of many years following the underlying statigraphy in a steep gradient hillside location. The original contamination was derived from metal cleaning operations after world war II at the synchrotron facility.

Plume migration is routinely monitored from well sites strategically located on the hillside where soil gas samples are readily available. The ease and rapidity with which well-head analytical chemistry data can be accumulated was augmented because each well had been secured using a 19mm rubber septum port. The sensing head of the SAW/GC was fitted with a water trap to moderate the potentially overwhelming effect of water vapor on the SAW. The sensing head was fitted with a male leur fitting which allowed a short 27swg needle to be used by directly puncture the well-head septum. In this manner procurement of samples was reduced to the time taken to approach the well head and puncture the septa.

Results

The site at Lawrence Berkeley Laboratories (figure 3) is a small site with quite densely packed buildings and as a consequence of this the wells were relatively few in number.

The air temperature varied significantly from one group of well sites to another which required continual recalibration of the instrument with tedlar bags containing two of the known

contaminants, TCE and PCE essential. Failure to continually update the calibration in terms of retention times would have resulted in false peak identification due to a temperature dependent shift in retention times. The lower panel of figure 4 shows an indication of this phenomenon with drift time of 0.12s and 0.24s for the two analytes.

A typical identification profile is shown in figure 4 were PCE and TCE have been detected by matching their retention times with known standard vapors provided *in situ* using a tedlar bag containing the two standards in vapor form at 1ppm concentration. Given that the average chromatogram



vapors provided *in situ* using a tedlar Figure 3 At the steeply sloping well-head gathering soil gas bag containing the two standards in chromatographic data on migrating DNAPL contaminants.

is only 15 s and the sample acquisition time 10 s, data gathering proceeded at 25s per run which provides ample time to run standards between each data set.

The chromatograms from each well head are usually quite complex and in these data sets the ubiquitous presence of a late eluting peak is seen at around 9s. This peak is often

associated with the reduction products of TCE and PCE to which the SAW is even more sensitive.

Conclusion

It has been effectively demonstrated that accurate and reproducible chromatograms can be generated in the field that closely emulate those derived during analytical chemical laboratory analysis. Even though the resolution provided by the SAW/GC does not compare with laboratory based equipment for the most part this feature is not required. The positive advantage during field screening or ground well monitoring is that data is acquired at an extremely rapid rate which allows only those samples containing analytes of interest to be



Figure 4: Site generated chromatograms with a TCE/PCE standard which is used to indicate the presence of these analytes.

selected for further in depth analysis at an off-site analytical lab. In addition the SAW is extremely sensitive providing detection levels in the low ppb range and further more its sensitivity is not linked to any chemical feature of the analyte. This last attribute ensures that analytes such as the volatile chlorinated hydrocarbons can be easily detected as the SAW is essentially a mass-sensitive detector.

Finally to ensure portability the SAW/GC itself is a compact device employing a solid state SAW detector: it is compact, lightweight and requires no addition fuel gas supply. When manufactured in quantity the likelihood is that its unit cost will decrease as has been the case with most lithographic microelectronic fabrications. When this detector is coupled to a short, fast capillary GC column via a trap and valve the practicalities of an ultra-rapid general purpose field gas chromatograph begin to become apparent.

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