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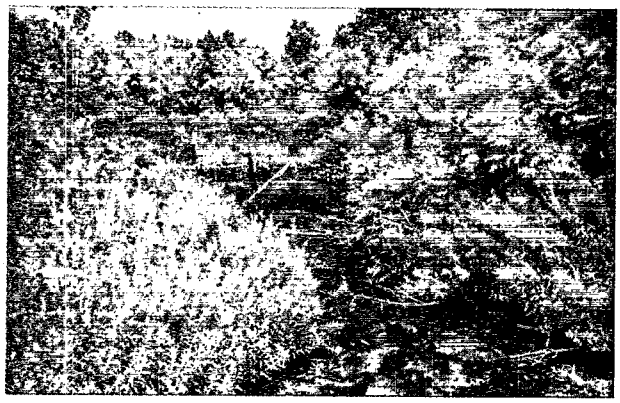
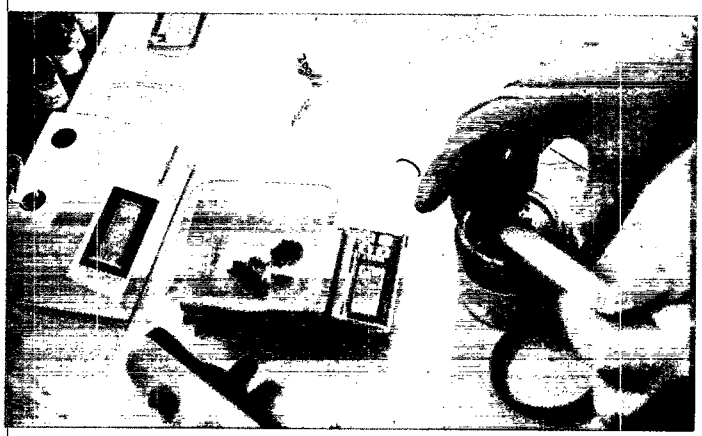
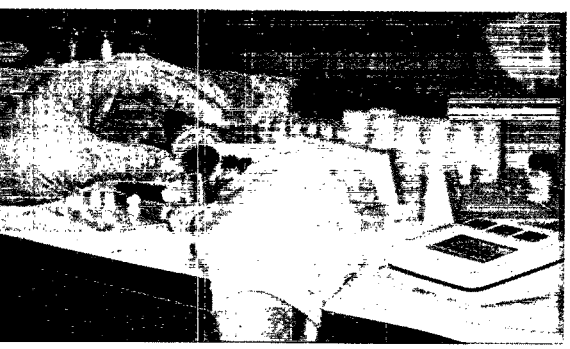
HNU-Hanby PCP Immunoassay Test Kit

Innovative Technology Evaluation Report







SITE
SUPERFUND INNOVATIVE
TECHNOLOGY EVALUATION

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EPA/540/R-95/515
August 1995

HNU-HANBY PCP IMMUNOASSAY TEST KIT

INNOVATIVE TECHNOLOGY EVALUATION REPORT

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Notice

The information in this document has been funded wholly or in part by the U.S. Environmental Protection Agency (EPA) in partial fulfillment of Contract No. 68-C0-0047, Work Assignment No. 0-40, to PRC Environmental Management, Inc. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. The opinions, findings, and conclusions expressed herein are those of the contractor and not necessarily those of the EPA or other cooperating agencies. Mention of company or product names is not to be construed as an endorsement by the agency.

Foreword

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory is the Agency's center for investigation of technological and management approaches for reducing risks from threats to human health and the environment. The focus of the Laboratory's research program is on methods for the prevention and control of pollution to air, land, water and subsurface resources; protection of water quality in public water systems ; remediation of contaminated sites and ground water; and prevention and control of indoor air pollution. The goal of this research effort is to catalyze development and implementation of innovative, cost-effective environmental technologies; develop scientific and engineering information needed by EPA to support regulatory and policy decisions; and provide technical support and information transfer to ensure effective implementation of environmental regulations and strategies.

This publication has been produced as part of the Laboratory's strategic long-term research plan. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

E. Timothy Oppelt, Director
National Risk Management Research Laboratory

Abstract

This innovative technology evaluation report describes a demonstration of the HNU-Hanby Environmental Test Kit for determining pentachlorophenol (PCP) contamination in soil. This kit was demonstrated in Morrisville, North Carolina, in August 1993. The objective of this demonstration was to evaluate the technology by comparing its results to those from a confirmatory laboratory that used standard EPA-approved analytical methods. The HNU-Hanby test kit can provide PCP results only in samples that also contain a petroleum hydrocarbon carrier such as gasoline, kerosene, diesel fuel, or fuel oil. The test kit uses the Friedel-Crafts alkylation reaction to detect the petroleum hydrocarbons. This reaction is colorimetric. A reflective photometer is used to quantitatively measure the reaction color. A site-specific calibration is needed to determine the ratio of PCP to carrier solvent. This ratio is then used to correct the results from the reflective photometer.

The detection limit reported by the test kit's developer is 1.0 part per million (ppm) for soil samples. A 5.0 ppm detection limit was used for this demonstration. The elevated detection limit was the result of reducing the sample mass used for extraction. During the demonstration, 47 soil samples were extracted and analyzed. The precision of the test kit was determined to be statistically the same as the precision of the confirmatory laboratory. The accuracy of the kit's data set was evaluated as a whole and by concentrations less than and greater than 100 ppm PCP. When the entire data set was evaluated, the test kit's results were determined to be statistically different from the confirmatory results. This was also the case for samples in which the PCP concentrations were greater than 100 ppm. The test kit's data for samples containing less than 100 ppm PCP was shown to be statistically similar to the corresponding confirmatory data. Based on this evaluation, the test kit produced Level 1 data for samples containing greater than 100 ppm PCP and Level 2 data for samples containing less than 100 ppm PCP. This indicates that there was a concentration effect on the test kit's accuracy. The test kit showed greater comparability to the confirmatory data when PCP concentrations in samples were below 100 ppm.

This report was submitted in partial fulfillment of 68-CO-0047 WA 0-40 by PRC Environmental Management, Inc. (PRC), under sponsorship of the U.S. Environmental Protection Agency. This report covers a period from July 1, 1993, to August 31, 1993, and work was completed as of February 1, 1994.

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List of Abbreviations and Acronyms

DCAA	2,4-dichlorophenylacetic acid
EMSL-LV	Environmental Monitoring Systems Laboratory-Las Vegas
EPA	Environmental Protection Agency
ERA	Environmental Research Associates
GC	gas chromatograph
GC/MS	gas chromatograph/mass spectrograph
IDW	investigation-derived waste
ITER	Innovative Technology Evaluation Report
Koppers	Koppers Company
µg/kg	micrograms per kilogram
mg/kg	milligrams per kilogram
MMTP	Monitoring and Measurement Technologies Program
NRMRL	National Risk Management Research Laboratory
ORD	Office of Research and Development
OSWER	Office of Solid Waste and Emergency Response
PCP	pentachlorophenol
PE	performance evaluation
ppm	part per million
PRC	PRC Environmental Management, Inc.
QADE	Quality Assurance and Data Evaluation
QA/QC	quality assurance/quality control
QAPjP	quality assurance project plan
r^2	correlation of determination
RCRA	Resource Conservation and Recovery Act
RECAP	Region 7 Environmental Collection and Analysis Program
RPD	relative percent difference
SARA	Superfund Amendments and Reauthorization Act of 1986
SITE	Superfund Innovative Technology Evaluation
SMO	Sample Management Office
SVOC	Semivolatile Organic Compound

Acknowledgments

This demonstration and the subsequent preparation of this report required the services of numerous personnel from the Environmental Protection Agency, Environmental Monitoring Systems Laboratory (Las Vegas, Nevada); Environmental Protection Agency, Region 7 (Kansas City, Kansas); HNU-Hanby Systems (Houston, Texas); HNU Systems (Boston, Massachusetts); Beazer East, Inc. (Pittsburgh, Pennsylvania); Winona Post, Inc. (Winona, Missouri); and PRC Environmental Management, Inc. (Kansas City, Kansas; Cincinnati, Ohio; and Chicago, Illinois). The cooperation and efforts of these organizations and personnel are gratefully acknowledged.

Section 1
Executive Summary

This innovative technology evaluation report (ITER) presents information on the demonstration of the HNU-Hanby Environmental Test Kit for determining pentachlorophenol (PCP) contamination in soil. This screening kit was demonstrated in Morrisville, North Carolina, in August 1993. The demonstration was conducted by PRC Environmental Management, Inc. (PRC), under contract with the Environmental Protection Agency's (EPA) Environmental Monitoring Systems Laboratory—Las Vegas (EMSL-LV). The demonstration was developed under the Monitoring and Measurement Technologies Program (MMTP) of the Superfund Innovative Technology Evaluation (SITE) Program.

This technology was demonstrated in conjunction with four other field screening technologies: (1) the Penta RISc Test System developed by EnSys Incorporated, (2) the EnviroGard PCP Test Kit developed by the Millipore Corporation, (3) the Penta RaPID Assay developed by Ohmicron Corporation, and (4) the Field Analytical Screening Program PCP Method developed by EPA's Region 7 through its Superfund Program. The results of the demonstrations of these other technologies are presented in separate reports similar to this one.

The objective of this demonstration was to evaluate the HNU-Hanby test kit for accuracy and precision at detecting high and low levels of PCP in soil samples by comparing its results to those from a confirmatory laboratory that used standard EPA-approved analytical methods. These EPA-approved methods are used to provide legally defensible analytical data for the purpose of monitoring or for the enforcement of environmental regulations. Because these EPA-approved methods are used by the regulatory community, they also were used for this demonstration for comparison of results. While these methods may include inherent tendencies which may bias data or may include procedures with which developers disagree, they are the best methods for providing legally defensible data as defined by the regulatory community. To remove as much of these inherent tendencies as possible, PRC used post hoc residual analysis to remove data outliers. The HNU-Hanby test kit also was qualitatively evaluated for the length of time required for analysis, ease of use, portability, and operating cost.

The site selected for demonstrating this technology was the former Koppers Company (Koppers) site in Morrisville, North Carolina. This site was selected because a Risk Reduction Engineering Laboratory (RREL) SITE demonstration was planned for this site allowing for a conjunction of logistical and support efforts between RREL and EMSL-LV. However the PCP at the former Koppers site was not introduced using a petroleum hydrocarbon carrier. Because the HNU-Hanby test kit provides results only for soil in which a petroleum hydrocarbon carrier is present, samples were collected from the Winona Post site in Missouri and shipped to the former Koppers site for inclusion as demonstration samples. PCP contamination at the Winona Post site had been introduced using a diesel fuel carrier solvent.

The HNU-Hanby test kit is designed to provide quick, semiquantitative and quantitative results for PCP concentrations in soil samples. The test kit can provide PCP results only in samples which also contain a petroleum hydrocarbon carrier such as gasoline, kerosene, diesel fuel, or fuel oil. It cannot be used to determine PCP results for samples in which no petroleum hydrocarbon carriers are present. The HNU-Hanby test kit measures PCP indirectly by measuring the petroleum hydrocarbons carrier solvent remaining in the soil. The ratio of PCP in a petroleum hydrocarbon carrier may vary due to manufacturing processes, dilution variances, and the volatility and weathering of the petroleum hydrocarbon carrier. Therefore, site samples must be obtained so that site-specific calibration data can be prepared. This can be done by analyzing the samples both by EPA-approved methods and using the test kit. Calibration data can then be generated by correlating the PCP confirmatory results against the kit's corresponding response. The test kit uses the Friedel-Crafts alkylation reaction to detect the petroleum hydrocarbons. This reaction is colorimetric. A reflective photometer is used

to quantitatively measure the reaction color. A site-specific calibration is needed to determine the ratio of PCP to carrier solvent. This ratio is then used to correct the results from the reflective photometer.

The HNU-Hanby test kit is portable and can be operated outdoors. Temperature extremes and humidity do not seem to affect its performance. The reagents used with the test kit do not require refrigeration. The reflective photometer requires electricity but can be operated using a rechargeable battery pack. The test kit was found to be easy to operate by individuals with no prior environmental testing experience.

The test kit costs $1,195. This test kit provides enough reagent and glassware to perform 30 soil sample analyses. The reflective photometer used to provide quantitative data costs $3,500. Other equipment, such as extraction vials and pipettes, may need to be purchased when using the test kit. The cost of these items will vary depending upon the number of samples that will be analyzed. The detection limits reported by the test kit's developer is 1.0 part per million (ppm) for soil samples. A 5.0 ppm detection limit was used for this demonstration. The elevated detection limit was the result of reducing the sample mass used for extraction.

During the demonstration, 47 soil samples were extracted and analyzed in two 8-hour days. The average time to analyze one soil sample was about 21 minutes. The precision of the test kit was determined to be statistically the same as the precision of the confirmatory laboratory. The kit's data set was evaluated for accuracy as a whole and by concentrations less than and greater than 100 ppm PCP. When the entire data set was evaluated, the test kit's results were determined to be statistically different from the confirmatory results. This was also the case for samples in which the PCP concentrations were greater than 100 ppm. The test kit's data for samples containing less than 100 ppm PCP was shown to be statistically similar to the corresponding confirmatory data. Based on this evaluation, the test kit produced Level 1 data for samples containing greater than 100 ppm PCP and Level 2 data for samples containing less than 100 ppm PCP. This indicates that there was a concentration effect on the test kit's accuracy. The test kit showed greater comparability to the confirmatory data when PCP concentrations in samples were below 100 ppm.

Section 2
Introduction

This ITER presents information on the demonstration of the HNU-Hanby Environmental Test Kit, a field screening technology designed to detect PCP in soil. The demonstration was conducted by PRC under the EPA's SITE Program. The test kit was demonstrated in conjunction with the demonstrations of four other field screening technologies: (1) the Penta RISc Test System developed by EnSys Incorporated, (2) the EnviroGard PCP Test Kit developed by the Millipore Corporation, (3) the Penta RaPID Assay developed by the Ohmicron Corporation, and (4) the Field Analytical Screening Program PCP Method developed by EPA's Region 7 through its Superfund Program. The results of these other demonstrations are presented in reports similar to this one.

EPA's Site Program and MMTP: an Overview

At the time of the Superfund Amendments and Reauthorization Act of 1986 (SARA), it was well recognized that the environmental cleanup problem needed new and better methods. The SITE Program, therefore, was created to fulfill a requirement of SARA that the EPA address the potential of alternative or innovative technologies. The EPA made this program a joint effort between the Office of Solid Waste and Emergency Response (OSWER) and the Office of Research and Development (ORD). The SITE Program includes four parts:

- The Demonstration Program
- The Emerging Technology Program
- The Monitoring and Measurement Technologies Program (MMTP)
- The Technology Transfer Program

The largest part of the SITE Program, the Demonstration Program, is concerned with treatment technologies and is administered by ORD's NRMRL in Cincinnati, Ohio. The MMTP component, though, is administered by EPA's EMSL-LV. The MMTP is concerned with monitoring and measurement technologies that identify, quantify, or monitor changes in contaminants occurring at hazardous waste sites or that are used to characterize a site.

The MMTP seeks to identify and demonstrate innovative technologies that may provide less expensive, better, faster, or safer means of completing this monitoring or characterization. The managers of hazardous waste sites are often reluctant to use any method, other than conventional ones, to generate critical data on the nature and extent of contamination. It is generally understood that the courts recognize data generated with conventional laboratory methods; still, there is a tremendous need to generate data more cost effectively. Therefore, the EPA must identify innovative approaches, and through verifiable testing of the technologies under the SITE Program, ensure that the innovative technologies are equivalent to or better than traditional technologies.

The Role of Monitoring and Measurement Technologies

Measurement and monitoring technologies are needed to assess the degree of contamination, to determine the effects of contamination on public health and the environment, to supply data for selection of appropriate remedial action, and to monitor the success or failure of selected remedies. Thus, the MMTP is concerned with evaluating screening technologies, including remote sensing, monitoring, and analytical technologies.

Candidate technologies may come from within the federal government or from the private sector. Through the program, developers are to rigorously evaluate the performance of their technologies. Finally, by distributing the results and recommendations of those evaluations, the market for the technologies is enhanced.

Defining the Process

The demonstration process begins by canvassing the EPA's 10 regional offices (with input from OSWER and ORD) to determine their needs. Concurrently, classes of technologies are identified. An ideal match is made when there is a clear need by EPA's regions and a number of technologies that can address that need. The demonstrations are designed to judge each technology against existing standards and not against each other.

The demonstration is designed to provide for detailed quality assurance and quality control (QA/QC) to ensure that a potential user can evaluate the accuracy, precision, representativeness, completeness, and compar-ability of data derived from the innovative technology. In addition, a description of the necessary steps and activities associated with operating the innovative technology is prepared. Cost data, critical to any environmental activity, is generated during the demonstration and allows a potential user to make economic comparisons. Finally, information on practical matters such as operator training requirements, detection levels, and ease of operation is reported. Thus, the demonstration report and other informational materials produced by the MMTP provide a real-world comparison of that technology to conventional technologies. With cost and performance data, as well as "how to" information, users can determine whether a new technology better meets their needs.

Components of a Demonstration

Once a decision has been made to demonstrate technologies to meet a particular EPA need, the MMTP performs a number of activities. First, the MMTP identifies potential participants and determines whether they are interested in participating. Each developer is advised of the general nature of the demonstration and is provided with information common to all MMTP demonstrations. Information is sought from each developer about its technology to ensure that the technology meets the parameters of the demonstration. Then, after evaluation of the information, all respondents are told whether they have been accepted into the demonstration or not. While participants are being identified, potential sites also are identified, and basic site information is obtained.

The next component, probably the most important, is the development of plans that describe how the demonstration will be conducted. A major part of the EPA's responsibility is the development of a demonstration plan, a quality assurance project plan (QAPjP), and a health and safety plan. While the EPA pays for and has the primary responsibility for these plans, each is developed with input from all of the demonstration's participants. The plans define how activities will be conducted and how the technologies will be evaluated. The MMTP also provides each developer with site information and often predemonstration samples so the developer can maximize the field performance of its innovative technology. Generally, the developers train EPA-designated personnel to operate their technologies so that performance is not based on the special expertise of the developers. This also ensures that potential users have valid information on training requirements and the types of operators who typically use a technology successfully.

The field demonstration itself is the shortest part of the process. During the field demonstration, data is obtained on cost, technical effectiveness (compared to standard methods), and limiting factors. In addition, standardized field methods are developed and daily logs of activities and observations (including photos or videotape) are produced. The EPA is also responsible for the comparative, conventional method analytical costs and the disposal of any wastes generated by the field demonstration.

The final component of an MMTP demonstration consists of reporting the results and ensuring distribution of demonstration information. The primary product of the demonstration is an ITER, like this one, which is peer-reviewed and distributed as part of the technology transfer responsibility of the MMTP. The ITER fully documents the procedures used during the field demonstration, QA/QC results, the field demonstration's results, and its conclusions. A separate QA/QC data package also is made available for those interested in evaluating the demonstration in greater depth. Two-page technical briefs are prepared to summarize the demonstration results and to ensure rapid and wide distribution of the information.

Each developer is responsible for providing the equipment or technology product to be demonstrated, funding its own mobilization costs, and training of EPA--designated operators. The MMTP does not provide any funds to developers for costs associated with preparing equipment for demonstration or for development, and it does not cover the costs developers incur to demonstrate their products.

Rationale for this Demonstration

PCP, a regulated chemical used in the wood treatment industry, is included on the EPA Extremely Hazardous Substances List. Recently, PCP regulations under the Resource Conservation and Recovery Act (RCRA) have been created specifically for wood treatment facilities. PCP is included as a target compound of many EPA-approved analytical methods, including EPA 500 Series Methods 515.1 and 525, EPA 600 Series Methods 604 and 625, and EPA SW-846 Manual Methods 8040, 8151, 8250, and 8270. All of these methods use solvent extraction and gas chromatography. Detection and quantitation is performed with flame ionization, electron capture, or mass spectrometer detectors. Analyzing samples for PCP using these methods is typically costly and time consuming. EMSL-LV, therefore, identified the need for effective, accurate, low-cost screening technologies that could provide near real-time analytical data for PCP to Superfund and RCRA decisionmakers.

Demonstration Purpose, Goals, and Objectives

The HNU-Hanby test kit was qualitatively evaluated for the length of time required for analysis, ease of use, portability, and operating cost. It also was evaluated for accuracy and precision at detecting high and low levels of PCP in soil samples. The test kit's accuracy and precision were statistically compared to the accuracy and precision of a conventional confirmatory laboratory that had used EPA-approved analytical methods. These comparisons also were used to determine the highest data quality level that the test kit could attain in field applications. For the purpose of this demonstration the three primary data quality levels are defined as follows (EPA 1990):

Level 1: This data is not necessarily analyte-specific. Technologies that generate Level 1 data provide only an indication of contamination. Generally, the use of these technologies requires sample documentation, instrument calibration, and performance checks of equipment.

Level 2: This data is analyte-specific. To provide an accuracy check, verification analysis for at least 10 percent of the samples by an EPA-approved method is necessary. The method's analytical error is quantified. Use of QC procedures such as sample documentation, chain-of-custody procedures, sample holding time criteria, initial and continuing instrument calibration, method blank analysis, rinsate blank analysis, and trip blank analysis is recommended.

Level 3: This data is considered formal or confirmatory analysis. It is analyte-specific and generally involves second-method confirm-ation on 100 percent of critical samples. Analytical error is quantified (precision, accuracy, coefficient of variation) and monitored. The following QC measures are used: sample documentation, chain of custody, sample holding time criteria, initial and continuing instrument calibration, rinsate blank analysis, trip blank analysis, and performance evaluation samples. Detection limits are determined and monitored.

Inherent in the concept of data quality levels is accuracy. Although PRC could not find a reference that defined the expected and quantified accuracy of each data quality level, it imposed common accuracy criteria in defining these data quality levels. Data quality Level 3 is considered the most accurate of the three levels; this data is obtained by formal analysis using approved methods. Data quality Level 2 is less accurate but does quantify compound concentrations. Data quality Level 1 is the least accurate and is often considered survey data, only identifying the presence or absence of a compound or class of compounds.

Section 3
Predemonstration Activities

Several activities were conducted by EMSL-LV, PRC, and other demonstration participants before the demonstration began. These activities included identifying developers, selecting the demonstration sites, selecting the confirmatory laboratory and analytical methods, and conducting predemonstration sampling. Predemonstration sampling and analysis are normally used to allow developers to refine their technologies and revise their operating instructions, if necessary, prior to the demonstration.

Identifying Developers

EMSL-LV supplied PRC with the names of the immunoassay developers demonstrating technologies and asked that PRC search for other technologies that could be demonstrated simultaneously and inexpensively. PRC identified EPA Region 7's field gas chromatograph (GC) method and the HNU-Hanby test kit for inclusion in the demonstration.

Selecting the Sites

To evaluate the HNU-Hanby test kit under field conditions, a hazardous waste site suitable for the demonstration was needed. The following criteria were used to select the appropriate site:

- The test kit needed to be demonstrated on samples with a wide range of PCP contamination.
- PCP concentrations at the site had to be well characterized and documented.
- The site had to be accessible for conducting demonstration activities without interfering with any other activities being conducted on site.
- Because the test kit can only be applied when a petroleum product is the PCP carrier, the site used had to be contaminated by PCP in a petroleum product carrier.

The former Koppers wood treatment site was selected for conducting the analyses because it met the criteria for the other demonstrations and because NRMRL was planning a SITE demonstration of the ETG Environmental, Inc., Base-Catalyzed Decomposition technology at the site, allowing logistical and support efforts between NRMRL and EMSL-LV to be combined. However, the former Koppers site is contaminated with PCP in butane and isopropyl ether carrier solvents. Therefore, demonstration samples were collected from the Winona Post site in Missouri and shipped to the former Koppers site. Soils at the Winona Post site are contaminated with PCP in a diesel fuel carrier solvent.

The Winona Post site is located in Winona, Missouri, on Old Highway 60 West. It has operated as a sawmilling and wood preserving facility since at least the early 1950s. It currently treats pine and oak lumber with a solution of 5 percent PCP in diesel fuel. The solution is stored in a 20,000-gallon aboveground storage tank located adjacent to the treatment building. In the past, the Winona Post Company mixed its own solution from concentrated PCP. Prior to the mid-1950s, the Winona Post Company treated wood with creosol.

PCP is an organic chemical with an empirical formula of C_5Cl_5OH and a molecular weight of 266 grams per mole. PCP has a melting point of 191 °C and a boiling point of 310 °C. The specific gravity of PCP is 1.978 grams per cubic centimeter. PCP is described as almost insoluble in water, with 8 milligrams able to dissolve into 100 milliliters of water. The octanol ratio coefficient of PCP is 6,400, which indicates that PCP is tightly bound to the soil matrix when it is released into the environment.

PCP is used as a wood preservative, an insecticide, a preharvest defoliant, a slimicide, and a defoaming agent. The largest user of PCP is the wood treating industry. PCP is applied to wooden utility poles, railroad ties, and lumber to protect them from weathering and deteriorating due to fungus and rot. About 0.23 kilogram of PCP is required for each cubic foot of wood treated. For treating

wood, PCP is usually diluted to a 5 percent solution with solvents such as mineral spirits, kerosene, diesel fuel, or fuel oil. PCP also has been applied to wood with methylene chloride and liquified petroleum gas, such as butane. PCP also is used in the manufacturing of leather and tanning products, masonry products, rope and paper products, adhesives, and paint.

Selecting the Confirmatory Laboratory and Analytical Methods

Before the demonstration, the EPA Region 7 Laboratory arranged for all samples to be analyzed under the Region 7 Environmental Collection and Analysis Program (RECAP) Contract. SW-846 protocols for Level 3 data were used to analyze the samples during this demonstration. All samples were extracted by EPA Method 3540A (Soxhlet Extraction) and analyzed by EPA Method 8270A (Semivolatile Organic Compounds by Gas Chromatograph/Mass Spectrometer [GC/MS]: capillary column). Any samples in which PCP was not detected using Method 8270A were reanalyzed by Method 8151A (chlorinated herbicides by GC: capillary column) calibrated to PCP. All of these analytical methods are well established and approved by EPA. The QA procedures, reporting requirements, and data quality objectives of these methods are consistent with the goals of the SITE Program.

Training Technology Operators

The technology was operated by a PRC operator. Before the demonstration began, this individual was trained on how to use the technology. This training involved a review of operating procedures and instructions provided by the developer, and formal training by the developer. Training was equivalent to that recommended by the developer for those using the test kit on actual site characterization projects.

Predemonstration Sampling and Analysis

In August 1993, while demonstration sampling for the other technologies was being conducted at the former Koppers site, PRC collected five predemonstration soil samples from areas at the Winona Post site previously identified as containing PCP. These samples were submitted to HNU-Hanby. These samples were not analyzed by a confirmatory laboratory. HNU-Hanby Systems analyzed the predemonstration samples with the test kit and by GC/MS. The developer used this data to calculate calibration factors for the test kit.

Section 4
Demonstration Design and Description

The primary objective of the demonstration was to evaluate this test kit for its effectiveness at detecting PCP in soil when operated in field conditions. This objective included defining the precision, accuracy, cost, and range of usefulness for the test kit. A secondary objective was to define the data quality objectives that the test kit can be used to address. The evaluation was designed so that the test kit results could be compared to those of a confirmatory laboratory that analyzed each sample using standard EPA-approved methods. The design limited, as much as possible, those elements of sample collection and analysis that would interfere with a direct comparison of the results. These elements included heterogeneity of the samples and interference from other chemicals or other controllable sources.

The design also ensured that the data was collected in a normal field environment. To do this, the test kit was operated in a trailer located at the former Koppers site. The operator was trained by the developer and was able to call the developer with questions when necessary. The operator, though, obtained all results on his own and reported the results once he believed the results were accurate and precise. Standard QC samples were analyzed with each batch of environmental samples. Numerous laboratory and field duplicate samples were included among those analyzed to ensure a proper measure of precision. The technology was tested for common interferants. Qualitative measures, such as portability and ease of operation, were also noted by the operator. Overall, the demonstration was executed as planned in the demonstration plan (PRC 1993), which included the QAPjP. The final version of that plan was approved by all participants and developers before the demonstration began. Below is a discussion of selected elements of that plan and a full discussion of deviations from it.

Implementation of the Demonstration Plan

Forty soil samples and five soil field duplicates were collected at the Winona Post site. The soil samples were collected in areas believed to be contaminated with high (greater than 1,000 ppm), medium (100 to 999 ppm), and low (less than 99 ppm) concentrations of PCP. The identification of these areas was based on past sampling data and visual signs of waste disposal. All of the samples were collected, packaged, and shipped to the former Koppers site. Each soil sample was thoroughly homogenized and then split into six replicate samples. One replicate from each soil sample was submitted to the confirmatory laboratory for analysis using the methods described in Section 3. The remaining replicates were analyzed in the trailer at the former Koppers site using the various technologies being evaluated.

Field Modifications to the Demonstration Plan

Two field modifications were made to the approved demonstration plan used to demonstrate the five technologies, but neither influenced the test kit's results. First, fluorescein was to be added to the soil samples from the former Koppers site prior to homogenization. This test kit, though, was used only on samples from the Winona Post site, and the saturated silty nature of the Winona Post soil samples allowed easy and thorough homogenization. PRC, therefore, used an EPA-approved homogenization method and applied it to each sample for 10 to 15 minutes.

Data Collection

The operator prepared a subjective evaluation of how difficult the test kit was to use. Other qualitative factors included portability, ruggedness, instrument reliability, and health and safety considerations. Information on these qualitative factors was collected both by the operator of the test kit and by the project's lead chemist.

Accuracy and precision were statistically evaluated during this demonstration. To evaluate accuracy and precision, all samples collected for the demonstration were split between the test kit and the confirmatory

laboratory for analysis. The results from the confirmatory laboratory, for the purposes of this demonstration, were considered the actual concentration of PCP in each sample. The statistical methods used for the comparison are detailed later in this section. The cost of using the test kit also was assessed. Cost, for the purposes of this demonstration, includes expendable supplies, nonexpendable equipment, labor, and investigation-derived waste (IDW) disposal. These costs were tracked during the demonstration.

Statistical Analysis of Results

Besides looking at the data set as a whole, PRC grouped the data into results greater than 100 ppm and less than 100 ppm PCP. This grouping was intended to assess potential concentration effects on the data analysis. These data sets were prepared for the statistical analysis following the approved demonstration plan. When comparing duplicate samples or when comparing the results of a technology to those from the confirmatory laboratory, sample pairs that contained a nondetect were removed from the data sets. While other statistical methods can be used when nondetects are encountered, PRC felt that the variance introduced by eliminating these data pairs would be less than, or no more than equal to, the variance produced by giving not detected results an arbitrary value.

Intramethod Comparisons

Sample results from the test kit were compared to their duplicate sample results and to other QA/QC sample results. These comparisons are called intramethod comparisons. Intramethod precision was assessed through the statistical analysis of relative percent differences (RPD) between duplicates. First, the RPDs of the results for each sample pair in which both the sample and its duplicate were found to contain PCP were determined. The RPDs then were compared to upper and lower control limits. When using conventional technologies, such data is often available from analysis of samples collected during previous investigations. Because the technology being demonstrated was itself being assessed, the control limits used were calculated from data provided during this investigation. To determine these control limits, the standard deviation of the RPDs was calculated. This standard deviation was then multiplied by two and added to its respective mean RPD. This established the upper control limit for the technology. Because an RPD of zero would mean that the duplicate samples matched their respective samples perfectly, zero was used as the lower control limit. This resulted in a large range of acceptable values. All samples that fell within the control limits were considered acceptable. PRC determined that if at least 90 percent of the duplicate samples fell within these control limits, the technology had acceptable intramethod precision.

Intermethod Comparisons

The data sets also were statistically compared to the results from the confirmatory laboratory, and the precision of the technology was statistically compared to the precision of the confirmatory laboratory. These comparisons are called intermethod comparisons. In both cases, the results from the confirmatory laboratory were considered as accurate and precise as analytically possible.

The statistical methods used to determine intermethod accuracy were linear regression analysis and the Wilcoxon Signed Ranks Test. PRC prepared the data sets for the linear regression by averaging the field duplicate results. This was done to ensure that those samples were not unduly weighted in the regression analysis. PRC calculated linear regression by the method of least squares. Calculating linear regression in this way makes it possible to determine whether two sets of data are reasonably related, and if so, how closely. Calculating linear regression results in an equation that can be visually expressed as a line. Three factors are determined during the calculations: the y-intercept, the slope of the line, and the coefficient of determination, also called r^2. All three of these factors had to have acceptable values before the technology's accuracy was considered to meet Level 3 data quality requirements. The r^2 expresses the mathematical relationship between two data sets. If r^2 is equal to one, then the two data sets are directly related. Lower r^2 values indicate less of a relationship. Because of the nature of environmental samples, r^2 values between 0.85 and 1 were considered to meet data quality Level 3 accuracy requirements; r^2 values between 0.75 and 0.85 were considered to meet data quality Level 2 accuracy requirements; and r^2 values below 0.75 were considered not accurate, meeting, at best, Level 1 data quality objectives. The classification of data as Level 1, 2, or 3 was implied in the approved demonstration plan; however, these specific criteria were not presented.

If the regression analysis resulted in an r^2 between 0.85 and 1, then the regression line's y-intercept and slope were examined to determine how closely the two data sets matched. A slope of 1 and a y-intercept of zero would mean that the results of the technology matched those of the confirmatory laboratory perfectly. Theoretically, the farther the slope and y-intercept differ from these expected values, the less accurate the technology. Still, a slope or y-intercept can differ slightly from its expected value without that difference being statistically

significant. To determine whether such differences were statistically significant, PRC used the normal deviate test statistic. This test statistic results in a value that is compared to a table. The value at the 90 percent confidence level was used for the comparison. To meet data quality Level 3 requirements, both the slope and y-intercept had to be statistically the same as their ideal values. If the r^2 was between 0.75 and 0.85, and one or both of the other two regression parameters was not equal to their ideal, the test kit's results were considered inaccurate but to be of Level 2 quality. Results in this case could be mathematically corrected if 10 to 20 percent of the samples were sent to a confirmatory laboratory. Analysis of a percentage of the samples by a confirmatory laboratory would provide a basis for determining a correction factor. Only in cases where the r^2, the y-intercept, and the slope were all found to be acceptable did PRC determine that the test kit's results were accurate, meeting Level 3 data quality requirements. Data placed in the Level 1 category had r^2 values less than 0.75, the data was not statistically similar to the confirmatory data, based on nonparametric testing, or the results did not meet the manufacturer's performance specifications.

A second statistical method used to assess inter-method accuracy was the Wilcoxon Signed Ranks Test. This test is a nonparametric method for comparing matched pairs of data. It can be used to evaluate whether two sets of data are significantly different. The test requires no assumption regarding the population distribution of the two sets of data being evaluated other than that the distributions will occur identically. In other words, when one data point deviates, its respective point in the other set of data will deviate similarly. Because the only deviation expected during the demonstration was a difference in the concentrations reported by each technology, the two sets of data were expected to deviate in the same way. The calculation performed in the Wilcoxon Signed Ranks Test uses the number of samples analyzed and a ranking of the difference between the result obtained from a technology and the corresponding result from the confirmatory laboratory. The rankings can be compared to predetermined values on a standard Wilcoxon distribution table, which indicates whether, overall, the two methods have produced similar results. In cases where the linear regression produced an r^2 less than 0.75 and the Wilcoxon Signed Ranks Test indicated that the data sets were statistically similar, the regression data was not considered correct. Such occurrences were due to one or both data sets not meeting the fundamental assumption for regression analysis, normally distributed data sets.

Finally, the test kit's precision was statistically compared to the precision of the confirmatory laboratory using Dunnett's Test. This test was used to assess whether the precision of the test kit and that of the confirmatory laboratory were statistically equivalent. First, the mean RPD for all samples and their respective duplicates analyzed by the confirmatory laboratory was determined. The RPDs of each duplicate pair analyzed by the test kit was then statistically compared to this mean. It should be noted that a Dunnett's Test result showing the precisions are not similar does not mean that the precision of the technology was not acceptable, only that it was different from the precision of the confirmatory laboratory. In particular, Dunnett's Test has no way of determining whether or not any difference between the two data sets actually resulted because a technology's data was more precise than the confirmatory laboratory's. Verification of the Dunnett's Test results was provided by the Wilcoxon Signed Ranks Test.

Overall, for this demonstration, the determination of significance for inferential statistics was set at 90 percent. However, regression analysis was considered to show a significant relationship if the coefficient of determination (r^2) was greater than 0.85 for Level 3 data and between 0.75 and 0.85 for Level 2 data.

Section 5
Confirmatory Analysis Results

All samples collected during this demonstration were submitted to the EPA Region 7 Laboratory for confirmatory analysis under the RECAP Contract. The result for each sample is presented in a table near the end of Section 6.

Confirmatory Laboratory Procedures

EPA Region 7 Laboratory Quality Assurance and Data Evaluation (QADE) Branch personnel conducted a Level II data review on the results provided by the confirmatory laboratory. A Level II data review does not include an evaluation of the raw data or a check of calculated sample values. A review of the raw data and a check of the calculations was performed by QC personnel from the confirmatory laboratory before submitting the data package to EPA Region 7 Laboratory QADE Branch. PRC was not able to review all of the raw data generated from the analysis of samples. However, PRC did review the laboratory case narratives and the EPA Region 7 Laboratory QADE Branch comments generated by the Level II data review. The following paragraphs discuss specific procedures used to identify and quantitate semivolatile organic compounds (SVOC), specifically PCP, using the following methods: EPA Method 8270A and EPA Method 8151A.

Sample Holding Times

All of the analytical methods used for confirmatory analysis require that all sample extractions be completed within 7 days from the time a sample was collected. Due to the stability of PCP, ORD's Methods Validation Section extended these holding time requirements by 4 days for this demonstration. The analysis of the sample extracts must be completed within 40 days of validated sample receipt. The holding time requirements for the samples collected during this demonstration were met.

Sample Extraction

The method used for the extraction of soil samples prior to analysis by EPA Method 8270A was EPA Method 3550. EPA Method 3550 involves sonication extraction of the soil using methylene chloride. The confirmatory laboratory used both the low concentration extraction method and the high concentration extraction method discussed in EPA Method 3550. To determine the appropriate extraction method to use for the analysis of individual soil samples, the confirmatory laboratory screened each sample using the screening techniques recommended in EPA Method 8270A. Soil samples with concentrations at or near the detection limits of Method 8270A were reanalyzed using Method 8151A. EPA Method 8151A includes an acidification of the soil sample followed by an ultrasonic extraction with methylene chloride. This extraction is similar to EPA Method 3550's sonication extraction. The soil sample extract was then taken through an acid-base partition. The acid-base partition was used to remove potentially interfering compounds from the sample extract. The sample extract was then concentrated and taken through a diazomethane derivatization. This procedure replaces the hydrogen atom of the alcohol group with a methyl anion. This derivatization removes the polarity associated with PCP and enables improved chromatographic behavior. PCP standards used for sample identification and quantitation were taken through the same derivatization steps to allow a direct comparison of concentration. That is, no correction factor needs to be used for the molecular weight of the derivatization product.

Detection Limits and Initial and Continuing Calibrations

The detection limit for samples analyzed by EPA Method 8270A was reported as 0.330 ppm. The detec-

tion limit for soil samples analyzed by EPA Method 8151A was reported as 0.076 parts per billion. Method-required initial and continuing calibration procedures were appropriately conducted, and all method-required criteria for these calibrations were met.

Sample Analysis

The confirmatory laboratory performed sample analysis by first screening samples using EPA Method 8270A. Based upon the screening results, the samples were extracted with either the low concentration method or the high concentration method discussed in EPA Method 3550. Samples that did not provide a positive response for PCP with EPA Method 8270A were analyzed by EPA Method 8151A.

For EPA Method 8270A, compound identification was required to meet two criteria: (1) the sample component relative retention time was to fall within $\pm$ 0.06 relative retention time units of the standard component, and (2) the mass spectrum of the sample compound was to correspond with the standard compound mass spectrum. If compound identification was not made, samples were analyzed by EPA Method 8151A. For EPA Method 8151A, compound identification was made if a sample peak eluted within the retention time window established during the initial calibration.

Quality Control Procedures

Method blanks are used to monitor the presence of laboratory-induced contamination. The EPA Region 7 Sample Management Office (SMO) provided blank soil for use as method blank samples. An acceptable method blank must not provide a positive response for the target compounds above the reported detection limit. Method blank samples were stored, extracted, and analyzed in exactly the same manner as the demonstration samples. Results for all method blank samples extracted and analyzed were found to be acceptable.

Internal standards were used for the analysis of demonstration samples by EPA Method 8270A. Internal standards were added to all standards, blanks, samples, and QC samples prior to injection into the GC/MS system. The internal standards were used to provide response factors for each of the target compounds. Six samples exhibited internal standard responses which were outside of the QC limits of 50 to 150 percent recovery. All of the affected samples provided internal standard responses which were less than 50 percent. The soil samples affected were samples 060, 062, 068, 090, 091, 095. Of these samples, three -- 090, 091, and 095 -- were found to contain no detectable levels of PCP, and no corrective action was taken. Instead, they were reanalyzed using EPA Method 8151A. The remaining samples were reanalyzed to verify that the internal standard response was below 50 percent recovery. The reanalysis showed that internal standard response was below 50 percent recovery. No corrective action was taken by the laboratory, which attributed the low recovery to matrix effects inherent to the samples. The Region 7 Laboratory QADE Branch reached the same conclusion during its review of the data.

Surrogate standards were used to evaluate the efficiency of the extraction and analysis processes and to evaluate matrix effects. Surrogate standards used for EPA Method 8270A include deuterated standards which provide a different mass spectrum when compared to the nondeuterated compound. The surrogate standard used for EPA Method 8151A was 2,4-dichlorophenylacetic acid (DCAA). The DCAA acceptance range was determined by the RECAP and Region 7 Laboratory through a statistical analysis of 30 or more standard surrogate recoveries. The mean and standard deviation were then calculated, and the acceptance range was determined by applying a $\pm$ 3 standard deviation around the mean. All samples analyzed with EPA Method 8151A provided surrogate recoveries that fell within the laboratory-generated control limits.

Matrix spike samples are aliquots of original sample into which a known concentration of the target compounds were added. The EPA Region 7 Laboratory SMO designated the samples which were to be used as matrix spike samples. The designated soil samples were samples 073, 087, and 098, all analyzed using EPA Method 8270A, and sample 089, analyzed using EPA Method 8151A. The soil matrix spike samples were spiked with all of the target compounds reported by the method. Soil matrix spike data for PCP is shown in Table 5-1. The recoveries of these samples were greatly influenced by the high concentrations of PCP present in the original sample relative to the amount spiked. Only one sample, 098, resulted in recoveries for both the matrix spike and matrix spike duplicate sample which could be considered acceptable. A clear evaluation of the effects of matrix on PCP recovery is not possible due to the high concentrations of PCP in the sample and the comparatively low levels of PCP added to the matrix spike samples.

Data Reporting

The data report PRC received from the EPA Region 7 Laboratory included a standard EPA Region 7 Analysis Request Report. Results were reported on a dry weight basis, as required in the methods. PRC obtained data on

TABLE 5-1. MATRIX SPIKE AND MATRIX SPIKE DUPLICATE RESULTS.

Sample No.	Amount Found In Original Sample (ppm)	Amount Added To Matrix Spike Sample (ppm)	Amount Found In Matrix Spike Sample (ppm)	Percent Recovery (%)
073	86.0	11.0	130	400
087	46.0	1.40	57.0	786
089	0.247	0.098	0.315	69
098	0.70	0.41	0.82	29

Sample No.	Amount Added To Matrix Spike Duplicate Sample (ppm)	Amount Found In Matrix Spike Duplicate Sample (ppm)	Percent Recovery (%)	Relative Percent Difference (%)
073	11.0	93.0	64	145
087	1.40	64.0	1,285	48
089	0.098	0.241	0	200
098	0.41	0.98	68	80

the loss-on-drying determination for each of the samples. The loss-on-drying values were used to convert the confirmatory laboratory data from a dry weight basis to a wet weight basis.

Results were reported by the confirmatory laboratory in micrograms per kilogram (μg/kg) for soil samples. Soil sample results were converted to milligrams per kilogram (mg/kg) so they could be compared to the results from the technologies, all of which reported results for soil samples in mg/kg.

Data Quality Assessment

Accuracy refers to the difference between the sample result and the true concentration of analyte in the sample. Bias, a measure of the departure from complete accuracy, can be caused by such processes as loss of analyte during the extraction process, interferences, and systematic contamination or carryover of an analyte from one sample to the next. Accuracy for the confirmatory laboratory was assessed through the use of two performance evaluation (PE) samples purchased from Environmental Research Associates (ERA). These samples contained a known quantity of PCP. ERA supplied data sheets for each PE sample which included the true concentration and an acceptance range for the sample based on the 95 percent confidence interval taken from data generated by ERA and EPA interlaboratory studies. The true value concentration of soil PE sample 099 (the low-level sample) was 7.44 ppm with an acceptance range of 1.1 to 13 ppm. The result reported by the confirmatory laboratory for this sample was 4.02 ppm, which was within the acceptance range. The percent recovery of this sample by the confirmatory laboratory was 54 percent. The true concentration of soil PE sample 100 (the high-level sample) was 101 ppm with an acceptance range of 15 to 177 ppm. The result reported for this sample by the confirmatory laboratory was 52.4 ppm, which was within the acceptance range. The percent recovery of this sample by the confirmatory laboratory was 52 percent.

Precision refers to the degree of mutual agreement among individual measurements and provides an estimate of random error. Precision for the confirmatory laboratory results was determined through the use of field duplicate samples. Normally laboratory duplicates are used for this. However, no laboratory duplicates were analyzed by the confirmatory laboratory. Field duplicates are two samples collected together but delivered to the laboratory with separate sample numbers. Typically, field duplicate samples are used to measure both sampling and analysis error. PRC established control limits for field duplicate RPDs. These control limits are similar to those used to determine matrix spike recovery acceptance control limits. To establish the control limits, all sample pairs that did not produce two positive results were removed from the data set. Then the RPD for each pair was calculated, and the mean RPD and standard deviation were determined. The lower control limit was set at zero because this would mean that the

results from a duplicate and its sample matched perfectly. The upper control limit was set by multiplying the standard deviation by two and adding it to the mean RPD. The RPD of each sample pair was then compared to these control limits. Each sample pair RPD was expected to fall within the control limits.

Five field duplicate samples were collected and analyzed by the confirmatory laboratory during this demonstration. RPD values for the duplicate pairs ranged from 4 to 58. The mean RPD value of the soil field duplicate pairs was 23 percent, with a standard deviation of 25 percent. For the soil field duplicate pairs the control limits were found to be 0 to 73 RPD. All of the five field duplicate sample pairs fell within this range. Overall, this data shows excellent agreement between the samples and their respective field duplicates, indicating a high degree of precision by the confirmatory laboratory. The mean RPD also indicated that the method used to homogenize the samples before splitting them for analysis was highly effective.

Completeness refers to the amount of data collected from a measurement process compared to the amount that was expected to be obtained (Stanley and Verner 1983). For this demonstration, completeness referred to the proportion of valid, acceptable data generated by the confirmatory laboratory. The completeness objective for this project was 95 percent. Completeness for the confirmatory laboratory was 100 percent.

Confirmatory Laboratory Costs and Turnaround Times

The cost for performing PCP analysis by EPA-approved analytical methods varies from laboratory to laboratory. The cost of analysis depends upon the number of samples submitted for analysis, the matrix, and the level of QC performed. The following costs are given as general guidelines. EPA Method 8270A analysis costs range from $250 to $400 per sample. EPA Method 8151A analysis costs range from $150 to $250 per sample. Turnaround times for samples submitted for analysis with EPA-approved analytical methods range from 14 to 30 days. The turnaround time also depends upon the number of samples submitted for analysis, the matrix, and the level of QC performed. Faster turnaround times may be available for an additional cost.

Section 6
HNU-Hanby Environmental Test Kit

The HNU-Hanby test kit is designed to provide quick, quantitative results for aromatic and petroleum compounds in soil samples. This test kit determines PCP concentrations in soil samples indirectly by measuring the carrier solvents used in wood treating that contain PCP. This application assumes that the ratio of carrier solvent concentration to PCP concentration is constant. HNU-Hanby Systems claims that the test kit can detect petroleum carrier solvents containing PCP at concentrations as low as 1 to 5 ppm in soil. The test kit uses the Friedel-Crafts alkylation reaction to detect aromatic and petroleum hydrocarbon compounds in soil. In the Friedel-Crafts alkylation reaction, an aromatic substitution occurs where the aromatic ring attacks a carbocation electrophile. The electrophile is formed by the reaction of a Lewis acid catalyst, such as aluminum chloride, with an alkyl halide. An excess amount of this catalyst is added to act as a dehydrant to enable the Friedel-Crafts reaction to proceed. Electrophile aromatic substitution products are generally very large molecules with a high degree of electron dislocation that cause intense coloring. When using the test kit, the sample's color is then compared to site-specific color standards for a semiquantitative assessment of PCP concentrations.

The standards are produced by analyzing several samples from the site. These samples should contain PCP concentrations representative of contamination at the site. The analysis is conducted using a GC/MS to determine the PCP-to-carrier solvent ratio. Alternatively, the change in the color can be read in millivolts using a reflective photometer. In this method, a PCP calibration chart is developed between millivolt readings and the concentration of PCP based on the GC/MS analysis. The sample reading as obtained from the reflective photometer is then cross-referenced with the calibration charts to obtain a quantitative sample result for PCP. HNU-Hanby Systems has said that the test kit is extremely sensitive due to the intense coloring that develops during the Friedel-Crafts reaction.

Because the Friedel-Crafts reaction involves only aromatic compounds, this test kit does not work on all PCP carriers. Only those carriers that have aromatic compounds, such as gasoline, diesel fuel, and kerosene, can be detected.

Generally, PCP is added in a certain percentage to the carrier solvent for application onto wood. This percentage may differ from site to site. To assess the ratio between the carrier solvent and PCP in the Winona Post samples, HNU-Hanby Systems obtained contaminated soil samples collected from Winona Post site, diluted these samples when required, and analyzed these samples for PCP. Later, the same samples were analyzed using the test kit, and the corresponding reflective photometer readings in millivolts were obtained. A regression line was then calculated to allow the kit's operator to predict PCP concentrations when millivolt readings were known. This type of site-specific calibration should minimize the effect of the weathering of the carrier solvent that could affect the ratio. Following the completion of the demonstration, HNU-Hanby Systems sent the PCP calibration data to PRC. This data is presented in Table 6-1.

TABLE 6-1. CALIBRATION DATA.

Reflective Photometer Reading (millivolts)	PCP Concentration (ppm)
890	0.00 (Blank)
826	0.20
738	0.50
670	1.00
556	2.00
434	5.00
223	25.0
111	100
89	200
79	1,000

Operational Characteristics

The HNU-Hanby test kit weighs about 17 pounds and comes in a rugged, plastic carrying case. The carrying case is 15 inches high by 19 inches wide by 8 inches deep. Overall, the test kit was found to be portable. Each test kit contains the following materials: (1) a 10-milliliter graduated cylinder, (2) a 50-milliliter beaker, (3) 36 screw-top test tubes, (4) 30 ampules of extraction solvent consisting of 20 percent carbon tetrachloride and 80 percent heptane, (5) 30 vials of color development reagent such as aluminum chloride, (6) a 500-milliliter separatory funnel, (7) a tripod ring stand, (8) one pair of safety glasses, (9) six pairs of plastic gloves, (10) an instructional video, (11) a color chart depicting test results, and (12) a reflective photometer.

Other materials used by the operator during the demonstration besides those mentioned above included: (1) a scale capable of measuring $\pm$ 0.05 grams, (2) a stainless-steel spatula, (3) laboratory wipes, (4) a stop watch, (5) pipette bulb, and (6) marking pens.

The test kit's logistical requirements include electricity or battery replacements. For this demonstration, a fume hood also was used because the extraction solvent contains carbon tetrachloride. All extraction and analysis can be carried out in a small open area or within a small fume hood. The test kit requires approximately 2 square feet of work surface. The reflective photometer can be operated using a 110-volt or 220-volt electrical supply. This instrument also is equipped with a rechargeable battery. This battery requires 8 to 24 hours of charging, and when fully charged, the battery can last up to 8 hours.

The operator chosen to analyze samples using the technology was Mr. Dan Fenton, an employee of PRC. Mr. Fenton has worked for PRC for 2 years. He has been primarily involved in environmental potentially responsible party searches and the writing of Superfund enforcement memorandums. He has had 6 credit hours of college inorganic chemistry and 4 credit hours of inorganic laboratory. Training was conducted by the technology developer. Mr. Fenton received training from HNU-Hanby Systems and reviewed a training videotape that explained the operation of the technology. HNU-Hanby Systems prepared the calibration factors for the final data evaluation.

Mr. Fenton found the test kit easy to operate. Prior experience in analytical chemistry is useful, but not required. Operation of the test kit involves weighing samples, carefully breaking open glass ampules, shaking vials, adding catalyst to vials and measuring readings on the reflective photometer. The test kit is designed for use either in the field or in a laboratory. Some of its instrumentation and equipment require special handling. This instrumentation includes the reflective photometer, the portable balance, and the pipettor. This equipment must be handled carefully to avoid damage. The prototype reflective photometer failed to give consistent results because the batteries were weak. The reflective photometer had no low battery indicator to warn the operator. When the weak battery was noted, the photometer was plugged into an available electricity outlet. Also, highly contaminated samples turned black and developed gas pockets. These samples seemed to interfere with the precision of the reflective photometer readings.

The photometer's reliability was monitored daily by checking a white calibration standard. The reflective photometer should read 1,020 millivolts when analyzing the white calibration standard. As the intensity of the color increases, the corresponding millivolt reading decreases. The calibration check should give the highest reading. During the two calibration checks conducted during the sample analysis, the reflective photometer read 812 and 866 millivolts. HNU-Hanby Systems said that these readings were within the acceptable range of a calibration check.

The test kit uses a proprietary solvent to extract organic compounds from different sample matrices. This solvent contains heptane and carbon tetrachloride. The test kit also uses aluminum chloride in large amounts as a Lewis acid catalyst. Care should be taken when using these chemicals. Heptane is a highly flammable solvent that tends to explode in the presence of an ignition source. Carbon tetrachloride is a probable human carcinogen. Aluminum chloride is a probable teratogen that reacts violently with alkenes. It is recommended that proper personal protective wear, such as gloves and safety glasses, be worn when handling these chemicals.

The HNU-Hanby test kit is priced at $1,195. This test kit contains color charts for color interpretation; it does not include a reflective photometer. Each test kit contains enough reagents and other supplies to analyze 30 samples. The cost of HNU-Hanby Systems' reflective photometer is $3,500. Other costs associated with the analysis were the cost of 40-milliliter vials, the cost of pipettes and a pipette bulb, and the operator cost. The operator cost depends on the operator's qualifications and experience. The total cost for quantitative application of this test kit , excluding operator's costs, was about $6,000 for the 52 samples analyzed, which is about $112 per sample. However, as more samples are analyzed, the cost of the reflective photometer will be

distributed among more samples, reducing the per sample cost. When used semiquantitatively, the cost of the reflective photometer can be deducted from the total cost. In the semiquantitative analysis, the color developed by each sample is compared to the standard color chart, which is included in the test kit for the determination of the concentration. In this case, the cost per sample for this demonstration would be about $48. Waste disposal cost is not included in the cost per sample described above. The waste generated during this demonstration filled approximately one-half of a 55-gallon drum. The disposal cost for this quantity of PCP-contaminated laboratory waste is approximately $1,000.

Performance Factors

The sensitivity of the method depends on the sensitivity of the reflective photometer. The literature on this method claims that aromatic compounds as low as 1.0 ppm can be detected in soils. In fact, the calibration chart prepared for the test kit shows a range from 0.2 ppm to 1,000 ppm. During this demonstration, all sample extracts that developed moderate to dark color were diluted with the proprietary solvent. This dilution was performed by taking 0.3 milliliter of sample extract and adding 10 milliliters of solvent. This produced a 172-fold dilution for a 1.0 gram soil sample. These dilutions increased the detection limits for the samples involved. The modified detection limit was 5 ppm.

HNU-Hanby Systems has stated that 50 samples can be analyzed in an 8-hour work day. During this demonstration, the average time taken to extract each sample and prepare it for analysis was 21 minutes. The analysis of the prepared sample in the reflective photometer required less than 1 minute. Based on the average time of 21 minutes per sample, approximately 22 samples were analyzed in an 8-hour day. This number was influenced by factors such as the number of samples that required dilution, and the analysis of QC samples.

The linear range of the test kit is dependent on the linear range of the reflective photometer. The linear range of the reflective photometer was not evaluated during the demonstration. However, HNU-Hanby Systems sent the calibration data which included a PCP concentration range of 0.2 ppm to 1,000 ppm. When this data between the millivolt readings and PCP concentrations was plotted on a normal-scale plot, the coefficient of determination (r^2) indicated that the response between the reflective photometer readings and corresponding PCP concentrations was not linear. A natural logarithm transformation of the data gave a linear response with an r^2 of 0.96.

Drift in this method was considered the instability associated with reflective photometer readings. As noted by the operator, whenever the battery was either fully charged or weak, sample readings fluctuated more. This problem was later solved by connecting the instrument to an outlet.

Intramethod Assessment

Reagent blank samples were prepared by taking reagents through all extraction and reaction steps of the analysis. Reagent blanks were prepared with each batch of 20 samples. Two reagent blanks were prepared and analyzed during the demonstration. The reagent blank samples did show some readings on the reflective photometer. When these millivolt readings were converted to PCP concentrations, they gave values of 2.19 ppm and 1.8 ppm. Both of these values are below the technology's detection limit of 5 ppm used during this demonstration. Therefore, none of the data was rejected because of reagent blank contamination.

Completeness refers to the amount of data collected from a measurement process compared to the amount that was expected to be obtained (Stanley and Verner 1983). For this demonstration, completeness refers to the proportion of valid, acceptable data generated using the technology. The completeness objective for this project was 90 percent. Forty-five soil samples including field duplicates were analyzed during the demonstration. Two reagent blanks and five laboratory duplicates were analyzed along with the 45 samples. Results were obtained from all samples. Completeness for the samples analyzed by the kit was 100 percent.

Intramethod precision was assessed by determining the method's ability to reproduce its results on duplicate samples. These duplicate samples included five laboratory duplicates and five field duplicates. Usually these duplicate samples are used to determine matrix variability and the effects of using several operators. To use the duplicates to measure the method's precision, PRC both controlled for matrix variability by thoroughly homogenizing the samples and controlled for operator effects by using only one operator for the entire demonstration. Laboratory duplicate samples are two analyses performed on a single sample delivered to a laboratory. Five laboratory duplicates were analyzed by this technology. The results of laboratory duplicate analyses are presented in Table 6-2. The initial analysis of the duplicate samples ranged from 158 to 4,590 ppm. When the analysis was duplicated, the results ranged from 130

TABLE 6-2. LABORATORY DUPLICATE RESULTS.

Sample No.	Original Sample Result (ppm)	Laboratory Duplicate Sample Result (ppm)	Relative Percent Difference (%)
059D	4,590	4,320	6
062	748	775	4
064	354	395	11
066	213	440	70
067	158	130	19

TABLE 6-3. FIELD DUPLICATE RESULTS.

Sample No.	Original Sample Result (ppm)	Field Duplicate Sample Result (ppm)	Relative Percent Difference (%)
059	3,130	4,590	38
073	8.60	7.42	15
074	40	32.5	21
086	7.54	5.86	25
087	4.94	4.17	17

to 4,320 ppm. Field duplicate samples also were analyzed during the demonstration. Field duplicates are two samples collected together but brought to the laboratory with separate sample numbers. Five field duplicate samples were collected and analyzed by this technology during the demonstration. The results for the field duplicate samples are included in Table 6-3. The RPDs between original samples and their duplicates were calculated. The RPDs for all duplicate samples ranged from 4 to 70 percent. Even the best technology that determines results quantitatively cannot reproduce its results every time. Therefore, PRC established control limits like those sometimes used to evaluate laboratory duplicates. These control limits were then used to determine whether the difference between a result from a duplicate and the result from its respective sample was reasonable. The RPD for each sample pair was calculated, and the mean RPD and population standard deviation were determined. The lower control limit was set at zero because this would mean that the results from a duplicate and its sample matched perfectly. The upper control limit was set by multiplying the standard deviation by two and adding it to the mean RPD. The RPD of each sample pair was then compared to these control limits. Each was expected to fall within them. If greater than 90 percent fell within this range, the technology's precision was considered adequate. If fewer than 90 percent of them fell within this range, the data was reviewed, and if no explanation could be found, the technology's precision was considered inadequate.

The control limits established using the procedure delineated above were from 0 to 61 percent. Comparing the RPDs to these control limits showed that only one sample's RPD was outside the control limit. As a result, 90 percent of RPDs fell within the control limits making the technology's precision acceptable.

Comparison of Results to Confirmatory Laboratory Results

The quantitative results of the test kit were analyzed by using the linear regression techniques and the inferential statistics detailed in Section 5. All of the data used for the analyses is presented in Table 6-4. The initial linear regression analysis was based on results from 32 samples. The concentrations found in eight of the samples were below the test kit's detection limit and, therefore, were not used in the comparative analysis. The r^2 for this regression was 0.19, indicating that little or no relationship exists between the data sets. A residual analysis of the data, though, identified samples 59 to 62, 65, 72, 75 and 76 as outliers. PRC removed these points, recalculated the regression, and defined an r^2 of 0.31, still indicating that little or no relationship exists between the two data sets. The parameters of this regression line are shown on Table 6-5. Figure 6-1 shows the regression graphically. The Wilcoxon Signed Ranks Test was used to verify these results. It indicated at a 90 percent confidence level that the data was significantly different from that of the confirmatory laboratory. These results indicate that this test kit is not accurate and that it cannot be mathematically corrected to estimate corresponding confirmatory data. This places test kit results for the combined soil data set into the Level 1 data quality category.

The confirmatory laboratory found that 16 of the 32 samples had concentrations less than 100 ppm. Of these the test kit detected contamination above the detection limit in only 10 samples. The initial linear regression on these 10 samples defined an r^2 of 0.23, indicating that little or no relationship exists between the two data sets. A residual analysis of the data identified no samples as outliers. However, the Wilcoxon Signed Ranks Test indicated at a 90 percent confidence level that the method's data was not significantly different from that of the confirmatory laboratory. This contradicts the regression analysis and indicates that one or both of the data sets do not meet the condition of normality required for regression analysis. Therefore, the regression data

TABLE 6-4. SUMMARY OF DEMONSTRATION DATA.

Sample No.[a]	HNU-Hanby Environmental Test Kit (5 ppm)[b]	Confirmatory Laboratory (ppm)	Sample No.[a]	HNU-Hanby Environmental Test Kit (5 ppm)[b]	Confirmatory Laboratory (ppm)
059	3,130	9,600	079	562	792.0
059D	4,590	10,260	080	263	2,550
060	1,030	1,008	081	8.16	125.0
061	1,400	2,744	082	127	2,400
062	748	138.0	083	9.46	270.0
063	445	1,610	084	83.4	1,140
064	354	1,978	085	5.27	57.70
065	1,200	1,577	086	7.54	6.59
066	213	57.80	086D	5.86	6.88
067	158	110.0	087	5.94	34.00
068	218	47.70	087D	5.17	51.80
069	540	798.0	088	2.72[d]	2.58
070	435	2,888	089	2.14[d]	0.21[c]
071	181	289.0	090	2.65[d]	0.55[c]
072	5,570	336.0	091	2.55[d]	0.28[c]
073	8.60	74.80	092	2.43[d]	0.57[c]
073D	7.42	78.20	093	2.36[d]	0.19[c]
074	40.0	836.0	094	4.47[d]	1.02[c]
074D	32.5	1,520	095	89.4	0.088[c]
075	303	3,692	096	108	59.80
076	751	4,590	097	7.63	14.60
077	508	2,040	098	2.78[d]	0.57
078	252	1,720			

Notes:

[a] All samples numbered before 059 were collected at the former Koppers site and, therefore, were not analyzed by the operator of this technology.

[b] Detection limit. When below the detection limit the sample's result was not considered during the regression analysis..

[c] Sample analyzed by Method 8151A; all other samples were analyzed by Method 8270A.

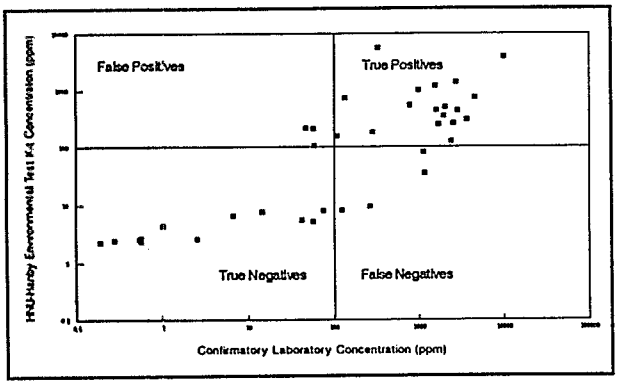
[d] Result is below detection limit.

TABLE 6-5. SUMMARY OF REGRESSION AND RESIDUAL STATISTICS

	N	r^2	Y-int	Slope	Wilcoxon Probability
All Data	37	0.27	126	0.16	Significant difference
<100 ppm	16	0.16	14	1.2	No significant difference
>100 ppm	20	0.04	308	0.22	Significant difference

Notes:
N Number of data points
r^2 Coefficient of determination adjusted for variance
Y-int Y-axis intercept of the regression line

FIGURE 6-1. REGRESSION OF DATA.



was considered suspect. These results indicate that this technology produces data statistically similar to the confirmatory laboratory. This factor places this technology into the level 2 data quality category for the samples with PCP concentrations less than 100 ppm; however, the data cannot be mathematically corrected.

The confirmatory laboratory found that 23 of the 32 samples contained PCP concentrations of more than 100 ppm. The initial linear regression on these samples defined an r^2 of 0.09, indicating that no relationship exists between the two data sets. A residual analysis of the data identified samples 59, 72, and 79 as outliers. PRC removed these three points, recalculated the regression, and defined an r^2 of 0.04, still indicating that no relationship exists between the two data sets. The Wilcoxon Signed Ranks Test verified these results. These results indicate that this test kit is not accurate and that it cannot be mathematically corrected to estimate corresponding confirmatory data. This factor places this technology for the samples with PCP concentrations above 100 ppm into the Level 1 data quality category.

To compare the precision of the test kit's results to the precision of the confirmatory laboratory's results, a Dunnett's Test was performed on the RPDs determined from the field duplicate samples and their respective samples. The Dunnett's Test determines the probability that the data sets on which it is based are the same. If the RPDs from the confirmatory laboratory and those from the technology are the same, then it can be assumed that the precisions are also similar. A Wilcoxon Signed Ranks Test was used to supplement the Dunnett's test results. The Wilcoxon Signed Ranks Test was used to test the hypothesis that no significant difference exists between the technology's RPDs and the confirmatory laboratory's RPDs. When the Dunnett's Test compared the RPDs between the method's data set and the confirmatory laboratory data set, it indicated the precisions were statistically similar. The Wilcoxon Signed Ranks Test confirmed this data.

Section 7
Applications Assessment

The principal advantage of the test kit is that it can analyze a large number of samples in a short period of time. Other advantages include the following: (1) the test kit is inexpensive when compared to formal laboratory analysis using EPA-approved methods for PCP, (2) it is simple to operate even for individuals with no prior experience using the test kit, (3) it is portable and can be operated outdoors, (4) it requires electricity, but a rechargeable battery can be used without the need for an electrical hookup at the site, and (5) its reagents do not require refrigeration.

The principal limitations of the test kit are (1) that it can only be used on sites where petroleum products are the carrier solvent for PCP, and (2) that it provides only an indirect measurement of PCP concentration. The test kit requires detailed site-specific calibration prior to use. This indirect measurement is performed through a measurement of petroleum hydrocarbons in a sample. An estimated ratio of PCP versus the petroleum hydrocarbon carrier is calculated and used to correct the sample results. The test kit, therefore, can only be used at sites where the PCP to petroleum carrier solvent ratio is stable, and it cannot be used to determine PCP results in samples where no petroleum hydrocarbon carriers are present. The ratio of PCP in a petroleum hydrocarbon carrier may vary due to manufacturing processes, dilution variances, and the volatility and weathering of petroleum hydrocarbon carriers. This volatility and weathering may change with depth, and thus, the ratio-based calibration may vary with depth. All of these variances can lead to errors when interpreting PCP results. It is essential that samples from the site be investigated and analyzed for the purpose of preparing site-specific calibration data.

The test kit's estimation of PCP concentrations in samples was generally found not to agree with results from the confirmatory laboratory. However, for samples contaminated with less than 100 ppm of PCP, the technology's data was statistically similar to the confirmatory data. The test kit contains the hazardous chemicals heptane, carbon tetrachloride, and aluminum chloride. Proper safety and disposal practices need to be employed when using the technology.

The test kit can be used to provide screening results for PCP soil samples. HNU-Hanby Systems also markets it for use on water samples. The demonstration results indicate that the test kit is most accurate with samples containing less than 100 ppm PCP. Therefore, it should only be used to produce Level 2 data at sites where the PCP action level is below 100 ppm.

Generally, the larger the site or the larger the number of samples which will be collected, the greater the advantage of using the test kit. The use of the test kit at these types of sites will decrease the cost of the investigation by enabling more work to be completed during a single sampling visit. The use of the test kit can allow work to continue without having to wait for confirmatory laboratory results. The results of the demonstration indicate that the test kit can be used as an EPA Level 1 screening tool over a wide concentration range. However, the kit will not detect PCP if the carrier solvent is heavily weathered and is no longer present in the sample. This could lead to a false determination of no PCP present in the sample. This failure to detect the presence of a contaminant does not meet Level 1 criteria. For PCP concentrations of less than 100 ppm at a site where the PCP-to-carrier ratio appears stable, this demonstration indicates that the test kit can produce Level 2 data. The determination of data quality levels will be site-specific and dependent on the stability of the PCP-to-carrier ratio. Field investigators should confirm that results obtained from the test kit correlate with confirmatory laboratory results. Field investigators must realize that the test kit is designed only as a screening tool to assist in evaluating petroleum contamination and its use as a PCP screening tool is very site-specific.

Section 8
References

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