

STATE OF CALIFORNIA  
AIR RESOURCES BOARD

AIR MONITORING QUALITY ASSURANCE

VOLUME V

AUDIT PROCEDURES  
FOR  
AIR QUALITY MONITORING

APPENDIX AI

LABORATORY PERFORMANCE AUDIT PROCEDURES  
FOR  
DIOXINS, FURANS AND POLYCHLORINATED BIPHENYLS

MONITORING AND LABORATORY DIVISION

OCTOBER 2003

## TABLE OF CONTENTS

### APPENDIX AI

#### LABORATORY PERFORMANCE AUDIT PROCEDURES FOR DIOXINS, FURANS AND POLYCHLORINATED BIPHENYLS

	<u>PAGES</u>	<u>REVISION</u>	<u>DATE</u>
<b>AI.1 - LABORATORY PERFORMANCE AUDIT PROCEDURES</b>			
<b>AI.1.0 INTRODUCTION</b>	1	0	03-28-03
AI.1.0.1 General Information			
<b>AI.1.1 AUDIT PROCEDURES</b>	2	0	03-28-03
AI.1.1.1 Audit Materials			
AI.1.1.2 Storage of Audit Materials			
AI.1.1.3 Initiation of Audit			
AI.1.1.4 Sample Analysis			
AI.1.1.5 Completion of Audit			
<b>AI.1.2 POST AUDIT CALCULATIONS</b>	4	1	10-23-03
AI.1.2.1 Calculation of Percent Difference (Accuracy)			
AI.1.2.2 Calculation of Relative Percent Difference (Precision)			
AI.1.2.2 Final Audit Report			

**APPENDIX AI**

**LABORATORY PERFORMANCE AUDIT PROCEDURES  
FOR  
DIOXINS, FURANS AND POLYCHLORINATED BIPHENYLS**

**FIGURES**

	<u>Page</u>
Figure AI.1.1.1. . . Dioxin Performance Evaluation Standard (PES) Protocol . . . . .	2
Figure AI.1.2.1. . . Dioxin, Furan, and PCB Laboratory Audit Final Results Cover Letter . . .	2

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MONITORING AND LABORATORY DIVISION

MARCH 2003

## **AI.1.0 INTRODUCTION**

### **AI.1.0.1 GENERAL INFORMATION**

Audits for dioxins, furans, and polychlorinated biphenyls (PCB) are conducted at AXYS Analytical Laboratory, a contract laboratory of the Air Resources Board's (ARB) Monitoring and Laboratory Division (MLD). On a one time basis, ARB purchases the performance evaluation standard (PES) sample sets from Wellington Laboratories Inc. A PES sample set is sent to the ARB's Quality Assurance Section (QAS) which forwards it along with chain-of-custody (COC) documentation and a written protocol to AXYS Analytical Laboratory for analysis. The PES sample set includes three ampoules, each at different concentrations appropriate for the calibration range of the analytical methods. The laboratory uses high resolution gas chromatography-mass spectrometry and follows Standard Operating Procedures (SOP) required under the contract for the California Ambient Dioxin Air Monitoring Program (CADAMP) for extraction, analysis, and data reporting. The sample is analyzed in duplicate to determine the amounts of the 2,3,7,8-substituted polychlorinated dioxins and furans, and dioxin-like PCBs. The results are returned to the QAS for calculation of the percent difference (accuracy) and relative percent difference (precision) of the sample and duplicate sample for each congener. Results are reported in percent difference and relative percent difference from picograms per sample (pg/sample) and submitted to the Operation Planning and Assessment Section (OPAS). An additional PES set was acquired to compare the CADAMP and National Dioxin Air Monitoring Network (NDAMN) operated by the U.S. EPA.

The purpose of the audit is to assess the precision and accuracy of the laboratory's standard operating practices and procedures.

## **AI.1.1      AUDIT PROCEDURES**

### **AI.1.1.1      AUDIT MATERIALS**

The audit materials will consist of three ampoules each containing Dioxins, Furans, and polychlorinated biphenyls at varying concentrations representative of the calibration range of the analytical methods and instrumentation.

### **AI.1.1.2      STORAGE OF AUDIT MATERIALS**

PES will be stored in accordance with the laboratory's Standard Operating Procedures for sample handling and storage. The PES will not be opened or analyzed until authorization from the California Air Resources Board's Quality Assurance Section.

### **AI.1.1.3      INITIATION OF AUDIT**

Upon receiving the Wellington Laboratory Inc. PES sample ampoules and certificate of analysis, the QAS will record the receipt of the ampoules on a COC document ([COC Field Operations for CADAMP](#)) which will accompany the PES and audit protocol (Fig. AI.1.1.1) that will be sent to AXYS Analytical Laboratory for analysis.

### **AI.1.1.4      SAMPLE ANALYSIS**

All PES ampoules supplied by the Wellington Laboratory Inc. and analyzed at the AXYS Analytical Laboratory are processed using the SOP approved for the CADAMP (U.S. EPA Methods TO-9A, 1613B, and 1668).

### **AI.1.1.5      COMPLETION OF AUDIT**

Upon completion of PES processing and analysis, AXYS Analytical Laboratory returns results containing raw data (chromatograms, both manual and software integrations, run logs, bench sheets, etc.), appropriate U.S. EPA data reporting forms, an executive summary, and any additional comments or information to the QAS via hardcopy and diskette deliverables.

Figure AI.1.1.1  
Dioxin Performance Evaluation Standard (PES) Protocol

**Dioxin Performance Evaluation Standard (PES) Protocol**

*California Dioxin Air Monitoring Network (CDAMP) and National Dioxin Air Monitoring Network (NDAMN) Comparison Study*

1. **DO NOT OPEN** ampoules without authorization from the California Air Resources Board's Quality Assurance Section staff. Please contact Mr. Michael Werst at 916-327-4757 or via email at [mwerst@arb.ca.gov](mailto:mwerst@arb.ca.gov).
2. Upon receipt, please log-in and store the ampoules under refrigeration and return a copy of the attached chain-of-custody with appropriate signatures within 72 hours to:  
  
Mr. Michael Werst  
California Air Resources Board  
P.O. Box 2815  
Sacramento, California 95812
3. Upon authorization, open the requested ampoule (PES-1, PES-2, or PES-3) and transfer to a teflon sealed, amber vial for spiking and storage. Any unused portion should be stored appropriately per the laboratory's SOP for sample storage and handling.
4. Using a calibrated, gas tight syringe, spike 75µl of the requested standard (PES-1, PES-2, or PES-3) onto a pre-cleaned and certified PUF:XAD:PUF matrix in a glass cartridge used for Dioxin/Furan/PCB analysis. Each PES will be conducted in **duplicate** to evaluate precision. Take care to spike the standard into the top section of PUF and the XAD layer.
5. Extract, split, clean-up, and analyze the PES with a pre-cleaned and certified quartz fiber filter along with appropriate Quality Control (appropriate standards including pre-spikes, method blanks, 2 laboratory control samples, etc.) using Methods TO-9A, 1613B, and 1668A (CADAMP and NDAMN specific). The performance evaluation standards should be extracted and analyzed with ambient samples that are currently in-house.
6. Review data and submit analysis results within **30 days** to the above address and contact person along with all appropriate QC information and U.S. EPA forms. Raw data (chromatograms, run logs, bench sheets, etc.) with all integrations (manual and software) will be required for a valid performance evaluation. All method specific QA/QC criteria must be met. Data will be submitted both in hardcopy and via diskette deliverables using CADAMP or NDAMN requirements, as appropriate.

## **AI.1.2 POST AUDIT CALCULATIONS**

### **AI.1.2.1 CALCULATION OF PERCENT DIFFERENCE (ACCURACY)**

The QAS will calculate the percent bias for each congener between AXYS Analytical Laboratory measured results and Wellington Laboratories, Inc., certified analysis using the following equation (results are reported in picograms (pg) /sample):

$$\text{Percent Difference} = \frac{(\text{Measured Concentration} - \text{Assigned Concentration})}{\text{Assigned Concentration}} \times 100$$

### **AI.1.2.2 CALCULATION OF RELATIVE PERCENT DIFFERENCE (PRECISION)**

The QAS will calculate the percent relative difference for each congener between AXYS Analytical Laboratory measured results for duplicate analysis using the following equation (results are reported in picograms (pg) /sample):

$$\text{Relative Percent Difference} = \frac{\text{Positive difference in duplicate concentrations}}{\text{average of the duplicate concentrations}} \times 100$$

### **AI.1.2.3 FINAL AUDIT REPORT**

The QAS will forward the final results with a cover letter (Fig. AI.1.2.1) to the OPAS. In the event that the percent difference exceeds  $\pm 30\%$  for the dioxins and furans (Method Accuracy for U.S. EPA TO-9A) and/or  $\pm 50\%$  for PCBs (Method Accuracy for U.S. EPA 1668), and/or  $\pm 30\%$  for percent relative difference (Method Precision for U.S. EPA TO-9A), the laboratory may be asked to investigate results by OPAS. Upon completion of the three PES samples, the QAS will perform an in-depth evaluation of the laboratory's performance. These results will be forwarded to the OPAS for appropriate follow-up with the laboratory, if necessary.





**Winston H. Hickox**  
Agency Secretary

## Air Resources Board

**Alan C. Lloyd, Ph.D.**  
Chairman

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**Gray Davis**  
Governor

### MEMORANDUM

TO: Jeff Cook, Chief  
Quality Management Branch

FROM: Michael Miguel, Manager  
Quality Assurance Section

DATE: February 24, 2003

SUBJECT: DIOXIN, FURAN, AND PCB LABORATORY PERFORMANCE EVALUATION  
STANDARD AUDIT RESULTS: PES-1

The following table represents audit results for the first quarter 2003 dioxins, furans, and polychlorinated biphenyls (PCB) laboratory performance audit. The performance audit was conducted using vendor-manufactured standards spiked onto a polyurethane-XAD resin-polyurethane cartridge. AXYS Analytical Laboratory utilized high resolution gas chromatography-mass spectrometry to determine the concentrations of 2,3,7,8-substituted polychlorinated dioxins, furans, and dioxin-like PCBs following U.S. EPA methods TO-9A, 1613B, and 1668A specific to the California Ambient Dioxin Air Monitoring Program (CADAMP). The laboratory results are as follows (concentration values are picograms (pg) per sample):

*The energy challenge facing California is real. Every Californian needs to take immediate action to reduce energy consumption. For a list of simple ways you can reduce demand and cut your energy costs, see our Website: <http://www.arb.ca.gov>.*

California Environmental Protection Agency

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[illegible]

$$\text{Relative Percent Difference} = \frac{\text{ABS} ([\text{PES-1}] - [\text{PES-1Dup}])}{([\text{PES-1}] + [\text{PES-1Dup}]) / 2} \times 100$$

Figure AI.1.2.1  
Dioxin, Furan, and PCB Laboratory Audit Final Results Cover Letter

Jeff Cook  
March 28, 2003  
Page 3

All compounds were within the targeted +/-30% and +/-50% control limits for dioxins/furans and PCBs, respectively; all compounds were within the +/-30% control limit for relative percent difference. All method accuracy and precision control limits were established using U.S. EPA Methods TO-9A and 1668.

The next scheduled audit is to take place during the fourth quarter, 2003.

Thank you for your participation in this program. If you have questions, please call Mr. Michael Werst at 327-4757 or via email at [mwerst@arb.ca.gov](mailto:mwerst@arb.ca.gov).

cc: Webster Tasat  
Monitoring and Laboratory Division  
Air Resources Board

Kevin Mongar  
Monitoring and Laboratory Division  
Air Resources Board

Michael Werst  
Monitoring and Laboratory Division  
Air Resources Board