

Field-Usable Portable Analyzer for Chlorinated Organic Compounds

**Topical Report
September 1992 - May 1994**

**William J. Buttner
Roger D. Williams**

May 1995

Work Performed Under Contract No.: DE-AC21-92MC29118

**U.S. Department of Energy
Office of Environmental Management
Office of Technology Development
Washington, DC**

For

**U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia**

**By
Transducer Research, Inc.
Naperville, Illinois**

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Acknowledgements

The authors gratefully acknowledge William Vickers for providing support on the software and the development of the external 10:1 diluter, Karen Schroeder and Ali Husain for testing and developing the condensed phase sampler; Greg Taylor and Li Pan for development of the preconcentrator; Chuck Wolfe for the development of the instrument software; Phil Loeb for the electronic layout of the instrument, Steve Parrish for the mechanical layout of the instrument, Denise King for providing the RCL sensors, Daryl Mortensen for evaluation of the sensors; and Dr. William Penrose, Mr. Melvin Findlay, and Dr. Joseph Stetter for additional support. A special thanks is extended to Cary Martin for facilitating our testing of this instrument at DOE Hanford, and our most cooperative and helpful colleagues at Morgantown Energy Technology Center, DOE Hanford, DOE Savannah River, and DOE Idaho National Engineering Laboratory.

Abstract

Through a U.S. DOE-funded program, an advanced chlorinated organic (RCL) vapor monitor has been built and tested in actual hazardous waste site operations. The monitor exploits the analytical capabilities of a solid-state sensor which was recently developed and has remarkable selectivity for chlorinated organic vapors at sub-parts-per-million sensitivity. The basic design goal of a user-friendly, reliable, instrument with a broad dynamic range for the selective detection of chlorinated solvent vapors was demonstrated. To date, no non-halogen-containing compound has been identified that induces a measurable response on the sensor, including commonly encountered contaminants such as BTXs (benzene, toluene, and xylenes) or POLs (petroleum, oils, lubricants). In addition to the development of the RCL MONITOR, advanced sampler systems were developed to further extend the analytical capability of this instrument, allowing chemical analyses to be performed for both vapor phase and condensed contamination. The sampling methods include fixed dilution, preconcentration, and closed-loop air stripping for condensed media. With uniform success, these different series of field tests were conducted at DOE facilities on several types of samples. Independent cost-benefit analysis has concluded that significant cost savings can be achieved using the RCL MONITOR in DOE applications. This effort provides a sound fundamental technology base for the development of advanced analytical methods that are needed by the US DOE. In addition, advanced methods for detecting chlorinated hydrocarbons that are made possible by this technology will save time, reduce costs, and improve human health and safety in restoration operations. To fully achieve all possible cost savings, continued effort is necessary to develop validated methods for the use of the RCL MONITOR. The development of methods through case studies is the theme of the Phase II effort, which is currently underway.

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Executive Summary

Background

In 1991, Transducer Research, Inc., (TRI) developed a solid state chemical sensor which exhibits a high degree of chemical selectivity in detecting vapors of chlorinated organic solvents. With this sensor, the selective sub-ppm_v detection of vapors of chlorinated organic compounds has been achieved, even in the presence of much higher levels of hydrocarbons and other organic and inorganic vapors. To date, no non-halogen containing chemical has been identified which induces a measurable response. By mid-1991, this device, which was called the RCL sensor, was retrofitted into an existing instrument system. The prototype instrument system found several applications within the Department of Energy (DOE). The ability to perform on-site analysis for chlorinated vapors was recognized as a strong advantage over the time delays and extra cost associated with conventional laboratory techniques. Ultimately however, the difficulty in using the prototype instrument system impeded its general application. To be generally useful to site personnel, the RCL sensor needed to be integrated into an easy to use, reliable instrument.

An opportunity to improve the instrument system for the RCL sensor was provided through the Morgantown Energy Technology Center (METC) Program Research and Development Announcement (PRDA). On September 30, 1992, TRI was authorized to redesign the chlorinated vapor monitor. Through this DOE-METC funded program (contract number DE-AC21-92MC29118), the analytical capabilities of this new device were to be exploited by designing and building an advanced instrument package. General design goals for the instrument included 1) reliable and sensitive measurements of vapors of chlorinated solvents; 2) a broad dynamic range provided by intelligent sampler systems; 3) versatility to fit several applications; and 4) a user-friendly, conveniently packaged, field-usable instrument.

Instrument Description

Through this program, a portable, user-friendly instrument for the field analysis of vapors of chlorinated solvents was designed, built, and field tested. This instrument, called the RCL MONITOR, was designed to operate in two modes, a manual mode of operation (SURVEY) and an automatic mode of operation (MONITOR). Both the manual mode and automatic mode have two concentration ranges--Low (0 to 25 ppm_v with a lower detection limit of 0.2 ppm_v) and High (0 to 500 ppm_v with a lower detection limit of 2 ppm_v). The analysis time is 90 seconds. Except for automatic repetition of analyses, MONITOR mode is equivalent to SURVEY mode. To expand the potential applications of the RCL MONITOR, specialized samplers were developed to improve the lower detection limit to 10 parts per billion by volume (ppb_v) with a preconcentrator; to extend the upper limit to 5,000 parts per million by volume (ppm_v) with a fixed 10:1 external diluter; and to perform analysis of chlorinated solvent contamination in water samples with a Condensed Phase Sampler (CPS).

Field Evaluations

Between July 19 and July 23, 1993, and between October 15 and October 19, Dr. William J. Buttner and Mr. Roger Williams field-tested the RCL MONITOR and specialized sampler systems at DOE-Hanford in Richland, Washington. For each series of field tests, two field prototype instruments were assembled and deployed for evaluation and one engineering prototype was used to provide field support. In addition to the field tests at DOE-Hanford, Dr. William Buttner used the RCL MONITOR during a portion of a regular monitoring exercise at the Idaho National Engineering Laboratory (INEL). The goal of the field testing was to confirm performance and specifications of the RCL MONITOR and specialized samplers under field conditions. During these evaluations, the instrument was tested in actual site activity, including well digging, routine surveys of well head spaces and soil gases, and other site remediation activity. During the field tests, the concentration of vapors varied from "no detection" (< 0.2 ppm_v) to over 1000 ppm_v.

Over 200 on-site analyses were made with *a single instrument* in one week of field tests. Battery power sustained operation for up to 6 hours of continuous operation (no attempt was made to operate the instrument for longer periods). The instrument weighs only 12 pounds, and was conveniently hand transported for on-site analyses. Training sessions lasting less than 5 minutes were sufficient for novice users to operate the instrument and obtain accurate measurements. Personnel in protective clothing, including gloves and supplied air, could operate the instrument. The RCL MONITOR was tested in each mode of operation (SURVEY and MONITOR). Rapid site surveys were achieved using the SURVEY/Low mode, which allows up to 10 chemical analyses in an hour. This mode was designed to allow chemical analyses (0 to 25 ppm_v) to be performed quickly, and was well-suited to assure worker safety. The SURVEY/High, was designed for a much broader range of vapor levels (0 to 500 ppm_v). This broader concentration vapor range was achieved through an internal feature which automatically dilutes the vapor concentration by blending the sample with clean air. Continuous vapor measurements were performed with the instrument in MONITOR mode. On several occasions, the instrument was tested in this mode of operation within the exclusion zone to which general access was restricted.

A comparison was made between the RCL MONITOR and alternative methods of analyses. The alternative methods included gas chromatographic analysis, portable photoionization detectors (PIDs), and detector tubes. Excellent agreement between gas chromatographic analysis and the RCL MONITOR was obtained in side by side analyses of actual field samples at INEL. In general, the RCL MONITOR provided better sensitivity and accuracy than detector tubes and photoionization detectors for the detection of chlorinated vapors.

The performance of specialized samplers was verified during the October field tests. Vapor levels down to 10 ppb_v were analyzed using the Preconcentrator, while the Fixed External 10:1 Diluter extended the dynamic range of the RCL MONITOR up to 5000 ppm_v. The Fixed External 10:1 Diluter interfaced to the RCL MONITOR was able to perform continuous measurements so that temporal data on fluctuating vapor levels, which are common in well head spaces and from soil gas probes, could be conveniently obtained. The performance of the Condensed Phase Sampler compared favorably with laboratory analyses of water samples with chlorinated solvent contamination ranging

from 10 to 10,000 ppb_{wt}. Unlike the laboratory methods which could take up to two weeks, results with the Condensed Phase Sampler were obtained within 30 minutes of sample collection.

Throughout the field testing, the RCL MONITOR performed reliably and provided measurements in a facile manner. No other field-portable instrument has been developed which provides the degree of selectivity and sensitivity obtained with the RCL MONITOR. Independent cost-benefit analysis has concluded that significant cost savings can be achieved using the RCL MONITOR in DOE applications. Through interactions with site personnel during these field tests, numerous applications were identified which would benefit from an inexpensive and simple method to measure contamination levels of chlorinated solvents. The applications can be categorized as:

- Environmental Compliance
- Health and Safety
- Process Monitor for Clean-Up Equipment
- Environmental Modeling
- Site Characterization

These categories serve as a working framework to organize and relate ongoing environmental chemical analyses into application groups. Within the above groupings, TRI has identified specific DOE activities which would benefit from using the analytical capabilities of the RCL MONITOR. Development of useful methods for several DOE operations is ongoing.

I Introduction

"We don't have the luxury of time in characterization. We need to characterize now and begin the remediation process. We need to get characterization technologies into the field."

Caroline Purdy, Tie Quarterly, Volume 1 (2), 1992.

I.1 Chlorinated Solvent Contamination

Past operations within many government facilities have resulted in major site contamination by hazardous chemicals. This has been especially true for weapon production facilities. Now that many of these operations are no longer needed, the mission for the facilities is being changed and many are being transferred to the private sector. Regardless of whether the site is transferred to the private sector or continues to operate under federal government control, it will be necessary to guarantee that the legacy of past operations does not pose a risk to future users. Accordingly, the U.S. Department of Energy (DOE), U.S. Department of Defense (DOD), and other government agencies have instituted extensive programs to restore the environment. Environmental restoration will be expensive, and without major breakthroughs in technologies, the cleanup cost has been estimated to be over \$1 trillion (DOE, 1991). One fortunate aspect of the problem is that in many cases the nature of contamination is surprisingly similar from site to site, typically consisting of organic solvents, petroleum-based oils and lubricants, and in some cases heavy metals. This facilitates transfer of technology between sites.

One example of an environmental problem common to many sites is contamination by chlorinated solvents. Chlorinated solvents were used extensively at government and industrial facilities as a degreasing agent. Many chlorinated solvents are toxic and have stringent exposure limits (e.g., American Conference of Governmental Industrial Hygienists--ACGIH, 1993). For example, the short term exposure limit for carbon tetrachloride and trichloroethylene are 10 ppm_v and 100 ppm_v, respectively, while the time-weighted-average for carbon tetrachloride and trichloroethylene are 5 and 50 ppm_v, respectively (ACGIH, 1993). Because of past disposal and storage practices, chlorinated solvent contamination is now a major environmental problem at many of these sites. In DOE alone, a recent study verified chlorinated solvent contamination was involved in all 14 facilities included in the study (U.S. Congress OTA, 1991). Worse yet, within each facility there are frequently multiple contaminated sites.

Efficient environmental restoration requires efficient analytical methods for quick, cost-effective analysis of toxic compounds whenever they are suspected to be present. Until recently, the only reliable means for performing such analyses were conventional laboratory methods with a bench top gas chromatograph. While conventional sample collection and transport to off-site laboratories can provide highly sensitive analyses for chlorinated solvent contamination, such methods are inefficient because of time delays and high costs. It has also been established that environmental samples containing volatile organic compounds are not stable and are prone to degradation during transport and storage. These methods are not cost effective and do not necessarily provide an

accurate representation of the site being characterized. Because of these problems, in the past few years Field Analytical Methods (FAMs) have become increasingly useful in performing chemical analyses with a higher degree of accuracy, at a lower cost, and with higher frequency than was possible with conventional methods (Carpenter et al., 1994). FAMS frequently provide more accurate results than conventional methods because of the problems associated with transporting samples containing volatile compounds to remote facilities. Therefore, a validated FAM for chlorinated solvents would be a powerful analytical tool for hazardous waste site operations.

I.2 The RCL Sensor

The development of a FAM is a multi-step process involving technical advances, validation of protocols, and finally acceptance by users, regulators, and stake holders. The first step in the development of a FAM is of course the development of viable technology, and in chemical analyses, the critical component is the detector system. In 1991, TRI developed a new chemical sensor which responds selectively to vapors of chlorinated solvents (Stetter and Cao, 1993). In the RCL sensor, no response is observed with common hydrocarbon organic compounds such as BTXs (benzene, toluene, xylene) or POLs (petroleum, oil, lubricants). No non-halogen containing chemical has been identified which induces a measurable response. While the sensor does exhibit a small response to brominated compounds, and an even smaller response to iodinated and fluorinated compounds, it responds quickly, reversibly, and with a high sensitivity to vapors of chlorinated compounds (Cao and Stetter, 1992), with a lower limit of detection of 0.1 ppm, (Buttner et al, 1993). The selectivity of the sensor is illustrated in Figure I-1. Because of the high response to chlorinated compounds, and to distinguish it from other sensor types, we have called it the "RCL" sensor. "RCL" is derived from the organic chemist's shorthand notation "R-Cl", denoting an unspecified chlorine-containing organic molecule.

I.3 History of Program

I.3.1 Technology Introduction (1992)

To exploit its analytical potential, the RCL sensor was retrofitted into an existing instrument system in mid-1991. The instrument and RCL sensor package was called the Odyssey 2001-05 (Penrose, et al., 1993). Because of the unique analytical capability of the RCL sensor, the Odyssey 2001-05 had numerous applications and exhibited an analytical capability for chlorinated solvent detection not available in any other portable chemical instruments (Vaughn and Martin, 1993). Highlights included:

1. Favorable performance comparison of the Odyssey 2001-05 with other technologies at the DOE Hanford site and several other non-DOE facilities.
2. Use of the instrument for multiple purposes including process control and point source monitoring.

3. Detection of chlorinated organic solvent contamination in a waste oil storage area where no chlorinated solvent was believed to be present.
4. Detection limit and selectivity to CCl_4 below the Hanford Action level, which is not readily achievable with photoionization detectors (PIDs).
5. Continuous monitoring of waste site clean up operations in various applications including:
 - measured in-coming vapor levels (process tracking)
 - measured emission vapor level (verification of compliance to environmental regulations)
 - detection of transient low level emissions
6. Designation as baseline technology for RCL vapor analysis at Hanford (October 1992).

The deployment of the Odyssey 2001 in actual ongoing hazardous waste cleanup operations demonstrated two important points. First of all, it was clearly demonstrated that a need existed for the monitoring capability of the RCL sensor. The ability to perform on-site analysis for chlorinated vapors was recognized as a strong advantage over the time delays and extra cost associated with conventional laboratory techniques. However, it was also realized that FAMs require easy to use, reliable instrumentation. The complexity of operation for the Odyssey 2001-05 impeded its general application. Quite simply, in spite of the strengths of its analytical capability, the RCL sensor would never be extensively deployed unless it was interfaced to an intelligently designed, easy to operate instrument system.

I.3.2 Development of the RCL MONITOR

An opportunity to redesign an instrument system centered around the RCL sensor came through the DOE Program Research and Development Announcement (PRDA) released through Morgantown Energy Technology Center (METC) in October 1991, and authorization to redesign the chlorinated vapor monitor was issued in September, 1992. This provided an opportunity to produce a powerful field deployable tool for the real-time analysis of a major class of environmental contamination. Project goals included:

- Development of a user-friendly, conveniently packaged instrument for DOE applications.
- Extension of the dynamic range of the instrument through intelligent sampler systems including:
 - direct sampling (for most applications)
 - autodilution (to extend to higher concentrations)
 - fixed dilution (for further extension)
 - preconcentration (for very low concentrations)
- Extension of the analytical applications beyond direct vapor monitoring by developing alternative media samplers, such as a condensed phase sampler for water and/or soil.

While the intrinsic range of the sensor does allow for broad analytical applications, it is limited and many applications would not be amenable to direct monitoring by the RCL sensor. Basically, high level vapors (>100 ppm_v) and extremely low level vapors (<0.1 ppm_v) would be outside the range of the sensor. Also, the sensor responds to vapor phase analytes, so water- or soil-bound contamination can not be monitored directly. Accordingly, TRI proposed the development of specialized samplers which would expand the effective range and applications of the RCL Instrument. Thus, in addition to a general sampler for direct monitoring, TRI proposed to build intelligent diluter systems, as well as a preconcentrator and a condensed media sampler. In specific terms, TRI proposed to design and build an RCL MONITOR with the following characteristics:

- All components in a single, hand-carried package.
- Field usable.
- Simplified operation which will not allow improper use. Intuitive protocols for operation, and/or well defined prompts on the display.
- Simple calibration procedure.
- Clearly legible display.
- Versatile sample interface for a broad dynamic range and applications to media other than air, gases and vapors.
- Controls accessible with gloved hands.
- Automatic features to protect the sensor and speed response.
- A range of 0 to 500 ppm_v with a LDL of 0.2 ppm_v, extended up to 5,000 ppm_v with external diluters and down to 0.005 ppm_v with a preconcentrator.
- Capable of performing water-phase analyses with a condensed phase sampler.

The preconcentrator and condensed phase samplers were constructed as modules separated from the basic RCL MONITOR.

I.3.3 Milestones for the RCL MONITOR

From the onset of the project, the criteria for the design and performance evaluation of the RCL MONITOR were to be determined from actual field applications and not from laboratory evaluations. Much of the information regarding the necessary design features were formulated during fact finding trips performed at the beginning of the project. Performance of the instrument and samplers was determined through a series of field tests. From the fact-finding trips and field tests, a list of design requirements were formulated and ultimately implemented in the instrument; Table I-1 summarizes these requirements. The analytical specifications of the RCL MONITOR built for DOE are summarized in Table I-2.

By July of 1993, prototype instruments had been designed, built, and made ready for field testing. The assessment of the instrument and samplers was based on their performance in a series of field tests. Initial testing of the instrument occurred at DOE-Hanford in July, 1993. As expected for new technology, shortcomings in the initial prototype design were identified in the first field test. The weaknesses included improper indication of over-range conditions; no indication in the report

as to which analytical mode was used; no internal zero filter; an overly complicated 10-point calibration procedure; an inadequate external 10:1 diluter; manual adjustment of the sensor heater voltage; and non-keyed pneumatic inputs on the front panel thus allowing improper connections to the instrument. For the most part, these were minor in nature, and were corrected prior to the second set of field tests, held in October, 1993. In the case of the pneumatic connectors, better labeling of pneumatic inputs was incorporated to minimize the chance of misconnections. The specialized samplers were also field tested in October, 1993. An additional opportunity to evaluate the RCL MONITOR in actual field operations came in April, 1993. This particular opportunity was especially valuable in that not only was it a mandatory site survey at the Radioactive Waste Management Complex at the Idaho National Engineering Laboratory, but we were also able to obtain side-by-side comparison of the RCL MONITOR to the results obtained with a gas chromatograph. A commercial version of the RCL MONITOR was released in November, 1993. Of particular interest was the receipt of the R&D 100 award. Figure I-2 summarizes the major milestones for the development of the RCL MONITOR.

I.4 Summary

The development of the RCL MONITOR was a multi-step process, starting with the development of the RCL Sensor. The technology introduction stage demonstrated the significant role the RCL sensor could play in environmental characterization, monitoring and cleanup activity, providing it could be packaged in a convenient, user-friendly instrument system. The performance of this instrument system, and the accessories developed to improve the overall operating specifications are the subject of this report. A detailed discussion of the instrument system developed in this project, the RCL MONITOR, is presented in Chapter III, and the evaluations and field demonstrations with the instrument will be covered in Chapter IV. Chapter V is dedicated to the specialized samplers.

Table I-1: Features of the RCL MONITOR vapor monitor.

Design Feature	Description
MEASUREMENT Discrete Repetitive Range	Direct Readout in ppm, Easy to set up 0 to 500 ppm, with a LDL of 0.2 ppm,
OPERATION Modes User Interface Startup Transport Display Duration (single charge)	1). SURVEY-LOW (a fast manual mode of analyses, 0.2 to 25 ppm,). 2). SURVEY-HIGH (a fast manual mode of analyses, 2 to 500 ppm,) 3). MONITOR (an automated mode of operation, with same choice of range as SURVEY- LOW or SURVEY-HIGH)) Push buttons (accessible with gloved hands) One button operation Handle and Shoulder Strap Results presented in "ppm," 6 Hours (25°C)
OPERATOR SKILL Basic use Advanced use	Minimal training (<5 min) 3 hours training
MAINTENANCE Sensor Internal Filters	Easily Accessible Easily Accessible
CALIBRATION Protocol Time Required	Automated 3 point, 0 to 10 ppm, procedure 1 hour (maximum), unattended, auto shutoff afterward
DATA STORAGE Format	Results stored in report: date, time, concentration, analysis number, mode used
PHYSICAL DESIGN Package Weight Power Pneumatics	All components in one unit 5" x 6" x 12" 5 kg (12 pounds) Internal battery (over 6 hours operation at 25°C) - robust quick connects - internal zero filter - internal particulate filter

Table I-2: Operating Specifications of the RCL MONITOR (April, 1994)

FEATURE	OPERATING MODES	
	SEARCH-LOW/ MONITOR-LOW	SEARCH-HIGH/ MONITOR-HIGH
Measurement Range (ppm _v)	0 to 25 ppm _v	0 to 500 ppm _v
Lower Detection Limit (ppm _v)	0.2 ppm _v	2 ppm _v
Cycle Time Measurement AUTOZERO (typical)	90 seconds 5 minutes (0 - 5 ppm _v) 10 minutes (5 -25 ppm _v)	90 seconds 10 minutes
Accuracy (typical)	indication (0.2-0.5 ppm _v) ±25% (0.5 - 25 ppm _v)	indication (2 - 5 ppm _v) ±30% (5 - 500 ppm _v)

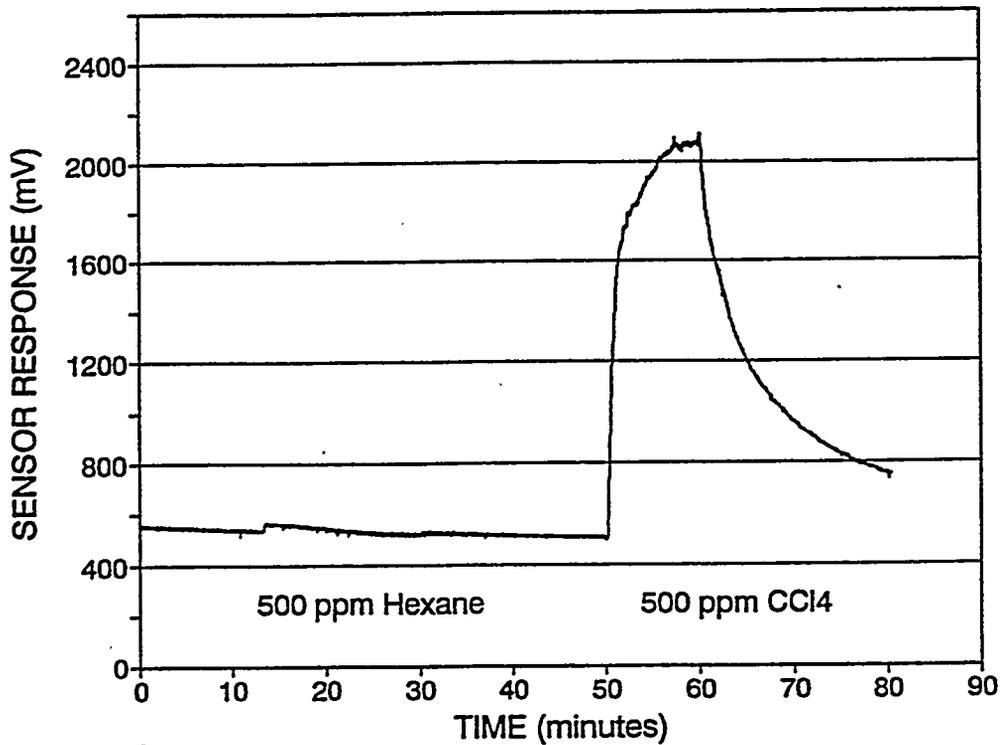


Figure I-1: Selectivity of the RCL Sensor. The Response of the RCL Sensor is highly selective to vapors of chlorinated solvents. No response is induced by hydrocarbons.

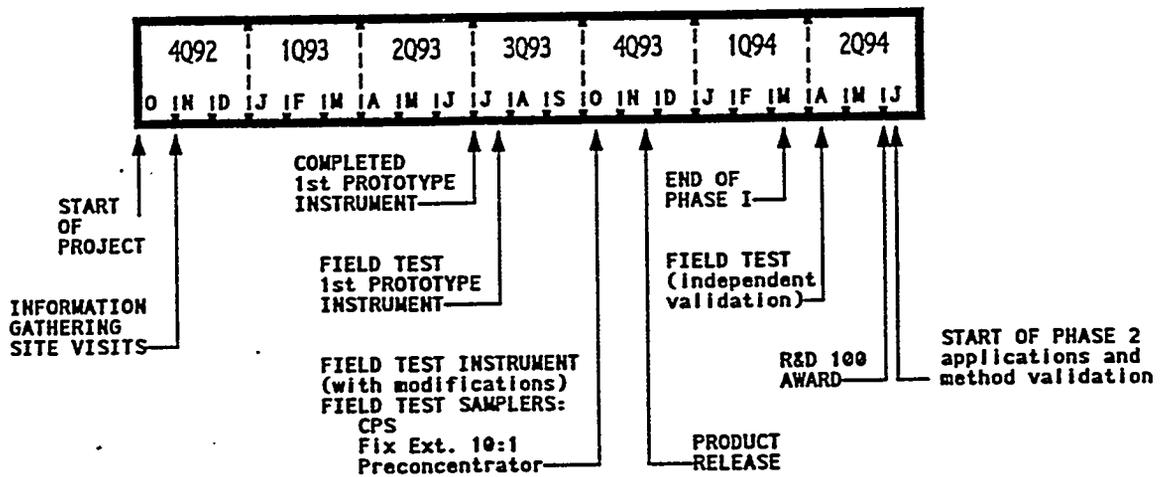


Figure I-2: Milestone schedule for the development and demonstration of the RCL MONITOR.

II. The RCL MONITOR

II.1 Overview of the RCL MONITOR

The design goals for the RCL MONITOR, i.e., rapid and accurate analytical capability in a user-friendly instrument, were achieved. The RCL MONITOR is shown in Figure II-1. A survey of potential customers indicated that ease of operation was perhaps the most important property for portable analytical instruments, perhaps even more important than a high degree of accuracy. The instrument is operated through simple intuitive commands from a logical menu tree (illustrated in Figure II-2). The commands are initiated through the pressure sensitive Key Pad (illustrated in Figure II-3) mounted on the top of the instrument. A summary of the specifications and functions of the advanced RCL instrument was presented in Table I-1. The RCL MONITOR was not created as an upgrade to the existing Model 2001-05, but was redesigned from the ground up as an entirely new device.

II.2 Basic Operation of The RCL MONITOR

For operation, there are two instrument states, the READY and SUPERVISORY. Upon powering up and following a short warm up period (<20 minutes), the instrument automatically defaults to the READY state in SURVEY-HIGH mode. At this point, the instrument is ready to perform an analysis and an operator only has to supply the sample and press SAMPLE on the key pad. All instrument functions are automated, including sampling, data collection, presentation of results, and storage of data in memory. Control of the RCL MONITOR is through an internal microprocessor. Manual operation is restricted to selection of analytical modes (e.g., SURVEY, MONITOR or CALIBRATE), setting SUPERVISORY parameters (e.g., date, time, alarm threshold), and initiation of measurements. Following the completion of a measurement, results (in ppm,) are presented on an LCD display specifically selected for its legibility. The results are also stored in an internal memory, which can be downloaded to an external computer at the operators convenience. The format of the data stored in memory is:

Date Time Results ID # MODE

"ID#" is an sequential identification number assigned to each measurement and is presented both on the display following completion of a measurement and stored in memory. "MODE" identifies whether the instrument was operated in SURVEY-LOW/HIGH or MONITOR-LOW/HIGH. Following the analysis, the instrument goes through an automatic recovery protocol, called AUTOZERO, to prepare for the next measurement. Upon completion of AUTOZERO, the instrument is ready for another analysis. From the default READY MODE state, there are only two options. The operator may chose to perform an analysis in the SURVEY-LOW and SURVEY-HIGH (discussed below in Section II.3). The SURVEY modes are manually initiated modes of analysis.

Instrument parameters, such as date and time, are accessed in SUPERVISORY. In Supervisory, the MODE SELECT sub-menu allows the operator to select the non-default mode of operation, including MONITOR, the automated repetitive mode of analyses, and CALIBRATE. The complete menu tree (for both READY and SUPERVISORY) is illustrated in Figure II-2.

II.3 Analytical Modes of Operation

There are two main analytical modes of operation. There is a manual mode, SURVEY, in which the operator initiates each analysis by pressing SAMPLE on the keypad. There is also an automated mode of operation, MONITOR, in which an analysis is performed repetitively at preset user-selected intervals. MONITOR MODE is selected from the MODE SELECT menu in SUPERVISORY. The interval time between measurements is accessed upon selection of MONITOR MODE, and can be set between 15 minutes and 24 hours. Both SURVEY and MONITOR can operate in LOW (0 to 25 ppm_v, with a lower detection limit of 0.2) and HIGH (0 to 500 ppm_v, with a lower detection limit of 2 ppm_v). Selection of HIGH or LOW range is made by pressing SAMPLE MODE on the key pad during standby periods. The HIGH range is achieved by an internal automated 10:1 dilution of incoming vapors. The results that are displayed and stored in memory are corrected for this dilution factor.

For analysis, the sample source is connected to the RCL MONITOR at the "SAMPLE In" pneumatic connector on the front panel. Results are obtained within 90 seconds after initiation of the analyses. During the first 30 seconds, an automated instrument setup protocol is initiated. During this time, the sensor baseline is measured and the pneumatic dead volume of the internal and external (up to 2 meters) sampling system are purged and primed with the sample. Following this instrument setup, actual analysis begins and the sensor is exposed to the sample vapors for 60 seconds. After exposure, the sensor response is compared to an internal calibration and the results are presented on the display and stored in internal memory.

Following the measurement, AUTOZERO is initiated to allow the sensor to recover for a new measurement. Typical AUTOZERO times were presented in Table I-2. In actual practice, the instrument performs automated baseline checks and AUTOZERO times may be shorter. In the case of samples with no detectable vapor, the recovery time is nearly zero seconds. It should be stressed that the internal control of the instrument is blind to the user and all operation following initiation of the measurement is microprocessor controlled. The effect of OVERRANGE is special. In this case, the instrument performs an automated 10 minute baseline recovery, but it is recommended that one or two background measurements (e.g., the sample is actually air that does not contain any vapors) be performed to facilitate sensor recovery.

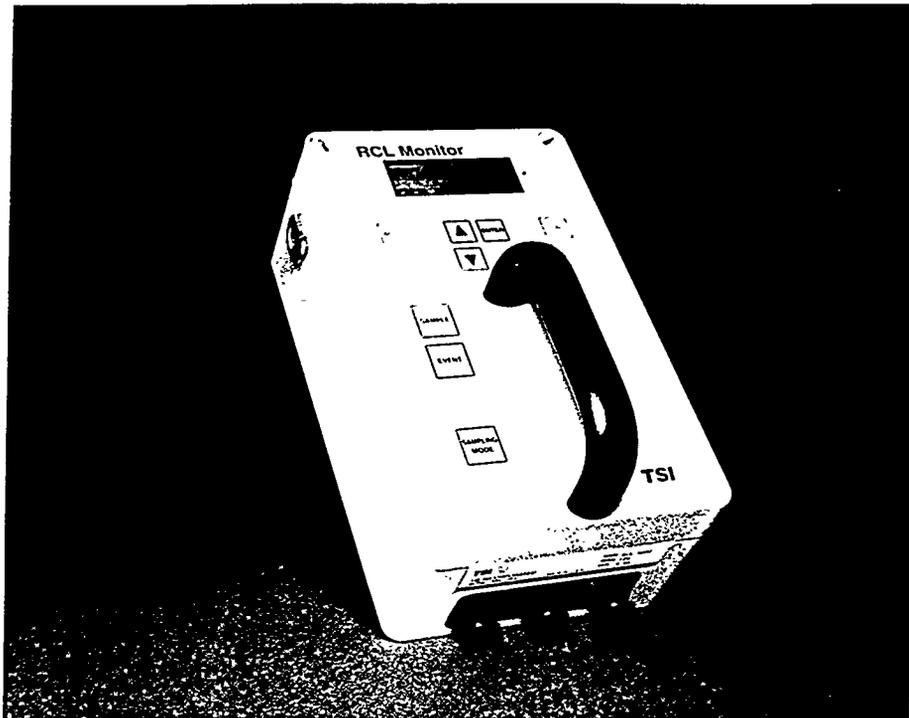


Figure II-1: The RCL MONITOR. The RCL MONITOR was designed and tested by TRI. Prototype instruments were built by TSI, Inc. (St. Paul, MN). TSI, Inc. is the parent company of TRI.

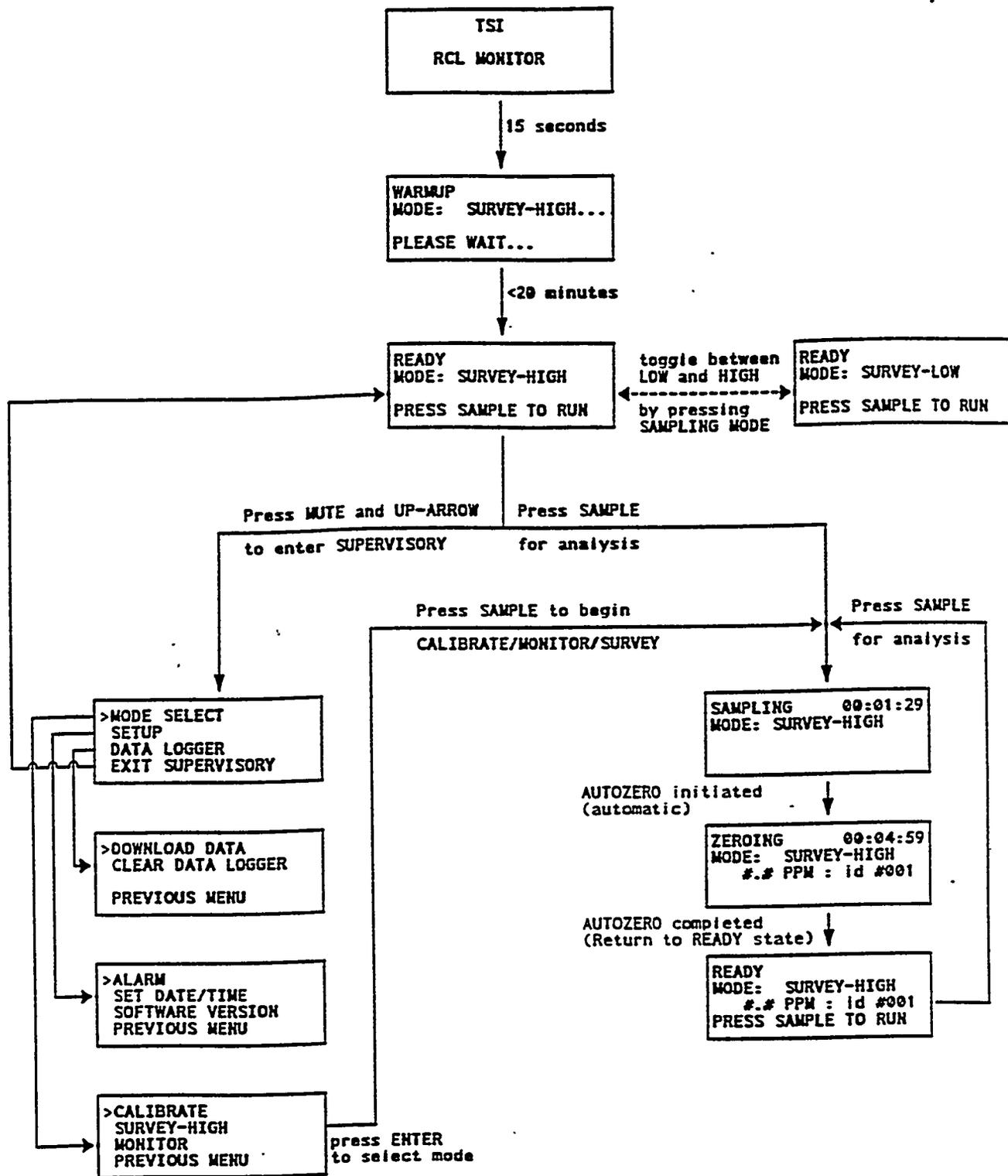
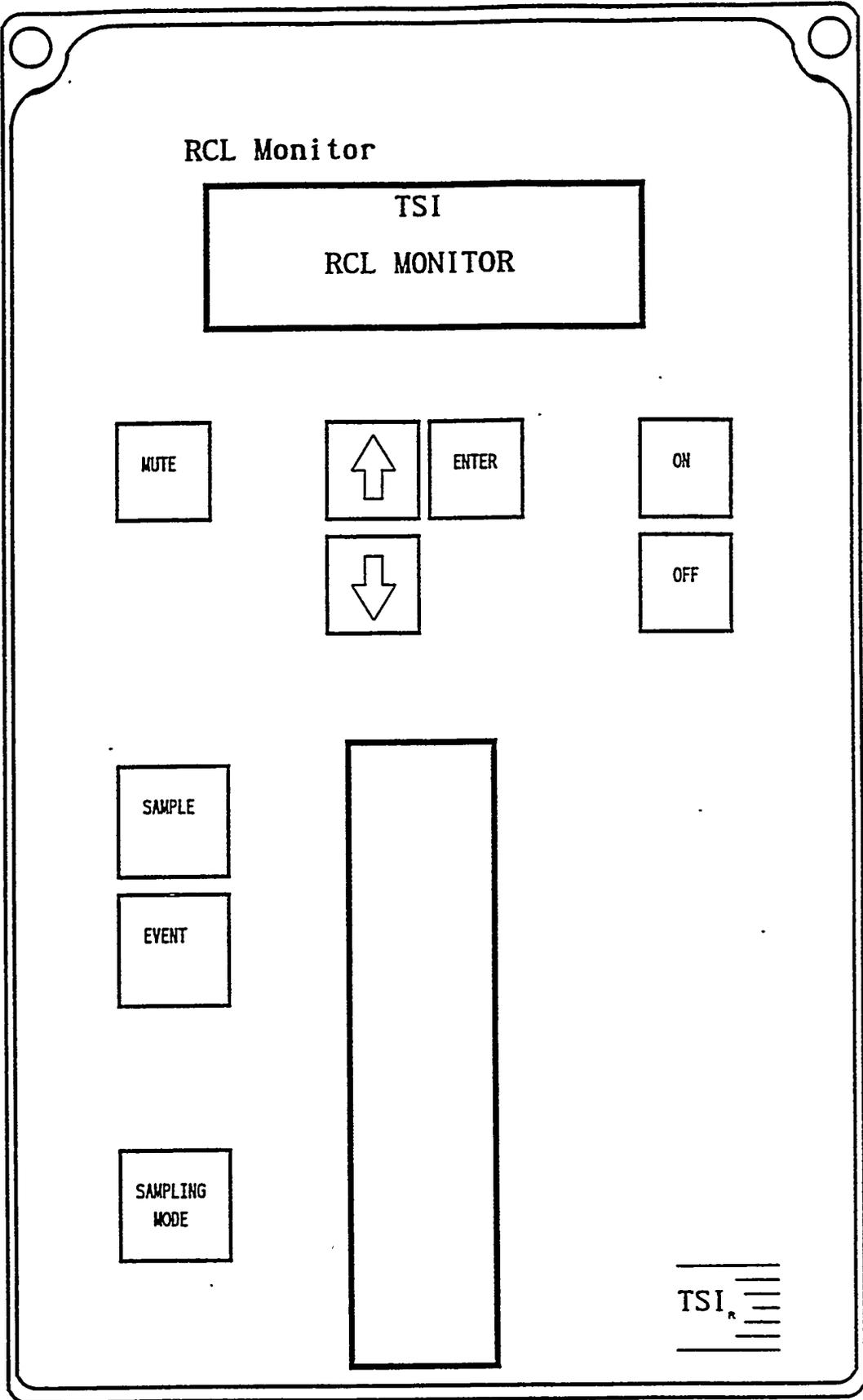


Figure II-2: The menu tree for the operation of the RCL MONITOR. Initiation of analyses is controlled from the READY MODE, while control parameters (e.g., date, time, alarm level, selection of mode of analyses) is performed in SUPERVISORY.



1 inch

Figure II-3: The KEYPAD for the RCL MONITOR.

III Performance and Evaluation of the RCL Monitor

III.1 Laboratory Evaluations of the RCL MONITOR

Validations: Following calibration, the accuracy of the RCL MONITOR was verified by exposing the instrument to known concentrations of vapors. Such challenges demonstrated that the RCL MONITOR is capable of provided accurate analytical results. Table III-1 summarizes a series of challenge vapors on two instruments. To assure accuracy, it is important that such validations be performed prior to deployment.

Table III-1: Typical response of the RCL MONITOR to known concentrations of a challenge vapor.

Test Vapor and Instrument Setting	RESULTS (Unit 1)	RESULTS (Unit 2)
10 ppm _v / SURVEY LOW	10.5	10.6
10 ppm _v / SURVEY LOW	9.5	10.3
1 ppm _v / SURVEY LOW	1.3	1.0
1 ppm _v / SURVEY LOW	1.2	1.0
10 ppm _v / SURVEY HIGH	11	10
10 ppm _v / SURVEY HIGH	10	10
25 ppm _v / SURVEY HIGH	26	25

Humidity dependence: The response of RCL sensor is insensitive to relative humidity (RH). This is important since it implies that the accuracy of the RCL MONITOR would not be affected by changes in RH. Thus the instrument can be calibrated with dry calibration gases but still provide accurate measurements in real-world applications where the RH is expected to vary significantly. The RH dependence of the RCL sensor and RCL MONITOR was evaluated using dry (%RH = 4 percent) and humidified (%RH = 87 percent) zero air and dry and humidified vapors of methylene chloride (20 ppm_v). The zero air was prepared in 40 liter bags and delivered to the RCL MONITOR without a zero filter; a zero filter was only used for ambient air. The RH of the ambient air was 56 percent. The results of these tests are summarized in Table III-2. These results demonstrate that changes in humidity do not affect the operation and accuracy of the RCL MONITOR.

Table III-2: Humidity dependence of the RCL MONITOR

READING	percent RH (SAMPLE)	%RH (ZERO AIR)
22.4, 21.0	4 percent	4 percent
22.3, 21.6	87 percent	4 percent
24.2, 24.4	87 percent	87 percent

Instrument Stability (shelf-life): Lifetime studies indicate that the performance of sensor remains constant when stored at 25°C in a normal indoor environment. The shelf-life of the sensor appears to be very long (measured in years), although it is recommended that the device be stored in a clean, dry atmosphere. This has significant implications for the stability of calibration in the RCL MONITOR. Since the sensor characteristics are stable at room temperature, the RCL MONITOR can be left indefinitely in storage and remain in calibration. Although the stability of the instrument has not been extensively evaluated, instruments have been found to maintain calibration for over 75 days when stored under no power. As with the sensor, it is recommended that the RCL MONITOR be stored in a clean, dry atmosphere.

Instrument Stability (operation): The limiting factor in instrument stability is the RCL sensor. During operation, the sensor has been found to remain constant over its useful life, but over time the sensitivity decreases and the sensor performance degrades to a level which is no longer useful. It has been found that the useful life of the sensor can be quite long under many circumstances, and a single sensor can provide hundreds of analyses. The major factors which limit sensor life are exposure level and exposure time. By minimizing exposure time and vapor levels, sensor lifetime can be increased. It is not unusual for the RCL sensor to maintain calibration for hundreds of analyses. Breathing zone measurements (vapor at 1 ppm, or less) have been performed for several months. High vapors levels (>100 ppm,) however, have been found to have deleterious effects on the RCL sensor.

Temperature dependence: Operation of the RCL MONITOR is affected slightly by changes in the ambient temperature. However, it was found that the effect of sample temperature is not significant, and that if the instrument is maintained at the temperature at which it was calibrated, accurate readings will be maintained. Table III-3 summarizes the temperature effect. Vapor and ambient temperature have a minor effect on the accuracy of the measurement. However, if the instrument is operated at depressed temperatures, there is some loss of accuracy. This has been alleviated by operating the instrument in a thermally controlled chamber.

Table III-3: Temperature Dependence of the RCL MONITOR

CONDITIONS (ambient)	Response to a 1 ppm _v Vapor	Response to a 10 ppm _v Vapor	Response to a 25 ppm _v Vapor
Instrument at 25°C Vapor at 25°C Zero Air at 25°C	1 ppm _v	10.0 ppm _v	25 ppm _v
Instrument at 25°C Vapor at 0°C Zero Air at 25°C	1.0 ppm _v	9.3 ppm _v	23.7 ppm _v
Instrument at 25°C Vapor at 0°C Zero Air at 0°C	1.0 ppm _v	9.0 ppm _v	21.8 ppm _v
Instrument at 0°C Vapor at 0°C Zero Air at 0°C	0.8 ppm _v	7.8 ppm _v	15.5 ppm _v

Cross sensitivity: The RCL MONITOR does not respond to hydrocarbons and, to date, no chemical not containing at least one halogen atom (e.g., fluorine, chlorine, bromine, and iodine) has been shown to induce a response. The sensor response is high for chlorine-containing analytes, with a much lower response for bromine containing analytes, and even lower response for iodine and fluorine containing vapors. The response of the RCL Sensor does vary for different chlorinated compounds. Table III-4 lists the relative selectivity for a variety of common chlorinated solvents (methylene chloride--MeCl₂, chloroform--CHCl₃, carbon tetrachloride--CCl₄, trichloroethylene--TCE, and perchloroethylene--PCE). Figure III-1 illustrates graphically the relative response factor for the various chlorinated solvents.

It should be stressed that Table III-4 summarizes the sensor response for various chlorinated solvents. Because of the non-linear nature of the RCL Sensor, a multi-point calibration curve is used in the RCL MONITOR, and the sensor response is not directly proportional to concentration for vapors concentrations greater than 1 ppm_v. The ramification of this is that for vapor levels greater than an equivalent 1 ppm_v response, the error in the RCL MONITOR data increases when measuring vapors different from that used for calibration. For example, 10 ppm_v methylene chloride induces a sensor response that is 84.5 percent of that induced by carbon tetrachloride. Using the calibration curve illustrated in Figure AI-2 (see Appendix I, Section AI-3), a response of this magnitude would provide a reading of approximately 6 ppm_v with the RCL MONITOR.

The RCL MONITOR also responds to other chlorinated compounds. One compound of potential interest is phosgene, a highly toxic chemical with an IDLH (immediate danger to life or health) of 2 ppm_v (ACGIH, 1992). The RCL MONITOR was able to detect this compound at the IDLH value.

Problems with cross-sensitivity can be eliminated by calibrating the RCL MONITOR with the analyte that is to be encountered in the field. It is recommended that whenever possible, the RCL MONITOR be calibrated with the vapor that is analyzed. Thus, if methylene chloride is the expected analyte, vapors consisting of 10 ppm, methylene chloride should be used as the calibration gas in order to maximize accuracy.

Table III-4: Relative Response for the RCL Sensor factors for various chlorinated solvents at 1 ppm, and 10 ppm, vapor levels (response factors are normalized to Carbon Tetrachloride)

Vapor	1 ppm, Response	10 ppm, Response
Methylene Chloride	0.66	8.45
Chloroform	0.94	8.03
Carbon Tetrachloride	1.00	10.00
Trichloroethylene	0.66	6.68
Perchloroethylene	0.61	6.90

III.2 Field Performance

AREA SURVEYS: Frequently, an "area" needs to be surveyed to assure that vapor levels are safe. In this sense, "area" can refer to a work location, a region of known or suspected contamination, or an unknown region. The RCL MONITOR is ideally suited for this application, and a complete survey of such "areas" can be accomplished in less than 1 hour. The time to perform a complete area survey is, of course, dependent upon the number of samples. Figure III-2 depicts graphically the results of a series of five soil gas measurements performed at a waste oil storage facility. The RCL MONITOR performed soil gas analysis on these five probes in less than 30 minutes. The vapor levels ranged between 0 and 2 ppm, and these soil gas levels were consistent with earlier measurements. This illustrates the many advantages of field analytical methods. Since samples did not have to be transported to a remote laboratory for analysis, results were obtained for a fraction of the time and cost.

Operation of the RCL MONITOR: The design goals for the RCL MONITOR were to produce an instrument whose basic operation is easily understood. This was achieved as indicated during the field testing in which Hanford site personnel were provided brief training sessions of approximately five minutes and were able to perform on-site measurements. The importance of having a user-friendly instrument was demonstrated since at several of the locations in which area surveys were performed, access was restricted because of ongoing activity (well drilling, etc.), and TRI personnel were not allowed site access.

Operation of the RCL MONITOR by personnel in protective equipment: Personal protection equipment is routinely worn by personnel involved in hazardous waste site operations. Such equipment did not impede operation of the RCL MONITOR. The KEYPAD was conveniently operated while wearing gloves. Even more important, analyses were performed with the RCL MONITOR during drilling operations around Well 299W18252 by Hanford personnel while wearing full protective equipment, including a respirator with supplied air, gloves, a face shield, and overalls. The protective equipment did not interfere with operation or reading of the instrument. The display was legible through a full-face respirator.

Effect of Hydrocarbon Interference: Figure III-2 depicts graphically the results of a series of five soil gas measurements performed at a waste oil storage facility. This area is contaminated primarily by oils which will produce large responses on photoionization detectors (PID). PIDs are routinely used for determining the presence of organic vapors, but are neither selective nor overly sensitive to chlorinated compounds. Both selectivity and sensitivity are necessary to quantify trace chlorinated contaminant levels in a matrix with a large background hydrocarbon contamination. Site records had indicated that no chlorinated solvent contamination should exist at this location. Measurement with the RCL instrument indicated the presence of chlorinated organic contamination, which was later confirmed by laboratory analysis. The RCL vapor monitor performed soil gas analysis on 5 probes in less than 30 minutes. The vapor levels ranged between 0 and 2 ppm, and were obtained without the oil interference that would have been observed using a photoionization or flame ionization detector. These soil gas levels were consistent with earlier measurements. This illustrates the importance of the selectivity of the RCL sensor and the utility of field rapid analysis for area survey applications.

Unattended Operation: MONITOR mode allows for unattended operation of the instrument. In MONITOR, the frequency of analysis can be adjusted from four analyses per hour to one analysis per day. This feature was evaluated using a cone penetrometer probe in the 200W area of Hanford. Figure III-3 illustrates the concentration of vapors at this location measured during overnight monitoring. Higher vapor levels were measured during the day versus the measurements during the night, which indicates that the ambient temperature has a significant effect on vapor levels. These temporal fluctuations are regularly observed (Rohay et al., 1993) and illustrate the dynamic nature of many hazardous waste sites and why an understanding of this dynamic nature is critical to understanding the site. To observe temporal changes in vapor levels such as those illustrated in Figure III-3, continuous automatic monitoring is required. Unattended operation is necessary for many applications such as process control, fugitive emission, and continuous breathing zone monitoring.

Comparison to Alternative Techniques: In order to validate the measurements of the RCL vapor monitor, other instruments and methods were tested in parallel. The alternative methods included gas chromatography, portable photoionization detectors, and detector tubes. In general, the RCL MONITOR provided better sensitivity, selectivity, and accuracy than detector tubes and photoionization detectors for carbon tetrachloride. For total chlorinated vapors, the RCL MONITOR was comparable to gas chromatography. Figure III-4 shows a side by side comparison between results obtained from gas chromatographic (GC) analyses and with the RCL MONITOR. The data

depicted in Figure III-4 was obtained during an actual field exercise. For these measurements, 1 liter sample bags were collected from the head space of wells and transported to a remote GC for analysis. The remaining sample was sufficient for analysis by the RCL MONITOR. The RCL monitor was operated in SURVEY/LOW Range mode, which has a dynamic range of 0 to 25 ppm, and a lower detection limit of 0.2 ppm. If necessary, SURVEY HIGH with a range of 2 to 500 ppm, could have been selected.

It must be kept in mind that both the RCL MONITOR and the GC have uncertainties in their measurements. The GC does not necessarily provide better data; it is simply the method currently used. Duplicate GC analyses varied by 12 percent. The accuracy specification RCL MONITOR in this concentration range is ± 25 percent; duplicate runs are typically within 10 percent. The discrepancies between the GC and RCL can be due to errors in sample collection and analytical errors (the sample could contain RCLs not detected by the GC, since the GC only detects those compounds which are chromatographable and respond on the detector). Validation runs on the calibration standards provide measurements well within specified accuracy specifications for the RCL MONITOR.

Battery Operation: At 25°C, the battery specifications allow for up to 8 hours of continuous operation under a single charge. Field deployment of the RCL MONITOR demonstrated that the instrument can operate under battery power for over 6.5 hours at 25°C. Longer operating times were not attempted. At 0°C, low battery alarms were registered after 5.5 hours of operation. At -10°C, a low battery alarm was registered after 4.5 hours of operation. However, a replacement, fully charged battery can be installed in the RCL MONITOR in less than 5 minutes.

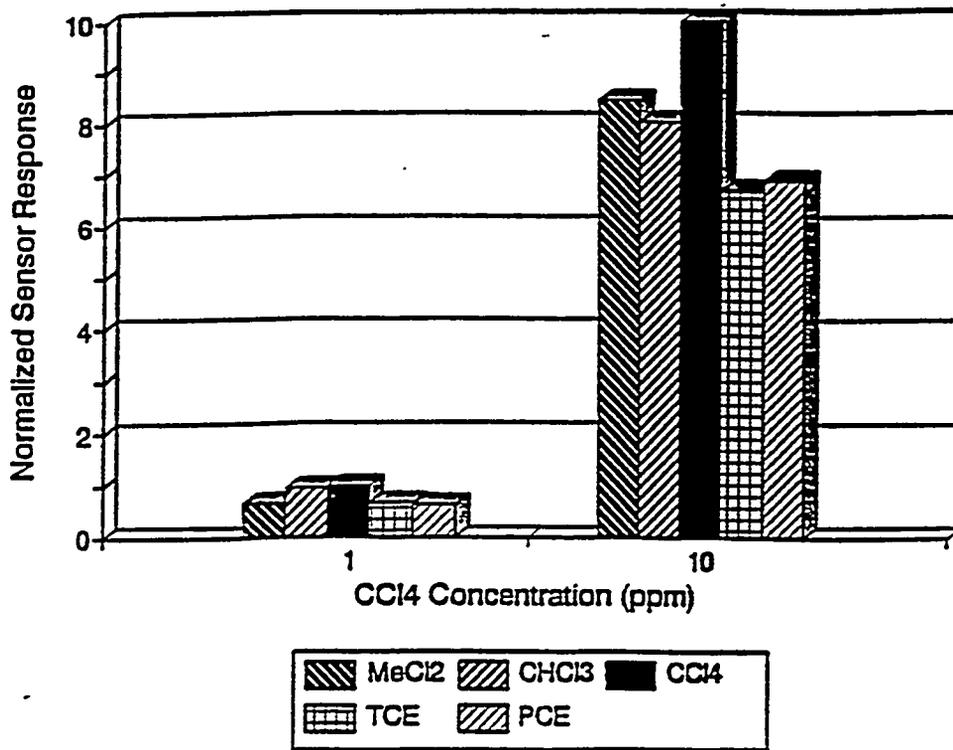


Figure III-1: Relative Selectivity of the RCL MONITOR to other chlorinated solvents.

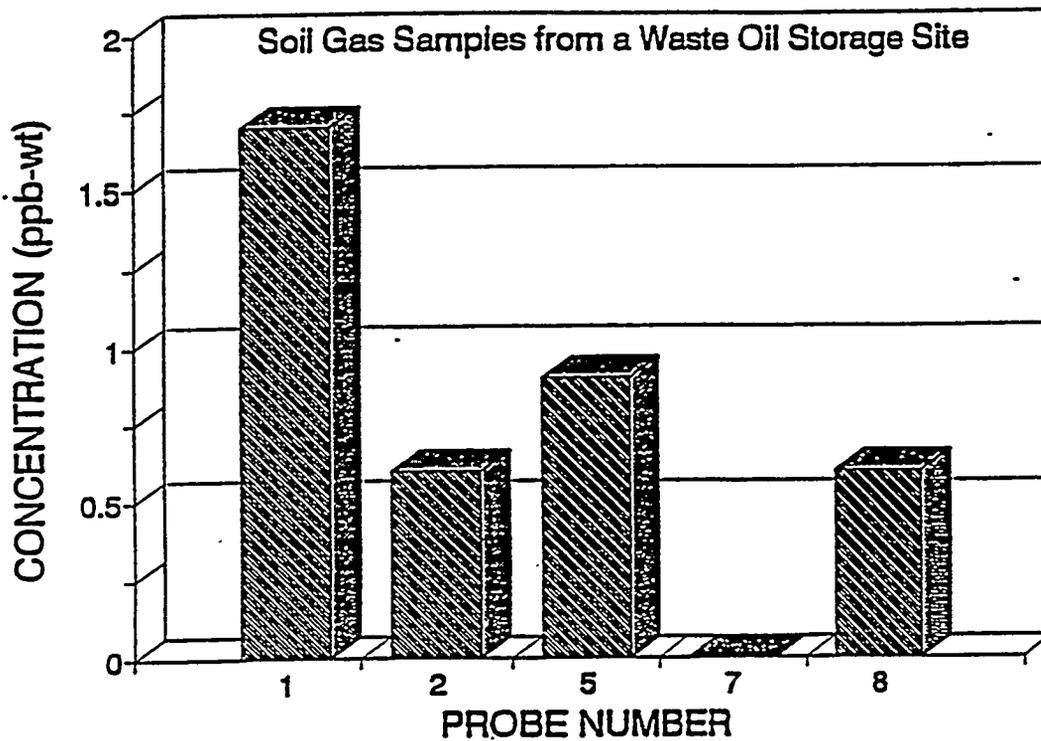


Figure III-2: Area survey performed on soil gas probes around a waste oil facility. Not only does the RCL MONITOR perform measurements quickly, it does so without interferences from the known oil contamination in the area.

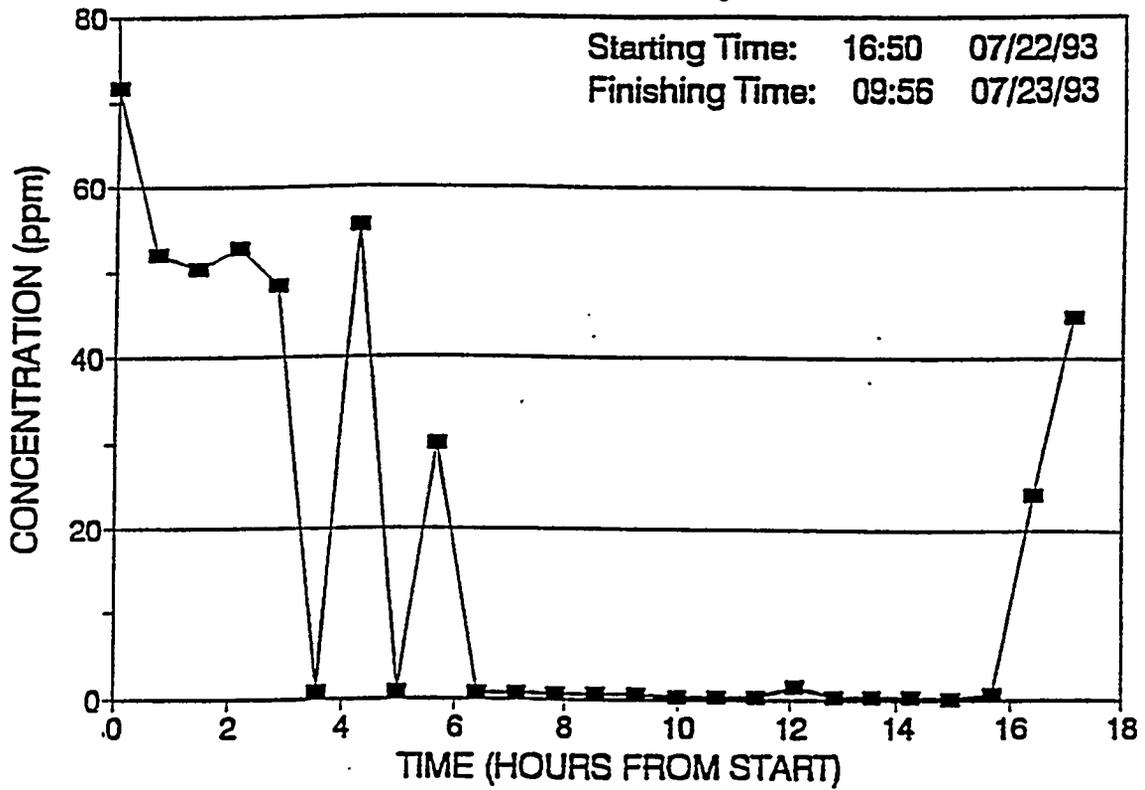


Figure III-3: Overnight continuous measurement of subsurface chlorinated vapor levels using the RCL MONITOR. Note that the vapor level increases during day as the ambient temperature increases.

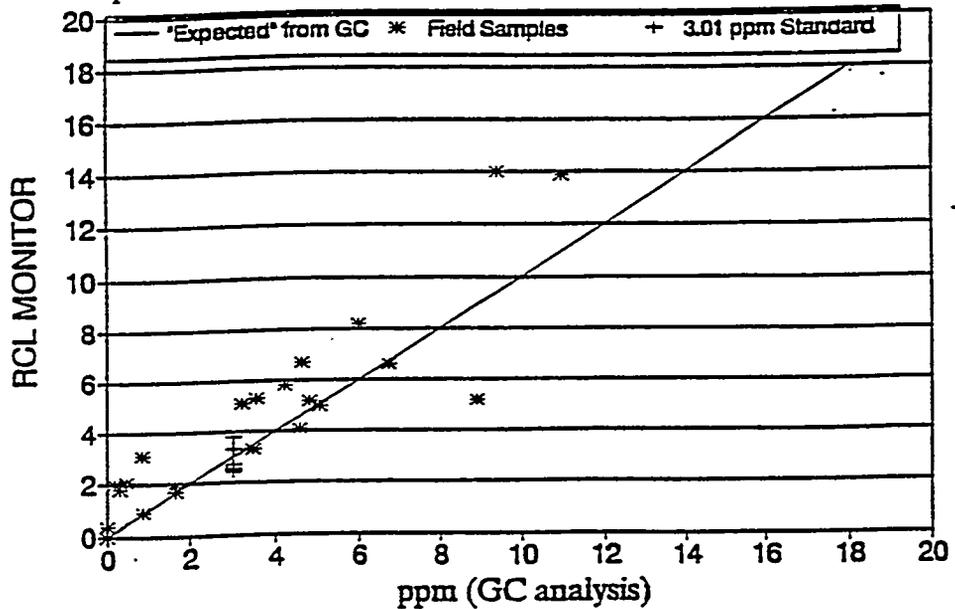


Figure III-4: Comparison between analyses by the GC (-) and the RCL MONITOR (*) on actual field samples. Laboratory standards (+) verified the calibration of the RCL MONITOR. The RCL MONITOR compared favorably with the GC for concentrations up to 500 ppm_v (5000 ppm_v with an external diluter).

IV The Specialized Samplers

Specialized samplers and sampling protocols were developed for the RCL MONITOR. These included direct sampling, internal dilution, external dilution, external preconcentration, internal autorange, and condensed phase sampling. The driving force behind the development of the samplers was to extend the dynamic range of the RCL MONITOR and increase the number of applications it can perform. The optimal range of the RCL sensor is between 0 and 25 ppm_v. The RCL MONITOR has a range of 0 to 500 ppm_v with a lower detection limit (LDL) of 0.2 ppm_v chlorinated hydrocarbon. This broad range had been achieved by incorporating an internal dilution of the vapor. While this range is adequate for many applications, it is limited and will exclude many other applications. Accordingly, TRI designed, built, and field tested a series of specialized samplers aimed explicitly at further expanding the analytical capabilities of the RCL MONITOR. Table IV-1 lists the samplers and presents a brief description of each function. Further details on the design and performance of the samplers is presented in the text.

Table IV-1: Specialized sampler developed to interface to the RCL MONITOR.

Sampler Name	Description and expected application
General Sampler	Provides a direct pneumatic interface between the sample and the instrument.
Internal Dilution (Fixed and AUTORANGE)	An internal-dilution system to expand the dynamic range of the instrument. Fixed dilution is user selected and is restricted to either no dilution or to a 10 times dilution of incoming vapors; a range of 0.2 to 25 ppm _v (LOW) or 2 to 500 ppm _v (HIGH) is obtained with fixed dilution. AUTORANGE was an automated protocol which required the measurement of incoming vapor levels at high dilution followed by an adjustment of the dilution factor. AUTORANGE required longer analyses times and longer recovery times than standard operation. A range of 0.2 to 500 ppm _v was possible.
Fixed External 10:1 diluter	Dilutes sample vapors by a factor of 10. In effect the range of the RCL MONITOR is extended to 5000 ppm _v . Used when high level vapors are expected (e.g., well head space analysis).
Preconcentrator	Concentrates sample vapors by a factor of 10 or 50. In effect the LDL of the RCL MONITOR is decreased to 5 ppb _v or less. Used when low level vapors are expected (e.g., workplace around well heads).
Condensed Phase Sampler	Extracts volatile organic contamination from aqueous media. Used to allow the RCL MONITOR to analyze water samples for chlorinated organic contamination

IV.1 General Sampler

The most fundamental sampler developed is the general sampler. It consists of a stainless steel probe that is connected to the RCL MONITOR through a 1.25 m length of an inert polypropylene sample tube. The general sampler was engineered to interface not only physically to the RCL MONITOR, but to field operations. The internal pneumatic system of the RCL MONITOR, as

discussed above, was designed to go through a purge/prime cycle to eliminate the dead volume of the external and internal pneumatic systems, and the general sampler was designed to merge with the capability of the purge/prime cycle. It should be noted that the use of the general sampler is up to the operator, but care should be taken to avoid using excessively long external pneumatic connections. If the tube is too long, the pneumatic time constant would be too large for the RCL MONITOR to obtain an accurate reading. The connection tube to the sample can be shorter than 1.25 m, but should be no longer than 2 m. When possible, the use of sample bags is recommended.

IV.2 Internal Dilution

The recovery time and lifetime of the RCL sensor are adversely affected by exposures to high vapor levels. Even vapor levels at 25 ppm_v can affect the sensor. In order to meet the specified maximum concentration of 500 ppm_v for the RCL MONITOR, dilution of the sample gas was necessary. This was accomplished by designing a diluter into the instrument itself. Two approaches were used: Fixed Internal Dilution and AUTORANGE. Ultimately, fixed internal dilution was selected because evaluations demonstrated that short exposures provided the same quality of data as that obtained with longer exposures, yet the shorter exposure had the advantage of improved sensor life and accelerated recovery.

IV.2.1 Internal AUTORANGE

The principle of AUTORANGE was based on switching flows of sample and zero gas with an electric solenoid valve operating on a precisely-timed duty cycle to precisely dilute the incoming vapor and then to measure the diluted vapor concentration. It took advantage of the electric solenoid valve already located internally in the sample line by establishing the baseline of the sensor during the measurement cycles (the internal design of the instrument is described in Appendix I and illustrated in Figure AI-1). When the valve is off, "zero air" (e.g., air that has been scrubbed by the internal chemical filter to remove all reactive impurities) passes through to the sensor. If energized, undiluted sample passes through. If, however, the solenoid is energized only 100 milliseconds in every second, the sample gas is diluted 10-fold. A mixing chamber allowed the pulses of sample to mix thoroughly with the diluting air before passing to the sensor. This method, though not generally used, has been employed with great reliability at TRI, and was the basis for a product.

AUTORANGE was an internal feature of the prototype version of the RCL MONITOR. It was developed to automatically adjust dilution levels of incoming vapors. The algorithm used for the autoranging is shown in Figure IV-1. The response of the sensor to a transient exposure to sample is used to adjust the range. Upon initiation of analyses, the vapor is assumed to be at a high level (>100 ppm_v) and is internally diluted 95 percent (e.g., 20 to 1--19 parts air, 1 part sample). If after a 1-minute sampling, the sensor response indicates that the incoming vapor level is between 100 to 500 ppm_v (the actual sensor exposure level would be between 5 and 20 ppm_v), the analysis is completed at 95 percent dilution. If the vapor level is below 100 ppm_v, the dilution factor is decreased to 75 percent (e.g., 4 to 1--3 parts air, 1 part sample). Again, if after a second 1-minute

sampling, the sensor response indicates that the vapor is between 20 and 100 ppm_v, the analysis would proceed at 75 percent dilution. If the vapor is below 20 ppm_v, the dilution factor is set to 0 percent (pure sample). If at any time, the vapor level being exposed to the sensor exceeds 25 ppm_v, (e.g., >500 ppm_v for the AUTORANGE Step 1, with 95 percent dilution), the instrument shuts down and indicates OVERRANGE. Once the appropriate dilution setting has been determined, exposure is allowed to continue until the steady state response is obtained (10 minutes). To achieve the full dilution, two 1-minute exposures are needed. The time required for these AUTORANGE steps is added to the total cycle time of the instrument. When AUTORANGE is active, the instrument range is 0.2 ppm_v to 500 ppm_v.

Two disadvantages with AUTORANGE have been identified. The analysis time is longer than expected and takes up to 12 minutes to complete. This is because the AUTORANGE procedure demands that the sensor reach steady state. The second disadvantage is the restrictive limitation on the effect of steady state sensor operation recovery time, i.e., recovery times of up to 10 minutes or longer are required following a measurement. Thus, only three analyses per hour can be performed. However, it was demonstrated that a one minute exposure provided accurate measurements comparable to a 10 minute exposure. Because of these limitations, AUTORANGE was not implemented in the final version of the RCL MONITOR, but was installed and field tested in the prototypes. Although not implemented in the present version of the RCL MONITOR, applications exist which could exploit the protocols developed in AUTORANGE.

IV.2.2 Fixed Internal Dilution

An alternative approach to AUTORANGE was to use fixed internal dilution. In this method, the user manually selects the concentration range. The options are Low (0.2 to 25 ppm_v) and High (2 to 500 ppm_v). Analysis times are 90 seconds with recovery times typically requiring either 5 minutes (for vapors < 5 ppm_v) or 10 minutes (for vapors > 5 ppm_v), but the sensor would be exposed to vapors for only 60 s. Fixed internal dilution is achieved by energizing the an internal solenoid valve (see Figure AI-1) 0.1 second out of every 1 second duty cycle. This essentially dilutes the incoming vapor to 10 percent of its concentration. An internal mixing chamber assures that the vapor/zero air blend has been homogenized. Fixed internal dilution is superior to AUTORANGE; the improved performance in terms of sensor lifetime and accelerated recovery far outweighed the broader dynamic range provided with AUTORANGE. Moreover, it was found that the performance of the RCL MONITOR is not compromised when operated with a one minute exposure on the sensor versus a 10 minute sensor exposure. Figure IV-2 compares the results obtained with the RCL MONITOR for both exposure times, along with an independent gas chromatographic analysis.

IV.3 Fixed External Dilution

Conditions are frequently encountered in which extremely high concentrations of vapors are encountered. For example, well head space and vadose zone vapor levels have been observed at concentrations well in excess of 1,000 ppm_v, and in rare cases, in excess of 10,000 ppm_v. Such high

concentrations are out of the RCL MONITOR range. To further extend the dynamic range of the RCL MONITOR, an external, fixed 10:1 diluter system was designed to actively blend vapors with zero air. When interfaced to the RCL MONITOR, the range of the monitor is extended to 5000 ppm_v for HIGH mode operation. The design of the fixed external 10:1 diluter is discussed in Appendix III. The principle of operation is such that the dilution factor can be increased to 100:1 without major modification of the design of the sampler.

It is worth noting that the 10:1 diluter uses active dilution; that is, the sample is collected and blended with zero air in an ambient-pressure chamber. Vapor from the chamber can be used to fill a sample bag or can be connected directly to the RCL MONITOR for analysis. Both approaches have been used. This sampler allows for the collection of sample through sizable lengths of tubing. Tests were performed with this sampler on soil gas probes inserted over 20 meters in the ground, and in fact, acceptable performance was obtained through 60 meters of sample tubing. Table IV-1 summarizes some of the results obtained with the 10:1 diluter system. It should be stressed that the active diluter design is critical for the RCL MONITOR. An early prototype external 10:1 diluter design based on parallel flow paths between sample and zero air was built. Precisely balanced flows were required, and this was nearly impossible to maintain in the field. Consequently, this approach was totally inadequate for the RCL MONITOR. Active external dilution is more cumbersome in that it requires a separate battery-powered module. However, it produces reliable results.

Table IV-2: Performance of the Fixed External 10:1 Diluter

Vapor Level (ppm _v)	Instrument Setting	Comments
34, 32, 31	RCL MONITOR/HIGH	20 m depth, vapor collected into a bag and analyzed (Well VVE1-Port 3, INEL)
32, 32, 31	RCL MONITOR/SURVEY LOW with 10:1 ext. dilution	20 m depth, vapor diluted and collected into a bag and analyzed. RCL MONITOR provided a reading that was scaled down by a factor of 10 (e.g., 3.2, 3.2, and 3.1 ppm _v) (Well VVE1-Port 3, INEL)

IV.4 The Preconcentrator

The LDL of the RCL monitor is 0.2 ppm_v, although it should be noted that the instrument may provide a reading of 0.1 ppm_v. A "0" ppm_v reading should be interpreted as below detection limits (i.e., vapor level is less than 0.2 ppm_v). It is often envisioned that the better the sensitivity, the better the capability of a field instrument. To improve the LDL of the RCL MONITOR, a preconcentrator was designed, built, and field tested.

The preconcentrator was developed to extend the lower detection limit of the RCL MONITOR to 10 ppb_v or less. Operationally, the vapors from a large volume of air are trapped on a sorbent and then thermally desorbed into 1 liter of air. The degree of enrichment is determined primarily by the ratio of sample (sorbed) volume to desorbed volume. Two basic preconcentration ratios were designed into the device: 1:10 and 1:50. In each mode, vapor collection was set at 1 liter/min. Thus a 1:10 preconcentration required 10 minutes, while the 1:50 preconcentration required 50 minutes. Prior to desorption, the sorbent tube is preheated. During desorption, the concentrated vapors are collected in a 1 liter sample bag and then analyzed by the RCL MONITOR in SURVEY/LOW. It is necessary for the bag to be manually connected to the instrument for analysis. Following the thermal desorption step, the sorbent tube is pretreated by a five minute purge with zero air at elevated temperature. The purge step pretreats the sorbent tube for subsequent sample collection. It should be noted that the purge step back-flushes the sorbent tube. Design of the preconcentrator is discussed in Appendix III.

IV.4.1 Laboratory Evaluations of the Preconcentrator

Vapors of known concentrations were collected on the preconcentrator for various degrees of enrichment. Reliable 50-fold enrichments with the 1:50 mode were not successfully produced. This may have been due to the difficulty of making and handling accurate vapor dilutions at such low concentrations. A more likely explanation is that the failure was due to inefficient trapping of vapors. For example, vapor breakthrough was observed after prolonged operation of the preconcentrator, with even moderate levels of carbon tetrachloride. It appears that continued operation of the heater, pumps, and solenoids heats the internal chamber of the preconcentrator, thus inducing desorption. There was no vent or cooling system in the sampler. In addition, it was found that for reproducible operation in the 1:10 mode, a long cool-down period was required. When the sorbent tube was allowed to completely cool down, reproducible and efficient 10-fold concentration enrichment was obtained. Performance of the preconcentrator is depicted in Figure IV-3. The LDL of the RCL MONITOR when used in conjunction with the 1:10 mode of the preconcentrator is 20 ppb_v.

IV.4.2 Field Testing of the Preconcentrator

The preconcentrator was tested at several locations during the October 1993 field test, and the results are summarized in Table IV-3. To validate the performance, simultaneous measurements were made with a Foxboro Miran IDX infrared spectrometer.

Several tests with the preconcentrator were performed at Well W15-217. The first test with the preconcentrator at 1:10 enrichment produced a 100 ppb_v¹ sample, indicating that the sample vapor was 10 ppb_v. This measurement was performed 5 feet southeast of the well. In addition to

¹It should be noted that while the RCL MONITOR will indicate vapor levels of 0.1 ppm_v, not all sensors can accurately measure vapors at this low level. Accordingly, the lower detection limit of the RCL MONITOR is specified at 0.2 ppm_v.

using the preconcentrator, several measurements were performed at this location directly with the RCL MONITOR and no vapor was detected (e.g., actual vapor level <100 ppb_v). To validate the performance of the preconcentrator/RCL MONITOR system, an infrared monitor was used (Foxboro Miran IDX). With the Miran, measurements were performed more frequently and vapor levels were found to vary with location and time. Levels from <0.1 ppm_v to over 8 ppm_v were observed, depending upon sample location. Typically, higher levels were observed as air was sampled nearer the well head, with the highest level found in the well head. A second test with the preconcentrator was performed at the well cap. For nearly 9 minutes of the 10 minute sample collection period, the Miran was used to continually monitor the vapor level near the point at which sample collection with the preconcentrator was performed. The Miran reading was recorded every 30s, with an average concentration of 1.94 ppm_v, as indicated in Table IV-3. Excellent agreement was obtained between the RCL MONITOR when the 1:10 preconcentrator was used with the Miran. The next day, a third measurement was performed at Well W15-217. The preconcentrated vapor was 0.5 ppm_v, indicating a vapor level of 0.05 ppm_v.

Additional tests of the preconcentrator were performed at Well 15-15. Again, the area was continuously monitored with the Miran. The preconcentrator produced a vapor level of 3.4 ppm_v, as measured with the RCL MONITOR, corresponding with an incoming (actual) vapor level of 0.34 ppm_v. The Miran was operated during the sample collection and read between 0.4 and 0.5 ppm_v. Again, excellent agreement was obtained.

Table IV-3: Sample collection and measurements performed using the RCL MONITOR with the preconcentrator.

Area around Well W15-217 (200 W Hanford)	
RCL MONITOR ¹	Foxboro Miran IDX
0.01	below detection limits ²
1.94	1.64 ppm _v
0.05	below detection limits ²
Head Space of Well 15-15 (200 W. Hanford)	
RCL MONITOR ¹	Foxboro Miran IDX
0.34	0.4 to 0.5 ppm _v

¹The listed concentrations have been corrected for a 10X preconcentration, the actual reading from the RCL MONITOR was 10 times the value presented.

²The lower detection limit of the Foxboro is 0.1 ppm_v.

IV.5 The Condensed Phase Sampler

Chlorinated solvent contamination does not always exist in the vapor phase. In fact, contamination of water supplies with chlorinated solvents is a major environmental issue. In order

to use the RCL MONITOR for water analysis, a sampler and method needed to be developed which would vaporize the volatile vapors from the condensed medium. Once in the vapor phase, the chlorinated solvent can be quickly and accurately analyzed using the RCL MONITOR.

It was originally envisioned that a silicone membrane permeation process could be used to extract vapors from an aqueous sample. While this procedure does work for higher concentrations, it was found to be slow and insensitive for aqueous samples contaminated with low levels of chlorinated solvents. Instead, a more active sampler system was developed using air stripping (sparging) to remove RCL vapors from water samples quickly and reproducibly. The design of the condensed media sampler is discussed in Appendix III. The condensed media sampler was designed to extract volatile vapors using a closed-loop air-stripping process in which 1 liter of air is recirculated through a 1 liter water sample. Following the 10 minute recirculation, the sample bag is manually connected to the RCL MONITOR. The CPS was designed to operate in two modes--a). sample collection and b). system purge (for cleaning purposes). The modes are manually selected, but each mode has several steps, again controlled by an internal microprocessor (Basic Stamp).

IV.5.1 Laboratory Evaluation of the Condensed Phase Sampler

The condensed media sampler was designed to strip the volatile vapors in a controlled manner. A closed-loop process was developed in which 1 liter of air is recirculated through a 1 liter water sample. Following the 10 minute recirculation, the sample bag is manually connected to the instrument for analysis. The closed loop air stripping process was found to be quick (less than 10 minutes), sensitive (lower detection limit of 10 ppb_{wt} CCl₄ aqueous contamination), proportional from 10 to 1,000 ppb_{wt} and reproducible. The performance is illustrated in Figure IV-4, in which a calibration curve (10 to 1000 ppb_{wt}) is plotted. Quantification was performed by comparison of the result of vapor analysis to the calibration curve. As shown by laboratory testing, a linear relationship exists between CCl₄ contamination level from 10 to 1000 ppb_{wt} in an aqueous sample for the vapor level collected by the condensed media sampler ($Vapor_{ppmv} = 0.063 Liquid_{ppb}$). The proportionality constant compares favorably to published Henry's Law constants for CCl₄ in water (Gossett, 1987). The condensed media sampler allows for the direct use of the RCL MONITOR to measure aqueous level contamination. Approximately 50 percent of the total chlorinated solvent was stripped from the aqueous phase for each 10-minute recirculation cycle. It was not possible to achieve significantly improved sensitivity with longer recirculation times.

IV.5.2 Field Testing of the Condensed Phase Sampler

During the October 1993 field test at the 200 W area of Hanford, aqueous samples were collected from three wells, W10-13, W15-15, and W15-16. The wells were chosen because it had been verified that no radioactive contamination existed. The concentrations ranged from around 10 ppb_{wt} to 7,000 ppb_{wt} (as determined by independent analysis using CLP methods). Laboratory evaluations were performed on aqueous samples of less than 5,000 ppb_{wt} levels greater than 1,000

ppb_{w_t} in water samples in the field were not expected. This turned out to be wrong--up to 800 ppm_{w_t} of CCl₄ can dissolve in water. It is not uncommon to encounter levels of over 10 ppm_{w_t}.

The water samples were analyzed by the CPS/RCL MONITOR system. The level of chlorinated contamination in each aqueous sample was obtained by comparing the vapor concentration as determined by the RCL MONITOR to the calibration curve illustrated in Figure IV-4. A comparison between the CLP results and the analysis obtained by the condensed media sampler and RCL unit is illustrated in Figure IV-5. The comparison between the contamination level as determined by the CLP method and our condensed phase sampler is impressive, considering that the expected accuracy of contract laboratory procedures (CLP) methods are ± 35 percent and that the laboratory analyses of volatile compounds are typically low because of loss of volatile compounds during transport and storage. It is important to note that there can be delays of up to two weeks using the CLP method for chlorinated solvent contamination in water. The condensed phase sampler and RCL instrument provides results within 30 minutes of sample collection. The ability to obtain results in a timely manner allows for intelligent decision making and potentially significant cost savings.

IV.6 Summary

With specialized samplers, the effective dynamic range of the RCL MONITOR was greatly extended. Figure IV-6 illustrates the range that can be achieved for the instrument when operated alone or in conjunction with the sampling systems and protocols developed in this project.

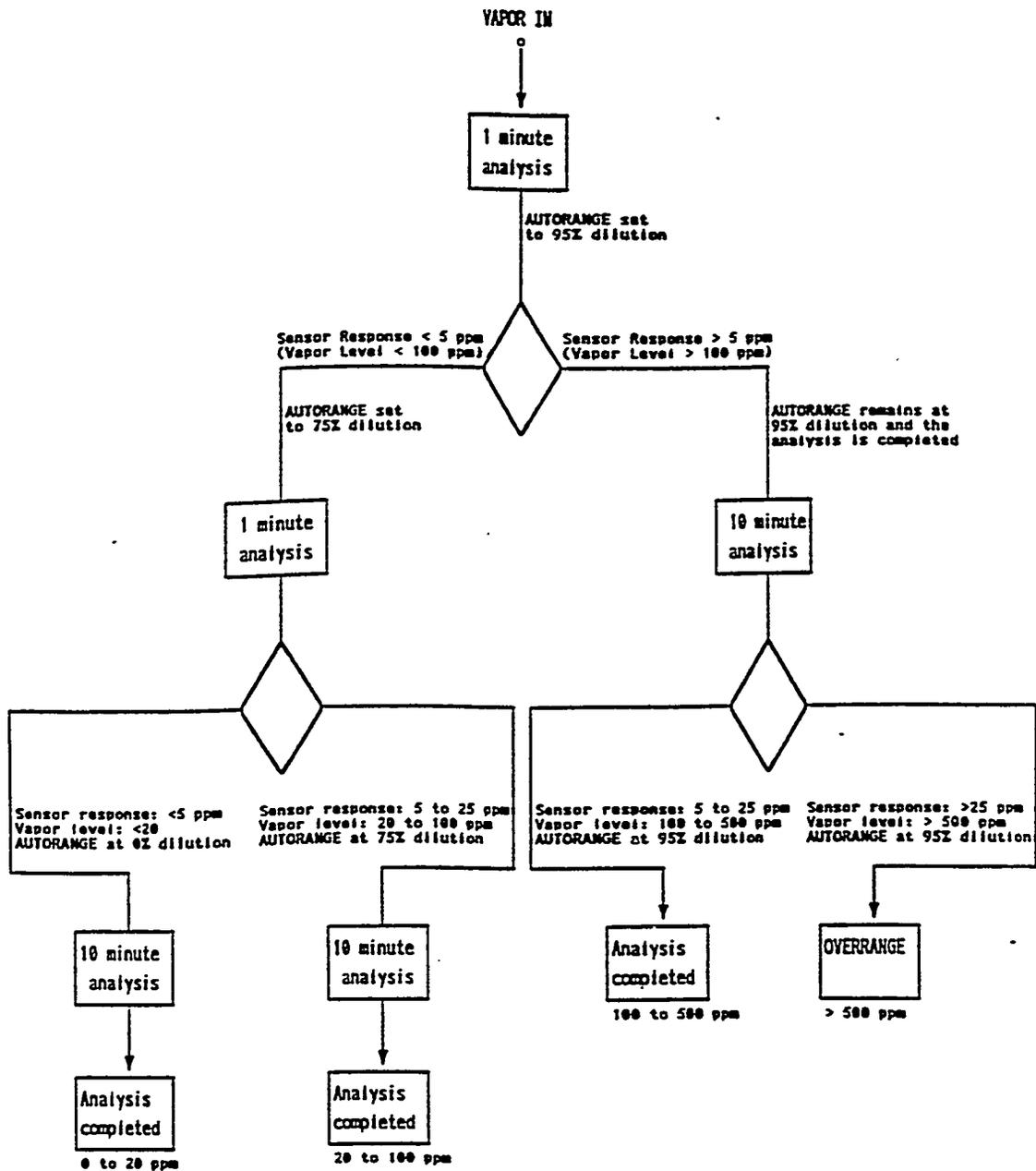


Figure IV-1: The AUTORANGE protocol. Incoming vapors were assumed to be at a high concentration and were diluted internally by 95%. If the incoming vapor level was between 100 and 500 ppm, the analysis was completed. If the incoming vapor level was between 20 and 100 ppm, the dilution factor was adjusted to 75%. No dilution was used for vapor levels less than 20 ppm.

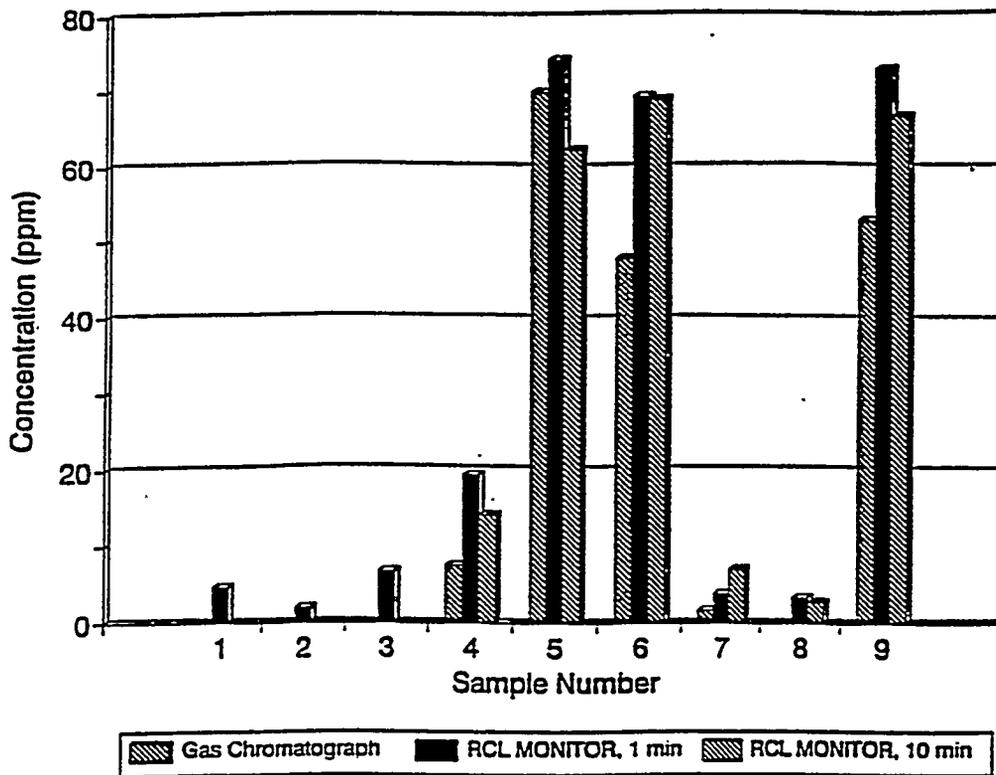


Figure IV-2: Comparison between the performance of the RCL MONITOR using a 10-minute exposure with AUTORANGE activated vs. the performance of the RCL MONITOR with a 1 minute exposure. The results of a gas chromatographic analysis is provided.

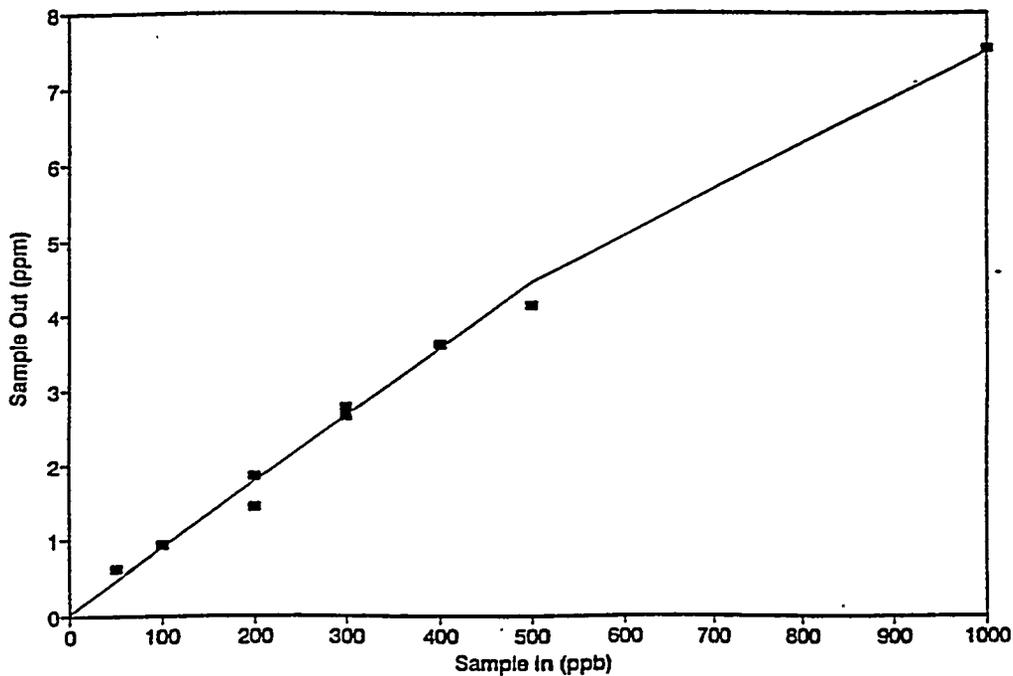


Figure IV-3: Laboratory performance of the preconcentrator. When coupled with the RCL MONITOR, the 1:10 mode of the preconcentrator extends the LDL to 20 ppb.

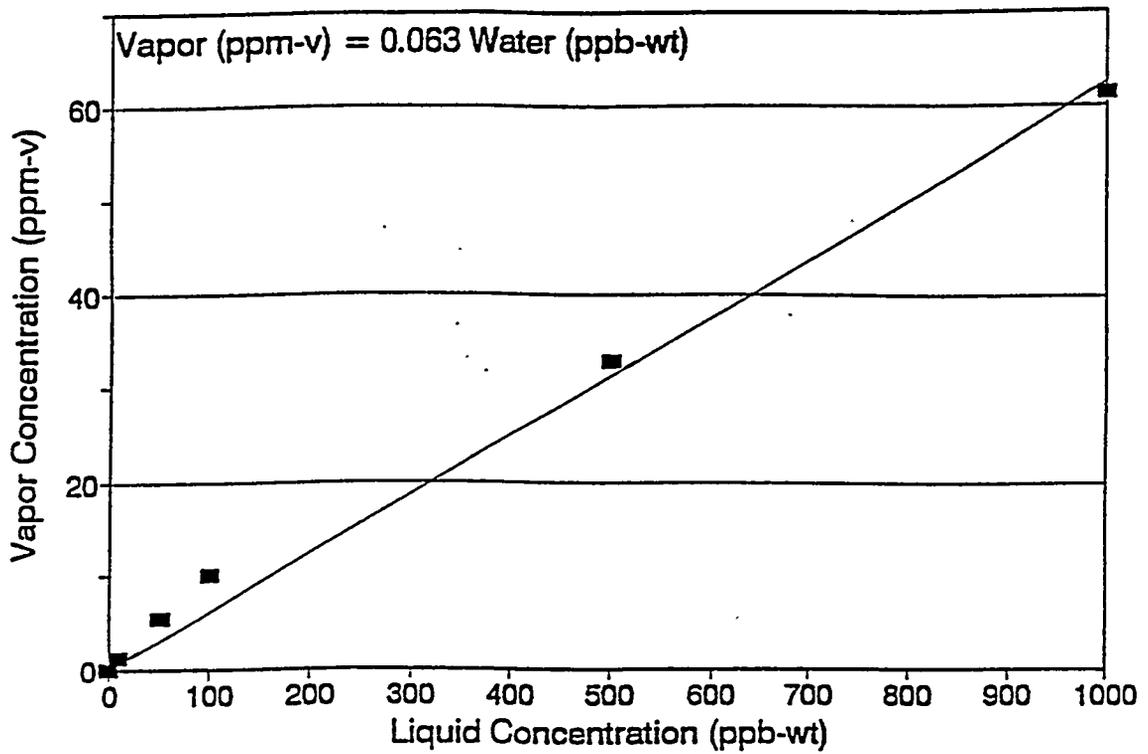


Figure IV-4: Calibration of the CPS. A linear relationship was found for water contamination from 10 ppb_{wr} to over 1000 ppb_{wr}.

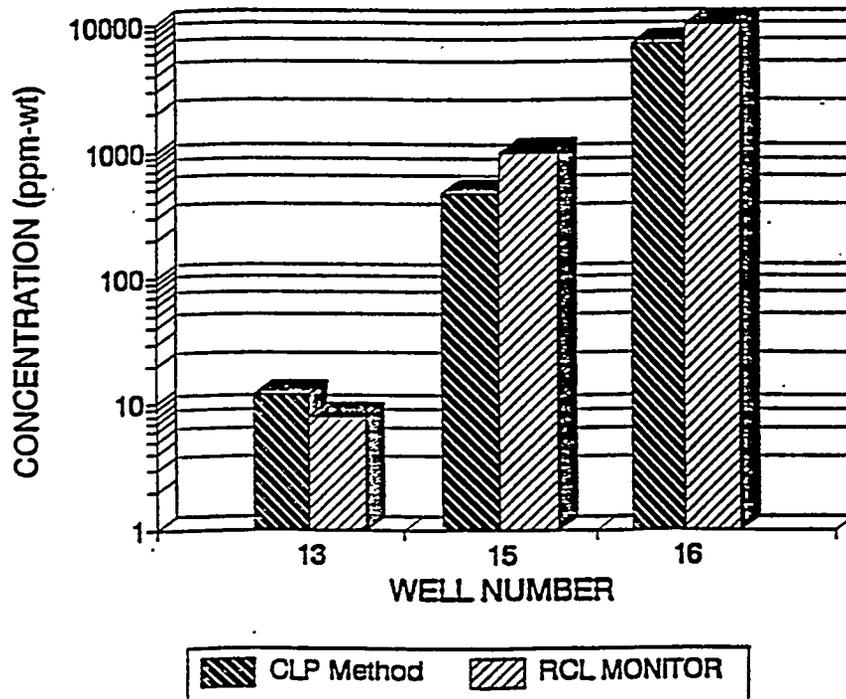


Figure IV-5: Analysis of chlorinated solvent contamination in water samples using the CPS interfaced to the RCL MONITOR and a comparison to the results obtained by CLP methods.

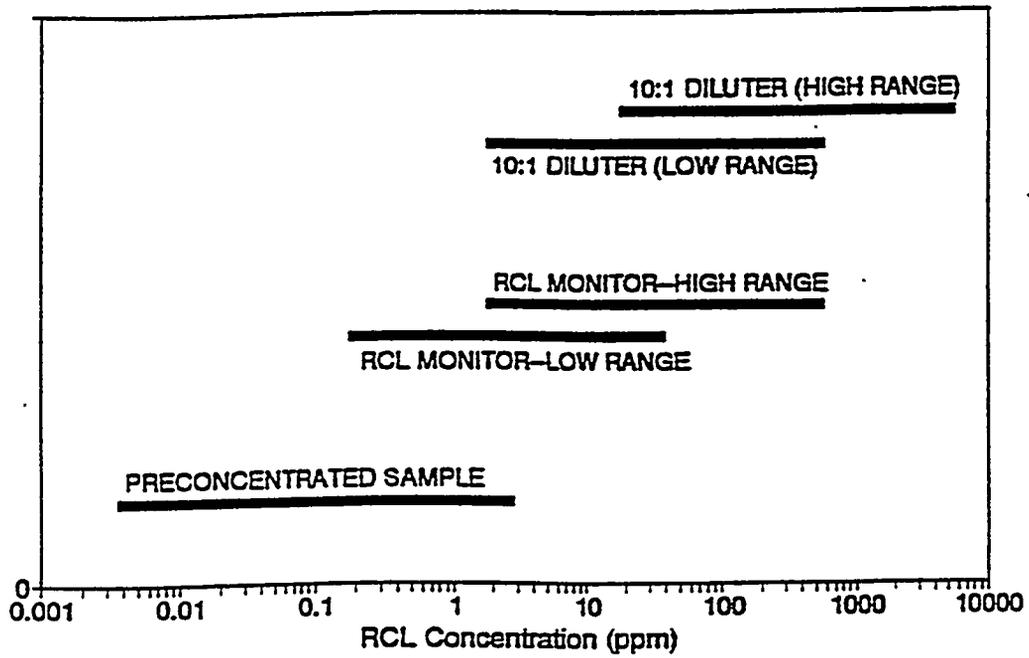


Figure IV-6: Range of the RCL MONITOR when used alone or with the specialized sampling systems and protocols developed in this project.

V Summary and Applications

V.1 Strengths of the Instrument

At the onset of the project, various design goals were formulated for the instrument. These goals recognized the fact that portable chemical analyzers must be truly portable and easy to use, yet still provide valuable information. Frequently, the term "portable" has been applied to instruments which weigh over 40 pounds or even to instrument systems which require vehicle transport. Our definition of portable implies an instrument which can be transported to the site conveniently by the average person and is not dependent on a nearby source of electric power. During the initial field test, it was demonstrated that the design goal to develop a user-friendly, easily transportable analytical tool for the measurement of chlorinated vapors was achieved. The following are the more obvious strengths and features of the instrument, as demonstrated in the field test:

1. The instrument is easily transportable. Operators had no difficulty in transporting the RCL MONITOR to the site and performing point sampling.
2. Rapid analysis with a range of 0.2 to 500 ppm_v is possible. Results can be obtained in 90 seconds. Site personnel can quickly obtain quantitative information essential for worker safety. A survey of an area can be performed in less than an hour and can be updated continuously.
3. The results obtained with the RCL MONITOR and GC analysis on a bag sample were comparable. It should be stressed that the analysis by RCL MONITOR provided only total chlorinated vapor concentration, while a GC analysis will speciate. The RCL MONITOR compared favorably with spectroscopic methods (e.g., the Miran IDX infrared spectrometer). The RCL MONITOR consistently provided more accurate readings than PIDs and detector tubes.
4. The RCL MONITOR can be used by personnel with minimal training. Following training sessions lasting less than 5 minutes, measurements were made within sites which have restricted access. The instrument was used successfully by personnel with various technical backgrounds.
5. The RCL MONITOR can be used by personnel in protective clothing, including full chemical protection suits (Level B) with supplied air.
6. The automatic calibration procedure allows operators to attend to other activity.
7. The display shows clearly the results of the measurements. Operators wearing full-face respirators can still read the display.
8. Results are presented in "ppm_v" both on the display and in memory.
9. Following an analysis, a clear, logical report is automatically generated with an external computer and using the communication software.
10. Reliable field operation is possible under battery power with continuous operation for over 6 hours.
11. Standard maintenance procedures are easy to perform. These include the replacement of the internal filters (zero and particle), battery replacement, sensor replacement.
12. The instrument can operate both in a manual mode (SURVEY) and in an automated, repetitive mode (MONITOR).

13. The instrument is cost effective. Independent cost analysis demonstrated that significant cost saving can be achieved with the RCL MONITOR for many applications (Energetics, 1994).

V.2 The Specialized Samplers

Although the RCL MONITOR has a broad dynamic range, it was recognized at the beginning of the project that these specifications would not be adequate for all applications. Accordingly, specialized samplers were developed which would extend the upper and lower concentration limits of the RCL MONITOR and expand its analytical capability to condensed (aqueous) media. Prior to field testing, the samplers were extensively characterized in laboratory simulations. Overall, the performance of the samplers in the field was favorable with no failure or erroneous behavior encountered. From our experience in the field, the following can be concluded:

Fixed External 10:1 Diluter: The range of the RCL MONITOR is 0.2 to 500 ppm_v. High vapor concentrations greater than 500 ppm_v are frequently encountered in the field. This was especially true for vapors collected from wells proximal to high levels of contamination, as well as for the incoming vapors in vapor extraction systems in operation at several DOE sites. The 10:1 diluter extends the range of the RCL MONITOR to 5000 ppm_v, a level for which there are immediate applications. In some circumstances, even high concentrations of vapors are encountered, and it may be necessary to extend the dilution factor further. The present sampler design could be easily modified to operate in a fixed 100:1 mode.

Condensed Phase Sampler: Water contamination by chlorinated solvents is a major environmental issue and immediate applications exist for the condensed phase sampler. Slightly improved lower detection limits for the condensed phase sampler are desirable. The existing system has a lower detection limit of 10 ppb_{wt} for carbon tetrachloride. Drinking water standards are 5 ppb_{wt}. However, in its present state of development, the condensed phase sampler can be used as a screening tool and waste stream monitor. The regulated level for waste streams is typically 50 ppb_{wt}. Further method development is required for the condensed phase sampler before universal application is possible.

Preconcentrator: The preconcentrator enabled the instrument to detect vapors as low as 10 ppb_v. There were a few technical problems associated with the design of the preconcentrator. Most notably, a long cool-down period was necessary to obtain reproducible measurements. Installation of a vented cooling fan would improve the internal ventilation and would facilitate the cooling process. However, the lower detection limit of the RCL MONITOR appears to be adequate, and there does not seem to be a major need for detecting chlorinated vapor at levels less than 0.2 ppm_v. User feedback indicated that those applications which would require detection limits less than 0.2 ppm_v would also require compound identification and speciation capability.

V.3 Applications

During the development of the chlorinated organic vapor monitor (the RCL MONITOR), Transducer Research, Inc. carried out field tests which demonstrated the performance of the instrument. As a result of interactions with DOE site personnel over the period of this project, we have concluded that there is no shortage of DOE applications which would benefit from an inexpensive and simple method to measure vapor levels of chlorinated solvents. The applications are identified as:

- Environmental Compliance
- Health and Safety
- Process Monitor for Clean-Up Equipment
- Tool for Research and Development (e.g., Environmental Modeling)
- Site Characterization

These groupings serve as a working framework to relate ongoing environmental chemical analyses into common themes and are not meant to correspond to official terminology. Within the above groupings, TRI has identified specific DOE activities which would benefit from the analytical capabilities of the RCL MONITOR. The development and validation of the methods for specific applications will serve as the central theme for Phase II, which is currently underway. TRI and METC are collaborating in ongoing environmental restoration activities within DOE that are representative of the above groupings. Particular emphasis will be on obtaining acceptance of developed methods by local regulators for specific applications. The ongoing effort will provide model studies for the deployment of the RCL MONITOR in "Real World" applications. Comparison to current methods, including both technical assessments and a cost benefit analysis, will be performed. Modifications in the RCL MONITOR, which are necessary for it to be successful in a specific application, will be identified and, if possible, incorporated into the instrument.

V.4 Case Studies

By the end of Phase I, specific applications had been identified and case studies initiated. These case studies can be classified within the groupings presented in Section V.3. From an operational point of view, these applications can be classified into two general categories--discrete sampling and unattended operation, since parameters and requirements for using the RCL MONITOR are defined primarily by whether the instrument is operated in either of these two modes.

Discrete Sampling Applications. The discrete sampling application is relevant for those situations where the operator manually initiates each analysis. It is certainly important in health and safety measurements when the results are needed immediately. These verifications are routinely performed at hazardous waste site operations. Discrete sampling is also used for area surveys which involve multiple analyses of same area, such as well head or soil gas probe sampling. Discrete sampling rapidly checks into the state of the site being analyzed. The RCL MONITOR

has proven itself to be a reliable analytical tool for discrete analyses, providing reliable measurements quickly and easily. Accuracy and reliability can be verified on-site simply by performing validation runs using vapor standards of known concentrations.

Continuous Monitoring Applications. It may not be convenient or even possible to manually perform analyses, especially if the measurements must be performed around the clock. Continuous monitoring allows for unattended repetitive operation and is useful both as a process monitor and as a continuous monitor for fugitive emissions. The major difference between continuous monitoring and discrete sampling applications is simply that the user does not have to be present during analyses. The instrument may be set up as a monitor to collect analytical data, or it may be set up to alarm when threshold concentrations are exceeded. Because of the need for extended reliable operation, continuous monitoring is significantly more demanding than discrete sampling.

The specific case studies initiated in the Phase II effort include:

The Routine Quarterly Monitoring (RQM): The RQM consists of quarterly groundwater and vapor sampling and analysis for chlorinated organic contamination in wells surrounding the Radioactive Waste Management Complex within INEL. It is an ideal example of the discrete sampling protocol and can be grouped as Site Characterization/Environmental Compliance. The RQM requires the collection and analyses of 66 vapors 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. 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. Protocols require the collection, transport, and remote analyses of all samples by gas chromatography. Approximately two man-weeks of effort are required for the vapor analyses, with an additional one to two man-weeks required for the water samples. Since it is performed four times annually, this is a labor-intensive exercise which ties up trained personnel.

Vapor Extraction Systems (VES): Site cleanup using vacuum extraction systems (VES) is an established method for removing subsurface soil contamination of volatile organic compounds, including chlorinated solvents. There are three basic applications from continuous monitoring in the VESs: (1) tracking the amount of chlorinated solvent that is being removed for the soil (Process Monitoring) ; (2) tracking the loading of chlorinated solvents on the granulated activated carbon (GAC) filter beds (Process Monitoring); and (3) verification that the vapor effluent does not exceed regulated levels (Environmental Compliance). There are three VESs in operation in the 200W area of Hanford. Vapors from the VES are currently being sampled using a time-shared instrument system and the analyses are performed manually. The RCL MONITOR will be deployed on two of the three VESs in operation at Hanford. It will track emissions to verify compliance to the site emission standards; it will track incoming vapor levels on one system; and it will monitor the vapor levels emanating from the first of the three carbon beds.

Environmental Modelling Studies (EMS): Hazardous waste sites are not static, and major temporal fluctuations of subsurface and external vapor levels have been observed around hazardous waste sites (see Figure III-3). Subsurface fluctuations of over 10,000 ppm, have been observed for CCl₄ vapors. While the exact nature of the fluctuations has not been fully characterized, the significance of such phenomena is clear. Subsurface fluctuations can arise only from migration of contamination. This migration may simply be caused by circulation of waste within a contained site, or may represent lateral migration. When migrating vapors enter an open well, they will vent out. Alternatively, changes in above-ground vapor levels arise from barometric pressure changes and result in passive emissions through the soil. Passive emission has probably occurred since the contamination was first present and could have a significant impact on the actual amount of contaminant. Both passive emissions and well vent may represent a cost-effective supplement to environmental restoration (Rohay, et al., 1993). To effectively exploit this "zero operating cost" clean up method, models must be developed which can be used to assess the effectiveness of lateral and vertical chemical migration of volatile contamination. Such studies require an analytical tool capable of continuous process monitoring.

Health and Safety (H&S): It is absolutely essential that safe conditions be assured for workers involved in hazardous waste site operations. Assurance of Health and Safety for site personnel working around potentially toxic chemicals is probably the most important application for chemical monitoring technology and illustrates the need for real-time measurements better than any other application. In order to maintain cost-effective site operations, analyses must be performed on-site. Applications for both continuous breathing zone monitoring and discrete point source monitoring exist.

Environmental Technology Demonstration (ETD): As part of DOE's commitment to environmental cleanup, the Environmental Technology Development (ETD) Program at the Savannah River Laboratory has been set up to validate the performance of new and emerging environmental technology for DOE's needs and to provide an avenue to gain acceptance of the new technology by local and regional regulators, including approval of the technology by the Environmental Protection Agency. The RCL MONITOR is currently being independently evaluated within the ETD program. This validation will provide precedence in demonstrating to local regulators that the RCL MONITOR provides data of sufficient quality for the application.

These case studies will expedite the general deployment of the RCL MONITOR throughout DOE and throughout the public sector through the development of validated methods for specific applications that have been accepted by the cognizant regulators.

V.5 Conclusions

The first step in developing a validated FAM is the availability of field analytical technology. The advanced features of the RCL MONITOR provide a unique analytical capability not available in any other truly field-portable instrument. Perhaps the most important feature is the ability to provide immediate on-site chemical analyses, providing operators with indispensable chemical data

when it is needed and allowing for informed decision making. No other portable instrument system exhibits comparable sensitivity, dynamic range, and selectivity to chlorinated organic compounds. Since conventional laboratory analyses are frequently impractical for many applications because of the associated delay times in obtaining and acting on results, the availability of a true field-usable analyzer will be a powerful tool for the analyses of chlorinated solvents.

The field analytical methods which will be developed in Phase II will result in significant cost savings through:

- reduced personnel costs,
- cheaper instrumentation cost,
- reduced waste,
- no transportation cost,
- rapid availability of results.

In addition to cost savings, we expect improvements in both the efficiency and safety of field operations. The accuracy of the RCL MONITOR was demonstrated in side by side analysis of actual field samples with the RCL MONITOR and a laboratory GC, assuring that high quality data will be obtained.

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APPENDIX I

Design of the RCL MONITOR

AI.1 Internal Design of the RCL MONITOR

Drawing from the experience and lessons learned from customer feedback from the Model 2001-05, coupled with the information gathered during the fact finding trips, an advanced and powerful instrument system was engineered. A Table of Specifications was compiled, based not on laboratory considerations but rather on client expectations and needs (Table I-1). These specifications did evolve over the course of the program, but never did they deviate from producing a user-friendly, powerful analytical tool for the analyses of chlorinated solvents.

The instrument design was also required to reconcile the characteristics of the RCL sensor with customer requirements. The sensor is extraordinarily sensitive, but it is also slower to respond and even slower to recover than customers would prefer. These latter problems were addressed by enforcing rigid measurement protocols. Ultimately, the final instrument specifications would have to accommodate the fundamental properties of the sensor.

Internal Pneumatic System: Figure AI-1 illustrates the internal pneumatic system of the RCL MONITOR. It consists of two solenoid valves (The Lee Co., P/N LFDX series), a pump (Brey G6/01), a mixing chamber, and the RCL SENSOR. The pump and solenoid valves were selected for small size, low power, and chemical inertness. There are also two filters, a) a zero filter (ZF) to remove all contaminants from the air stream to provide clean air (zero air) for AUTOZERO and baseline measurements; and b) a particulate filter (PF) to remove dust and other particulate from the vapor stream. A filter housing was designed for the two internal filters. The PF is connected to the sample input of the RCL MONITOR, and the ZF is connected to the air input. Screw caps on the two filter chambers allow the operator to easily replace filters in the field. When developing the zero filter, we found that carbon tetrachloride tended to break through most types of activated charcoal. Several samples of granulated carbon were screened before a suitable one was found. Both the type of carbon and the pellet size were critical.

The primary function of Solenoid Valve 1 is sample control. Vapor is allowed to enter the instrument only at precise times. During an analysis mode, the Solenoid is activated to allow vapor to pass by the RCL sensor. In SURVEY-High and MONITOR-High, the valve 1 is activated 0.1 seconds for each second, so that 1 part sample is mixed with 9 parts zero air in the mixing chamber. This provides a 10:1 dilution of the vapor stream, e.g., in High Mode, a 100 ppm_v vapor would expose the sensor to only 10 ppm_v.

The analysis time is 90 seconds, but the first 30 seconds are dedicated to an automated instrument setup procedures. At the start of an analysis, a purge and prime cycle is automatically initiated to assure that the external and internal pneumatic system will measure only the sample of interest and that residues from previous measurements are purged. Once primed, the sensor baseline will be measured with zero air, followed by a 60 seconds exposure to vapor. At the end of 60 seconds, the sensor response will be measured and compared to a stored calibration curve. These

operations are all automated and transparent to the user. A 90 second clock will count down on the display to indicate the time remaining in the measurement cycle. Upon completion of the measurement cycle, AUTOZERO will automatically begin and is 5 minutes for vapors < 5 ppm, and 10 minutes for vapors >5 ppm. A count-down timer will be displayed on the screen to indicate the time remaining in AUTOZERO. Table AI-1 summarizes the timing and component logic for the various steps involved in an analysis; these operations are blind to the user.

Table AI-1: Component logic table for the RCL MONITOR for the Measurement Cycle and AUTORANGE steps

INSTRUMENT STATE	COMPONENT LOGIC TABLE			DURATION
	S1	S2	P	
MEASUREMENT CYCLE				
Prime	+	+	+	15 seconds
Purge	-	+	+	5 seconds
Baseline measurement	-	-	+	10 seconds
Sample	+ ¹	-	+	60 seconds
AUTOZERO	-	-	+	5 to 10 minutes ²
STANDBY	-	-	+	User Defined

¹ In an High mode of analysis, S1 is activated only 10 percent of the time on a 1 second duty cycle.

² AUTOZERO is 5 minutes for vapors levels less than 5 ppm, and is 10 minutes for vapor levels greater than 5 ppm.

Temperature Control (sensor): Because the strong temperature dependency in the RCL Sensor, an active temperature control protocol has been designed into the RCL MONITOR. The operating temperature of the RCL sensor is 800 ± 10 °C.

Case: The case used in the RCL MONITOR was a Hammond fiberglass instrument case (P/N R130-162-000) with hinged lid and a gasket seal. This off-the-shelf component was selected in order to reduce development time and dollars. This case was required to be water and dust resistant, rugged, and large enough to house the battery, circuit board and pneumatics. The selected case also had large captive screws, allowing it to be easily opened for servicing.

Software: The software is the instructions to the microcontroller for controlling all instrument processes. Assembly language was chosen for its compactness, flexibility, ease of interfacing to hardware, and requirement for the minimum amount of external circuitry. Use of a high-level compiler, such as C or ADA, would have required more than the 16K program memory available on-chip, and required external memory circuitry to be designed into the system. The length of the assembly language software was approximately 8 kilobytes, which fitted into the on-chip memory with plenty of room for future expansion of features, if required.

Display: The front panel display is a 4 line x 20 character LCD display with a LED backlight. The LCD technology was chosen for its low power consumption and clarity. The LED backlight allows for viewing in dim light and has very long operating life. A 4 line display was chosen to provide the operator with an uncrowded display. The use of cryptic prompts was minimized.

Front Panel: The front panel was a Mylar overlay, a material that is commonly used in instrumentation for its good appearance and its ruggedness in an outdoors industrial environment. Push-buttons were molded into the panel by the manufacturer to our specifications. The keys were spaced to allow for operation using a gloved hand with little chance of false key entries. The KEYPAD layout is illustrated in Figure II-3.

Battery: A battery is required for hand-carried, portable use. The added weight of a lead-acid battery was considered acceptable because of the good low-temperature performance of this battery type, as well as cost. The battery size selected was the smallest that would provide 8 hours continuous operation in the field. A 12 volt, 7 ampere-hour sealed lead acid battery was chosen. This battery weighs about 6 pounds. It is internal to the RCL MONITOR and represents nearly 50 percent of its total weight. The internal battery may be replaced with a spare battery in the field at any time. Power should be turned off first. Data and instrument settings will not be lost during charging and during battery replacement because of the circuit board memory is backed up with an separate low-power battery that is independent of the main battery.

Adapter/Charger: The RCL MONITOR comes complete with an Adapter/Charger. The instrument will operate on either internal battery power or the external Adapter/Charger (for AC line operation). The Adapter/Charger is used to either operate the instrument on AC power or to charge the battery. When the power is off, the Adapter/Charger will charge the battery. However, the battery will not charge with power on. The Adapter/Charger will detect a fully charged battery and switch to "float" mode, so that the battery cannot be destroyed by overcharging. An indicator light on the charger will be illuminated while the battery is charging or when the instrument is in operation. The light will turn off when the battery is fully charged.

Microprocessor Control: Control of the RCL MONITOR is through an internal microprocessor (Intel 87C51FB microcontroller, 12 MHz with 32K reprogrammable program memory). Manual operation is restricted to selection of analytical modes (e.g., SURVEY, MONITOR or CALIBRATE), setting SUPERVISORY parameters (e.g., date, time, alarm threshold), and initiation of measurements. The operating system controls all instrument functions, including sample analyses, data collection, workup and storage in memory, as well as the internal operation of the instrument subsystems (e.g., pumps, flow regulation, solenoids, sensor temperature regulation).

Instrument parameters, such as date and time, are accessed in SUPERVISORY. In Supervisory, the MODE SELECT sub-menu allows the operator to select the non-default mode of operation, including MONITOR, the automated repetitive mode of analyses, and CALIBRATE. The complete menu tree (for both READY and SUPERVISORY) is illustrated in Figure II-2.

AI.2 Calibration of the RCL MONITOR

All analytical instruments require calibration. In the case of the RCL MONITOR, it is necessary when a new sensor is installed in the unit because of variability in the response of the sensors. At this time, the manufacture control of the sensor produces devices with a broad range of performance characteristics, especially in terms of sensitivity and kinetics of recovery following exposure to vapors. Although the sensor produces a stable response for its useful life, it may also be necessary to recalibrate the unit without replacement of the sensor. This is usually indicated when the unit will not validate with a challenge vapor, but is only slightly out of calibration (e.g., a reading of 7.4 ppm, when challenged with a 10 ppm, vapor). A validation measurement should be performed regularly to verify stable sensor operation. It is recommended that a 10 ppm, sample is attached to the inlet, and a measurement made. The displayed value should be between 7.5 and 12.5 ppm,. This should be done at the end of the day, before and after calibration, and more often in critical applications. If the sensor is out of specification, then the instrument should be recalibrated. The sensor should be replaced if it has undergone two recalibrations since installation.

One special case where calibration may be necessary is when the vapor that is being measured is known to be a different compound from the vapor used for calibration. Since it is known that the RCL Sensor has different sensitivity factors for different vapors, it is recommended that the calibration gas consist of the analyte of interest. Without any knowledge of the analyte, the RCL MONITOR will still provide quantitative and selective analysis on the total chlorinated solvent vapor level, measurements, but with a higher uncertainty.

An automated multi-point calibration protocol was developed for the RCL MONITOR. CALIBRATE is initiated from the MODE SELECT submenu in SUPERVISORY. In CALIBRATE, a 10 ppm, carbon tetrachloride solvent vapor source is attached to the instrument. two liters of vapor are required. Although a 10 ppm, vapor source is required, the actual calibration is multi-point with the 10 ppm, vapor diluted internally during calibration. Thus, from a single 10 ppm, source, a calibration curve of 1, 4, and 10 ppm, is obtained. A multi-point calibration procedure was selected because of the non-linear nature of the RCL sensor (illustrated in Figure AI-2). The actual instrument calibration is initiated by pressing SAMPLE on the Keypad. From this point on, the procedure is fully automated and the instrument can be left unattended. The total time required for calibration is typically 45 minutes. Should the instrument be left unattended, it will automatically turn off 15 minutes after calibration. This allows the battery to recharge. The new calibration data will be stored in the memory of the instrument.

AI.3 Routine Maintenance of the RCL MONITOR

A brief listing of the display messages and error modes produced by the RCL MONITOR is presented in Appendix II. Routine maintenance procedures were designed to be simple and pertains primarily to sensor replacement and filter replacement:

Sensor Replacement: The sensor should be replaced when the instrument indicates a burned out heater coil (TROUBLE code #030) or when the sensor fails a validation test two days in a row. To replace the sensor, power should be turned off. The large screws are loosened and the case is opened. The sensor is a translucent plastic cylinder 0.625" diameter and 1.25" high; two gas tubes are attached to the sides. The tubes are disconnected, and the sensor can be pulled straight out of its socket. A new sensor can be plugged in and the tubes reconnected. Following sensor replacement, it is necessary to calibrate the instrument using the procedure described in Section AI.2.

Filter Replacement: Two low-cost internal filters are used in the RCL MONITOR. Filters are replaced by opening the lid and removing the screw caps from the filter holder. The Zero Filter (ZF) scrubs organic compounds from the sample stream. It provides clean air for establishing baseline and to allow the sensor to recover. Its capacity is limited, and it should be replaced daily under normal use. The Particulate Filter (PF) should be replaced every month under normal conditions, and more often in dusty conditions.

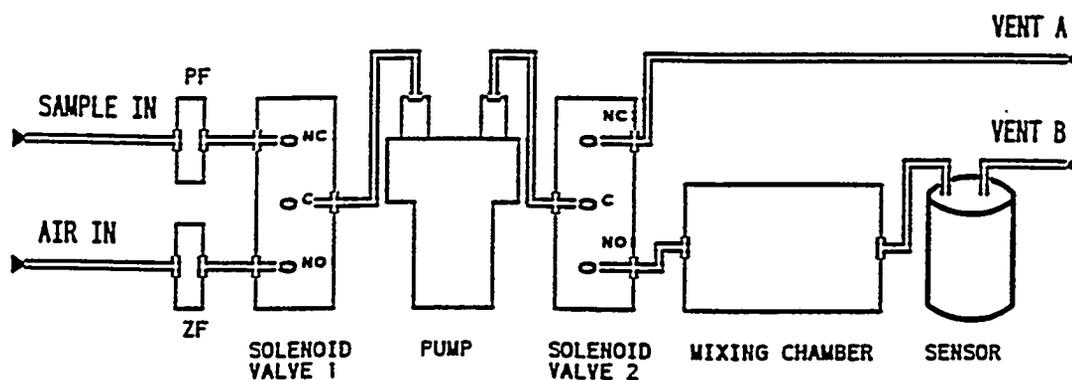


Figure AI-1: The internal pneumatic system of the RCL MONITOR. Details in text.

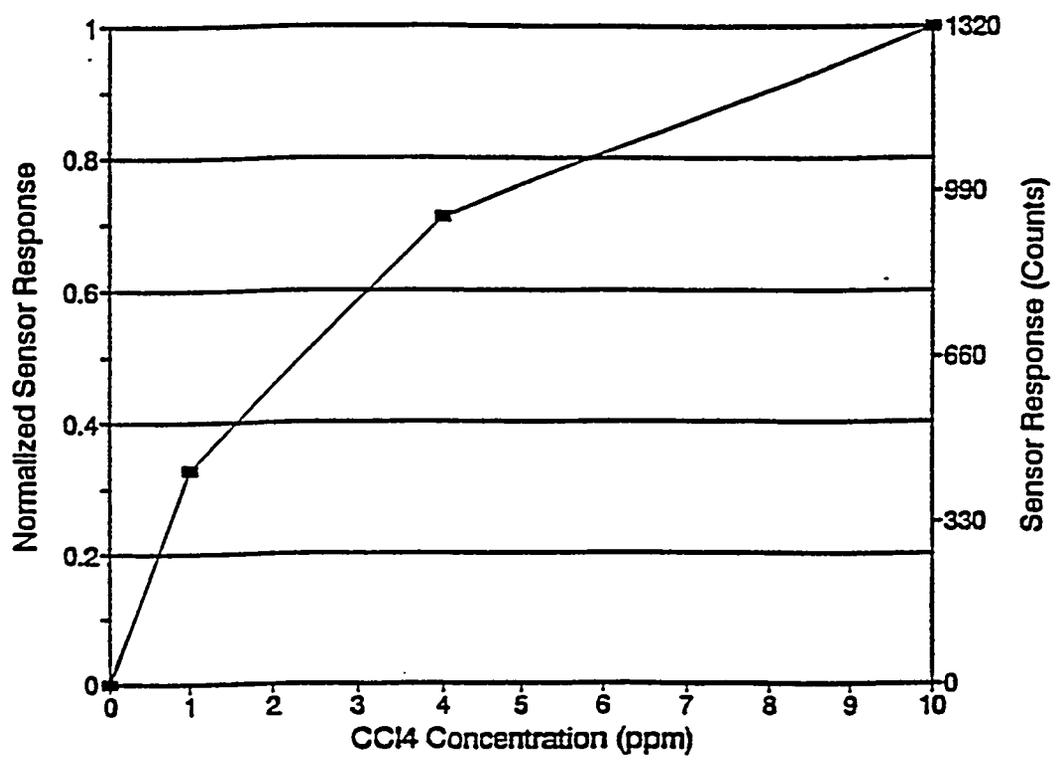
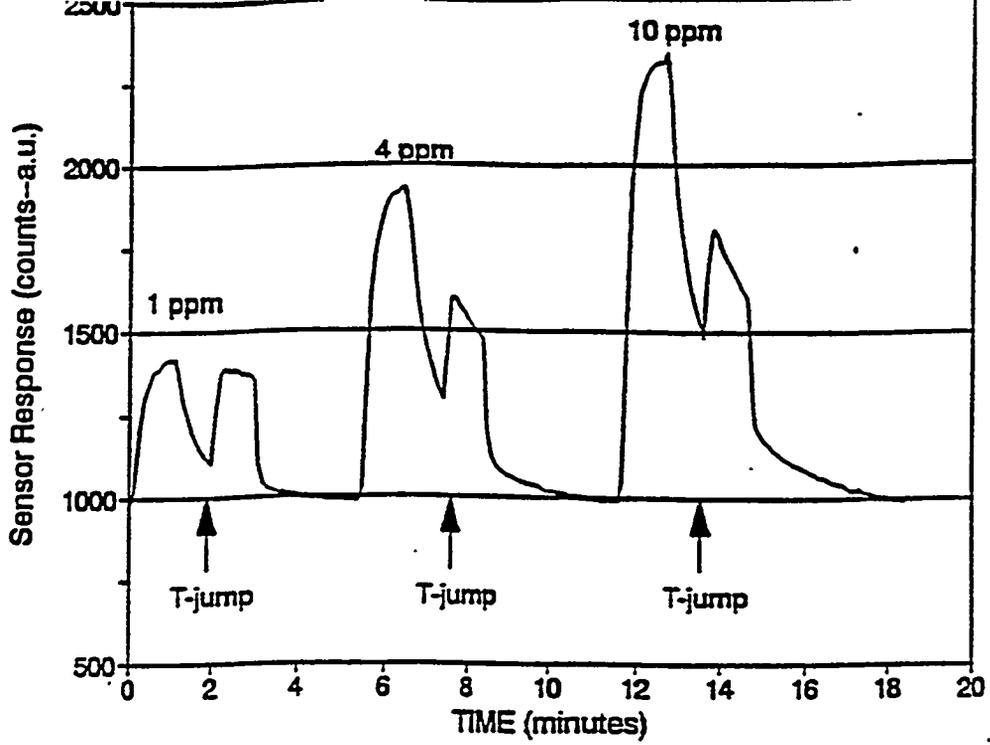


Figure AI-2: The RCL MONITOR automated calibration (CALIBRATE) protocol. A 10 ppm vapor source is attached to the RCL MONITOR and is diluted internally to generate vapor standards of 1, 4 and 10 ppm. The procedure requires less than 1 hour, but can be significantly shorter for a sensor which recovers to baseline quickly. To facilitate the sensor recovery, a temperature jump is automatically implemented for 1 minute during AUTOZERO.

APPENDIX II

Warnings and Messages

AII.1 Troubleshooting

AII.1.1 Common Problems Resulting in Measurement Errors

The purpose of this section is to provide users with the information necessary to prevent measurement problems. Many of the items listed are issues common to gas-measurement instrumentation. Attention to these items will minimize errors, problems, and lost time.

Sampling tube too long: The maximum length of the sample tube is 6 feet.

Unacceptable material in flow path: Many materials absorb chlorinated vapors under low flow and/or low temperature conditions, and desorb chlorinated vapors under high flow and/or high temperature conditions.

Pressure/vacuum at sample source: Even a slight difference in pressure between the SAMPLE IN port and the AIR In port can cause a measurement error.

Calibration sample concentration inaccurate: Accuracy in preparing the sample bags for validation and calibration is critical to obtain reliable results.

Restricted or kinked tubing: Any flow restriction in the tubing or ports will cause major errors

Sample being measured contains a mixture of chlorinated organic compounds: It is important to remember that the RCL MONITOR measures the total of all chlorinated compounds present. Example: If the sample contains 5 ppm_v of carbon tetrachloride and 5 ppm_v of trichloroethylene, the instrument will indicate a concentration of 10 ppm_v.

Table AII-1: Troubleshooting Guide

Symptom	Possible Causes	Solution
Battery fails to Charge	Instrument power turned on during charging Internal fuse blown Battery weak or dead	Turn instrument power off during charging Replace fuse Replace Battery
Operating time on battery less than expected	Cold weather operation Battery Weak	Operate from AC power or carry spare battery Replace battery
Power shuts off	Automatic shut off after calibration Automatic shut off after <LOW BATTERY> warning Defective battery Automatic shut off when self-diagnostics detect power supply failure	Normal Operation. Turn power on when ready to use instrument Normal protective operation. Recharge battery. Recharge battery. If battery fails to power unit for longer than two hours, replace battery. Recharge battery. If unit fails to turn on, factory service may be required.
Validation tests fails after calibration	Sample bag or tubing faulty Test Vapor old or faulty	Inspect system, repair or replace as necessary Make fresh sample, then calibrate and validate
Questionable Measurements	Instrument is not in calibration Kinked or restricted tubing Leaks in external pneumatics Positive or negative pressure at sample source Sample tube too long Incomplete sensor recovery Sensor Expended Sample has more than one chlorinated compound Instrument was calibrated with different chlorinated vapor than sample being measured Filters depleted Mis-connected sample/vent tubing	Perform validation test. Calibrate if necessary. Inspect and remove restriction Inspect and remove restriction Test source to ensure zero pressure. If not zero, try collecting sample in a sample bag and measure bag concentration. Tube should not exceed 6 feet (2 m) Perform validation test. Calibrate if necessary. Replace sensor if necessary Most likely to occur after exposure to high concentrations. Run several blank measurements of clean air to clear sensor and pneumatics RCL MONITOR measures the total of all chlorinated vapors present Calibrate instrument with gas to be measured Replace filters Inspect and correct connections

AII.1.2 Diagnostic Messages

The RCL MONITOR contains diagnostic circuitry and firmware that continuously monitor system performance. Diagnostic messages are displayed so that appropriate action may be taken

There are three types of diagnostic messages:

Status messages advise the operator of instrument capacity conditions. An audible beep occurs when these messages are displayed.

Service messages indicate instrument service needs.

Alarm messages may appear on the display to alert the operator to conditions that need immediate attention. A message is displayed, the alarm sounds, the alarm LED lights, and the relay contacts close to indicate an alarm. The event is recorded in the data logger. Silence the alarm by pressing the MUTE key. The alarm LED, display message, and relay contact closure will remain energized until acknowledged (reset) via the Supervisory menu.

Each of the diagnostic messages is described below in alphabetical order. The message type is enclosed in parentheses:

"<ALARM CONDITION>", (alarm)

The measured gas level exceeded the user-defined alarm trigger level.

"<CALIBRATE LOG FULL>", (status)

The section of the data logger memory that stores calibration events is full. Measurements can still be taken and measurement results will still be saved. Calibrations may be performed but will not be saved. Download and clear the data logger to allow new calibration information to be saved. The capacity of the calibrate log is approximately 30 calibrations.

"<LOG ALMOST FULL>", (status)

The data logger memory is almost full. There is sufficient room for about 100 additional measurements. Download the stored data to a computer using the supplied software and then clear the data logger. This measurement remains visible until the memory is cleared or the "<SAMPLE LOG FULL>" message appears

"<LOW BATTERY>", (status)

The battery requires charging. When the message is first displayed, there is sufficient battery power remaining for one additional measurement cycle. Power is automatically turned off when the battery voltage becomes too low to operate the instrument.

"<OVER 25 PPM>", (status)

The input sample gas concentration exceeds the full scale limit of 25 ppm, in low range and a measurement is not possible. A record indicating that an over-range measurement was made is stored in data logger. Change to high range to measure this sample

Since the sensor has been exposed to a vapor concentration level above acceptable range, recovery time will be longer than normal. To speed clearing of the sensor and flow path, perform a blank measurement by sampling from clean ambient air. It is also advisable to run a validation test to determine if calibration is necessary.

"<OVER 500 PPM>", (status)

The input sample gas concentration exceeds the full scale limit of 500 ppm, in high range and a measurement is not possible. A record indicating that an over-range measurement was made is stored in data logger. This sample may be measured using an external gas diluter to reduce the concentration to a measurable level.

Since the sensor has been exposed to a vapor concentration level above acceptable range, recovery time will be longer than normal. To speed clearing of the sensor and flow path, perform a blank measurement by sampling from clean ambient air. It is also advisable to run a validation test to determine if calibration is necessary.

"<PLEASE CALIBRATE>", (service)

Calibration is required before any accurate measurements can be taken.

"<REPLACE SENSOR>", (service)

Self-diagnostic tests have determined that the sensor can no longer be perform accurate measurements. Replace the sensor. This message can only appear immediately after a calibration has been performed.

"<REPLACE ZERO FLTR>", (status)

The zero filter needs replacement or the tubing on the vent or sampling ports is connected improperly.

"<SAMPLE LOG FULL>", (status)

The data logger memory is full. Measurements can still be taken but they will not be saved. Data stored will not be corrupted. Download to a computer using the supplied software and clear the datalogger. This message will remain visible until datalogger memory is cleared.

"<TROUBLE # 00>", (alarm)

This message indicates that there is a problem with the LCD display. Turn power off and then on again. If the trouble persists, turn power off and call Customer Service.

"<TROUBLE # 01>", (alarm)

This message indicates that there is a problem with the EEPROM. Turn power off and then on again. If the trouble persists, turn power off and call Customer Service.

"<TROUBLE # 02>", (alarm)

This message indicates that there is a problem with the Serial I/O. Turn power off and then on again. If the trouble persists, turn power off and call Customer Service.

"<TROUBLE # 030>", (alarm)

This message indicates the absence of electrical current to sensor heater. The most common cause is the burn-out of the sensor coil. Replace the sensor. If sensor replacement does not resolve the problem, call Customer Service.

APPENDIX III
Design of the Specialized Samplers

AIII.1 The Fixed External 10:1 Diluter

Figure AIII-1 illustrates the internal pneumatics of the fixed external 10:1 diluter. In this version, sample vapor is continuously collected into a venter reservoir. Similarly, ZERO AIR is vented into a second vented reservoir. During analyses, the solenoid is activated on a 10 percent duty cycle. The vapor and zero air are homogenized in the mixing chamber and the resulting diluted sample is analyzed by the RCL MONITOR. The principle of operation is such that the dilution factor can be increased to 100:1 without major modification of the design.

AIII.2 The Preconcentrator

A block diagram of the preconcentrator is illustrated in Figure AIII-1 and a logic table of the components is presented in Table AIII-1. A Carotrap 300 Multi-Bed Thermal Desorption Tube (Supelco) was modified for use as the trap. The Carotrap 300 tube was designed for vapors of chlorinated solvents and consists of three different sorbents (Carotrap C, Carotrap B, and Carboseive S-III) separated by silinized glass wool. Desorption was induced by a heater coil wrapped around the sorbent tube. The heater consisted of 20 cm of 0.013 mm diameter NiChrome wire and encapsulated with a high temperature ceramic operating at 300°C. The preconcentrator is controlled by a Basic Stamp controller.

Table AIII-1: Component logic table for the Preconcentrator

PRECONCENTRATOR (Step)	COMPONENT LOGIC TABLE							DURATION
	S1	S2	S3	S4	PI	H1	Fan	
Sampling	-	-	-	-	+	-	-	10 or 50 minutes
Preheat	-	+	+	+	+	+	-	3 minutes
Desorb	+	+	+	-	+	+	-	1 minute
Purge	+	+	+	-	+	+	-	1 minute
Cool	+	-	-	-	+	-	+	10 minutes

AIII.3 The Condensed Phase Sampler (CPS)

The design of the condensed media sampler is illustrated in Figure AIII-3. The condensed media sampler was designed to extract volatile vapors using a closed-loop air-stripping process in which 1 L of air is recirculated through a 1 L water sample. Following the 10 minute recirculation, the sample bag is manually connected to the RCL MONITOR. The CPS was designed to operate in two modes--a). sample collection and b). system purge (for cleaning purposes). The modes are manually selected, but each mode has several steps, again controlled by an internal microprocessor (Basic Stamp). Table AIII-2 provides the component logic table for the Condensed Phase Sampler.

Table AIII-2: Component logic table for the Condensed Phase Sampler

Condensed Phase Sampler (Step)	COMPONENT LOGIC TABLE					DURATION
	S1 ¹	S2	S3	P1	P2	
SAMPLE COLLECTION						
Fill Bag	-	-	-	+	-	1 minute
Sampling	-	+	+	-	+	10 minute
SYSTEM PURGE²						
Circulate & Empty Bag	-	+	-	-	+	5 minutes
Fill Bag	-	-	-	+	-	1 minute
Circulate & Empty Bag	-	-	-	+	-	5 minutes
Fill Bag	-	-	-	+	-	1 minute
Circulate & Empty Bag	-	+	-	-	+	5 minutes

¹S1 was not used in the present design for the CPS, but was included to allow for an automated interface to the RCL MONITOR; when energized, S1 would provide a pneumatic connection to the RCL MONITOR

²The SYSTEM PURGE step was to be performed two times; once with the sample vessel filled with clean water and once with the sample vessel empty.

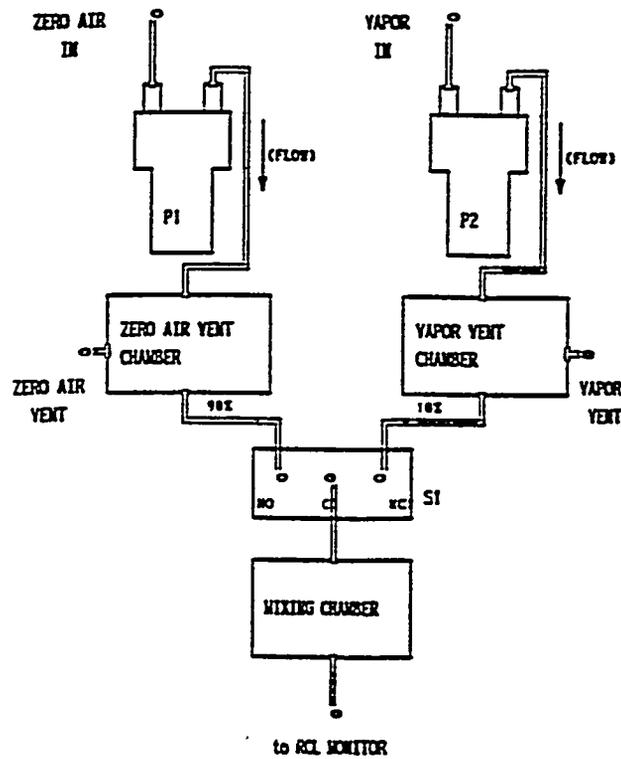


Figure AIII-1: Block diagram of the pneumatic system of the fixed external 10:1 diluter. To expand the range of the RCL MONITOR to 5,000 ppm_v, an external diluter was built which dilutes samples by a factor of 10.

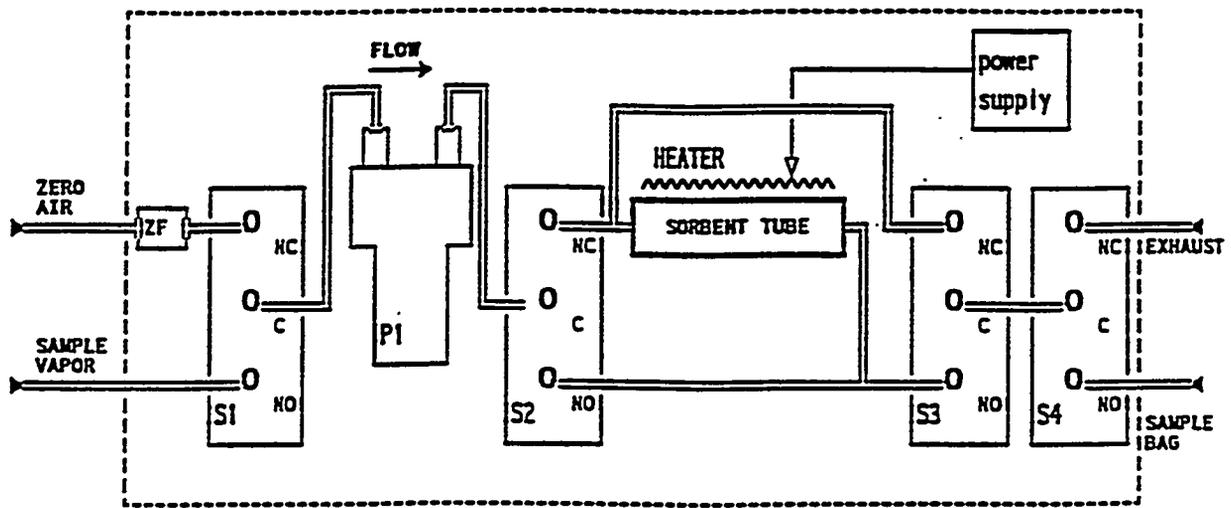


Figure AIII-2: Block diagram of the pneumatic system of the preconcentrator, which was developed to enrich incoming vapor levels by a factor of 10 or 50.

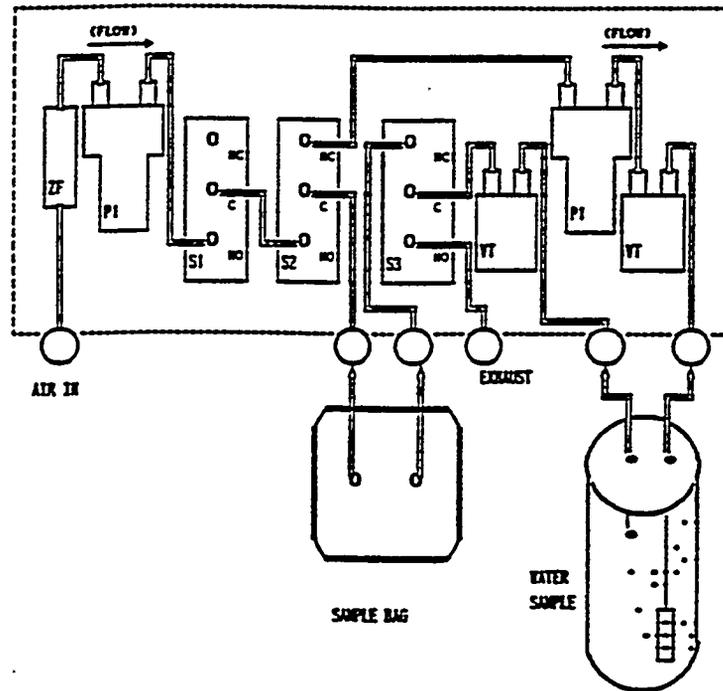


Figure AIII-3: Block diagram for the pneumatic system of the Condensed Phase Sampler (CPS). The CPS was developed to extract chlorinated vapors from aqueous samples and to analyzed the vapors with the RCL MONITOR.

APPENDIX IV
List of Abbreviations

ACGIH	American Conference of Government Industrial Hygienist
BTX	Benzene, Toluene, Xylene; a group of common hydrocarbon organic solvents and possible environmental contamination noted for the <i>aromatic</i> properties
CLP	Contract Laboratory Procedure. Typically conventional off-site laboratory analytical procedure
CPS	Condensed Phase Sampler
DOD	Department of Defense
DOE	Department of Energy
ETD	Environmental Technology Development
EMS	Environmental Modelling Studies
FAM	Field Analytical Method
GAC	Granulated Activated Carbon
GC	Gas Chromatograph
H&S	Health and Safety
IDLH	Immediate danger to life or health
INEL	Idaho National Engineering Laboratory
LDL	Lower Detection Limit
MeCl ₂	Methylene chloride
METC	Morgantown Energy Technology Center
OTA	Office of Technology Assessment
OTD	Office of Technology Development

OVM	Organic Vapor Monitor
P# (# = 1, 2)	Pump Number
PID	Photoionization Detector
PNL	Pacific Northwest Laboratory
POL	Petroleum, Oils, and Lubricants. Common environmental contaminants
ppb _v	Parts Per Billion by volume, a measure of vapor concentrations
ppb _{wt}	Parts Per Billion by weight, a measure of concentration in aqueous samples
ppm _v	Parts Per Million by volume, a measure of vapor concentrations
ppm _{wt}	Parts Per Million by weight, a measure of concentration in aqueous samples
PRDA	Program Research Development Announcement
% RH	Per Cent Relative Humidity
RCL	A chlorine-containing chemical (R-Cl)
RQM	Routine Quarterly Monitoring
S# (# = 1, 2, 3, 4)	Solenoid Number
SRL	Savannah River Laboratory
TCE	Trichlorethylene
TRI	Transducer Research, Inc.
VES	Vacuum Extraction System
WHC	Westinghouse Hanford Company