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# Innovations in Site Characterization

## Case Study: Dexsil L2000 PCB/Chloride Analyzer for Drum Surfaces





**Innovations in Site Characterization**  
**Case Study: Dextsil L2000 PCB/Chloride Analyzer for Drum Surfaces**

U.S. Environmental Protection Agency  
Office of Solid Waste and Emergency Response  
Technology Innovation Office  
Washington, D.C. 20460

## Notice

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Comments or questions about this report may be directed to the United States Environmental Protection Agency, Technology Innovation Office (5102G), 401 M Street, SW, Washington, D.C. 20460; telephone (703) 603-9910.

## **Foreword**

This case study is one of a series designed to provide cost and performance information for innovative tools that support less costly and more representative site characterization. These case studies will include reports on new technologies as well as novel applications of familiar tools or processes. They are prepared to offer operational experience and to further disseminate information about ways to improve the efficiency of data collection at hazardous waste sites. The ultimate goal is enhancing the cost-effectiveness and defensibility of decisions regarding the disposition of hazardous waste sites.

## **Acknowledgments**

This document was prepared for the United States Environmental Protection Agency's (EPA) Technology Innovation Office. Special acknowledgment is given to EPA Region 4 and the staff of Oak Ridge National Laboratory for their thoughtful suggestions and support in preparing this case study. Acknowledgment is also given to the Office of Emergency and Remedial Response and the Waste Policy Institute for their review and suggestions.

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## Dexsil L2000 PCB/Chloride Analyzer for Drum Surfaces Case Study Abstract

### Dexsil L2000 PCB/Chloride Analyzer for Sampling Drum Surfaces East Tennessee Technology Park, Oak Ridge, Tennessee

<p><b>Project Name and Location:</b> East Tennessee Technology Park Oak Ridge, Anderson County, TN 37831</p>	<p><b>Sampling and Analytical Technologies:</b> 1. Wipe sampling 2. Dexsil L2000 PCB/Chloride Analyzer</p>	<p><b>CERCLIS #</b> Not applicable</p>
<p><b>Period of Project Operation:</b> 1940 to current</p> <p><b>Operable Unit:</b> Not applicable</p>		<p><b>Current Project Activities:</b> Environmental and waste management support for the Department of Energy including operation of an incinerator for wastes regulated by the Toxic Substances and Control Act (TSCA).</p>
<p><b>Point of Contact:</b> David M. Carden U.S. Department of Energy P.O. Box 2001 Oak Ridge, TN 37831 423-576-9262 cardendm@oro.doe.gov</p>	<p><b>Media and Contaminants:</b> Metal drum surfaces contaminated with oily waste and soil residues from drum contents which had consisted of various polychlorinated biphenyls (PCB) waste materials.</p>	<p><b>Technology Demonstrator:</b> Department of Energy, Oak Ridge Operations Oak Ridge, TN 37831</p>
<p><b>Number of samples analyzed during investigation:</b> 26 wipe samples (Note: The original intent of PCB analyses was to monitor the clean-up of 7,000 empty drums, requiring 400 wipe samples. However, the clean-up work was aborted when the clean-up technology was found to be ineffective during the initial phase of the work during which 26 wipe samples were analyzed.)</p>		
<p><b>Project Cost Savings:</b> Analytical per sample costs (not including instrument cost or rental) for the Dexsil method is \$12.50 compared to \$50.00 for the GC/ECD laboratory method. Had the project not been aborted, use of the analytical method would have resulted in more than \$10,000 in analytical cost savings.</p>		
<p><b>Results:</b> A field method for PCB analysis provided rapid feedback regarding the effectiveness of a process for removing PCB surficial contamination from empty drums. Rapid turnaround in field analyses resulted in the data user's ability to abort the clean-up work before expending additional resources on a drum clean-up process that was not working.</p>		

## Dexsil L2000 PCB/Chloride Analyzer for Drum Surfaces

**Description:**

This case study describes how a field analytical method was used to measure PCB surficial contamination in empty drums that were cleaned by a new process. The Department of Energy (DOE) Oak Ridge Operations had obtained approval from the Environmental Protection Agency (EPA)-Region 4 to demonstrate the cleanup of 7,000 empty TSCA-regulated drums using a new pelletized-CO<sub>2</sub> scouring technique. DOE proposed and EPA approved a sampling program to determine the effectiveness of the clean-up technology and evaluate compliance with EPA's regulatory limits for releasing TSCA-regulated items. The proposed sampling program consisted of (1) statistical control limits for process monitoring, (2) random sampling of processed drums, (3) wipe sampling of container surfaces, and (4) rapid analysis of the wipe samples by a field method. During the trial period, the clean-up technology vendor attempted to clean about 20 of the most highly contaminated drums. Field analyses of residual PCB contamination, which provided results within one hour of wipe sample collection, showed that the clean-up technology was not working as expected. On the basis of the field results, which were later confirmed when the results of gas chromatography analyses became available, DOE aborted the drum clean-up project and the sampling program was terminated.

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# TECHNOLOGY QUICK REFERENCE SHEET

Case Study Name: Dexsil L2000 PCB/Chloride Analyzer for Drum Surfaces

<b>Technology:</b> Dexsil L2000 PCB/Chloride Analyzer			
<b>Summary of Case Study's Performance Information</b>			
<b>Project Role:</b> Used to measure residual surface PCB contamination in drums cleaned by a new process.		<b>Cost/Performance Information:</b> Analytical per sample cost (not including instrument cost or rental) for the Dexsil method is \$12.50 per sample compared to ~\$50.00 for the GC/ECD laboratory method. If the drum cleaning project proceeded as planned, use of the analytical method to verify regulatory compliance would have resulted in more than \$10,000 in analytical cost savings.	
<b>Total Cost:</b> Information not available			
<b>Project Cost Breakdown</b>			
<b>Instrument Cost:</b> \$3500	<b>Consumables Cost:</b> Test kit reagents, \$12.50 per sample	<b>Labor Cost:</b> Information not available	<b>Waste Disposal Cost:</b> Information not available
<b>Site-Specific Performance Observed:</b> Blanks analysis results ranged from 0.6 to 3.1 ug/100 cm <sup>2</sup> . Recoveries on Arochlor 1260 10 ug/100 cm <sup>2</sup> standards (reported as Arochlor 1242) were greater than 100% (range: 118-263%). Although the Dexsil field results were qualitatively consistent with the lab verification analyses, the latter values tended to be higher than corresponding field measurements. Oily residues on the wipe samples may have exacerbated differences in extraction efficiencies between the field and laboratory methods, each of which used different solvents and extraction times.			
<b>General Commercial Information (Information valid as of August 1998)</b>			
<b>Vendor Contact:</b> John Siliman Technical Support	<b>Vendor Information:</b> Dexsil Corporation One Hamden Park Drive Hamden, CT 06517 203-288-3509	<b>Limitations on Performance:</b> Cannot distinguish PCB congeners; identification of Aroclor not possible.	
<b>Availability/Rates:</b> Instrument and test kits (reagents + extraction vessels) can be purchased from Dexsil	<b>Principle of Operation:</b> Metallic sodium strips PCB molecules of chlorine; chloride levels are measured by a chloride-ion-specific electrode and converted to PCB concentration using known chlorine percentages present in Aroclors.	<b>Power Requirements:</b> 120 V	
<b>General Performance Information</b>			
<b>Rate of Throughput:</b> 5 samples per hour when sample preparation and analyses were done outdoors; 10 samples per hour when sample preparation and analyses were done indoors (from ETV study)		<b>Known or Potential Interferences:</b> Other chlorinated organics that are preferentially soluble in a non-polar solvent; iodine and bromine	
<b>Applicable Media/Matrices:</b> Soil, surface wipes, dielectric fluids and oils	<b>Analytes Measurable with Commonly Achieved Detection Limit Ranges:</b> PCBs, 2 ppm or 2 ug/100cm <sup>2</sup> (if a 1000 cm <sup>2</sup> area is wipe sampled).	<b>Other General Accuracy/Precision Information:</b> (from ETV report EPA/600/R-98/109; see website <a href="http://www.epa.gov/etv/library.htm#verifications">www.epa.gov/etv/library.htm#verifications</a> )  Average recovery in soil samples: 208% Average recovery in extract samples: 149%	

Precision in soil samples as relative standard deviation (RSD): 23%  
Precision in simulated extract samples as RSD: 14%

## Dexsil L2000 PCB/Chloride Analyzer for Drum Surfaces

<p><b>Wastes Generated Requiring Special Disposal:</b> All materials and reagents that contact PCB-contaminated material may be considered TSCA waste; applicable regulations for TSCA waste disposal should be checked before disposal of used materials and reagents.</p>		
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## Dexsil L2000 PCB/Chloride Analyzer for Drum Surfaces

### EXECUTIVE SUMMARY

This case study describes a field analytical method that was used to measure PCB surficial contamination in empty drums to be cleaned by a new process. Approximately 7,000 empty 55-gallon drums that previously contained PCB-contaminated material had accumulated at the Department of Energy (DOE)'s East Tennessee Technology Park in Oak Ridge, TN. Because disposal of these drums following regulator-approved methods would have been very costly, DOE requested permission from the Environmental Protection Agency (EPA)-Region 4 to demonstrate the cleanup of these drums using a new CO<sub>2</sub> scouring technology. DOE also proposed and EPA approved a sampling program to demonstrate the effectiveness of the clean-up technology and evaluate compliance with EPA's regulatory limits for releasing PCB-contaminated items. The proposed sampling program consisted of (1) statistical control limits for process monitoring, (2) random sampling of processed drums, (3) wipe sampling of container surfaces, and (4) rapid analysis of the wipe samples by a field method.

While taking advantage of the cost effectiveness and quick turnaround of field methods, DOE minimized the risk of violating regulatory limits by selecting the field method based on the following criteria: (1) if field results are biased, they must be biased high, (2) the field technique should provide a low probability of false negative results, (3) the detection limit should be well below the lowest action/decision level, and (4) the field technique should provide quantitative results rather than results in the form of ranges or intervals. Of the six field methods evaluated during the Environmental Technology Verification (ETV) project co-sponsored by EPA and DOE, only the Dexsil L2000 PCB/Chloride Analyzer satisfied these criteria and was thus selected for monitoring the drum cleaning process.

During the initial phase of the project, the CO<sub>2</sub> scouring technology vendor attempted to clean 20 of the most highly contaminated drums. The Dexsil PCB Analyzer was used to monitor residual PCB contamination in the processed drums during this trial period. Field analyses, completed and reported within one hour of sample collection, showed that the clean-up technology was not working as expected. On the basis of the field-generated results, which were confirmed by wipe samples sent to an off-site laboratory for gas chromatography analysis, DOE decided to abort the drum clean-up project before additional resources were expended. Although only a limited data set was obtained to evaluate the overall performance of the Dexsil field method, this case study demonstrates the usefulness of field methods for rapid decision-making.

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## Dexsil L2000 PCB/Chloride Analyzer for Drum Surfaces

### PROJECT INFORMATION

#### Identifying Information

Demonstration Project for Pelletized CO<sub>2</sub> Drum Cleaning Process  
East Tennessee Technology Park  
Oak Ridge, Anderson County, TN 37831

#### Background [1, 2]

**Project Use:** The East Tennessee Technology Park (ETTP), formerly the K-25 project, was built in the 1940s as the Oak Ridge Gaseous Diffusion Plant, a facility where highly enriched uranium was produced for the U.S. Army's Manhattan Project. Since then, facility ownership has been transferred to the U.S. Department of Energy (DOE), and its mission has evolved to support environmental management activities within DOE's Oak Ridge Operations (ORO). Specific activities currently being conducted at ETTP include the operation of a Toxic Substances Control Act (TSCA) incinerator, which receives TSCA-regulated waste for disposal from DOE facilities, and technical support for waste management within the DOE/ORO complex. ETTP is currently managed by Bechtel Jacobs Company, LLC for DOE.

**Release Investigation/History:** As of early 1998, approximately 7,000 empty drums that previously contained materials contaminated with polychlorinated biphenyls (PCBs) were stored at ETTP. At one time the drums contained TSCA-regulated waste generated within the DOE complex that were either repackaged or disposed of in the ETTP's TSCA incinerator. Drum contents ranged from transformer oils to contaminated soils with PCB levels exceeding 50 ppm. Records regarding the contaminant characteristics of the previous contents exist for most of these drums, however residual PCB surficial contamination in these drums had not yet been characterized.

**Regulatory Context:** Under TSCA rules, the handling and disposal of empty drums that previously contained PCB-contaminated material depends on the level of PCBs that were in the drums. If the contents exceed 500 ppm of PCBs, the empty drum must be disposed of in an incinerator that complies with 40 CFR 761.70, or in a chemical waste landfill that complies with 40 CFR 761.75. Alternatively, the drum can be triple-rinsed according to the standard procedures in 40 CFR 761.79.

Some of the 7,000 empty drums at ETTP contained wastes that exceeded 500 ppm. Because disposal of these drums in an incinerator or chemical waste landfill would be very costly, and decontamination by triple-rinsing would generate a large volume of TSCA waste [2], DOE requested approval from EPA Region 4 to demonstrate an innovative scouring technology by which pelletized CO<sub>2</sub> is utilized to remove surficial contamination from the drums. Pursuant to the Oak Ridge Reservation PCB Federal Facility Compliance Agreement (FFCA) between EPA and DOE, containers cleaned using a process other than triple-rinsing must be tested for residual PCB

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### PROJECT INFORMATION, CONT'D.

contamination before disposal. PCB surface levels must not exceed 10  $\mu\text{g}/100\text{ cm}^2$  if the cleaned drum is to be free-released, or 100  $\mu\text{g}/100\text{ cm}^2$  if the drum is to undergo metal recycling. Vendor claims regarding the  $\text{CO}_2$  scouring technology led DOE to believe that drums cleaned by this process would show residual PCB levels acceptable for free-release. Furthermore, the waste generated by this clean-up technology and the overall clean-up cost per drum would be an order of magnitude less than that associated with triple-rinsing.

Because the pelletized  $\text{CO}_2$  clean-up process was not an EPA-approved technique, DOE proposed implementing a testing program to ensure that EPA's established surface cleanup standards would be met. The testing program was designed to include (1) statistical control limits for process monitoring, (2) statistical random sampling of processed drums, (3) wipe sampling of container surfaces, and (4) rapid analysis of the wipe samples by an on-site measurement method. Through a memorandum issued to DOE [2], EPA Region 4 approved the demonstration of the  $\text{CO}_2$  cleaning technology, and concurred with the testing program DOE had proposed with minor modifications. Within the context of the Oak Ridge Reservation PCB Federal Facility Compliance Agreement, flexibility is accorded to the Region in applying PCB regulations to DOE's particular problems with managing PCB/radioactive waste streams.

#### **Project Logistics/Contacts**

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**Federal Lead Agency:** U.S. Department of Energy, Oak Ridge Operations

**Federal Oversight Agency:** Environmental Protection Agency, Region 4

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Atlanta, GA 30303-8909

**Dexsil L2000 PCB/Chloride Analyzer for Drum Surfaces**

**PROJECT INFORMATION, CONT'D.**

404-562-8990

## Dexsil L2000 PCB/Chloride Analyzer for Drum Surfaces

### **MEDIA AND CONTAMINANTS**

#### **Matrix Identification**

**Type of matrix sampled and analyzed:** Drum surfaces of 55-gallon drums

#### **Project Geology/Stratigraphy**

This information is not relevant to this project.

#### **Contaminant Characterization**

**Primary contaminant groups:** Polychlorinated biphenyls (PCBs)

#### **Matrix Characteristics Affecting Characterization Cost or Performance**

PCB surface contamination in the processed drums was characterized by wipe sampling using gauze pads saturated by a solvent (see detailed description under Characterization Technologies). The presumption is that all the PCB contaminants on the sampled surface are effectively collected by the gauze pad. However, if a significant oily residue is present, the gauze pad can become saturated and cannot absorb all the oil present on the sampled surface. Under such conditions, the measured surface contamination can be negatively biased. These effects would apply for both the field and laboratory analyses of the wipe samples. According to personnel involved with the project, oily residues were observed in some of the drums even after they had been processed. Thus, the analytical results for the highly contaminated drums may underestimate the actual levels of residual surface contamination.

Oily residue on the wipe samples could also exacerbate differences in extraction efficiency between the field and laboratory methods. This is discussed in more detail under the Section on Performance Evaluation.

### **PROJECT CHARACTERIZATION PROCESS**

#### **Goal of Characterization**

DOE obtained approval from EPA to demonstrate an innovative CO<sub>2</sub> scouring technology to remove surficial contamination from 7,000 empty TSCA drums that were in storage at ETPP. Because this new technology had not been approved by EPA as a substitute for the standard triple-rinsing procedure outlined in 40 CFR 761.79, monitoring of the clean-up process was required to certify its effectiveness. DOE and EPA agreed on a sampling and analysis plan [2] which would establish with a known level of confidence that the clean-up process was meeting regulatory goals, i.e., that residual PCB surface levels were below 10 µg/100 cm<sup>2</sup> if the cleaned drums were to be free-released, or below 100 µg/100 cm<sup>2</sup> if the cleaned drums were to be

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subjected to metal smelting. Using the Data Quality Objectives Process to organize the goals and expectations of this project produces the following outputs:

1. **State the Problem:** This problem can be stated in two parts:
  - C Demonstrate a cheaper, effective drum cleanup method.
  - C Use a cheaper, rapid turn-around analytical method to sample and analyze a representative number of the drums to ensure cleanup goals are met.
  
2. **State the Project Decision(s):**
  - C Determine whether the new cleaning process can achieve one of two preferred drum disposal options by meeting applicable regulatory levels: free-release ( $10 \mu\text{g}/100 \text{ cm}^2$ ) and/or metal recycling ( $100 \mu\text{g}/100 \text{ cm}^2$ ).
  - C Designate each 500-drum batch as appropriate for one or the other disposal option.
  
3. **Define the appropriate data inputs:**
  - PCB concentrations (as  $\mu\text{g}/100 \text{ cm}^2$ ) in any residues remaining on the inside surfaces of drums after cleaning.
  
4. **Define the conditions under which to collect data and other study boundaries:**
  - C Wipe samples will be taken from the drum's inside surfaces, and analyzed by a method which can provide the required PCB data.
  - C The number of drums from each 500-drum batch that will be sampled will be determined according to a statistically-designed sampling plan.
  - C The collection and analysis of samples will use a field analytical method with a defensible quality assurance plan.
  
5. **State the Decision Rule(s):**
  - C Decision Rule for using the new cleaning process: If the process is unable to clean drums to either the free-release or metal recycling regulatory criteria, then the new process cannot be used.
  - C Decision Rule for the free-release disposal option: If the nominal action level of  $10 \mu\text{g}/100 \text{ cm}^2$  of total PCBs cannot be achieved, the free-release option cannot be used to dispose of drums.
  - C Decision Rule for the metal recycling disposal option: If the nominal action level of  $100 \mu\text{g}/100 \text{ cm}^2$  cannot be achieved, the metal recycling option cannot be used to dispose of drums.
  
6. **Specify limits on decision errors:** For each batch of 500 drums, under a worst case-scenario, there must be 95% confidence that no more than 10% of the drums in the batch exceed the nominal action level and a 95% confidence that no more than 10% false negative analytical results are produced by the analytical method. It was expected that, with the safety factors built into the statistical and analytical design, actual exceedances would be much less. After generation of the statistical data for each batch of drums, the actual probability of exceeding the nominal

## Dexsil L2000 PCB/Chloride Analyzer for Drum Surfaces

action level will be determined from the analytical data sets, and the statistical confidence actually achieved will be documented in the project report.

*[The reader is cautioned that depending on the regulatory context, the use of a sampling and analysis plan that permits any statistical exceedance of TSCA regulatory limits for PCBs might not be acceptable to the regulating entity. Under the Oak Ridge Reservation PCB Federal Facility Compliance Agreement, flexibility in setting statistical limits on decision errors was permitted by Region 4 for this project evaluating an innovative drum cleanup method.]*

### 7. *Optimize the Design:*

C Optimization of the sampling and analysis plan will be carried out according to detailed quality control and corrective action measures. With the exception of the use of periodic field duplicates as described in the analytical QA/QC plan, a single sample will be taken to characterize each drum, as long as the following assumption is demonstrated to be valid: Any PCBs remaining after drum cleaning are uniformly distributed on the inner surfaces of the drums.

Since it was discovered during the initial evaluation of the cleaning process that it could not achieve even the 100 µg/100cm<sup>2</sup> regulatory limit, it could be said the project was “optimized” by aborting it so that no more resources than necessary were expended on an unworkable project.

The analytical Data Quality Objective (DQO) Summary Statement for this project is “Verify with at least 95% confidence that no more than 10% of 7,000 drums remain contaminated at applicable regulatory levels after being cleaned with the new process.”

## **Sampling Workplan**

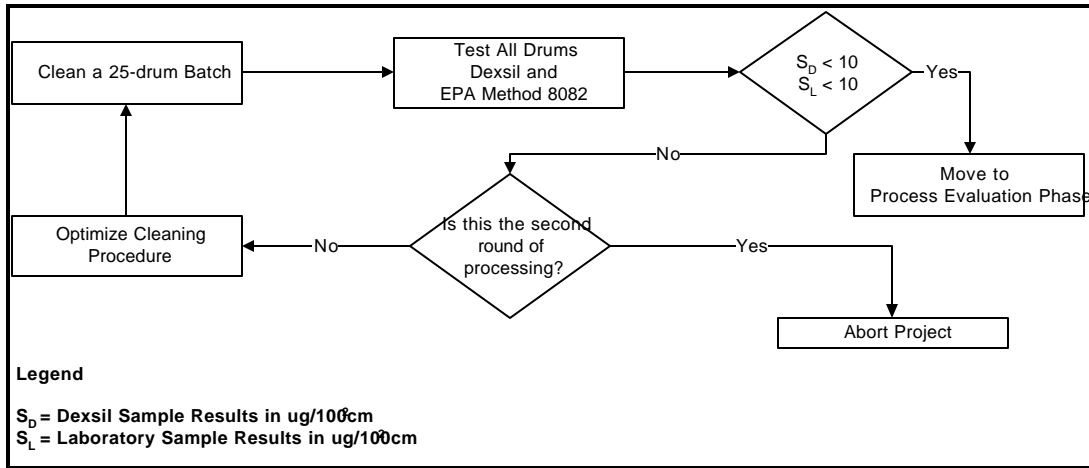
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Monitoring of the drum clean-up process was divided into an initial intensive sampling phase for process optimization followed by a production sampling phase for process control and effectiveness verification. A discussion of each sampling phase is provided below, and follows the decision tree graphics presented in Boxes 1 and 2, below.

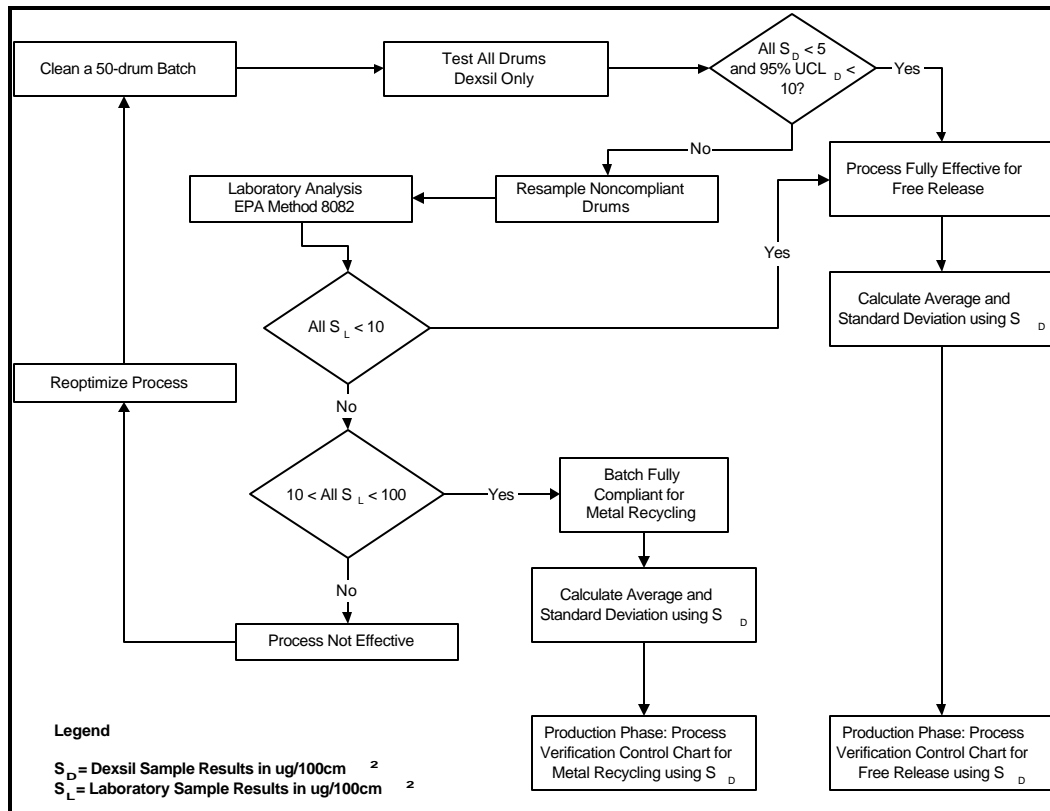
### *Process Optimization: Initial Intensive Sampling* (See Box 1)

The objectives of this phase were (1) to determine whether the CO<sub>2</sub> process can achieve at least one of the regulatory goals (100 µg/100 cm<sup>2</sup> for metal recycling, or 10 µg/100 cm<sup>2</sup> for free release), and (2) to obtain process control information that will be used to monitor the clean-up process during the subsequent production phase.

## Dexsil L2000 PCB/Chloride Analyzer for Drum Surfaces



**Box 1: Process Optimization Decision Tree**



**Box 2: Process Evaluation Decision Tree**

## Dexsil L2000 PCB/Chloride Analyzer for Drum Surfaces

For this initial phase, 75 of the most contaminated drums were selected based on visual inspection and records of prior contents. The clean-up technology vendor was permitted to process 25 of the 75 drums in order to determine the optimum amount of CO<sub>2</sub> scouring time needed to remove surficial contamination to acceptable levels (see Box 1). Residual contamination during this optimization stage was measured by taking wipe samples from the inner surfaces of the processed drums, and analyzing the wipes using the Dexsil PCB test kit. Duplicate samplings of 10 drums were sent to the laboratory for confirmatory analysis by gas chromatography. Wipe sampling and the Dexsil PCB test kit are described in more detail in the Characterization Technologies section, below.

Unfortunately, it quickly became clear that neither regulatory goal could be achieved. The demonstration was discontinued because the process was deemed “ineffective” before the next step of the process optimization and evaluation plan was reached. For the educational purposes of this case study, however, further discussion of the project plan will continue in order to explain the rationale of this study.

After optimization, the vendor was to process the remaining 50 drums using the optimized conditions to demonstrate process effectiveness to DOE and EPA (see Box 2). The surfaces of those 50 processed drums would then be wiped, and the sample results used to determine whether or not the process can achieve the regulatory goal of 10 µg/100 cm<sup>2</sup> for free-release of the drums, or 100 µg/100 cm<sup>2</sup> for metal smelting of the drums. The decision rules are as follows:

### *Acceptance Criteria for Process Effectiveness*

- (1) If the residual surficial contamination as measured by the Dexsil PCB test is less than 5 µg/100 cm<sup>2</sup> for all 50 drums, then the process is deemed “fully effective for free release.” There is an additional requirement in the workplan that “the upper 95% confidence level on the mean of the 50 consecutively processed drums must be less than the regulatory cleaning goals.” Depending on the variability present in the 50 sample results, it is possible to have an upper 95% confidence level that is greater than the regulatory cleaning goal, even though each of the 50 samples is less than the regulatory cleaning goal. If the mean of the data were *significantly* less than the regulatory cleaning goal, then this outcome might not occur. But if the mean of the data is close to the regulatory goal with enough (expected) variability in the data, there is a good chance that the upper 95% confidence level would exceed the regulatory limit.
- (2) If one or more drums has residual levels above 5 µg/100 cm<sup>2</sup> as determined by the field test, those drums will be re-sampled and the wipes will be sent to a fixed laboratory for analysis by EPA Method 8082 (Polychlorinated Biphenyls (PCBs) by Capillary Column Gas Chromatography) [8]. If the fixed lab analysis results are less than 10 µg/100 cm<sup>2</sup> for all samples, then the re-sampled drums are considered acceptable and the process deemed “fully effective for free release.” If the fixed lab analysis results are greater than 10 µg/100 cm<sup>2</sup> but less than 100 µg/100 cm<sup>2</sup> for all samples, then the process is deemed “fully effective for metal recycling.” If at least one of the fixed lab results is



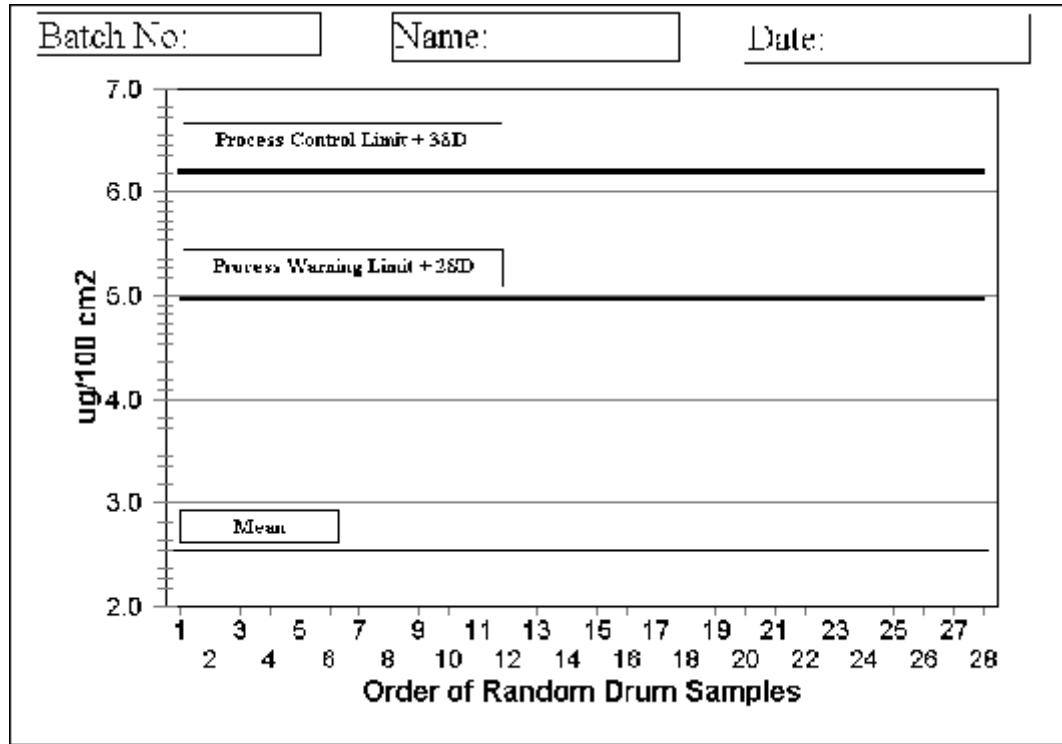
### **Dexsil L2000 PCB/Chloride Analyzer for Drum Surfaces**

greater than  $100 \mu\text{g}/100 \text{ cm}^2$ , then the process is deemed “ineffective” and the clean-up vendor may be asked to re-optimize the process and demonstrate technology effectiveness using another set of 50 drums.

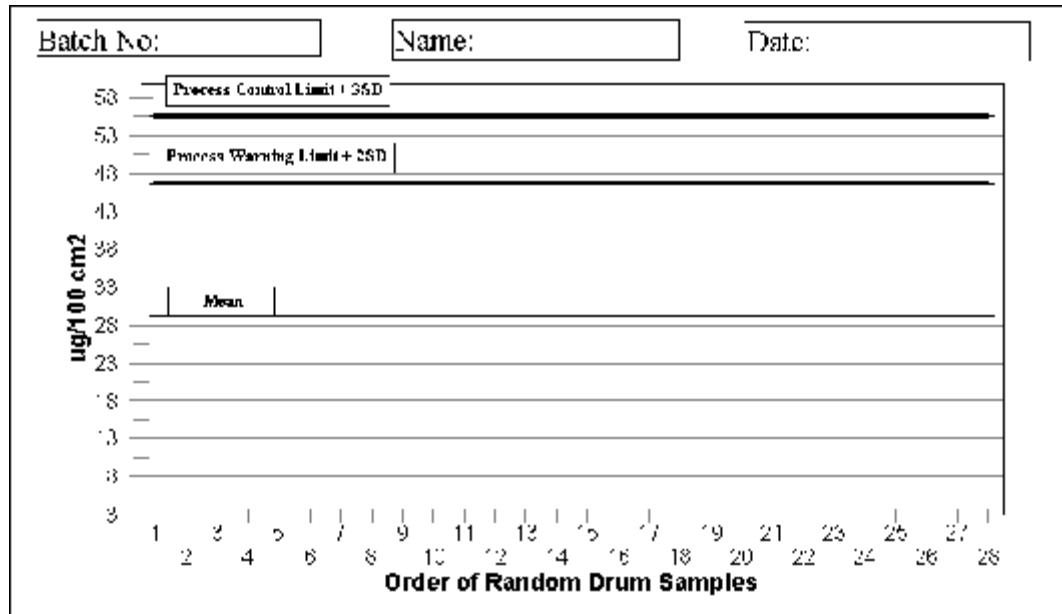
The original project design was directed at meeting the free release regulatory standard of  $10 \mu\text{g}/100 \text{ cm}^2$ . However, if the cleanup process was unable to meet that stringent standard, the same design, with minimal modifications, could be used to meet the standard for metal recycling of  $100 \mu\text{g}/100 \text{ cm}^2$ . For example, 50 and  $100 \mu\text{g}/100 \text{ cm}^2$  could replace 5 and  $10 \mu\text{g}/100 \text{ cm}^2$  as the field-specific and nominal regulatory action levels, respectively.

The decision trees above (Boxes 1 and 2) establish the role and usefulness of the Dexsil kit as a screening tool to select samples that require testing by Method 8082 to confirm regulatory compliance during these initial phases of work which were designed to establish process effectiveness. If the cleaning contractor had been able to satisfy the “full process effectiveness” criteria for at least one of the two goals and had successfully processed a batch of 50 drums according to the decision tree above, the mean and standard deviation (SD) of residual surface contamination in these 50 drums, as determined by results of the Dexsil PCB test kit, would be used as parameters for process control during the production phase. This is accomplished by the development of a control chart. An example of a control chart is provided in Figure 1 using a fictitious data set that might have resembled the data generated during the 50-drum process-effectiveness evaluation, had the cleaning process proven “fully effective for free release.” Figure 2 shows a control chart that may have been created had the cleaning technology failed the free-release goal, but was demonstrated “fully effective for metal recycling.” The Mean, Process Warning Limit, and Process Control Limit for a control chart would be derived from the data generated during the 50-drum Process Evaluation Procedure, during which the cleaning process would be maximally optimized. Later, during the production phase of work, data collected from each of 28 randomly selected drums from each 500-drum batch would be plotted on the chart as a means of assessing whether the cleaning process continued to perform optimally as all 7,000 drums were cleaned (described in more detail below).

### Dexsil L2000 PCB/Chloride Analyzer for Drum Surfaces



**Figure 1: Process Control Chart for Free Release**

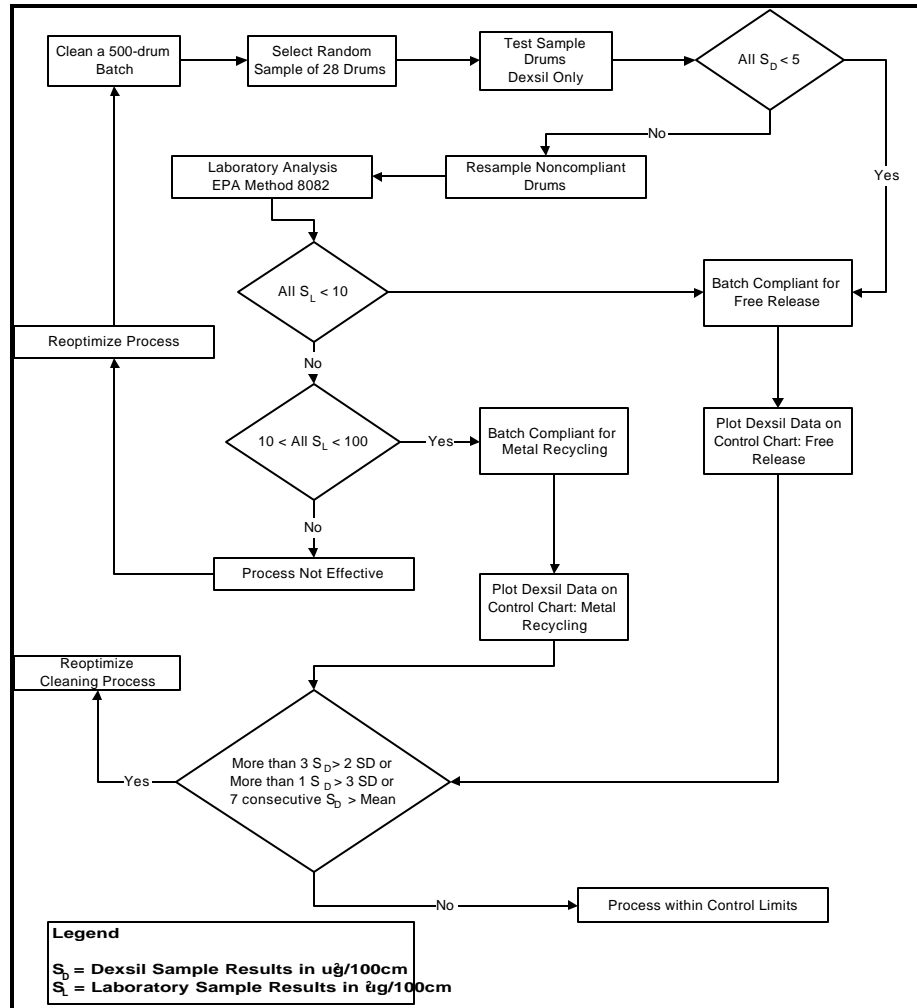


**Figure 2: Process Control Chart for Metal Recycling**

## Dexsil L2000 PCB/Chloride Analyzer for Drum Surfaces

### *Process Verification and Control: Production Phase Sampling*

Had the process been deemed “fully effective” either for free release or metal recycling, production phase sampling would be conducted with random verification sampling to ensure that the process remains in control and that process action limits, established during the Process Evaluation Procedure and used to prepare the Process Control Chart, are not exceeded (see Box 3).



**Box 3: Production Phase Decision Tree**

### **Dexsil L2000 PCB/Chloride Analyzer for Drum Surfaces**

The drums will be processed in batches of 500, and 28 drums per batch will be randomly selected for wipe sampling and analysis using Dexsil PCB test kits, and the results plotted on a Control Chart (28 sample results plotted on each chart, with one chart plotted per batch of 500 drums).

A discussion of two easily implemented protocols for random sampling of these drums appears in Box 4. The number of samples per batch was determined based on the statistical design proposed for this project, which was a nonparametric one-sided tolerance limit that does not require a presumption about the normality of the distribution of the measurements [4]. Using a sample size of 28 randomly selected drums allows one to state with 95% confidence that no more than 10% of a 500-drum batch will have residual levels greater than the highest result in the set of 28 random samples. Stated another way, the statistical design assures that there is less than a 5% chance that more than 50 drums out of a 500-drum batch will have a surficial PCB concentration greater than the highest result within the set of 28 randomly selected samples. It is possible with this statistical test to select more stringent tolerance limits, for example, instead of using the criteria that no more than 10% of a 500-drum batch would have residual levels greater than the highest result at the 95% confidence level, it is possible to specify that only 1% of a 500-drum batch (or only 5 drums) would have levels greater than the highest result at the 95% confidence level. Choosing this tolerance limit would raise the required number of randomly selected drums to be sampled to about 298, rather than 28, substantially increasing the cost and effort involved. Because of all the other conservatively stringent controls in place for this sampling plan, EPA Region 4 was comfortable permitting a less rigorous confidence level for this aspect of the sampling design. The reader should also recall from previous discussions that this type of statistical sampling design may not be acceptable to regulators under other PCB cleanup or decontamination scenarios.

Note that the data from the 28 randomly sampled drums from each 500-drum batch serve at least two, and possibly three, distinct purposes:

- 1) Use of the data (specifically, using the highest result of the 28-sample data set) in determining compliance with the nonparametric one-sided tolerance limit statistic used to predict residual levels of PCBs in the 500-drum batch after cleaning [4] and ensure meeting the defined Decision Error Limit (see the Acceptance Criteria for Processed Drums, p. 13);
- 2) Plotting the 28 data points on control charts to permit close monitoring of the efficiency of the cleaning process so that re-optimization of the CO<sub>2</sub> scouring process can be performed at the first indication of a loss of efficiency (see Process Control, below); and
- 3) The possible use of the data to calculate parametric or nonparametric statistical parameters, as appropriate (such as a confidence limit on the 99th percentile for a “not-to-exceed” regulatory standard) [8].

The decision tree in Box 3 assumes that the initial testing had demonstrated that the process

## Dexsil L2000 PCB/Chloride Analyzer for Drum Surfaces

could achieve the regulatory limit for free release, but routing batches of drums to the metal

### Box 4: Hypothetical Random Sampling Protocol

The statistical procedure for selecting the number of drums that would be sampled in each batch for the one-sided non-parametric tolerance limit is as follows: [7]

$$n = \log(\alpha)/\log(P) = \log(0.05)/\log(.90)$$

$$n = -1.3010/-0.0458 = 28$$

Where:

alpha = 1 - level of confidence desired; and

P = the percent of compliant drums.

A 500-drum batch is assembled (from the total of about 7,000 drums) in an area in preparation for the cleaning process. A random number generator is used to select 28 numbers between 1 and 500. (For example, say that 34 and 79 are two of the random numbers selected.) Before any drums are cleaned, the selected 28 random numbers are ordered on a list, from lowest to highest in numerical order. Then the cleaning process is begun. As each drum is about to be subjected to the cleaning process, it is assigned the next consecutive number (from 1 to 500). When the 34th drum is cleaned, it is immediately sampled before being stacked with the rest of the cleaned drums. When the 79th is cleaned, it is sampled before being stacked, and so on.

For example:

Order of Sampling	1	2	3	4	5	...	25	26	27	28
Order of Drum Cleaning & Drum ID Number	34	79	101	128	188	...	305	420	452	463

Alternatively, all 500 drums could be numbered as they are assembled in preparation for cleaning. After all have been assigned numbers, use a random number generator to select the numbers of the 28 drums to be sampled, and record those numbers in the order in which they were chosen. Cleaning does not have to proceed in any particular order. When a drum is cleaned which was previously selected for the set of 28, it is sampled before being stacked with the rest of the cleaned drums. The order of cleaning of these numbered drums must be preserved, but the numbers themselves do not have to be in order.

For example:

Order of Sampling (after cleaning)	1	2	3	4	5	...	25	26	27	28
Drum ID Number	305	251	301	34	101	...	452	292	197	79

recycling option is possible if some batches did not meet the criteria for free-release, but did meet the less stringent recycling criteria.

## **Dexsil L2000 PCB/Chloride Analyzer for Drum Surfaces**

### *Acceptance Criteria for Processed Drums*

- (1) If all 28 randomly-selected drums have residual contamination less than  $5 \mu\text{g}/100 \text{ cm}^2$  using the Dexsil test kits, the batch of 500 drums are deemed clean enough for free release. Since the nonparametric statistical procedure used ensures that no more than 10% of the 500 drums in a batch would exceed the highest result in the data set, and since the highest result is less than  $5 \mu\text{g}/100 \text{ cm}^2$ , such a data set meets the defined statistical goal given in Step 6 of the DQO Process that no more than 10% of the batch exceed the regulatory limit of  $10 \mu\text{g}/100 \text{ cm}^2$ .
  
- (2) If one or more of the 28 drums has residual contamination greater than  $5 \mu\text{g}/100 \text{ cm}^2$  using the Dexsil test kits, these drums will be re-sampled and the wipes analyzed using EPA Method 8082. If all of the fixed lab analysis results are less than  $10 \mu\text{g}/100 \text{ cm}^2$ , then the 500 drums are deemed clean enough for free release. If at least one of the fixed lab analysis results is greater than  $10 \mu\text{g}/100 \text{ cm}^2$  but less than  $100 \mu\text{g}/100 \text{ cm}^2$ , then the 500 drums are deemed acceptable for metal recycling. If at least one of the fixed lab analysis results is greater than  $100 \mu\text{g}/100 \text{ cm}^2$ , then the drums are deemed unacceptable for free release or recycling and the vendor may be required to re-process all 500 drums until random sampling demonstrates that one of the regulatory limits has been achieved.

### *Process Control*

After the data from the 28 random samples are evaluated using the applicable decision tree, and the corresponding 500-drum batch is deemed “clean,” the data from the 28 random samples will be used to indicate whether process effectiveness is beginning to degrade. This is done by plotting the data on a control chart. Each batch of 500 drums would have its 28 samples plotted on a copy of the control chart generated during Process Evaluation, and the cleaning order must be preserved when plotting the data on the chart. Deterioration of cleaning effectiveness would be apparent if the results of any of the 28 random samples began to rise above the limits established on control charts during process optimization. Even if those results were not yet exceeding the regulatory limit, it would be a signal that the cleaning process might again need to be optimized, and early corrective action could be implemented. The following criteria would have been used as indicators of diminishing process effectiveness.

1. Three or more of the 28 samples exceeds  $\bar{O} + 2 \text{ SD}$  (i.e., the Process Warning Limit), where  $\bar{O}$  and SD are the mean and standard deviation respectively of the residual levels in the 50 drums used to initially demonstrate “full effectiveness” and prepare control charts.
  
2. At least one of the 28 samples exceeds  $\bar{O} + 3 \text{ SD}$  (i.e., the Process Control Limit).
  
3. If any seven consecutive data points have residual levels greater than  $\bar{O}$ .

## **Dexsil L2000 PCB/Chloride Analyzer for Drum Surfaces**

### *On-Going Process Control Validation*

The random sampling scheme used for process verification does not guarantee that none of the 500 drums will exceed the regulatory limits. However, the sampling scheme does ensure with a 95% confidence level that the maximum number of drums that can violate the regulatory limit in a batch of 500 drums is 50, under a worst case scenario. It is possible that data from the 28 random samples in a batch might be used to project the probability that an individual drum within that batch would exceed a regulatory limit. As the project proceeds, the data from each round of 28 random samples is added to the data collected during previous rounds. The mean and standard deviations of these data are calculated, and the results compared with the process control limits for the project. If the comparison shows a significant difference between the calculated mean or standard deviations and the process control assumptions, this will serve as a warning that the early assumptions about the variability of the concentrations in the drums to be cleaned may not be valid.

### Wipe Sampling

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Residual PCB contamination in the processed drums is tested by wipe sampling, a standard EPA technique for sampling contamination on smooth surfaces [5]. Wipe sampling is accomplished by applying 2 mL of chromatographic-grade hexane to a sterile gauze pad, then using the soaked gauze pad to wipe a pre-determined, pre-measured area (1000 cm<sup>2</sup> or 12.5-in x 12.5-in) on the surface of a drum. Pre-measured aliquots of hexane were provided by Dexsil in sealed glass ampules to prevent contamination from external sources prior to use. After sampling, the hexane was allowed to evaporate, and the wipe was then extracted and analyzed following procedures for the Dexsil PCB test method (see below).

As noted in the section on quality control measures below, a significant component of measurement variability in wipe samples can be from heterogeneous analyte distribution of the surface being sampled. This must be considered when establishing QC criteria for replicate measurements and comparisons between different analytical methods (e.g., field vs lab) using separately collected wipe samples.

As discussed elsewhere in this case study, a number of factors can complicate wipe sampling (such as the amount and character of the sampled residue) and compromise analytical integrity. If complicating factors are anticipated during project planning, modifications to the wipe sampling procedure can be evaluated to ensure the representativeness and comparability of the analytical testing.

### PCB Analysis Using the Dexsil L2000 PCB/Chloride Analyzer

The Dexsil L2000 PCB/Chloride Analyzer is a field-portable instrument designed to quantify PCB concentration in soils, dielectric fluids, and surface wipes. For wipe samples, PCBs are extracted from the wiped sample by solvating the wipe with 10 mL of isooctane for 30 seconds. Inorganic chloride and water are removed from the isooctane extract by passing it through a Florisil cartridge, then the extract is mixed with a reaction solution and metallic sodium (which dechlorinates the PCB molecules). The free chloride released into the reaction solution is measured with an ion-specific electrode. Only chloride which was part of any organic molecule contributes to the signal (the Dexsil PCB kit is not specific for PCBs); inorganic chloride originally present in the sample does not interfere. The output of the chloride-specific electrode is electronically converted to the surficial PCB contamination (in µg/100 cm<sup>2</sup>) of a 1000 cm<sup>2</sup> wipe sample area. The free chloride concentration is converted to a Arochlor concentration based on the analyst's choice of one of four different settings—Arochlor 1242, Arochlor 1260, Askarel A (60% Arochlor 1260/40% trichlorobenzene), and total chloride. The instrument does not report Arochlor 1254. Arochlor identification can not be made because the measurement technique can not distinguish among the PCB congeners. Hence, the user needs to use site history or previous data to set the analyzer to convert the chloride concentration to the appropriate PCB congener. Alternatively, the user can set the analyzer to report results as Arochlor 1242, which has the



lowest percentage of chlorine, to obtain the most conservative (highest) PCB sample concentrations.

### **Quality Assurance/Quality Control Measures**

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The key to an effective QA/QC plan is that it take into consideration the limitations and strengths of the sampling and analytical methods involved, and the goals of the project. To meet the goals set forth in the preceding section, the Dexsil kit must be shown to produce data which meet the needs of site-specific decision process. One of the most important needs is that the site-specific results are consistently comparable (or consistently and predictably conservative) as compared to the 'reference methods' by which the TSCA action levels were derived. Had the drum cleaning method worked, that is, had the pelletized CO<sub>2</sub> process been able to physically remove the oily, often viscous, residue coating the inside surfaces of many of the drums, demonstrating comparability between the wipe sample results obtained by the Dexsil kit and those obtained by a traditional laboratory may have been a simple matter.

Unfortunately, since the cleaning process was ineffective at removing the oily residue, wipe sampling and analysis became a difficult task for a number of reasons which are discussed in more detail later in this section. If good comparability between laboratory and field measurements at all analyte concentrations is to be expected to provide data defensibility, representative sampling and analysis issues must be addressed, or this aspect of the quality assurance plan will fail.

Since it was not expected that the drum cleanup method would leave so much oily material, the sampling and analytical difficulties encountered were not anticipated. Compliance with all aspects of the QA/QC plan (as it was designed) could not be demonstrated in the limited data set generated. However, since the first goal of the project was to establish whether or not the innovative drum cleanup method could work, and since both the physical and analytical evidence was overwhelming that it did not, compliance with the QA/QC plan was not relevant to the decision to abort the pelletized CO<sub>2</sub> demonstration project due to a lack of effectiveness.

A defensible QA plan requires refinement of analytical and sampling procedures to cope with matrix issues if the data are to be expected to support complex decision-making. This is best done by a pilot study which establishes the optimum sample selection, collection, extraction, cleanup, analysis and interpretation procedures to address site-specific conditions and decision goals. It should be kept in mind that some studies have found variability due to sampling factors to routinely be 3 or more times as large as variability stemming from the analytical method [9]. The uncertainty stemming from variability in sample selection and collection needs to be quantified or estimated to avoid undue efforts to eliminate insignificant analytical uncertainty, while the sampling uncertainty remains substantial and unaddressed.

## Dexsil L2000 PCB/Chloride Analyzer for Drum Surfaces

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### CHARACTERIZATION TECHNOLOGIES, CONT'D.

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#### Measurement Quality Objectives (MQOs)

Measurement Quality Objectives are the QC requirements an analytical method must be able to achieve to meet the goals of the project as expressed in the Data Quality Objectives. In selecting a field technique for monitoring the drum cleanup process, DOE set criteria (the MQOs) to reduce the risk of violating regulatory limits. These criteria were: (1) if field results are biased, these must be biased high (i.e., expected recoveries relative to the “true values” must be greater than or equal to 100%), (2) the field technique should provide a rate of false negatives at less than 10% at a 95% confidence limit, (3) the detection limit should be well below 5  $\mu\text{g}/100\text{ cm}^2$ , and (4) the field technique should provide quantitative results in  $\mu\text{g}/100\text{ cm}^2$  (as opposed to results in the form of a concentration range or interval). Of the 6 field methods evaluated during the Environmental Technology Verification (ETV) project co-sponsored by EPA and DOE [3], only the Dexsil test kit satisfied these criteria and was thus selected for monitoring the drum cleaning process.

#### Analytical Data Quality Control

Quality control (QC) measures specified for the Dexsil field method are summarized in Table 1. The laboratory utilized the QC measures discussed in EPA Method 8082.

The performance data collected during the ETV evaluation of the Dexsil PCB test kit [3] and the data needs of the project were used to establish realistic expectations for the precision criteria in Table 1. It was recognized that measurement variability can be attributed to the following: (1) analytical variability, as affected by operator proficiency and consistency, and by potential variability in extraction efficiency which depends on the nature of the materials collected by the wipe sample, and (2) spatial variability or a heterogeneous distribution of the analyte across the inside surfaces of the drum. Analytical variability due to operator proficiency and consistency is monitored through the use of control charts on the blank and standard results. In the ETV study, replicate analyses of standards and well-mixed soils by the Dexsil field method showed relative standard deviations (RSDs) of 14% and 23%, respectively [3]. These RSDs, which correspond to relative percent differences (RPDs) of 19% and 33% ( $\text{RPD} = \sqrt{2}\text{RSD}$ ), were obtained under near-ideal conditions of sample-to-sample homogeneity. The choice of the precision limit follows from the discussion below setting the accuracy MQO.

The lower accuracy limit (9.5 for the 10  $\mu\text{g}/100\text{ cm}^2$  standard) was selected such that this value would be rounded to the corresponding standard value. This corresponds to a lower recovery limits of 95%, and ensures that field analytical results will not be biased low due to the determinative step itself. The upper accuracy limits were derived from the recovery values determined during the ETV demonstration [3]: the recovery for 10 ppm standards (equivalent to the 10  $\mu\text{g}/100\text{ cm}^2$  regulatory limit for the free-release scenario) was 207%, while the recovery for 100 ppm standards was 91%. (Note that these recoveries were achieved in the absence of other sources of variability in sample results, such as sampling heterogeneity or extraction

**Dexsil L2000 PCB/Chloride Analyzer for Drum Surfaces**

**CHARACTERIZATION TECHNOLOGIES, CONT'D.**

inefficiencies.) A recovery of 207% for a 10 µg/100 cm<sup>2</sup> standard is 20 µg/100 cm<sup>2</sup>, and thus is equivalent to 100% RPD. Since under the free-release scenario outlined in Box 3, all results greater than 5 µg/100 cm<sup>2</sup> are sent to the laboratory for confirmation testing anyway, using an initial RPD of 100% is reasonable. If sample heterogeneity and analytical performance permit more stringent limits on duplicate precision, this will be determined during the preparation of an analytical control chart (see Table 1).

**Table 1. Analytical Data Quality Indicators (DQIs), Measurement Quality Objectives (MQOs), and Corrective Actions for Dexsil Field Method**

Data Quality Indicator (DQI) for Method	Measurement Quality Objective (MQO)	Corrective Actions (if control limits are exceeded)
Blanks: A field blank, consisting of an unused wipe or gauze pad soaked with 2 mL of chromatographic grade hexane, will be analyzed by the field method for every 20 field samples.	Blank results will not be greater than the lowest action level (5.0 µg/100 cm <sup>2</sup> ). Precision of blanks will be less than 100% RSD. All blanks will produce a numerical result, therefore a project-specific MDL is recommended. Permissible rate of false positive results*: the MDL must be determined before the rate of false positives can be evaluated. The development and use of an analytical control chart for blanks is recommended: after obtaining 20-30 blank results, the data is used to calculate the mean and standard deviation to prepare a control chart to record subsequent blank results.	If a blank result exceeds 5.0 µg/100 cm <sup>2</sup> or the 2 SD line of the control chart, a second blank will be immediately run. If that blank result is within the QC limits, the method will be considered to be in control. If the 2nd blank is also outside control limits, troubleshooting <sup>1</sup> of the analyst and equipment will be performed before other drum wipe samples are analyzed.
Accuracy: A quality control solution spiked at 10 µg/mL (corresponds to 10 µg/100 cm <sup>2</sup> regulatory limit for free release) will be analyzed for every 20 field samples.	For a 10 µg/100 cm <sup>2</sup> standard, the result must be \$9.5 and #30 µg/100 cm <sup>2</sup> . Permissible rate of false negative results*: 0% (It is unacceptable for the 10 µg/mL standard to produce a result less than the MDL.) The use of an analytical control chart is recommended: after obtaining 20-30 standard results, the data is used to calculate the mean and standard deviation to prepare a control chart to record subsequent standard results.	If a standard result exceeds the criterion or the 2 SD line of the control chart, a second standard will be run immediately. If that result is within the QC limits, the method will be considered to be in control. If the 2nd standard result is also outside control limits, troubleshooting <sup>1</sup> of the analyst and equipment will be performed before other drum wipe samples are analyzed.

**Dexsil L2000 PCB/Chloride Analyzer for Drum Surfaces**

**CHARACTERIZATION TECHNOLOGIES, CONT'D.**

**Table 1. Analytical Data Quality Indicators (DQIs), Measurement Quality Objectives (MQOs), and Corrective Actions for Dexsil Field Method**

Data Quality Indicator (DQI) for Method	Measurement Quality Objective (MQO)	Corrective Actions (if control limits are exceeded)
Precision: A duplicate field sample will be collected for every 20 field samples.	Maximum acceptable relative percent difference of 100% between duplicates.	If the same drum is not resampled, the next drum to be sampled will have duplicate samples taken. If the criterion is still exceeded, duplicate measurements of blanks and the standard will be performed to verify instrument performance. If acceptable precision cannot be achieved with the blanks and standards, troubleshooting <sup>1</sup> of the analyst and equipment will be performed before other drum wipe samples are analyzed.

**Table 1. Analytical Data Quality Indicators (DQIs), Measurement Quality Objectives (MQOs), and Corrective Actions for Dexsil Field Method (continued).**

Data Quality Indicator (DQI) for Method	Measurement Quality Objective (MQO)	Corrective Actions (if control limits are exceeded)
Laboratory verification of field analyses/Comparability: During the initial and production phase of sampling, 10% and 5% respectively of all field test kit results will be verified by EPA SW-846 Method 8082. Under a free-release decision tree, all Dexsil results >5 will be verified.	Field results will be compared to lab results to ensure conservatism; that is, most field results must be equal to or higher than laboratory results. If field results are trending lower than lab results, a the project statistician will be consulted to determine whether trend is significant (that is, the integrity of the decision-making process is in question). Corrective action will be implemented if the statistician believes it is necessary.	If other QC measures are acceptable, a re-evaluation of the extraction step of the field procedure will be undertaken to identify correctable extraction inefficiencies for this project-specific matrix. If modification of the method cannot ensure conservative results, yet the bias appears to be predictable and relatively constant, consultation with a statistician will determine if the field method-specific action level may be adjusted to restore the desired margin of safety.

## Dexsil L2000 PCB/Chloride Analyzer for Drum Surfaces

### CHARACTERIZATION TECHNOLOGIES, CONT'D.

Data Quality Indicator (DQI) for Method	Measurement Quality Objective (MQO)	Corrective Actions (if control limits are exceeded)
<p><sup>1</sup> Troubleshooting of the analyst will involve an experienced chemist observing the analyst to verify that correct procedures are being followed during sample collection, extraction, and analysis. Tiered troubleshooting of the equipment should be performed by an experienced chemist and will involve any of the following depending on the nature of the problem: (1) evaluate sources of contamination: open a new box or lot of wipe pads, open a new lot of hexane or extraction solvent, (2) evaluate blank or standard integrity: prepare fresh blank or standard solutions with new solvent, (3) evaluate reagent/kit integrity: open a new Dexsil test kit box or lot, assess the condition and performance of the chloride-specific electrode, (4) resumption of drum sampling will not resume until acceptable performance of the field method is obtained.</p> <p>* A false negative result is one where the analyte is not detected above the reporting limit when it is actually present above the reporting limit. A false positive result is one where the analyte is detected above the reporting limit when it is not actually present.</p>		

One other factor needs to be considered when setting the initial upper limit on the 10 µg/100 cm<sup>2</sup> standard: the standard used in this project is Aroclor 1260, yet the Dexsil instrument was set to report its readings as Aroclor 1242, which will additionally bias the results high. So a reasonable starting value for the upper limit on the field QC standard is 30 µg/100 cm<sup>2</sup>. This value can be adjusted during the project if warranted by the applicable analytical control chart. Just as the process control charts monitor possible drifting of performance that signals the need for re-optimization of process parameters, so too, the use of analytical control charts continually monitor the analytical method for instrument drift or other causes of deteriorating analytical performance.

The laboratory method selected for verifying the field analyses was SW-846 Method 8082, Polychlorinated Biphenyls (PCBs) by Capillary Column Gas Chromatography (GC/ECD). The wipe samples for lab analysis were immediately immersed in 10 mL of hexane and transported to the fixed laboratory where aliquots of the hexane extracts were injected into the GC/ECD for PCB quantification. Thus, the laboratory and field methods were different in the following aspects: (1) extraction solvent (hexane vs isooctane), (2) length of time for extraction solvent exposure, and (3) determinative technique (GC/ECD vs. ion-specific electrode).

An extensive evaluation of several PCB field technologies was performed under the ETV program co-sponsored by EPA and DOE. Table 2 lists the performance characteristics obtained from the ETV evaluation of the Dexsil PCB kit [3], and illustrates that the Dexsil PCB kit met the criteria set by DOE for selecting a field method to monitor the drum clean-up process.

**Table 2. Performance characteristics of the Dexsil L2000 PCB/Chloride analyzer based on the EPA/DOE ETV study [3] and DOE criteria for selecting a field method to monitor the drum clean-up process [2].**

**Dexsil L2000 PCB/Chloride Analyzer for Drum Surfaces**

**CHARACTERIZATION TECHNOLOGIES, CONT'D.**

<b>Performance Characteristics</b>	<b>ETV Study Result</b>	<b>DOE Selection Criterion</b>
Accuracy	Average recovery in soil samples was 208%. Average recovery in simulated extract samples (correspond best to wipe samples) was 149%.	If the field method is biased, it must be biased high (i.e., recoveries must be $\geq 100\%$ ).
Detection Errors	PCBs were detected above the generic MDL for four out of eight blank samples; there were no false negative results.	There must be a low probability of false negatives using the field method.
Detection limits	The method detection limit (MDL) following the EPA definition was 7.1 ppm. After compensation for bias, the resulting MDL agreed with Dexsil's specified MDL of 2 ppm. The latter is numerically equivalent to $2 \mu\text{g}/100 \text{ cm}^2$ of a $1,000 \text{ cm}^2$ sample wipe area extracted with 10 mL of iso-octane.	The detection limit must be less than the lowest action level. The project-specific MDL may be defined by a pilot study to address matrix effects.
Measurement range	Manufacturer-specified measurement range is between 2 and 2,000 ppm. Quantitative results were determined for extract samples with levels of 10 and 100 ppm.	The field method should provide quantitative results around the critical values selected for the project.
Precision	The overall precision based on relative standard deviations (RSDs) was 23% for soil samples and 14% for extract samples.	None specified
Cost	Equipment purchase: \$3,500; \$5 to \$16 per sample (matrix dependent)	None specified

## Dexsil L2000 PCB/Chloride Analyzer for Drum Surfaces

### PERFORMANCE EVALUATION

#### Sampling Results and Cleaning Process Performance

Over a period of four days, the drum-cleaning technology vendor was permitted to treat 20 to 25 drums to optimize the cleaning process. During this trial period, the Dexsil PCB test kit was used to monitor residual PCB surface levels in the processed drums. Some of the drums were re-cleaned and re-sampled several times for a total of 27 field samples. The field testing provided immediate feedback regarding the effectiveness of the cleaning process, and showed that the process was unable to consistently and reliably achieve the action limit of 5 µg/100 cm<sup>2</sup> (see Table 3,[6]). Even reproducibly achieving an action limit of 50 µg/100 cm<sup>2</sup> (appropriate for the metal smelting goal) proved difficult, with several drums exceeding 2,000 µg/100 cm<sup>2</sup> of residual contamination. During the first day of the trial period, five out of six drums had residual levels greater than 200 µg/100 cm<sup>2</sup>. Corresponding laboratory measurements later confirmed the field test results (see Table 3). On the fourth and last day of the trial period, six out of eight drums had residual levels measured by the Dexsil test kit as exceeding 200 µg/100 cm<sup>2</sup>, with some levels exceeding 2,000 µg/100 cm<sup>2</sup>. These field results were also confirmed by laboratory analysis (see Table 3). At this point, DOE aborted the project before additional resources were expended on a drum cleaning process that was clearly not working. The production phase of the sampling workplan described previously was never implemented.

**Table 3. Residual PCB levels in processed drums measured using the Dexsil L2000 PCB/chloride analyzer and EPA SW-846 Method 8082 [6].**

Sample ID	Dexsil Test Method <sup>1</sup>	Method 8082	
		µg/100 cm <sup>2</sup>	Aroclor <sup>2</sup>
July 7, 1998			
1	4.8	11	1254
2	>200	5,397	1254
3	>200	2,123	1254
4	>200	1,169	1254
5	>200	1,857	1254
6	>200	1,810	1254
July 8, 1998			
1	6.3	NP	
2	3.9	NP	
3	3.8	NP	
4	4.8	NP	

**Dexsil L2000 PCB/Chloride Analyzer for Drum Surfaces**  
**PERFORMANCE EVALUATION, CONT'D.**

**Table 3. Residual PCB levels in processed drums measured using the Dexsil L2000 PCB/chloride analyzer and EPA SW-846 Method 8082 [6].**

Sample ID	Dexsil Test Method <sup>1</sup>	Method 8082	
1	7.8	NP	

**Table 3. Residual PCB levels in processed drums measured using the Dexsil L2000 PCB/chloride analyzer and EPA SW-846 Method 8082 [6] (continued).**

Sample ID	Dexsil Test Method <sup>1</sup>	Method 8082	
	μg/100 cm <sup>2</sup> as Aroclor 1242	μg/100 cm <sup>2</sup>	Aroclor <sup>2</sup>
July 9, 1998			
2	>100	NP	
3	14.1	NP	
4	22.0	NP	
6	4.0	NP	
7	3.9	NP	
8	82.7	NP	
9	3.8	NP	
July 15, 1998			
1	>200	NP	
2	>200	NP	
3	>200	NP	
4	>2,000	17,749	1254
5	>1,000	NP	
6	3.2	5	1260
7	9.8	26.3	1254
8	>1,000	19,098	1260

<sup>1</sup>Although the Dexsil analyzer is capable of reporting quantitative results up to 2,000 μg/100 cm<sup>2</sup>, field results during this phase of the project were reported quantitatively only if the levels were below 100 μg/100 cm<sup>2</sup>. Over 100 μg/100 cm<sup>2</sup>, the results were reported variously as ">100", ">200", ">1,000" or ">2,000".

<sup>2</sup> Aroclor identified in sample based on relative amounts of PCB congeners detected.

NP = Not Performed (No sample sent for laboratory confirmation.)



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**Performance of Analytical Technology**

The performance of the Dexsil test kit can only be evaluated based on the limited data set that was collected before the clean-up project was aborted [6]. Table 4 shows the results of the field blanks and of the 10 µg/100 cm<sup>2</sup> standards used as QC samples. The field blank results are comparable to those measured during the ETV evaluation of the Dexsil test kit [3] where the average PCB level measured in unspiked simulated extract samples (analogous to field blanks) was 2.3 ppm.

**Table 4. Field analytical results of quality control samples [6].**

Quality Control Sample	Field Method Result (µg/100 cm <sup>2</sup> reported as Aroclor 1242)	Applicable MQO (from Table 1) (µg/100 cm <sup>2</sup> )
<b>Blanks</b>		
Analyzed on July 7, 1998	2.0	<5.0
Analyzed on July 8, 1998	0.6	<5.0
Analyzed on July 9, 1998	3.1	<5.0
Analyzed on July 9, 1998	1.0	<5.0
Analyzed on July 13, 1998	2.3	<5.0
Analyzed on July 14, 1998	3.7	<5.0
Analyzed on July 15, 1998	2.4	<5.0
Summary of Blank Performance	Mean (O) = 2.5; SD = 1.0 Precision (RSD): 40%	Establish Control Chart RSD#100%
<b>10 µg/100 cm<sup>2</sup> Arochlor 1260 Standard</b>		
Analyzed July 7, 1998	26.3	\$9.5 and #30
Analyzed July 8, 1998	11.8	\$9.5 and #30
Analyzed July 9, 1998	21.0	\$9.5 and #30
Analyzed July 13, 1998	23.8	\$9.5 and #30
Analyzed July 14, 1998	24.1	\$9.5 and #30
Analyzed July 15, 1998	12.6	\$9.5 and #30
Summary of Standard Performance	Mean (O) = 19.9; SD = 6.2 Accuracy (as % recovery): 199% Precision (RSD): 31%	Establish Control Chart RSD#100%

In this study, the mean was 2.5 ppm, and the precision for the blank readings was 40%. Analysis

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### PERFORMANCE EVALUATION, CONT'D.

of the QC standard samples showed that false negatives at the regulatory control limit of 10  $\mu\text{g}/100\text{ cm}^2$  are unlikely. All recoveries for the 10  $\mu\text{g}/100\text{ cm}^2$  standard samples were greater than 100%. The high recoveries are consistent with the ETV study [3] which showed that the Dexsil test results were biased high in both soil and simulated extract samples. High recoveries in this study are also expected because Aroclor 1260 was used for the QC standard, yet the Dexsil kit was set to report the result as Aroclor 1242. The precision of the Dexsil kit for the 10  $\mu\text{g}/100\text{ cm}^2$  QC standard was 31%. The precision of neither the Dexsil test kit nor the laboratory method with respect to the actual samples could be evaluated from the data set because no field duplicates were collected.

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### PERFORMANCE EVALUATION, CONT'D.

The comparability MQO (laboratory verification analyses) was evaluated by comparing the field results with the corresponding ten laboratory analyses. In general, the lab analyses were consistent with the field method results when compared against the field action level of 5  $\mu\text{g}/100\text{ cm}^2$  (see Table 3), although the desired MQO that the field results be at least as high, or higher, than the lab results (to maintain conservative decision-making in the field) was not achieved in this initial limited data set. Had this project continued, corrective action would have been performed before implementing the applicable decision tree.

A previous evaluation of the Dexsil PCB test kit (the ETV study) showed that results strongly tend to be biased high with average recoveries of 149% for simulated extract samples at concentrations of 10 and 100  $\mu\text{g}/100\text{ cm}^2$  [3]. This bias was evident in this project in that the 10  $\mu\text{g}/100\text{ cm}^2$  standard had recoveries up to 260%, as discussed previously. However, the data set in Table 3 suggests that the Dexsil results are biased low compared to the laboratory results. Further, even lower results would be expected had the Dexsil analyzer been set to report results as Aroclor 1260 (the Aroclor occasionally reported by the laboratory method and closer in chlorine content to Aroclor 1254, which was the Aroclor most reported by the laboratory), instead of Aroclor 1242. Reporting of Dexsil results as Aroclor 1242 was chosen to add additional conservatism to the field results. Therefore, it is surprising that the quantitative Dexsil results underestimated the confirmatory laboratory results. One can speculate that this negative bias may be due to a less efficient extraction of PCBs from the matrices collected on the wipe pads using isooctane as compared to hexane, which was the solvent used for Method 8082. In the ETV study, wipe sample extracts were simulated by the use of spiked solvent aliquots, and as a consequence, the efficiency of isooctane for extracting PCBs collected on wipes/gauze pads was not evaluated. Extraction efficiency differences may be further exacerbated if the wipes are saturated with oily residues, i.e., hexane may be more effective at extracting PCBs from viscous residues than isooctane. In addition to differences in solvent, the extraction times were also drastically different between the field and laboratory methods. The wipes were extracted for only 30 seconds using the Dexsil method, while the wipes for laboratory analyses were immersed in hexane for a much longer time as they were transported to the fixed analytical laboratory.

Another potential reason for the bias may be reflected in the sequence in which the laboratory and field wipe sample duplicates were collected. Since a 1,000  $\text{cm}^2$  area was required for each wipe-sampling, it was difficult to allocate accurately delineated non-overlapping sample areas for the field and lab samples due to the size of the drums. If the laboratory wipe samples were collected first and the field sample areas overlapped with the lab sample areas, it is possible that the laboratory wipe samples would have demonstrated higher PCB levels.

Had the cleaning procedure proved effective and the project gone forward, any significant negative bias between field and laboratory results would have been addressed by troubleshooting.

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### COST COMPARISON

Table 5 lists estimated costs for the testing program that DOE had planned for verifying the drum cleanup process. The calculations in this table assume that approximately 400 wipe samples will be analyzed (7,000 drums processed in 14 batches of 500 from which 28 are wipe sampled). For 400 wipe samples, at least 60 QA/QC samples (blanks, standards and replicates) would have been required according to the sampling plan using the Dexsil test kit. It is assumed that the same number of QA/QC samples would have been required if a laboratory method were used. The sampling program using the field method also includes laboratory verification of 40 samples (10%), assuming that with an effective cleaning program, few field analyses would have exceeded the criteria of the decision tree requiring additional laboratory confirmation. Under ideal circumstances, the total cost of the sampling program using the Dexsil kit (including the purchase of the Dexsil analyzer) is less than 50% of a similar program using a laboratory method. Had this project been executed to completion, considerable savings would have resulted from the use of the field method for clean-up verification with the added benefit of immediate turn-around of results.

Although the sampling program was not completed, use of the Dexsil test kit during the vendor's trial period was clearly advantageous for DOE because rapid feedback was provided to the clean-up technology vendor that the process was not working. The immediate availability of analytical results also allowed DOE to rapidly reach a decision to abort the project, thereby avoiding expending more resources and accumulating more liability to the vendor.

**Table 5. Comparison of costs for a sampling program using the Dexsil PCB field method and EPA Method 8082.**

Cost Element	Dexsil PCB Method	EPA Method 8082
Equipment cost (capital)	\$3,500	\$0
Analysis of samples	\$12.50 x 400 samples = \$5,000	\$50 x 400 samples = \$20,000
Analysis of QA/QC samples	\$12.50 x 60 samples = \$750	\$50 x 60 samples = \$3,000
Analysis of laboratory verification samples	\$50 x 40 samples = \$2,000	\$0
<b>TOTAL</b>	<b>\$11,250</b>	<b>\$23,000</b>

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## Dexsil L2000 PCB/Chloride Analyzer for Drum Surfaces

### OBSERVATIONS AND LESSONS LEARNED

Because the project was aborted during its initial phase and the full sampling program was never implemented, this case study represents a very limited data set from which to draw observations and lessons learned in using the Dexsil PCB field method. However, the case study does illustrate that the use of a field method enabled rapid decision-making by the data users. The benefits of the field PCB method are identified as follows [6]:

- blank QC samples showed no false negative analytical results (a false negative analytical result is one where the analyte is not detected when it is actually present);
- C reduced per sample costs (\$12.50 per sample vs. approximately \$50 per sample using Method 8082); and
- rapid turn-around for results (within an hour of the last sample taken).

Use of the field method proved itself by immediately identifying to DOE that the process was not working as expected. Therefore, the process was stopped before DOE had assumed a larger liability [6].

#### *Lesson learned concerning process control tools:*

- C Depending on how the first 50 samples used to prove process effectiveness are distributed,  $\bar{O} + 2SD$  and  $\bar{O} + 3SD$  could possibly be greater than the action limit. If this were true, then the statistical control charts may be superfluous.

#### *Lesson learned concerning the analytical QA/QC plan:*

- C Had the project gone forward, the value of a detailed, well-planned and documented quality assurance plan would have been vital to detecting, correcting or compensating for any matrix interferences or other problems related to non-representative sampling and analysis. (On the other hand, had the cleaning procedure worked, matrix problems would not have existed, since the contaminated matrix would have been removed.) Detailed QA plans and project-specific standard operating procedures (SOPs) are critical to implementing field analytical methods to produce reliable data which supports defensible decision-making. Clearly defined MQOs and corrective measures ensure that field analytical data will be of known and documented quality.
- C If a project's data defensibility depends partly on good comparability between laboratory and field measurements, representative sampling and analysis issues *must* be addressed, or the data will not be able to support project decision-making.
- C Although much of the technical detail of rigorous QA plans may seem complex, designing and implementing statistically valid analytical quality assurance plans is a routine matter for experienced analytical chemists and statisticians. Tapping into appropriate expertise during project planning, and then at critical junctures during execution, will substantially increase

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the likelihood that projects will successfully meet the goals of public safety and confidence.

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