Field-Usable Portable Analyzer for Chlorinated Organic Compounds

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4.2 Field-Usable Portable Analyzer for Chlorinated Organic Compounds

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INTRODUCTION

Transducer Research, Inc. (TRI) has been working with the DOE Morgantown Energy Technology Center to develop a new chemical monitor based on a unique sensor which responds selectively to vapors of chlorinated solvents. We are also developing field applications for the monitor in actual DOE cleanup operations. During the initial phase, prototype instruments were built and field tested. Because of the high degree of selectivity that is obtained, no response was observed with common hydrocarbon organic compounds such as BTX (benzene, toluene, xylene) or POLS (petroleum, oil, lubricants), and in fact, no non-halogen-containing chemical has been identified which induces a measurable response. By the end of the Phase I effort, a finished instrument system was developed and test marketed. This instrument, called the RCL MONITOR (Figure 1), was designed to analyze individual samples or monitor an area with automated repetitive analyses. Vapor levels between 0 and 500 ppm can be determined in 90 s with a lower detection limit of 0.2 ppm using the hand-portable instrument. In addition to the development of the RCL MONITOR, advanced sampler systems are being developed to: (1) extend the dynamic range of the instrument through autodilution of the vapor and (2) allow chemical analyses to be performed on aqueous samples. When interfaced to the samplers, the RCL MONITOR is capable of measuring chlorinated solvent contamination in the vapor phase up to 5000 ppm and in water and other condensed media from 10 to over 10,000 ppb(wt)—without hydrocarbon and other organic interferences.

OBJECTIVES

Chlorinated solvents, such as carbon tetrachloride or trichloroethylene, were extensively used as degreasing agents in industrial operations. Because of past handling, storage, and disposal procedures, environmental contamination occurred at many of these sites. Chlorinated solvent contamination of soil and ground water is recognized as a major hazardous waste problem at numerous government and private installations (OTA, 1991). There are extensive
ongoing environmental restoration programs for the removal of subsurface RCL contamination. During the remediation process, from site characterization to closure, chemical monitoring is necessary to assure worker safety, locate contaminants, verify environmental compliance of emissions, and track the actual cleanup process. Until recently, the only available technology to selectively analyze for chlorinated organics was a gas chromatograph (GC) equipped with electron capture detector or mass spectrometer detector. In addition to being expensive, gas chromatography requires grab samples and does not provide real-time answers. The shortcomings of laboratory methods have been recognized for certain applications that demand quick response or analyses on large numbers of samples. Field analytical methods (FAMs) are being developed as attractive and cost-effective alternatives (Carpenter et al., 1994). The first step in the development of FAMs is the availability of field-usable instrumentation and the heart of any field instrument is the detector.

APPROACH

A solid state chemical sensor has been developed which exhibits a high degree of chemical selectivity in detecting vapors of chlorine-containing organic molecule, this sensor was named the "RCL" sensor. To exploit its analytical potential, an advanced chemical monitor was designed, built, and field tested using the RCL sensor as the detector system. A two-phase program was developed with support from METC. In the initial phase, an instrument system (the RCL MONITOR and specialized samplers) was developed and field tested. Specifications for the RCL MONITOR are presented in Table I. Independent cost analysis demonstrated that significant cost saving can be achieved with the RCL MONITOR for many applications (Energetics, 1993). At the conclusion of the Phase I effort, specific applications were identified which would benefit from the RCL technology:

- Environmental Compliance
- Health and Safety
- Process Monitor (Vacuum Extraction)
- Environmental Modeling
- Site Characterization

Case studies using the RCL MONITOR are currently underway as part of the Phase II effort. Details on the Phase I development and performance of the RCL MONITOR were presented elsewhere (Buttner et al., 1995).

PROJECT DESCRIPTION

The general theme for the current activity is technology deployment and method development. To accomplish this, several EM40 operations were identified that would benefit from the selective detection and quantitation afforded by the RCL MONITOR. Case studies are currently underway at DOE Hanford, Savannah River Laboratory (SRL) and the Idaho National Engineering Laboratory (INEL), and represent specific Phase II tasks. The selected operations are representative of activities
throughout DOE. Specifically, in the Phase II program, the RCL MONITOR was deployed and evaluated in the following EM40 activity:

- Routine Quarterly Monitoring (INEL)
- Health and Safety Applications (Hanford)
- Vapor Extraction System (Hanford)
- Environmental Modeling Studies (Hanford)
- Environmental Technology Demonstration (SRL)

The deployment plan includes use of the RCL MONITOR for the specific operation, interaction with the cognizant regulator (including Project Manager, State Environmental Officers, and local DOE Officers), and assessment of benefits. To facilitate deployment, TRI has developed a formal training class on operation of the RCL MONITOR.

RESULTS

Routine Quarterly Monitoring (INEL)

The Routine Quarterly Monitoring (RQM) consists of quarterly groundwater and vapor sampling and analysis for chlorinated organic contamination in wells surrounding the Radioactive Waste Management Complex within the INEL site, and is an ideal example of the discrete sampling protocol. Samples are obtained from vapor ports and analyzed using a remote on-site gas chromatograph to determine the total concentration of chlorinated organic constituents. Groundwater samples are collected and sent off-site to an analytical laboratory. The RQM requires the collection and analyses of 66 vapor samples from 21 wells and six water samples from six wells. The wells are sampled to characterize the distribution of organic contaminants in the saturated and vadose zones. Original protocols required the collection, transport, and remote analyses of all samples by gas chromatography. Approximately two man-weeks of effort were required for the vapor analyses, and an additional one to two man-weeks for the water samples. Being performed four times annually, this was a labor-intensive exercise which ties up trained personnel. The RCL MONITOR was deployed as an auxiliary analytical tool for the vapor portion of the RQM in June of 1994. Excellent agreement was obtained between the two methods. Because of this agreement, the RCL MONITOR is now being used as the baseline technology for the vapor portion of the RQM. Since samples no longer need to be transported to a remote laboratory for analysis, a significant time and cost saving is achieved with using the RCL MONITOR. The vapor analyses can be completed in less than 2.5 days, compared to the 2 man-weeks normally required. A cost analysis, presented in Table II, summarizes the expected savings.

The condensed phase sampler was used on the water samples collected from the six wells, but no contamination was detected. Independent analyses indicate that the total chlorinated solvent contamination is low, typically less than 5 ppb. This concentration is below the LDL of the sampler/RCL MONITOR instrument system. Methods to improve the condensed phase sampler, as well as alternative methods of water analysis (W. Buttner, 1995) are currently underway.

Health and Safety (Hanford)

Assurance of Health and Safety for site workers is probably the most important application for vapor monitoring technology and illustrates the need for real-time measurements better than any other application. Two basic applications are being developed—continuous breathing zone monitoring and discrete survey measurements (spot checks). During a four
month period, nearly 100 H&S related spot-check analyses were performed with the RCL MONITOR. Table III summarizes some these measurements. These measurements provided invaluable support to ongoing Hanford clean-up activity.

It is recognized that spot checks will not satisfy those applications requiring real-time monitoring. In many circumstances, continuous monitoring is necessary, and such capability does exist for the RCL MONITOR. Figure 2 depicts measurements performed over a one week period at the PURUS1 facility. Analyses were performed at 15 min. intervals. This deployment supported the evaluation of a developing remediation technology being tested in an enclosed quonset tent within the 200W area of Hanford over a four month period. Vapor levels were found to range from 0 to nearly 20 ppm, with the higher levels occurring overnight during unattended operation. There was not a single failure during the four month deployment.

Vapor Extraction System (Hanford)

Between 363,000 and 580,000 L of carbon tetrachloride were discharged in three locations within DOE Hanford. As part of the Accelerated Cleanup Activities (the Carbon Tetrachloride Site Expedited Response Activity), vacuum extraction systems have been installed in the 200W area to remove the volatile chlorinated solvents. With the vacuum extraction systems, vapors are extracted from subsurface through a high-powered vacuum system. To prevent atmospheric pollution, it is necessary that exhaust be filtered through an array of three chemical filter stacks containing granulated activated carbon (GACs) in series. Most vapor is scrubbed by the first GAC, while the second and third provide backup. The RCL MONITOR was installed to monitor the air stream passing through the primary GAC. In this configuration, likely vapor levels would range between 5 and 2000 ppm. Although outside the range of the RCL MONITOR, a custom interface system was built and deployed which extended the range of the instrument; details on this sampling system were presented earlier (Penrose et al., 1995). Although a separate interface system was built, its operation could, in principle, be performed by the RCL MONITOR. Data was collected over a 5 month period. During this time, the RCL MONITOR was operated for a week between downloading the data and validating performance. Representative results are provided in Figure 3. During the deployment of the RCL MONITOR, vapor excursions could be directly correlated to event on the VES, such as GAC breakthrough, system shut downs, and diurnal variations. Overall, we had a success rate of only 65%, where a failure is defined as loss of part or a weekly data set, but for the last half of operation, the success rate increased to over 80%. The major modes of failure were due to the sensor and to external causes (e.g., power shut down, lightning strikes). In a final assessment, we discontinued this activity at Hanford because it is unlikely that the RCL MONITOR would be adopted for this application at this site. Nevertheless, we demonstrated that the RCL MONITOR can operate as a Process Monitor or Process Controller.

Environmental Modelling Studies (Hanford)

Geological and geophysical modelling studies are ongoing at Hanford and other DOE sites to support the active cleanup technologies, such as the VES. One promising technology is the passive venting of VOCs, in which vapor

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1The PURUS system vacuum extract soil vapor and condenses it to the liquid state.
excursions are induced by transient barometric pressure changes. Pressure changes drive air in and out of soils, and that this is facilitated by wells. During periods of decreasing pressure, the vapor levels in outgassing of wells increase dramatically. What is not known is the overall efficiency of the process; this requires measurement of both vapor levels and flow rates over long time periods. While passive venting may not replace active cleanup methodologies, it is viewed as a potential cost-effective complement (Rohay et al, 1994). With METC support, TRI provided RCL MONITORS to Hanford geologists to track vapor excursions. These experiments are ongoing, and expected to continue through to the end of the Phase II effort. Data for a one month period is illustrated in Figure 4. Current activity is ongoing to evaluate method to enhance this process, notably the use of one-way valves to prevent air uptake by the soil.

Environmental Technology Demonstration (SRL)

The Environmental Technology Demonstration (ETD) program was set up to support DOE clean up operations by providing assessments, demonstrations, and training sessions on new and emerging technologies. TRI provided an RCL MONITOR and gas samplers/diluters for use in this demonstration. A second monitor was provided to support necessary H&S activity around wells. Numerous technologies were evaluated, including vapor analyzers (the TRI RCL MONITOR, Quantum FTIR, and the B&K 1302) along with other hardware (e.g., drilling rigs, penetrometers, and sensors). During the assessment, a "Sniff-Off" was performed to compare technologies. These are listed in Table IV. The RCL MONITOR provide true portable analytical capability, and provided quick measurements. Initially, all technologies provided comparable results, but it must be reported that the sensor failed during the evaluation and the instrument would no longer validate.

**BENEFITS**

The RCL MONITOR provides cost-effective analytical capability not found in any other truly portable instrument system. It is a powerful tool for the on-site determination of chlorinated solvent vapors. A range of 0 to 500 ppm was achieved (5000 ppm with the fixed external 10:1 diluter) and a LDL of 0.2 ppm was achieved. Direct analysis of water samples was possible with the condensed phase sampler. Performance of the instrument for vapor and condensed phase analyses compared favorably with CLP methods now in use. Independent cost analysis demonstrated that significant cost saving can be achieved with the RCL MONITOR for many applications.

The instrumentation is simple to use. Field personnel can be trained in less than five minutes to operate the instrument (a full training session requires about 2 hours). Real time data collection, heretofore not possible, on the temporal and spatial characteristics of chlorinated vapor emissions has been obtained. The application of this instrumentation and the development of validated methods should provide for improved field operations, better worker safety, and significant cost savings in hazardous waste management operations.

**FUTURE ACTIVITIES**

The RCL MONITOR has been formally accepted for at least one application, namely the Routine Quarterly Monitoring, and has been informally adopted by some groups for H&S and
research applications. Continuous monitoring activity was achieved with the instrument, with some reservations about reliability of the sensor over very long-term measurements. An extensive effort is underway to improve sensor performance.

ACKNOWLEDGEMENTS

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REFERENCES

Buttner, W.J. "In-Situ Sampling of Aqueous-Phase Contamination by Chlorinated Solvents", Lockheed Idaho Technology Company (LITCO) Contract #: C95-175582.


Figure 1: The RCL MONITOR

Figure 2: Representative data obtained from the RCL MONITOR during continuous monitoring of the work space air during testing of the PURUS system
Figure 3: Representative data obtained from the RCL MONITOR during continuous monitoring of the post-primary GAC exhaust. Vapor spikes correlated to VES activity, including saturation of GAC, GAC changes, changeovers, etc.

Figure 4: Monthly logging of passive venting of vapors as measured by the RCL MONITOR and barometric pressure.
Table I: Features of the RCL MONITOR vapor monitor.

<table>
<thead>
<tr>
<th>Design Feature</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measurement</td>
<td>Direct readout 90 s after start of analysis, presented in ppm with a range of 0 to 500 ppm and a LDL of 0.2 ppm. The results are presented on display and stored in memory</td>
</tr>
</tbody>
</table>
| Modes of Operation | - SURVEY-LOW (a fast manual mode of analysis, 0.2 to 25 ppm).  
                          - SURVEY-HIGH (a fast manual mode of analysis, 2 to 500 ppm).  
                          - MONITOR (an automated mode of operation, with HIGH and LOW ranges) |
| Physical Design | All components in one unit (5" x 6" x 12") |
| Package        | 5 kg (12 pounds) |
| Weight         | Internal battery (over 6 hours operation at 25°C) or AC operation |

Table II: Cost Benefit Analysis for using the RCL MONITOR instead of a gas chromatograph for the RQM

<table>
<thead>
<tr>
<th>VAPOR SAMPLES</th>
<th>GC</th>
<th>RCL MONITOR</th>
</tr>
</thead>
<tbody>
<tr>
<td>SINGLE TIME EXPENSE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Capital Equipment:</td>
<td>$30,000</td>
<td>$17,500</td>
</tr>
<tr>
<td>Capital Equipment (samplers):</td>
<td>1,000</td>
<td>5,000</td>
</tr>
<tr>
<td>TOTAL:</td>
<td>$31,000</td>
<td>$22,500</td>
</tr>
<tr>
<td>MANPOWER Requirements</td>
<td>man-hrs</td>
<td>cost</td>
</tr>
<tr>
<td>LABOR ($62.50/hr)</td>
<td>80</td>
<td>$5,000</td>
</tr>
<tr>
<td>EQUIPMENT COST</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Annual Maintenance Cost:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Supplies:</td>
<td>100</td>
<td>2,000</td>
</tr>
<tr>
<td>Equipment Preparation Cost:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bags:</td>
<td>500</td>
<td>2,000</td>
</tr>
<tr>
<td>Vehicle Expense</td>
<td></td>
<td></td>
</tr>
<tr>
<td>daily fee ($50.00/day)</td>
<td>400</td>
<td>1,600</td>
</tr>
<tr>
<td>Mileage (120 miles/day)</td>
<td>288</td>
<td>1,152</td>
</tr>
<tr>
<td>TOTAL:</td>
<td>$6,788</td>
<td>$29,152</td>
</tr>
</tbody>
</table>
Table III: Specific H&S Spot-Check Measurements Performed with the RCL MONITOR at HANFORD. All are breathing zone measurements.

<table>
<thead>
<tr>
<th>Application</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Well Perforation</td>
<td>0-2 ppm (OVM read 200 ppm—therefore nonchlorinated)</td>
</tr>
<tr>
<td>Well drilling operations</td>
<td>0-2 ppm</td>
</tr>
<tr>
<td>Examine Well cuttings</td>
<td>0-1 ppm</td>
</tr>
<tr>
<td>Investigate CCl_4 in enclosure</td>
<td>11-39 ppm</td>
</tr>
<tr>
<td>Outside air checks at 200W</td>
<td>(0.1-0.2 ppm)</td>
</tr>
</tbody>
</table>

Table IV: Technologies for chlorinated hydrocarbon analysis evaluated during the March Demonstration of the ETC program at SRL

<table>
<thead>
<tr>
<th>Technology</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>RCL MONITOR</td>
<td>$8,500</td>
</tr>
<tr>
<td>Quantum FTIR</td>
<td>$50,000</td>
</tr>
<tr>
<td>B&amp;K 1302</td>
<td>$30,000</td>
</tr>
</tbody>
</table>