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Project 1263-23
Final Report
October 1986



Field Evaluation of the S-Cubed Model PCBA-102 PCB Analyzer

Prepared by
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MONS 018398

REPORT SUMMARY

SUBJECT: Hazardous/toxic substances

TOPICS: PCB; Chemical analysis; Waste management; Gas chromatography; Field testing

AUDIENCE: Environmental and R&D engineers and scientists

Field Evaluation of the S-Cubed Model PCBA-102 PCB Analyzer

In laboratory and field tests, a portable gas chromatograph showed potential for measuring PCBs in fluids and soils at utility transformer sites. Compared with conventional laboratory analyses, on-site tests with the EPRI-developed instrument would be faster and less costly and thus expedite cleanup decisions.

BACKGROUND Current regulations require utilities to test for soil and fluid contamination at transformer sites where there has been an accidental release of polychlorinated biphenyls (PCBs). Typically, analyses of sample materials from the sites are conducted at commercial laboratories using gas chromatography techniques. Such off-site testing, however, can cause undesirable delays in obtaining test results. To speed up the process, EPRI sponsored development of a portable gas chromatograph—the PCBA-102 analyzer (EPRI report CS-4175).

OBJECTIVE To evaluate the PCBA-102 analyzer for precision and accuracy, reliability, operator proficiency requirements, and cost-effectiveness.

APPROACH The project team installed a PCBA-102 analyzer in a van fully equipped for on-site testing. Field crews in five utilities then used the van-mounted unit to analyze fluids and soils at transformer sites where there had been PCB releases. Each crew examined a minimum of 25 samples and, to evaluate the results, arranged for a representative portion of each sample to be analyzed with EPA-approved methods in an independent laboratory. In a separate laboratory investigation, the project team analyzed oil and soil samples using both the PCBA-102 and the EPA-approved methods. Then, employing rigorously controlled analytic procedures, they used the instrument to test 501 soil samples at 23 transformer substations.

RESULTS Utility experience with the analyzer varied widely. In some cases, statistical comparisons of analyzer data with commercial laboratory data showed that the analyzer provided accurate and precise results. In other cases, there was no correlation between field and laboratory analyses. After initial hardware problems were resolved, the factor found most critical in operating the analyzer was the gas chromatography experience of the operator.

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In both laboratory and on-site tests by the project team, analyzer measurements were precise and accurate. Obtaining reliable results required rigorous control of analytic procedures, experienced chromatograph operators, and high-quality reagents.

EPRI PERSPECTIVE

Compared with off-site PCB contamination analyses, on-site evaluations have such advantages as increased sampling efficiency and rapid identification of anomalous data. The small gas chromatograph tested in this project demonstrated reliable on-site performance when operated by a skilled technician. Minor improvements recommended in this report—such as redesign of the injection port—would eliminate operating problems encountered during field testing and will be made before commercialization. Information on other EPRI-developed devices for on-site analysis—the Clor-n-Oil® kit and the Horiba Mesa-200 analyzer—is available in EPRI report EL-3766.

PROJECT RP1263-23
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MONS 018402

ABSTRACT

This report presents the results of field tests for a new portable polychlorinated biphenyl (PCB) analyzer. S-Cubed developed a prototype unit, the PCBA-102, and furnished it to Brown and Caldwell for the study.

Electric Power Research Institute member utilities conducted the first evaluation of the PCBA-102. In this program, the PCBA-102 was outfitted in a half-ton van and loaned to five utilities. They used it in both soil and transformer oil analysis. Each utility returned comments concerning operation and outside lab comparison data. Failures of both hardware and software were reported along with concerns about instrument breakdown during travel. Favorable reviews were obtained by utilities having experienced gas chromatograph (GC) operators performing the evaluation. Problems in operation increased with decreasing GC experience. Regression analysis was used to compare data from split samples between the PCBA-102 and outside laboratories. Regression slopes for individual utilities varied from fairly accurate, 0.88 ± 0.05 to very inaccurate 25.6 ± 52000. Correlation of methods was directly related to the experience and ability of the analyst.

Next, Brown and Caldwell evaluated the PCBA-102 both in the laboratory and in the field. Chemists compared laboratory data from the PCBA-102 to data from Environmental Protection Agency method 8080 using regression statistics. The regression slope was 1.03 ± 0.36 at the 95 percent confidence limit. Results demonstrated linearity from 10 to 1000 parts per million (ppm).

The field study consisted of on-site soil analysis at a number of transformer substations. On the whole, the PCBA-102 performed well. Field data and the outside laboratory's confirmation data were compared, again with regression analysis. At the 95 percent confidence limit, the regression slope was 1.20 ± 0.37. Relative standard deviation of the PCBA-102 (from replicate analyses) during the study was 35.8 percent, while accuracy (from spiked samples) was 65.6 percent ± 32.4 percent. Sample throughput averaged 27 injections per 8 hour day. Downtime was less than 2 percent. Software inability to recognize detectable levels of PCB occurred in 3.4 percent of samples. Instrument start-up time to achieve linearity over the 10 to 1000 ppm range exceeded the one hour target duration.

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ACKNOWLEDGMENTS

The author would like to thank several individuals whose contributions made this report possible. Special thanks are extended to Daniel Mew for his dedication and efforts during the field evaluation. Elaine Archibald and Randy Jackson also deserve recognition for their efforts in the field evaluation. In addition, appreciation is due to Steven Fisher and Denny Parker for their guidance throughout the project.

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Section 1

SUMMARY

In September of 1984, Brown and Caldwell began an evaluation of a new field instrument for polychlorinated biphenyl (PCB) analysis. S-Cubed developed the instrument under a previous research study by the Electric Power Research Institute (EPRI). The marketing philosophy behind the design of the instrument emphasized simplicity, low cost, accuracy, and operation by nonskilled individuals. To meet these goals, pattern recognition software for PCB quantitation was incorporated into a small rugged field gas chromatograph. The objectives of this study were to evaluate the instrument for precision and accuracy, for the level of technical ability necessary for operation, and for cost efficiency. Both EPRI member utilities as well as Brown and Caldwell evaluated the instrument. Brown and Caldwell performed laboratory bench testing as well as field testing.

Evaluations from the utilities ranged from very positive to negative. Those utilities with the most experienced gas chromatograph (GC) operators had the most success with the instrument. Each utility analyzed both oil and soil samples with the PCBA-102. In addition, they sent split samples to outside laboratories to compare results. Regression statistics comparing the two sets of data showed extreme variation among utilities. A 95 percent confidence interval (CI) was chosen to define the variance about the calculated regression slope. Using the 95 percent CI, there would be only a 1-in-20 chance that the true regression slope would be outside the limits. Regression slopes and variances were calculated for each individual utility. Statistical data varied from 0.88 ± 0.05 (relatively accurate and precise) to 26 ± 52000 (no correlation between methods). The ability of the individual analyst appeared to be critical in obtaining accurate and precise data.

The PCBA-102 did experience appreciable downtime. Some of these difficulties were due to damage during travel and shipment and some were due to a poorly designed injection port. Certain utilities were impressed with the instrument and expressed interest in future purchase. Others were skeptical and expressed the need for redesign of both hardware and software.

Brown and Caldwell personnel found the PCBA-102 relatively easy to operate in the laboratory. Testing was performed under ideal conditions with results that were

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comparable to in-house GCs in precision, accuracy and linearity. The results obtained with the laboratory bench testing represent the maximum potential of the PCBA-102.

Brown and Caldwell tested the PCB analyzer under field conditions over a 3-month period from October through December, 1985. The field testing defined the extent of PCB contamination of soil at 23 transformer substations. Personnel took surface samples and analyzed them with the PCBA-102 at the site. If detectable levels of PCBs were found, subsurface samples were taken at increasing depths until a "none detected" result was obtained. The detection limit was 10 mg/kg.

On the average, contamination at each substation was fully defined in 2 working days. Instrument downtime was less than 2 percent. An average of 12 samples were analyzed per day. The relative standard deviation over the entire concentration range of samples was 35.8 percent, and accuracy from spiked samples was 65.6 percent $\pm$ 32.4 percent. A total of 501 samples were analyzed in the field; 81 of these analyses were confirmed by an outside laboratory. Comparisons were again made through regression statistics. At the 95 percent confidence limit, the regression slope was 1.20 $\pm$ 0.37.

Throughout the contaminated site study, results obtained by the software of the PCBA-102 were compared with results from chromatogram interpretation of a strip chart recorder. Statistically, there was no difference in precision and accuracy between methods at the 95 percent confidence limit. The software did miss certain detectable levels of PCB in 30 of the 501 samples analyzed (see Appendix A). Because of this omission and the need for a visual output of detector response, the use of a strip chart recorder is highly recommended as a complement to the software. The software identified specific aroclor compounds adequately, although it appeared to confuse Aroclor 1016 with Aroclor 1242 at times.

In general, the PCBA-102 performed quite well in the field study. Good agreement was obtained with samples analyzed by the outside lab. Precision and accuracy were acceptable in light of the inherent variation in PCB soil analysis. The PCBA-102 is not currently approved by the U.S. Environmental Protection Agency for quantitive measurement for PCBs. It can be used quite effectively as a screening tool when a quality assurance plan with conformation analyses is utilized. The PCBA-102 is particularly effective in applications involving complex sample matrices or when relatively low detection limits are required.

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Actual costs incurred in the on-site study were compared with projected costs that would have been incurred had the study been conducted with conventional sampling and lab analysis. In this study, costs for these two approaches were similar. Reduced indirect costs in project management, sampling efficiency, the ability to investigate and explain anomalous data, and the overall quality of decision making weighed heavily in favor of on-site analysis. The ability of the engineer to evaluate the data in the field provided a powerful means to make rapid and accurate assessments of site contamination.

Section 2

INTRODUCTION

BACKGROUND

The analysis of polychlorinated biphenyls (PCB) in transformer oils and in environmental samples must often be accomplished under severe time constraints. Usually, a sample is collected in the field and transported to a commercial laboratory for analysis. This procedure evolved because personnel of limited technical ability can collect samples, but analysis requires highly technical personnel and sophisticated instrumentation. Techniques are now being introduced that allow rapid on-site analysis of PCBs. These techniques have the same goals: high sample throughput, simple operation to eliminate the need for technical personnel, accuracy, and cost-effectiveness. The chemical principles used to detect and quantify PCBs vary among techniques, and correspondingly, so does the success in achieving these goals.

PCBs can occur in the environment in a variety of matrices. PCB aroclors are themselves complex mixtures containing many cogeners of chlorinated biphenyl. As analytical techniques become less sophisticated, their limitations in precision, accuracy, and applicability become more pronounced. In the long term, they can become cost liabilities when decisions concerning soil removal are made with inaccurate data. At present, there are four major manufacturers of instrumentation for rapid field measurement of PCBs (Table 2-1).

S-Cubed modified an existing field instrument used for gas detection in developing the PCBA-102. This adaptation permitted the use of methodology similar to U.S. Environmental Protection Agency (EPA) method 8080 because the basic technique was gas chromatography with Electron Capture Detection. The similarity in techniques may improve the possibility of gaining future EPA approval as an alternative method.

S-Cubed built the gas chromatograph (GC) with field durability and designed a microprocessor to handle data interpretation and quantitation. These capabilities reduced the need for experienced personnel. Sample preparation was modeled after EPA methods. The technique was simplified to a single methanol extraction followed by sulfuric acid cleanup. In addition, S-Cubed provided prepackaged reagents to reduce the responsibilities of the analyst in the field.

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Table 2-1

MANUFACTURERS OF FIELD INSTRUMENTATION FOR PCB ANALYSIS

Manufacturer	Technique	Quantification	Selectivity	Sensitivity	Oils	Soils	Analysis Time	Sample Preparation
S-Cubed	Gas chromatography/ electron capture detection	Yes	Yes	1 ppm	Yes	Yes	12 minutes	Yes
McGraw Edison	Chemical conversion of organic Cl to inorganic/ specific ion electrode detection	Yes	No	5 ppm	Yes	Yes	5 minutes	Yes
Horiba Instruments	X-ray fluorescence	Yes	No	5 ppm	Yes	No	5 minutes	No
Dussii CHLOR-N-OIL[TM]	Chemical conversion of organic Cl to inorganic/colorimetric detection	No	No	50 ppm	Yes	Yes	5 minutes	Yes

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Four prototype PCBA-102 units were produced and successfully tested by August 1985. Brown and Caldwell received one of these units to conduct a rigorous, independent evaluation.

OBJECTIVES

The objectives of the study were to evaluate the PCBA-102 for precision and accuracy, convenience of operation, level of technical ability needed for operation, and ability to detect PCBs in a variety of matrices.

Three major testing programs were performed. The first program was conducted by utility companies. The PCBA-102 was outfitted in a half-ton van, and loaned to five utilities. They used it in PCB analysis applications of their own choosing. Each utility was asked to confirm a minimum of 25 analyses using approved methodology. The PCBA-102 received mixed reviews. Most problems could be attributed directly to the lack of GC experience on the part of the operator, but some were inherent in the hardware and software capabilities of the instrument.

The second program was Brown and Caldwell's in-house laboratory study. This consisted of a series of comparisons of performance between EPA methodology and S-Cubed methodology. Results showed that the unit performed quite well.

The third program was a field investigation involving on-site soil analysis for PCBs. The vertical and horizontal zones of contamination were defined at a number of transformer substations over a 2-month period. The unit performed quite well. Downtime was less than 5 percent. Twenty-three substations were studied in the 2-month period.

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Section 3

INSTRUMENT DESCRIPTION

DESIGN PHILOSOPHY

The PCBA-102 was developed for rapid field measurement of polychlorinated biphenyls (PCBs) in transformer fluids and soils. It was designed for ruggedness, portability, and operation by nonskilled personnel. Prepackaged reagents are provided for sample preparation. A microprocessor with pattern recognition software performs the difficult task of chromatogram interpretation and PCB quantitation. Instrument start-up time is relatively short with high sample throughput.

SPECIFICATIONS

The PCBA-102 is a portable gas chromatograph (GC) equipped with a ^{63}Ni Electron Capture Detector (ECD). Instrument functions are completely controlled by an internal microprocessor. These include timed events, temperature zone control, calibration, data acquisition, quantitation, and report generation (see Figure 3-1). The run time and zone temperatures are preset at the factory and cannot be adjusted. Column flow rate is adjusted by the head pressure from the carrier gas tank pressure regulator. Technical specifications are listed in Table 3-1.

CAPABILITIES

The PCBA-102 is capable of detecting and quantitating four PCB aroclors: 1016, 1242, 1254, and 1260. Because the technique is gas chromatography/electron capture detection (GC/ECD), there is no theoretical limitation to sample matrix applications. Although only oils and soils have been studied, the PCBA-102 can be used for analysis of air, wipe, wastewater, sludge, or hazardous waste samples. Limitations would occur only if sample preparation techniques do not remove non-PCB electron capturing interferences that may be present in the sample matrix. Problems of this sort can affect even the most sophisticated PCB analytical techniques such as capillary GC with selected ion monitoring mass spectrometry.

Sensitivity of the PCBA-102 for PCB is routinely 10 parts per million (ppm) weight/weight. Detection limits of 1 ppm and lower may be achieved by modification of preparation techniques. Analysis time is approximately 12 minutes per sample. Actual field conditions over a 2-month period indicate that up to 45

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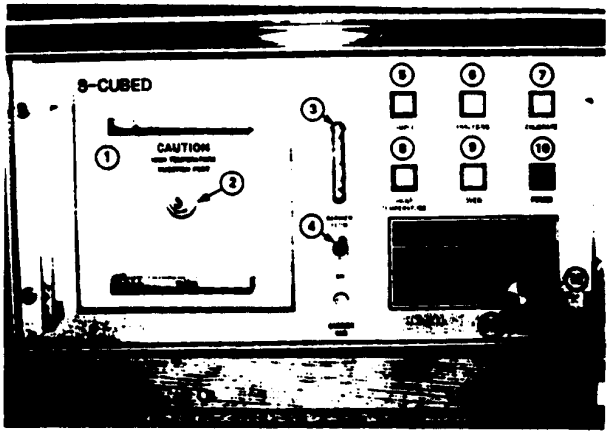

1	OVEN MODULE	7	CALIBRATION SWITCH
2	INJECTION PORT	8	TEMPERATURE PRINT SWITCH
3	ROTAMETER	9	OVEN POWER SWITCH
4	ROTAMETER SWITCH	10	MAIN POWER SWITCH
5	SAMPLE SWITCH	11	PRINTER RELEASE
6	ANALYZING INDICATOR	12	PRINTER PAPER FEED

[1]Adapted from "PCB Analyzer Instruction Manual" S-Cubed La Jolla, California March 1984, page 4.

Figure 3-1. PCBA-102 Front Panel Display

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Table 3-1

TECHNICAL SPECIFICATIONS

Analyzer Electron-Capture Detector

TYPE: 63_{Ni} foil

5 mCi sealed beta source

OPERATING TEMPERATURE: 250 ± 5° C

LINEAR DYNAMIC RANGE: 10^6

Analysis Capabilities

OPERATING RANGE:

Normal: 10 to 1000 ppm PCB

Alternative Procedure: 0.5 to 100 ppm PCB

Precision: 10 percent relative standard deviation

Sampling System

CHROMATOGRAPHIC COLUMN: 6' x 1/8" OD glass-lined stainless steel
3 percent SP-2100 on 100/200 mesh Supelcoport

CARRIER GAS: External supply of Argon 5 percent Methane

DATA OUTPUT: Paper tape printer, optional output, external strip chart recorder (not included)

Physical Characteristics

SIZE: 20" x 19" x 10" (DWH)

WEIGHT: Approximately 55 lbs

Power Requirements

1. 115-125 V AC 50-400 Hz, or
2. Vehicle equipped with heavy duty 50-amp alternator and inverter or
3. Rechargeable battery pack (2-50 amp hr 12 V DC) plus inverter (optional)

Power Consumption

200 watts

Source: PCB Analyzer Instruction Manual, S-Cubed, La Jolla, California, March 1984, page 27.

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injections can be made in a 10-hour day. Recalibration, precision and accuracy testing, and reanalyzing certain samples to bring them within the linear working range also require time. Field testing showed that 20 to 30 samples can be analyzed in one 10-hour day.

The software design of the PCBA-102 displays printed messages to assist in operation. Table 3-2 presents these messages which include system status reports, operational prompts, error messages, results, and run comments. The most important of these is the reported results. Four pieces of information are included in the result message: the specific aroclor detected (1016, 1242, 1254, or 1260), the concentration in ppm, the accuracy of the reported concentration, and the match number (a correlation of fit between the PCB pattern in memory and the PCB pattern in the sample run).

In addition to quantitation by software, the PCBA-102 has an analog output signal that can be monitored with a strip chart recorder. Brown and Caldwell took advantage of this feature throughout the utility loan program and the bench-scale and field testing. Quantitation from the strip chart recorder by peak height was compared to the software quantitation. Results of the comparisons are discussed throughout the report.

SAMPLE PREPARATION

Samples are prepared by isolating PCBs from the sample matrix in hexane. Chemical oxidation with sulfuric acid removes interfering components in hexane extracts. The technique is designed to simplify the EPA preparation method, yet provide a representative, reproducible extract free of interference. Field studies show that one analyst can perform both sample analysis and sample preparation during a daily routine.

The reagents used in sample preparation are prepackaged for easy use. Measurement devices such as Eppendorf pipets and electronic top-loading balances deliver rapid, accurate volumes and weights. Sample containers and pipet tips are disposable which reduces the risk of cross contamination between samples. Table 3-3 details the procedures for preparation of oil and soil samples.

ANALYSIS

A precision microliter syringe is used to inject the hexane extract into the PCBA-102. The injection technique is critical to reproducibility and to efficient

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Table 3-2

PRINTED SYSTEM MESSAGES

Operator interface with the PCBA-102 is accomplished through several means: activation of switches or buttons, observation of lights, injection of samples, and responding to printed messages or prompts. The printer messages provide information on analysis results, operating status, analysis problems or error conditions.

Each of these messages is presented in the following pages along with the operating conditions or circumstances that cause them to be generated. For messages that require remedial action, the recommended course of action is prescribed.

A.1 INFORMATIONAL MESSAGES AND PROMPTS

Printed Message	Reason For Message	Required Action
PCBA-102 ENABLED ENSURE OVEN IS ON	Power button has been turned on.	
PCBA-102 READY	Instrument has reached operating temperature.	
CALIBRATION REQUIRED	Request for instrument calibration issued after ovens have reached operating temperature. Request for instrument calibration issued after analysis of every ten samples. Request for instrument calibration issued after clean-out of contaminated system. Request for another attempt at calibration if calibration run fails.	
INJECT SAMPLE	SAMPLE button has been pushed and instrument is ready for injection of calibration sample. SAMPLE button has been pushed and instrument is ready for injection of oil/soil sample.	
XXX XXX XXX INJ COL DET TEMPERATURES (C)	PRINT TEMP button has been depressed. Information message after notification of EMERGENCY SHUTDOWN-TEMP LIMIT EXCEEDED error condition.	

A.2 CALIBRATION FAILURE MESSAGES

SYSTEM CONTAMINATED	Instrument cannot perform required automatic zeroing function prior to calibration run.	Check rotameter to verify that gas is flowing through instrument. Check gas supply to make sure it is carrier grade argon methane as specified in Table 3-1. Allow system to bake-out impurities by leaving on power, ovens, and gas flow for approximately 24 hours. Call S-CUBED Customer Service.

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Table 3-2 (continued)

Printed Message	Reason For Message	Required Action
CHECK FLOW	CALIBRATION analysis fails due to sample passing through system too fast or too slow.	Check gas flow through instrument and adjust accordingly. Check temperature of ovens to determine if within operating range. Call S-CUBED Customer Service.
CAL STANDARD OR SYRINGE CONTAMINATED	CALIBRATION analysis fails to recognize standard with the degree of confidence required.	Check that correct standard was injected - if not, inject correct standard. Thoroughly flush syringe with hexane and reinject calibration standard. Check septum, as prescribed in Section 3.3.1.2 of this manual. Call S-CUBED Customer Service.
A.3 ANALYSIS RESULT MESSAGES		
A.3.1 NORMAL RESULTS		
XXppm +/- Xppm MATCH = XXX PCB, XXXX	Quantitation results of calibration analysis. Quantitation results of oil/soil sample analysis.	
NO PCB DETECTED	Sample analyzed did not match any of the PCB's the instrument was looking for.	
A.3.2 EXCEPTION RESULTS		
SAMPLE TOO COMPLEX FOR AUTOMATED ANALYSIS	There are other compounds in the sample that are causing inference in automated analysis - SAMPLE SHOULD BE SENT FOR DETAILED LABORATORY ANALYSIS.	
HIGH CONCENTRATION 30 MINUTE DELAY TO CLEAN SYSTEM. DILUTE AND REINJECT	Injected sample has high concentrations of unidentified compound(s). After 30 minutes, system will request recalibration. After successful calibration, dilute sample as prescribed in Section 3.1.4 and inject for analysis.	
A.4. MISCELLANEOUS ERRORS		
CUMPUTER ERROR SYSTEM RESTART	Nondescript software error has occurred.	System will restart from beginning as if power had been interrupted. CALIBRATION will be required Please document events, actions, and circumstances leading up to this error condition, and notify the S-CUBED Customer Service Representative.

Source: PCB Analyzer Instruction Manual, S-CUBED, La Jolla, California. March 1984, pp. 29-31.

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Table 3-3

PREPARATION OF OIL AND SOIL SAMPLES

	Oil		Soil
Step 1.	Measure 100 ul of sample with Eppendorf pipet.	Step 1.	Weigh 1.0 gram of soil in a prepackaged vial containing methanol - a 10-fold dilution.
Step 2.	Deliver into hexane/H_2SO_4 prepackaged vial - a 10-fold dilution.	Step 2.	Shake for 2 minutes.
Step 3.	Shake for 2 minutes.	Step 3.	Allow soil suspension to settle.
Step 4.	Allow layers to separate.	Step 4.	Remove 1.0 ml of methanol with Eppendorf pipet and transfer to hexane/H_2SO_4 vial - a second 10-fold dilution.
Step 5.	Decant hexane layer into separate clean vial.	Step 5.	Shake for 2 minutes.
Step 6.	Hexane extract is ready for analysis.	Step 6.	Allow layers to separate.
		Step 7.	Decant hexane layer into separate clean vial.
		Step 8.	Hexane extract is ready for analysis.

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operation of the instrument. Prior GC experience or training is necessary to carry out this step properly. Improper injection technique can cause imprecision, inaccuracy, cross contamination of samples, septum damage, column damage, and obstruction of carrier gas flow. Many of the problems encountered in the operation of the PCBA-102 originated at this step in the analysis.

The instrument must be calibrated before the software will accept sample runs. Calibration depends on conditioning the instrument at the proper temperatures and flows, then injecting the proper amount of a 1 ppm standard of Aroclor 1254. Calibration runs are differentiated from sample runs by using the calibration control button. Difficulties in calibration arise from contaminated syringes, improper flow rates, and bad injections. During the in-house evaluation, the strip chart recorder was used quite effectively to monitor the signal from the ECD to troubleshoot the problem during difficult calibrations.

A 1 ppm calibration run of Aroclor 1254 is stored in the permanent memory of the microprocessor. Daily calibration is obtained only when operating parameters are similar to those during the original calibration run. This procedure permits pattern recognition of PCBs in subsequent sample runs. The sensitivity of the ECD will vary over time because of changes in factors such as gas purity, gas flow rate, and column efficiency. The calibration procedure compensates for these variations by storing the data points of the last calibration run for subsequent quantitation of sample runs. In fact, the instrument is programmed to accept only nine sample runs before recalibration is required.

The software is designed to print out the actual sample concentration of PCB. It quantitates based on multiple peak areas using a "cos θ" algorithm. Aroclor identifications are accomplished first, followed by quantitation. The 100-fold dilution of the sample during preparation is taken into account in the calculation. For example, a sample extract having 2 ppm Aroclor 1260 would be reported as 200 ppm Aroclor 1260. If modifications are made to the prescribed steps during sample preparations that would change the 100-fold dilution factor, adjustment of the result must be made independently of the PCBA-102.

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Section 4

MOBILE OUTFITTING

For the field testing, Brown and Caldwell mounted the PCBA-102 in a one-half ton 1984 Ford Econoline Van (see Figures 4-1, 4-2, 4-3, and 4-4). The van was specially equipped with plywood flooring and bench space with sufficient drawer and counter space to store all reagents and instrumentation. A heavy-duty alternator was installed to handle power requirements. A 110-volt AC power converter provided power from the battery to the electonic devices. Power fluctuation required the use of a voltage regulator to further condition the power. In the field, an outside power source was used if it was available. If not, the van was able to provide power to the PCBA-102, the strip chart recorder, the electronic balance, and inside lighting for all-day operation. Engine overheating was not a problem; however, field tests were run when ambient temperatures did not exceed 55 degrees F to 60 degrees F.

All instruments were fastened to the countertop with metal brackets. Foam rubber padding was placed under the PCBA-102 while the study was in progress to reduce the constant vibration that was loosening nuts and screws and may have caused intermittent electrical connections or broken wires.

Gas tanks containing 95 percent Argon/5 percent methane carrier gas were fitted into a holder and strapped against the wall of the van. Also included were a fire extinguisher, sink, and eyewash equipment. Operators usad protective clothing, safety glasses, and gloves during the tests. The effluent from the ^{63}Ni Electron Capture Detector (ECD) was scrubbed by a charcoal filter and discharged to the surrounding air outside the van.

MONS 018422

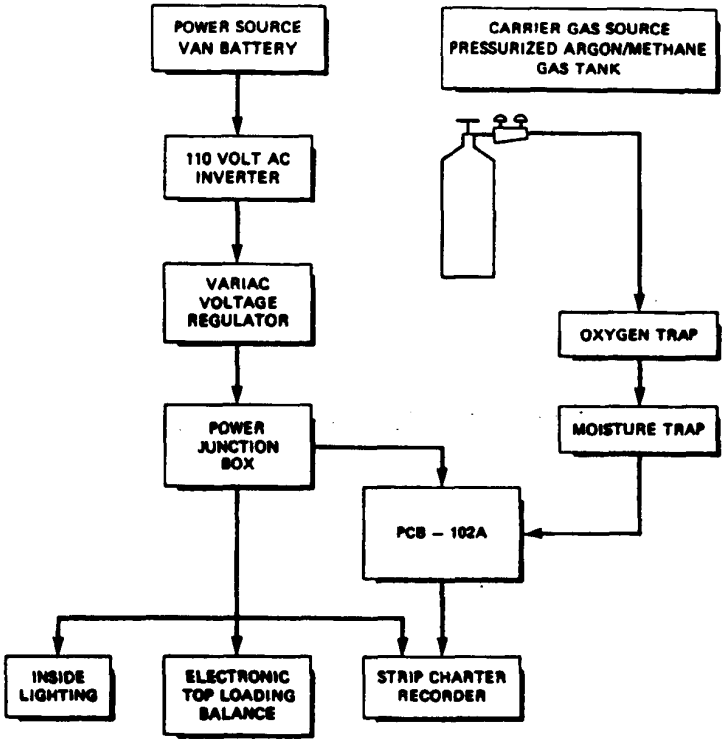

Figure 4-1. Design of Mobile Outfitting

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Figure 4-2. Econoline 250 Ford Van

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Figure 4-3. Interior of Van. View from the Side.

MONS 018425



Figure 4-4. Interior of Van. View from the Rear.

Section 5

UTILITY LOAN PROGRAM

TRAVEL LOG

Northern Indiana Service Company received the van and PCBA-102 in February 1985. The vehicle and instrument were shipped separately from Emeryville, California. A chemist from Brown and Caldwell spent a week with the personnel at the utility to help with start-up and sample analysis. Initially, a flow problem prevented calibration. A leak inside the oven module was detected in the swagelock fittings that connect the column to the injector port. Certain electronic components were inadvertently damaged when the leak was fixed. S-Cubed immediately sent out a new oven module. This new module was incompatible with the existing electronic configuration of the instrument. The resulting fluctuations in oven temperatures caused retention time shifts from run to run. At this point, the instrument was returned to S-Cubed in San Diego, California, for repairs. The initial flow problem apparently occurred during transit because Brown and Caldwell regularly obtained calibration at the laboratory in Emeryville, California before shipping. Northern Indiana Public Service Company was unable to calibrate the instrument due to hardware problems and thus could not participate in the program.

After repairs were completed, the instrument was shipped to Detroit Edison Company by air freight. Problems again occurred during start-up, and the instrument could not be calibrated. Again, it appears that problems arose during transportation because S-Cubed performed a thorough inspection of the instrument before shipping. A representative from S-Cubed flew out to Detroit Edison with a second prototype unit. This instrument was set up in the lab at Detroit Edison and successfully calibrated. Detroit Edison then installed the unit in the van and conducted their own field evaluation. They analyzed both soils and oils with good success. In one instance, they responded to a spill and obtained the result in a very timely fashion. A split sample was sent to an outside lab, and comparison of results showed good agreement between methods.

Staff from New York State Electric & Gas Corporation in Binghamton, New York, picked up the van in Detroit and drove it back to New York. They experienced little difficulty and were able to calibrate and operate the PCBA-102 successfully.

MONS 018427

In early May, staff from Central Hudson Gas and Electric Corporation picked up the van and drove it to Poughkeepsie, New York. Start-up problems occurred, and they could not calibrate the instrument. The problem was traced to a blockage of flow in the front part of the column. S-Cubed sent out a new oven module and Central Hudson installed it, which solved the problem. The new model worked appropriately and Central Hudson staff proceeded with their evaluation.

The blockage was caused by small pieces of septum that had lodged in the front of the column. The design of the injection port lends itself to this problem, especially if the septum is not changed after several injections. The blockage recurred several times in the utility loan program. The problem occurred again at the end of the Central Hudson study. Consolidated Edison Company of New York experienced the problem twice. In attempting to resolve the problem, Brown and Caldwell chemists were able to cause the blockage on purpose with only a few injections. When the blockage occurs, the flow rate is restricted, which causes shifts in retention time, a decrease in sensitivity, and distortion of peak shapes. The software cannot calibrate under these conditions because the chromatography is so different from the run stored in memory.

Consolidated Edison was the last utility to evaluate the PCBA-102. As mentioned before, they had repeated difficulty caused by the blockage problem. An inspection of the chromatogram (from the strip chart recorder) for a calibration run (1 parts per million (ppm) Aroclor 1254) showed very poor chromatography - a direct result of the flow problem. Because of this problem, Consolidated Edison's comparison of PCBA-102 results with the outside lab data showed no correlation whatsoever.

The van and PCBA-102 were shipped back to Brown and Caldwell in Emeryville in August 1985 where the instrument received a thorough inspection. A number of problems were immediately apparent: (1) nuts and screws holding circuit boards in place were loose or missing, (2) screws that fastened the detector base to the chassis were loose, allowing the detector to vibrate during transportation (3) a significant build-up of finely pulverized insulation material inside the oven module covered all connections and components with a layer of dust, and (4) the pressure regulator was inoperative and unable to properly regulate the head pressure to the column.

A new regulator was installed and calibration was attempted. The maximum flow rate was 5 milliliter per minute (ml/min) instead of the 40 ml/min needed for calibration. The oven module was opened, the column removed, and 4 separate pieces of septum removed from the front of the column. When the column was replaced, the flow rate was 40 ml/min, which permitted calibration. The polychlorinated biphenyl (PCB) pattern on the strip chart recorder then showed unacceptable resolution. A new column was prepared, conditioned, and tested. The instrument was calibrated with good separation between peaks of the Aroclor 1254 standard and was again ready for service.

COMPARISON TESTING

Each utility was asked to analyze a minimum of 25 samples using the PCBA-102. In addition, the samples were to be split and a representative portion sent to an outside lab (or their own lab) where approved U.S. Environmental Protection Agency EPA analytical methods were used to analyze the sample. A comparison of the PCBA-102 results versus the outside lab results formed the basis of the accuracy testing.

Regression analysis displayed in Table 5-1 was used to compare methods. A fifth set of data is included from the Pacific Gas and Electric Company, San Ramon, California, Department of Environmental Research. They evaluated the instrument in July 1984. This form of regression analysis was chosen because it is sufficiently rigorous to support the observations and comments made during the utility loan program. The method requires the assumption that data shown on the Y axis is accurate and data on the X axis is in error. For this reason, even though there is inherent error in precision and accuracy in both laboratory testing and PCBA-102 testing in the field, it was assumed that the PCBA-102 data contained the error and the outside lab data was true. In addition, the variation in the outside lab data could not be obtained.

The data from the PCBA-102 was entered as the X coordinate, and the outside lab data was entered as the Y coordinate. The slope of the regression curve for each utility was determined as follows:

$$b = \frac{\Sigma xy}{\Sigma x^2} = \frac{\Sigma XY - \Sigma X \Sigma Y/n}{\Sigma X^2 - (\Sigma X)^2/n}$$

MONS 018429

Table 5-1

ACCURACY COMPARISON IN UTILITY LOAN PROGRAM, PCBA-102 VERSUS EPA METHOD 8080

Utility	Regression Curve Slope	95 Percent Confidence Interval	Number of Data Points	Years of Experience of Analyst
Detroit Edison Company	0.70	± 0.16	23	>5
New York State Electric and Gas Corporation	1.6	± 28	24	>2
Central Hudson Gas and Electric Corporation	0.35	± 0.13	34	<1
Consolidated Edison Company of New York	26	± 52000	17	<1
Pacific Gas and Electric Company, Dept. of Environmental Research	0.88	± 0.05	97	>5

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where

b = slope of the regression curve

xy = sum of the cross products

x^2 = sum of the squares of X values

The variance about the regression curve can be expressed with a 95 percent confidence interval about the slope. It is determined as follows:

$$S^2_{y.x} = \frac{\Sigma y^2 - (\Sigma xy)^2 / x^2}{n-2} = \frac{Y^2 - (\Sigma Y)^2/n - (\Sigma xy)^2/\Sigma x^2}{n-2}$$

where $S^2y.x$ is the variance about the regression curve. The standard deviation is the square root of the variance.

$$S_{y.x} = \sqrt{S^2_{y.x}}$$

where Sy.x is the standard deviation about the regression curve. And, finally the 95 percent confidence interval is determined as follows:

$$CI_{.95} = \frac{t_{.05}\, Sy.x}{\sqrt{x^2}}$$

where

$CI_{.95}$ = the 95 percent confidence interval

$t_{.05}$ = student's t value at n degrees of freedom

A perfect correlation of accuracy between methods would yield a number very close to one with an extremely small confidence interval. Table 5-1 shows the variation in accuracy obtained by the utilities.

DISCUSSION

The variation in accuracy among utilities was directly related to the ability of each utility to ensure proper operation of the instrument. Adequate chromatography must be maintained during sample analysis. Poor chromatography will produce poor results regardless of the power of the software system. Many differences in comparative data were directly attributable to inadequate chromatography.

MONS 018431

Operational problems made it difficult to assess the error contribution of the software system. Two observations stand out. First, the injection port design must be changed to eliminate the blockage of the column with pieces of septum. Chemists at Brown and Caldwell were surprised at how easily they could cause this blockage to occur. Second, there is no substitute for an experienced gas chromatographer to minimize operational problems and obtain accurate data. Nontechnical people could possibly be trained in a short period of time to operate the PCBA-102 but an experienced GC chemist must troubleshoot, maintain equipment, and supervise operations.

One of the marketing objectives in the development of the PCBA-102 was operation by nonskilled personnel. The pattern recognition software was designed to make that aspect of operation simple enough to meet this goal. An equally important task, however, is the overall operation of the gas chromatograph. It became apparent that nonskilled personnel could not successfully operate the PCBA-102 to desired expectations. In this sense, the marketing objective of easy operation was not met.

COMMENTS FROM THE UTILITIES

Comments regarding the PCBA-102 ranged from positive to negative. Two utilities were impressed enough with the overall operation that they are proposing to purchase instruments. Other utilities expressed interest but wanted certain modifications as well as better accuracy and precision. It is interesting that the outside lab data was perceived to be the "correct" result in the comparison tests, even though a certain amount of variation is inherent even in EPA approved methodology. This perception may be partially due to the software printout of the PCBA-102, which gives not only concentration but also an accuracy range. Outside lab data included only the concentration, and therefore was perceived to be more accurate. The host utilities made the following additional comments to improve operation:

1. The ability of the instrument to maintain integrity during transportation is questionable. Shock mounting was suggested.

2. The start-up time of 1 hour is too short to achieve calibration and linearity over the 10 ppm to 1000 ppm range.

3. The van should have some type of climate control to protect the software on hot days.

4. The carrier gas flow control should be adjusted by more effective means than the gas tank regulator.

5. The injector port needs redesign to avoid clogging. Changing the septum daily instead of weekly, as the instruction manual directs, was suggested.

6. Troubleshooting was difficult because there were no gauges for critical parameters such as oven temperature and injector temperature. One utility did not trust software readouts of these conditions. Provision of gauges should be considered.

7. A better method of packaging and storing the prepackaged reagents is needed because evaporation of solvent, degradation of acid, and leakage occurred.

8. The troubleshooting section of the manual is too short.

9. Problems in recalibration arose when extracts with very high concentrations of PCB were inadvertently injected into the instrument. On one occasion a 41,000 ppm sample was injected. Overnight conditioning was needed before recalibration.

10. At times, the PCBA-102 does not distinguish between Aroclors 1242 and 1016 effectively.

Each utility recognized the potential of the S-Cubed PCBA-102. Varying degrees of success were achieved during the time each performed its evaluation. Expectations also varied, which led to differences in perceived instrument performance. The ideal instrument would not only provide results with the same degree of precision and accuracy as conventional lab methods, but would also provide the answer more rapidly, under field conditions, and with an operator of minimum technical skill. With these expectations, the PCB-102A was doomed to fail. There must be a realistic utilization of the PCBA-102 in the context of providing supporting data in field assessments. The presence of an experienced gas chromatograph chemist to operate the instrument is absolutely necessary to ensure success. Future design changes may enable the PCB-102A to become an EPA approved, quantitative method for rapid measurement of PCBs in the field.

Section 6

IN-HOUSE EVALUATION

OPERATION

Brown and Caldwell chemists found the PCBA-102 relatively easy to operate. S-Cubed personnel were present to help with initial start-up of the instrument. In addition to the in-house evaluation, the PCBA-102 was used effectively in daily operations in the lab to screen sample extracts for polychlorinated biphenyls (PCB). The sample extracts were injected into the PCBA-102 first, then, based on the result, the proper dilution (if any) was made before analysis with the Environmental Protection Agency (EPA) 608 or 8080 method. This procedure greatly facilitated operations because virtually all samples analyzed fell within the linear working range of the instrument and thus were able to be fully quantitated.

Throughout the in-house evaluation, rigid control was exercised during analytical procedures. Split samples were not compared if homogeneous, representative portions could not be obtained. High purity Argon/methane with freshly conditioned in-line traps for oxygen, moisture, and particulate were used to provide the same quality carrier gas as used with in-house gas chromotographs (GC). Power was obtained from a dedicated 110 volt source. Heated zones were maintained at proper temperatures with carrier gas flow on 24 hours a day to ensure a conditioned system. Lastly, Brown and Caldwell's staff of highly trained analytical chemists operated the instrument. To eliminate variation in injection techniques, only one chemist (B.S. degree in chemistry with 5 years experience) performed the analyses that produced the data used in this report.

PRECISION AND LINEARITY

The precision and linear range of the PCBA-102 were compared to a Hewlett Packard 5840A GC equipped with an auto sampler (see Tables 6-1 and 6-2). Results showed virtually no difference between the two instruments. The data was obtained during optimum operating conditions and after the analyst had conditioned the PCBA-102 and familiarized himself with its operation.

COMPARISON TESTING

Brown and Caldwell performed accuracy testing similar to that in the utility loan program. Soil and oil samples were split and analyzed by the PCBA-102 and by EPA 8080. Soil samples were sieved through a 1-millimeter sieve before splitting.

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Table 6-1

PRECISION OF PCBA-102

1. Concentration of Aroclor 1254 STD. Injected: 0.18 ppm

Trial	Aroclor	Software Result (ppm)	Recorder Result (ppm)
1	1254	0.19 ± 0.03	0.20
2	1254	0.16 ± 0.03	0.21
3	1254	0.17 ± 0.02	0.20
4	1254	0.17 ± 0.02	0.20
5	1254	0.16 ± 0.03	0.20

2. Concentration of Aroclor 1254 STD. Injected: 0.055 ppm

1	1254	0.05 ± 0.01	0.06
2	1254	0.05 ± 0.01	0.06
3	1254	0.05 ± 0.01	0.06
4	1254	0.06 ± 0.01	0.06
5	1254	0.06 ± 0.01	0.06

MONS 018435

Table 6-2

LINEARITY OF PCBA-102

Arochlor 1254 (ppm)	Software Result[1] (ppm)	Recorder Result[2] (ppm)
0.05	0.06 ± 0.01	0.06
0.10	0.12 ± 0.00	0.13
0.50	0.60 ± 0.07	0.60
2.00	1.95 ± 0.29	2.02

[1]Correlation coefficient = 0.9984
[2]Correlation coefficient = 0.9989

MONS 018436

Sixty-five samples were compared. Regression statistics yielded a slope of 1.03 ± 0.36 at the 95 percent confidence limit. The agreement between methods was excellent. Control over both sets of data and the experience of the analyst were probably contributing factors to the high accuracy of the results.

The modified sample preparation technique was also singled out for comparison testing. Here, split samples were prepared by the two different methods but analyzed by EPA 8080. This removed the variation in instrumentation as a source of error. Twenty-two soil samples containing concentrations of Aroclor 1260 ranging from 0.05 milligrams per kilogram (mg/kg) to 1200 mg/kg were compared in this study. Again, regression statistics were used to compare techniques. A slope of 0.95 ± 0.07 at the 95 percent confidence limit was obtained. These data indicate the methanol extraction to be very comparable to the more rigorous EPA technique. Homogeneous, finely sieved soils with relatively small clay content were analyzed. Field results may show more variation because of the wide range of sample types that may be encountered. Organic content, clay content, and particle size distribution could affect extraction recovery efficiencies.

The precision and accuracy obtained in the in-house study represents the potential of the PCBA-102. Controlled conditions, experienced analysts, and high quality reagents are all major factors affecting results. As seen in the utility loan program, variations that lead to error occur when control and experience are reduced.

COMMENTS/FINDINGS

The in-house testing program brought to light certain features of the PCBA-102's performance.

1. The PCBA-102 can identify and quantitate four aroclors (1016, 1242, 1254, and 1260). Other aroclors will be reported as one of these four, and the printed result message will differ from the true value.

2. If there are two or more aroclors in the sample, the software will report only the one that is present at the higher concentration. The reported concentration appears to be the sum of all aroclors present.

3. Interfering peaks (peaks with the same retention times as particular aroclor peaks) may cause the software to report a false positive finding.

4. A clean sample will usually be reported as "No PCB Detected" but occasionally the printed message "Analysis for automated sample too complex" appears.

MONS 018437

5. The software message, "High concentration thirty minute delay to clean system. Dilute and reinject," is not necessarily the result of an injection containing high PCB concentration. It might also occur when the extract contains low concentrations of PCB but high concentrations of interfering compounds not removed by the sulfuric acid cleanup.

6. The chart recorder can help verify PCBA-102 result messages. With the chart recorder more than one Aroclor can be identified and quantitated although it is difficult to distinguish between early eluting aroclors, such as 1016, 1242, and 1248.

7. The match number in the result message is not an indication of the accuracy of the result. A sample that contains a low concentration of a single aroclor and no interferences may give an accurate result but a low match number. Conversely, samples with significant interferences have been quantitated inaccurately, yet assigned a relatively high match number.

Section 7

CONTAMINATED SITE STUDY

OPERATION

The field study to characterize the extent of polychlorinated biphenyls (PCB) contamination in soils began on October 17, 1985 when the van and PCBA-102, a chemist, and the sampling crew arrived at the first transformer substation. The crew took soil samples with an impact core soil sampler. The soil was removed from each core and placed in an aluminum tray where it was homogenized. A representative portion was placed in a glass container, labeled, and given to the chemist for analysis.

Sampling equipment was washed between samplings with alconox. This cleansing was followed by rinses with tap water, deionized water, and acetone to avoid cross-contamination between samples during collection.

Sampling strategy involved taking surface grab samples at selected locations. The locations were chosen based on observation, proximity to capacitors, and past site history. If detectable levels of PCB were found, subsurface samples were taken at that location. Each location was sampled at increasing depths until a "none detected" result was obtained. The detection limit was 10 milligrams per kilogram (mg/kg).

On two occasions early in the study (10/18/85 and 10/25/85), calibration was unattainable. In each case the chemist opened and inspected the oven module and found a disconnected wire to the detector heating block. The wire was reconnected, the oven module reassembled and reseated into the gas chromatograph (GC) chassis and power was restored. In the first case, temperatures did not equilibrate properly, which indicated a bad connection. After many attempts, the oven module was successfully reseated and temperatures equilibrated properly. The second time, no problems were encountered in powering up the PCBA-102. These were the only two breakdowns that caused delays in analysis, and in the case of the second breakdown, 17 samples were analyzed that day after repairs.

At the start of the project, the goal was to characterize one substation per day. In actuality, about 2 days were spent on each substation because of weather

conditions, the length of time required for sample throughput on the PCBA-102, and the complexity of site contamination. Twenty-three substations were characterized in 41 days of sampling and analysis.

During these 41 days a total of 1104 injections were made, averaging 27 injections per day. 501 samples were analyzed, averaging a little over 12 per day. Twenty percent of injections were for quality control. These included blanks, duplicate analysis, spike analysis, and linearity checks. A certain portion of the samples were screened before analysis. This screening entailed diluting the extract 1 to 20 or 1 to 50 and injecting before analysis. The purpose was to avoid too high a concentration, which contaminates the instrument's detector and causes delays. The frequency of screening was determined solely by the analyst's choice. Forty-four percent of the samples analyzed were screened before analysis. A detailed account of daily activities is included as Appendix B.

Start-up time or instrument warmup was found to be longer than specified in the manual. All temperature zones would equilibrate well before the first hour after engaging power, but to achieve linearity over the 10 parts per million (ppm) to 1000 ppm range, a minimum of 3 hours of conditioning was required (see Figure 7-1). This phenomenon is due to the design of the Electron Capture Detector (ECD). The detector measures extremely small changes in voltage. The system may require a different period of time to stabilize depending on the type and/or magnitude of background contamination. These may be things such as the type of septum being used, the condition of the column, or the purity of the carrier gas. Variation in both response and linearity are somewhat compensated for by recalibrating the software's requirement for each set of 10 samples. A calibration curve should be run once a week to verify instrument performance.

After recognition of the time required for proper conditioning, the instrument was conditioned overnight from an outside power source. During transportation, the source of power was switched to the van battery, then 110 volt power from the substation was used at the site throughout the day.

Calibration was achieved relatively easily during the entire contaminated site study. Flow rates were monitored daily and adjusted to yield correct retention times for calibration. Septums were changed daily to prevent clogging of the column. The analyst noted the concentration value that was printed out with the daily calibration run. The result is based on data stored in memory of the PCBA-102. When a new oven module was inserted, concentration readings of

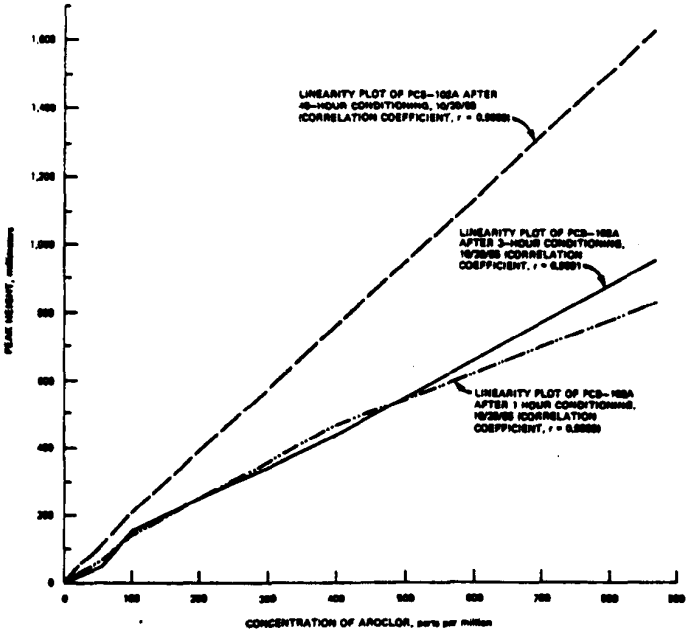

Figure 7-1. Linearity Plot of PCBA-102A

MONS 018441

300 ppm ± 50 ppm were obtained during calibration. This is probably due to sensitivity variation among individual ECDs. Precision and accuracy was not affected by this change in the relative sensitivity of the PCBA-102. On certain occasions successive calibration runs were performed because of imprecision in the concentration readout. It is not understood why precision varied between calibration runs.

As the study progressed, the resolving power of the column decreased. Near-baseline resolution was achieved at the beginning of the study. This decreased into valley to valley resolution and reached a point 31 days into the study when it was necessary to replace the oven module. Without the aid of a strip chart recorder it would be very difficult to know if the column is resolving properly.

Also, as the study progressed it became apparent that the inability to control the run time was a drawback. The vast majority of PCB detected in the transformer substations was Aroclor 1016. This particular aroclor elutes quite rapidly. For all intents and purposes the analysis is complete within five minutes; however, data continues to be acquired for another 5 to 7 minutes. In the case of Aroclor 1016 contamination, throughput could be doubled if the run time could be adjusted to 5 to 6 minutes. As an alternative, the analyst can choose to operate the instrument without engaging the software. In this case, the detector signal is monitored by the strip chart recorder. Manual calculations must be performed while operating in this mode.

On the whole, the unit performed quite well. Downtime was limited to less than 2 percent. Sample throughput averaged 12 samples per day with a high level of quality assurance and screening of extracts. The versatility of the instrument displayed itself throughout the study. Rinse water from sample collection activities was monitored for PCBs for proper disposal. Oil samples were analyzed to detect the presence of PCBs. Difficult samples of rock and gravel were analyzed by modifying sample preparation procedures. In one instance a localized fresh spill of highly contaminated oil was found. This spill was immediately cleaned up to prevent further migration of PCBs into the soil.

PRECISION AND ACCURACY

One goal of the S-Cubed PCB analysis system was consistent automation of chromatographic quantification. To help determine the accuracy and precision of the supplied software, a strip chart recorder was connected in parallel while an extensive series of soils were tested. An experienced chromatographer calculated

PCB concentrations from the strip chart recorder for comparison with the answers generated by the instrument software. Manual calculations of PCB were based on a point-to-point comparison of peak height using the most prominent peak in the PCB fingerprint pattern.

Once these figures were assembled, each data block was evaluated for precision and accuracy. Precision was based on results of duplicate samples, while accuracy calculations were derived from percent recoveries on spiked soil samples. These results are displayed in Table 7-1.

For determination of precision, no samples yielding results below detection limits were included. There were 15 pairs of duplicates above detection limits by the automated software and 23 pairs by strip chart calculation. For each series, the variance was calculated by the formula:

$$s^2_p = \frac{1}{2K} \sum_{1}^{K} d_i^2 .$$

Once the variances for the two quantitation techniques were determined, it was possible to compare them by using a standard F test. In this test, the larger variance was divided by the smaller, with the resulting ratio compared to tabulated F values. A "two-tailed" F test was selected to determine if the precisions were different without postulating that one was better than the other. The null hypothesis was that there was no significant difference between the methods. The null hypothesis was rejected if the F ratio calculated exceeded the tabulated value. This result would suggest that the data were significantly different. For convenient comparison with conventional discussions of precision, the standard deviation was determined as the square root of the variance. The relative standard deviation was calculated by dividing this value by the mean result and expressing the fraction as a percentage.

For accuracy comparison, it was first necessary to determine if the recoveries had equivalent distributions. The precision of the recoveries were then compared before making observations about their mean values. For this comparison, the mean recovery, variance, and standard deviations for the two methods were calculated. Once again, the larger variance was divided by the smaller, and the result compared with tabulated F values. It was appropriate to compare the means if the

MONS 018443

Table 7-1

CONTAMINATED SITE STUDY PRECISON AND ACCURACY OF PCBA-102

	Software Results	Strip Chart Recorder Results
Number of comparisons	15	23
Mean, mg/kg	1,540	914
Standard deviation over entire range based on duplicates	552	359
Relative standard deviation, percent	35.8	39.3
Mean spike recovery, percent	65.6	71.8
Relative standard deviation of spike recovery, percent	32.4	24.8

MONS 018444

deviations were found to be indistinguishable. For that comparison, a student's t test was used. In this test, the null hypothesis was that the recoveries were not significantly different. If the calculated t value was larger than the tabulated value at the chosen confidence interval, we rejected the hypothesis and concluded that the results were different.

The t value was calculated from:

$$t = (\bar{x}_1 - \bar{x}_2) \Big/ \sqrt{s \left(\frac{1}{N_1} + \frac{1}{N_2} \right)}$$

where s was the pooled standard deviation, which was derived from the deviations of the two methods:

$$s^2 = \left[(N_1-1)\, s_1^2 + (N_2-1) s_2^2 \right] / (N_1+N_2-2).$$

N1 and N2 were the number of observations in each set: 36 recoveries for the software and 41 for the strip chart.

For the S-Cubed software technique, the standard deviation based on duplicates was 552 mg/kg. For the strip chart, it was 359 mg/kg. The corresponding variances provide an F value of 2.36. For a numerator with 15 degrees of freedom and a denominator with 23, the tabulated F value for 95 percent confidence is 2.47. The null hypothesis was retained with the conclusion that the methods were not significantly different in precision. The mean of software results was 1540 mg/kg for a relative standard deviation (RSD) of 35.8 percent. The mean for the strip chart method was 914 mg/kg, for an RSD of 39.3 percent.

For accuracy, the mean spike recovery was 65.6 percent for the software and 71.8 percent for the strip chart. The respective variances were 1055 and 618, for a ratio of 1.71. The tabulated F value at 95 percent was 1.88 for a numerator with 40 degrees of freedom and a denominator with 40. The data sets had 35 degrees and 40 degrees, respectively, so even by this more conservative

MONS 018445

estimation the null hypothesis was retained, with a conclusion that the variation in recovery was not significantly different. Since the deviations were comparable, a pooled standard deviation of 28.7 was calculated along with a t value of 0.95. The tabulated t value for 75 degrees of freedom is not directly available, so the more conservative value of 1.96 at infinite degrees of freedom was chosen. Because this value was larger than the calculated value, the null hypothesis was retained with the conclusion that mean recoveries were not significantly different.

DISCUSSION

All of the calculations performed pointed to similarity for the two calculation methods. The higher mean value for the software was primarily caused by eliminating those values below detection limit from calculation. The higher software detection limit removed many low level samples from that set which remained available in the strip chart set.

The 95 percent confidence level was selected for these tests to reduce the risk of ascribing a random result falsely to some cause. At this level, the chances of making such an error were only 1 in 20. It is worth noting, however, that if the risk level were raised to 1 in 10 (the 90 percent level), the standard deviations from precision would be significantly different. The assessment of no difference is well supported when the relative standard deviations are reversed in comparison with the absolute deviations. In reviewing those figures it is important to remember that there was no true "mean" analytical result in this series because many different samples were tested.

Bellar and Lichtenberg discussed the variability in precision and accuracy in PCB soil analysis[1]. Factors influencing variability include sample pretreatment, method of extraction, sample container, sample matrix, sample preservation during storage, equilibration time of the spiked sample, and analytical measurement error. Bellar has reported PCB spike recoveries from bottom sediments with a mean of 61 percent and a standard deviation of 22 percent[2]. A more comprehensive study by Daly, reported variations in PCB analysis in sediments[3]. Twelve laboratories participated in the study. They analyzed three sets of 6 sediment samples, each set containing one particular PCB arocior. The data appear in Appendix C. Significant variations in reported concentrations between laboratories is seen throughout the concentration range and in all arocIors studied. Given this overall perspective, the variation in precision and accuracy reported in the contaminated site study conforms to other investigations.

MONS 018446

COMPARISON TESTING

Of the 501 samples analyzed by the PCBA-102, 80 were also analyzed by an outside laboratory using U.S. Environmental Protection Agency Method 8080. Samples were split from a homogenized portion of the soil. In certain cases sample matrix prevented adequate mixing. This condition occurred with unusually oily, wet, or rocky samples. In these cases, the split samples were prepared in a representative fashion to the best of the field personnel's ability. Variation in sample character should be considered as one source of error when interpreting the data.

Results were obtained from the PCBA-102 in two ways: one from the software readout, the other from the strip chart recorder. Each of these was compared individually to the result obtained by the outside laboratory, to see if there was any difference in the methods of quantification. These comparisons are presented in detail in Appendix D.

The same statistical treatment was used in this site study as in the utility loan program (see Table 7-2). The regression slopes were very similar, 1.14 ± 0.14 for the strip chart data versus 1.20 ± 0.37 for the software data. Thus, there is a 95 percent chance that the true regression slope of the strip chart data versus the outside lab data is between 1.28 and 1.00. Similarly, for the PCBA-102 data comparison with the outside lab data, the true regression slope is between 1.57 and 0.83. Since both intervals contain the regression slope of 1.00 and the interval itself is relatively small in comparison to the slope, it is assumed the methods are statistically equivalent at the 95 percent confidence limit.

In the comparison of data sets where one or both of the results was below the detection limit, excellent agreement was achieved. The detection limit of the software was 30 mg/kg; the strip chart was 10 mg/kg. Comparing the PCBA-102 software data with the outside lab data showed that 31 out of 32 data sets agreed. Thirty-one out of 33 agreed in the comparison of the strip chart recorder data with the outside lab data.

The identification of aroclors was somewhat suspect in that 29 percent of the identifications by the PCBA-102 software disagreed with the outside laboratory. In most of these cases, the PCBA-102 software identified the presence of Aroclor 1242 while the outside lab found 1016. This result may be due to the early elution pattern of both aroclors obtained with the 3 percent SP-2100 column. The patterns are also difficult to distinguish on the strip chart recorder.

MONS 018447

Table 7-2

CONTAMINATED SITE STUDY-COMPARISON STATISTICS

Statistical Parameter	PCBA-102 Software Results Versus Outside Lab Results	Strip Chart Recorder Results Versus Outside Lab Results
Number of data points	37	44
Regression slope	1.20	1.14
Standard deviation of regression slope	5,342	2,664
95 percent confidence interval	±0.37	±0.14
Number of comparisons of none detected results	32	33
Agreement, percent	97	94
Number of Aroclor identification comparisons	37	NA
Agreement, percent	71	NA

MONS 018448

On certain occasions the software failed to quantitate detectable levels of PCB (see Appendix A). Normal PCB patterns were obtained on the chromatograms produced by the strip chart recorder on these runs. The failures fell into two main categories: (1) a lack of sufficient sensitivity and (2) an inability to interpret relatively high levels of Aroclor 1016. The sensitivity problem occurred when levels of Aroclor 1016 in the 20 ppm to 50 ppm range were encountered. The software reported "None Detected" in 20 out of 884 runs, or 2.3 percent. The second type of failure occurred in 9 runs. The software reported "Sample Too Complex For Automated Analysis," even though normal interference-free PCB patterns were obtained and quantitated from the strip chart recorder chromatograms. The concentrations of Aroclor 1016 ranged from 100 ppm to 200 ppm in these cases.

The cause of these failures is not known, although intuition would suggest that differences in chromatography between the calibration run in memory and the daily calibration run may be the cause. These failures were greatly reduced near the and of the study after a new column and oven module were installed. There were no apparent differences in the software acceptance of the calibration run throughout the study, which may suggest that certain bugs may still exist in either the calibration program or the peak detection programs.

ECONOMIC COMPARISONS

Conventional approaches to site characterization involve field sampling coupled with laboratory analysis. Results are evaluated by the engineer within 1 day to 3 weeks, depending upon the urgency of the need for results and the ability of the lab to provide the results. Site characterization with the PCBA-102 in the field provides the engineer with results in 15 to 30 minutes after sample collection. In both cases, the data is evaluated to determine (1) the extent, if any, of PCB contamination, (2) the necessity for further sampling, and (3) the specific location(s) for further sampling if applicable. The regulated cleanup level is the overriding criteria in the engineer's decision making. There is no question that the quality of decision making is best served by the on-site real-time data provided by field instrumentation.

Comparisons of cost between approaches may be made both directly and indirectly. Direct costs include labor (engineering and sample collection), equipment, supplies, and analytical fees. Indirect costs include characterization efficiency, project duration, explanation of anomalous data, cleanup costs, verification costs, and noncompliance costs.

MONS 018449

Direct costs are displayed in Table 7-3. Costs incurred during the contaminated site study were determined as follows:

- Engineering Labor - labor costs expended from October 18, 1985, through December 20, 1985, for sample collection, data evaluation, and project management.
- Field Analysis Labor - labor costs expended from October 18, 1985, through December 20, 1985 for on-site field analysis.
- Expendable Supplies - costs incurred in outfitting the van, collecting samples, analyzing samples, and other miscellaneous costs.
- Equipment - costs for vehicle rental, instrument rental, recorder, balance, inverter and depreciated items necessary to the collection, analysis, and evaluation of samples and data.
- Analytical Fees - costs in Table 7-3 are based on $75.00 per sample fee, typical of commercial laboratories. The total ($75.00 x 80) is based on the 80 samples analyzed by the outside lab for confirmation.

To compare the conventional approach to the field characterization, direct costs for the contaminated site study were projected for the conventional approach. These costs were determined as follows:

- Engineering Labor - direct costs are assumed to be similar to the field characterization since the same basic level of sample collection, data evaluation, and project management would be required.
- Field Analysis Labor - the cost is zero since all analysis is performed by the outside laboratory.
- Expendable Supplies - costs incurred only in sample collection.
- Equipment - costs incurred in vehicle rental and those depreciated items necessary to the collection of samples and evaluation of data.
- Analytical fees - the same base per sample cost of $75.00 is used in calculations. A 50 percent premium is added to simulate commercial laboratory practices for providing rapid turnarounds. In actuality, this is a conservative adjustment of cost because 100 percent markups are typical for 24- to 48-hour turnarounds. Field results with the PCBA-102 are obtained within 15 to 30 minutes of sample collection.

Table 7-3 shows a $17,500 difference in bottom line direct costs between approaches. This difference may vary according to the assumptions made in assigning dollar amounts to specific costs. In addition, the direct costs for any site characterization are probably site specific. Also, the costs incurred in

Table 7-3

DIRECT COSTS: A COMPARISON OF APPROACHES TO CONTAMINATED SITE CHARACTERISTICS

	On-site approach, dollars	Conventional approach, dollars
Engineering labor	45,000	45,000
Field analysis labor	21,000	0
Expendable supplies	9,000	2,500
Equipment costs	4,500	2,500
Analytical fees	9,000	56,000
Total	88,500	106,000

MONS 018451

subcontracting laboratory analysis vary and may be a significant percentage of the total project cost with the conventional approach. For these reasons, it seems appropriate to view the direct costs incurred by each approach as essentially similar. It is quite another matter with the indirect costs.

Indirect costs are difficult to quantify, but that does not make them any less real or less important to the bottom line of site characterization costs. The manner in which the data is obtained by the engineer greatly influences the quality, timeliness, and effectiveness of decisions made during the investigation. These decisions have a great impact on the overall management of the project as viewed by the client. When the data can be obtained in the field, a number of advantages are realized.

The engineer is in "real-time control" of investigation operations. Should an anomalous data point be obtained, resampling and reanalysis can occur immediately. If the results are confirmed, the engineer is on hand to observe the area, make an evaluation, and proceed with additional sampling if necessary. In the short term, this control minimizes the guesswork in contamination definition. In the long run, client liabilities and costs are reduced in subsequent cleanup and verification.

On-site characterization maximizes the efficiency of sample location selection. The regulated cleanup level is usually the determining factor in deciding the extent of sampling. "Real-time control" allows the engineer to sample either vertically or horizontally until clean soil is found. This capability reduces the number of samples collected and facilitates thorough site characterization.

Other intangible benefits include an increased level of confidence when planning the site cleanup. The cleanup phase of waste site treatment is by far the most expensive. Excessive costs occur when verification testing turns up contamination that was not removed.

Lastly, the "real-time control" exercised by the engineer improves the quality and timeliness of communication to the client. The engineer can estimate project duration more precisely and can communicate unanticipated findings faster, improving decision making. The quality of decisions concerning compliance with regulatory agencies and client/regulator relationships is also improved.

MONS 018452

Section 8

CONCLUSIONS

POTENTIAL AND CAPABILITIES

The PCBA-102 has great potential as a rapid, effective screening tool for polychlorinated biphenyls (PCBs) in the field. It can handle a variety of matrices, reach relatively sensitive levels of detection [1 parts per million (ppm)], and conceivably analyze 30 samples in a 10-hour day. These capabilities depend on having an experienced analytical chemist with sufficient training to operate the instrument. The results obtained with the PCBA-102 agreed favorably with outside laboratory data when the instrument was operated under good chromatographic conditions. When chromatography was less than adequate, PCBA-102 results showed little correlation with outside lab results.

Most other field techniques lack selectivity--an important characteristic of the S-Cubed PCBA-102. The PCBA-102 can distinguish not only between PCBs and other chlorinated organic material but also among PCB aroclor mixtures. This feature permits tracing spills to the source. It may also prevent the false positive inference that other field techniques are susceptible to.

EASE OF OPERATION

The PCBA-102, a gas chromatograph (GC) equipped with an electron capture detector, is a sophisticated instrument. This study has shown that effective operation and maintenance requires field personnel experienced in gas chromatography analysis. Maintenance of good chromatography is essential and can only be achieved by someone knowledgeable in gas chromatography. The study has also shown that rugged field conditions and transportation can loosen parts and connections, which can cause instrument failures.

On the positive side, study results show that the PCBA-102 can be an effective tool for site characterization and assessment of PCB contamination. Twenty-three transformer substations were characterized (20 samples per substation) during 41 working days.

PRECISION AND ACCURACY

In the contaminated site study, relative standard deviation over the entire range of sample means was 35.8 percent based on 15 sets of duplicate analyses. Accuracy at the 95 percent confidence level was 65.6 percent $\pm$ 32.4 percent based on 15 sets of spike recovery data.

MONS 018453

RECOMMENDATIONS

The following recommendations are made to improve durability, operations, data throughput, and data interpretation of the PCBA-102:

1. Use locking nut and bolt fasteners throughout the gas chromatograph chassis that are vibration resistant to avoid loosening.
2. Provide shock mounts on the instrument for mobile outfitting.
3. Redesign injection port to eliminate clogging.
4. Incorporate flow controller to adjust carrier gas.
5. Allow for adjustment of run time.
6. Eliminate prepackaged reagents; they have a relatively short shelf-life and contain chemicals that require special handling for safe transportation.
7. Eliminate the match number component of printed result message. The correlation between the match number and the accuracy of results is inconsistent.
8. Encourage all users to complement software results with a strip chart recorder.
9. Develop training strategy for potential users and implement before initial user operation.

An optimistic marketing strategy during the development of the PCBA-102 led to expectations of high performance. Essentially a GC equal in performance to laboratory GCs was to be operated by non-skilled personnel who were to achieve both precise and accurate data under field conditions. This study has shown that only under very controlled conditions can laboratory precision be achieved. It has also shown that non-skilled personnel cannot successfully operate the instrument. But most importantly, it has shown that in real field situations trained operators can effectively characterize sites contaminated with PCBs given a realistic appreciation for the variation in precision and accuracy in PCB analysis.

REFERENCES

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MONS 018454

2. T. A. Bellar, J. J. Lichtenberg, and S. Lonnesman. "Recovery of Organic Compounds from Environmentally Contaminated Bottom Materials." In Contaminants and Sediments, vol. 2, ed. R. Baker. Ann Arbor, Michigan: Ann Arbor Science Publication, Inc., 1980.

3. James C. Daily. "An Assessment of the Performance of Laboratories Providing PCB Data for the PCB Settlement." Environmental Health Center. Division of Laboratories and Research. New York State Department of Health. September 1979.

Appendix A

SOFTWARE FAILURES

Date	Run Number	Software Result, ppm	Strip Chart Recorder Result, ppm	Comment
10/20/85	12	ND*	22	Sensitivity problem.
	15	ND	26	Sensitivity problem.
10/23/85	13	ND	43	Sensitivity problem.
10/24/85	2	Too complex	ND	Large peak detected, but not PCB.
	18	ND	80	
10/25/85	12	ND	39	
	18	ND	36	
	22	ND	31	
10/29/85	16	ND	53	Duplicate run had software of 42 ppb, recorder of 40 ppb.
	17	ND	84	This was a spiked sample.
10/30/85	15	Too complex	130	Duplicate run was okay. Software of 150 ppb, recorder of 130 ppb.
	29	ND	42	Sensitivity problem.
10/31/85	6	Too complex	98	This was an Aroclor 1016, 100 ppm standard.
	13	ND	41	Sensitivity problem.
	19	Too complex	152	
	32	ND	32	Duplicate run had software of 39 ppm, recorder of 26.
	34	Too complex	130	
11/5/85	7	Too complex	ND	Outside lab result was 0.5 ppm.
11/6/85	7	Too complex	240	
	23	ND	35	Next run had software of 60 ppm, recorder of 30 ppm.
11/7/85	7	ND	90	Sensitivity problem.
	8	Too complex	120	
	33	ND	51	Sensitivity problem.
	34	ND	87	Sensitivity problem.
11/8/85	5	Too complex	190	
	9	Too complex	160	
11/11/85	8	ND	43	Sensitivity problem.
11/14/85	6	Too complex	140	
	13	ND	120	
12/4/85	6	ND	30	Sensitivity problem.
12/6/86	13	ND	30	Sensitivity problem, subsequent spiked sample had software of 49 ppm, recorder of 28 ppm.

*None detected.

MONS 018456

Appendix B

CONTAMINATED SITE STUDY LOG

Date	Total Inj	Cal Inj	Screen Inj	QA/QC Inj	Sample Inj	Comments
10/17/85	15	2	2	3	8	First day
10/18/85	0	0	0	0	0	Instrument down, oven module failure
10/20/85	27	3	5	9	10	Performed linearity check
10/22/85	16	2	2	0	12	
10/23/85	17	2	6	2	7	No sampling, samples collected earlier were analyzed
10/24/85	24	4	2	5	13	
10/25/85	27	3	4	3	17	Repair over module prior to analysis
10/26/85	18	2	2	7	7	No sampling, samples collected earlier were analyzed
10/29/85	37	4	8	8	17	Performed linearity check
10/30/85	37	4	3	13	17	Performed linearity check
10/31/85	40	4	8	8	20	Analyzed today's samples plus sample backlog
11/1/85	23	2	7	3	11	One sample > 100,000 ppm
11/5/85	22	3	3	4	12	One sample needed extra H_2SO_4 cleanup
11/6/85	27	4	3	4	16	
11/7/85	36	4	9	5	17	
11/8/85	47	11	9	7	20	Multiple recalibration done twice
11/11/85	10	1	0	6	3	Finished up samples collected on 11/6/85
11/12/85	27	3	8	2	14	
11/13/85	34	8	7	7	12	
11/14/85	30	5	5	4	16	
11/15/85	40	5	10	3	21	
11/18/85	28	8	3	6	11	Second full day of sampling at this substation
11/19/85	30	9	4	6	20	
11/20/85	27	3	4	4	16	Six calibration runs accepted but variation in percision
11/21/85	42	12	6	12	12	
11/26/85	20	2	0	7	11	
11/27/85	32	5	10	5	12	Began screening samples with software off

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Date	Total Inj	Cal Inj	Screen Inj	QA/QC Inj	Sample Inj	Comments
12/2/85	10	5	0	5	0	Only QA testing
12/3/85	9	1	0	3	5	
12/4/85	13	2	3	5	3	
12/6/85	27	3	8	8	8	Installed new oven module at days ends Condition over the weekend
12/9/85	42	5	15	3	19	
12/10/85	22	3	8	2	9	Visited two sites
12/11/85	33	4	6	17	6	
12/12/85	31	3	12	2	14	
12/13/85	23	2	6	5	10	Installed original oven module with new column Condition over weekend
12/16/85	25	3	2	7	13	QC resolution is improved to original state
12/17/85	21	3	0	13	5	
12/18/85	37	4	11	8	14	
12/19/85	31	3	8	9	11	
12/20/85	39	4	14	3	18	
Total	1,104	160	220	223	501	

MONS 018458

Appendix C

RANKED DATA SHOWING PERFORMANCE RELATIVE TO OTHER PARTICIPANTS

Aroclor 1254 in Sediment — Test Date 4/9/79

Sample No. 791330		Sample No. 791380		Sample No. 791360		Sample No. 791360		Sample No. 791340		Sample No. 791370	
Reported Value	Lab Code	Reported Value	Lab Code	Reported Value	Lab Code	Reported Value	Lab Code	Reported Value	Lab Code	Reported Value	Lab Code
1.30	(15)	0.500	(09)	0.090	(09)	1.0	(13)	0.062	(09)	1.6	(12)
1.4	(12)	1.54	(15)	0.01	(15)	1.02	(09)	0.11	(10)	1.6	(13)
2.0	(10)	2.7	(10)	1.1	(12)	1.13	(15)	0.2	(02)	2.50	(15)
3.4	(10)	3.7	(12)	1.2	(10)	1.2	(10)	0.2	(12)	5.1	(09)
3.97	(09)	4.3	(08)	2.15	(08)	2.15	(08)	0.3	(14)	6.8	(02)
4.25	(08)	4.96	(08)	2.6	(02)	2.4	(02)	0.34	(13)	7.25	(09)
4.7	(02)	7.01	(03)	3.23	(03)	1.73	(03)	0.38	(08)	11.1	(10)
7.8	(14)	8.5	(10)	4.2	(06)	3.6	(10)	0.39	(03)	11.3	(03)
7.86	(09)	10.3	(06)	4.8	(10)	4.75	(06)	0.51	(06)	17	(10)
7.79	(03)	11	(14)	5.1	(14)	4.8	(10)	0.75	(13)	22.2	(06)
16.2	(10)	14.7	(10)	8.46	(16)	6.83	(16)	2.44	(04)	25.8	(04)
41	(04)	15	(04)	21.5	(04)	8.42	(04)	10.7	(16)	25.3	(15)
Median Values											
4.48		5.99		2.82		2.37		0.36		9.18	

Aroclor 1221 in Sediment — Test Date 4/9/79

3.112	(15)	0.997	(15)	0.695	(15)	0.73	(15)	0.0	(05)	3.01	(15)
3.5	(12)	11.0	(12)	2.7	(12)	2.1	(13)	0.01	(15)	3.7	(12)
8.1	(14)	22	(02)	10	(02)	9.6	(02)	<0.02	(10)	24	(13)
19.6	(04)	39.0	(10)	29.3	(16)	25.0	(10)	<0.05	(10)	50.6	(10)
24	(02)	43.6	(16)	29.7	(08)	27.6	(08)	<0.1	(02)	71.7	(08)
31.2	(10)	43.6	(08)	32.8	(09)	46.7	(10)	<0.1	(13)	84.6	(16)
44.0	(08)	61.9	(08)	35.0	(10)	56.2	(08)	<0.1	(14)	101	(08)
58.7	(16)	110	(04)	44.6	(04)	62.8	(09)	0.1	(12)	154	(03)
80.0	(09)	141	(03)	63.0	(03)	67.4	(03)	0.102	(09)	183	(09)
86.4	(10)	153	(09)	88	(14)	79.4	(09)	0.562	(04)	215	(13)
137	(03)	174	(14)	88.8	(10)	79.8	(10)	0.88	(16)	260	(10)
188	(09)	208	(10)	114	(09)	92	(14)	9.8	(10)	308	(04)
Median Values											
37.8		52.7		36.3		51.5		<0.1		98.7	

Aroclor 1016 in Sediment — Test Date 4/9/79

<0.1	(12)	<0.1	(12)	<0.1	(12)	<0.1	(12)	0.01	(15)	<0.1	(12)
5.3	(15)	7.26	(15)	4.73	(13)	0.58	(15)	0.08	(08)	7.2	(15)
15.7	(10)	42.8	(08)	16.4	(09)	17.3	(10)	<0.08	(10)	40.7	(10)
33.6	(10)	41.3	(10)	18.1	(10)	20.0	(08)	0.05	(05)	47.7	(08)
44.0	(08)	46.1	(08)	19.2	(08)	20.5	(09)	<0.10	(02)	52.8	(16)
49.1	(08)	51.2	(09)	23.2	(06)	28	(02)	<0.10	(13)	95	(13)
54.6	(04)	61.7	(16)	33.2	(16)	29.7	(05)	<0.10	(14)	96.	(16)
56.0	(09)	64	(02)	34	(02)	34.6	(16)	<0.10	(12)	101	(10)
68.4	(16)	84.5	(03)	39.2	(03)	39.9	(03)	0.34	(14)	111	(13)
80	(02)	85.0	(10)	46.2	(10)	48.0	(10)	1.0	(13)	115	(13)
88.2	(03)	272	(04)	69	(14)	98	(16)	8.59	(16)	244	(14)
150	(14)	330	(14)	114	(04)	129	(04)	-		468	(04)
Median Values											
49.8		61.7		33.2		29.7		<0.1		93.4	

SOURCE: From James C. Daly, "An Assessment of the Performance of Laboratories Providing PCB Data for the PCB Settlement," Environmental Health Center, Division of Laboratories and Research, New York State Department of Health, September, 1979.

Note: PCB concentrations in ug/g. Reported values ranked in ascending order. Lab code of reporting laboratory in parenthesis after each reported value.

MONS 018459

Appendix D

CONTAMINATED SITE STUDY-COMPARISON DATA

Sample Number	PCB-102A Software Result (mg/kg)	PCB-102A Chart Recorder Result (mg/kg)	Outside Lab Result (mg/kg)
1	-	<10	0.2
2	-	21	33
3	11,000	11,000	7,700
4	-	<10	2
5	<30	30	13
6	77	53	94
7	16,000	31,000	46,000
8	-	430	310
9	75	45	5
10	20,000	20,000	13,000
11	60	30	16
12	Analysis too complex No quantitation	<10	0.5
13	<30	<10	ND*
14	500	530	190
15	37	25	20
16	8,100	4,900	4,600
17	<30	17	9
18	<30	<10	2
19	<30	<10	1.0
20	<30	<10	0.20
21	<30	<10	0.76
22	<30	<10	0.64
23	<30	<10	0.18
24	<30	<10	4.6
25	<30	<10	ND*
26	88	67	230
27	-	110	1,300
28	-	26	33
29	46	34	36
30	100	81	100
31	<10	<10	2.5
32	620	800	ND*
33	42	37	43
34	71	-	ND*
35	72	92	53
36	<30	<10	4
37	<30	<10	ND*
38	<30	<10	0.8
39	<17	-	4
40	11,000	4,500	3,900
41	390	260	170
42	<30	<10	0.8
43	760	1,200	750
44	<30	<10	2
45	3,600	2,400	1,300
46	8,000	7,000	7,000
47	<30	<10	0.4
48	3,000	2,500	2,900
49	1,900	1,400	2,400
50	-	<10	5
51	<30	<10	0.7
52	<30	<10	ND*

*None detected.

MONS 018460

Sample Number	PCB-102A Software Result (mg/kg)	PCB-102A Chart Recorder Result (mg/kg)	Outside Lab Result (mg/kg)
53	<30	<10	4
54	<30	19	6
55	-	27	11
56	6,300	12,000	6,000
57	-	47	57
58	1,800	1,600	1,460
59	<30	<10	3,240
60	<30	<10	3
61	<30	<10	0.3
62	22	32	4
63	-	<10	2
64	4	8	1
65	140	190	130
66	47	71	28
67	62	120	60
68	73	140	19
69	13	16	13
70	<30	<10	1
71	21	13	9
72	13	14	2
73	<30	<10	ND*
74	320	440	320
75	<30	<10	0.2
76	<30	10	4
77	3,600	5,300	3,100
78	3,800	5,300	4,800
79	<30	<10	0.3
80	<30	<10	0.2

*None detected

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