

DETERMINATION OF 2,3,7,8-TCDD LEVELS

Prepared for:
Pattle Delamore Partners Ltd.
Attn: Richard Lucy
PO Box 6136
Wellington
New Zealand



This report contains 18 pages.

The results reported herein conform to the most current NELAC standards, where applicable, unless otherwise narrated in the body of the report.

Project: Chemical Analysis

Client Purchase Order Number: NA

REPORT OF LABORATORY ANALYSIS

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REPORT OF: CHEMICAL ANALYSES

PROJECT: TCDD ANALYSES

DATE: August 7, 2002

ISSUED TO: Pattle Delamore Partners Ltd.
Attn: Mr. Richard Lucy
PO Box 6136
Wellington
New Zealand

REPORT NO: 02-1060110

INTRODUCTION

This report presents the results from the analysis performed on two samples which were submitted by a representative of Pattle Delamore Partners Ltd. The samples were analyzed for the presence or absence of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) using a modified version of USEPA Method 1613 as described below.

SAMPLE IDENTIFICATION

<u>Client ID</u>	<u>Sample Type</u>	<u>Date Received</u>	<u>Pace ID</u>
SS#2 188-3	Solid	07/05/02	103695656
SS#5 188-8	Solid	07/05/02	103695664

METHODOLOGY

Sample Extraction

A portion of each sample was spiked with 2.0 nanograms (ng) of ¹³C₁₂-labeled 2,3,7,8-TCDD internal standard and extracted with methylene chloride in a separatory funnel. Each extract was quantitatively transferred to a Kuderna-Danish flask, concentrated, solvent exchanged to hexane, and processed through the analyte enrichment procedures described below.

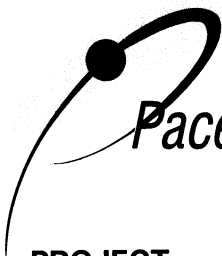
Analyte Enrichment

The extraction procedure often removes a variety of compounds, in addition to 2,3,7,8-TCDD from the sample matrix. Some of these compounds, for example polychlorinated biphenyls, can directly interfere with the analyses. Other compounds can overload the capillary column, causing a degradation in chromatographic resolution or sensitivity. The analyte enrichment steps described below were used to remove interfering compounds from the extract.

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Analyte Enrichment (Continued)

Each extract was diluted to 100 mL with hexane, spiked with $^{37}\text{Cl}_4$ -2,3,7,8-TCDD and washed with concentrated sulfuric acid, 1 N sodium hydroxide, and aqueous sodium chloride (5% w/v) as needed. Each extract was then quantitatively transferred to a liquid chromatography column containing alternating layers of silica gel, 40% concentrated sulfuric acid on silica gel, and 33% 1 N sodium hydroxide on silica gel. The column was eluted with 90 mL of hexane and the entire eluate was collected and concentrated, under ambient conditions, to a volume of 1 mL.

Each extract was then fractionated on a liquid chromatography column containing 4 g of activated alumina. The column was eluted with 20 mL of hexane followed by 15 mL of 60% methylene chloride/hexane. The 60% methylene chloride/hexane fraction was concentrated to 1 mL under a stream of dry nitrogen and applied to the top of a chromatography column containing 1 g of 5% AX-21 activated carbon in silica gel. The column was eluted with two 2 mL portions of hexane, 2 mL of cyclohexane/methylene chloride (50:50 v/v) and cyclohexane/methanol/toluene (75:20:5 v/v) in the forward direction, and then with toluene in the reverse direction. The toluene fraction was collected, spiked with recovery standards (1,2,3,4-TCDD- $^{13}\text{C}_{12}$) and taken to a final volume of 20 μL .

HRGC/HRMS Analyses

Each sample extract was analyzed for the presence of 2,3,7,8-TCDD using combined capillary column gas chromatography/high resolution mass spectrometry (HRGC/HRMS). The instrumentation consisted of a Hewlett Packard Model 6890 gas chromatograph interfaced to a Micromass Ultima high-resolution mass spectrometer. The capillary column was interfaced directly into the ion source of the mass spectrometer, thus providing the highest possible sensitivity while minimizing degradation of the chromatographic resolution.

The mass spectrometer was operated in the electron impact ionization mode at a mass resolution of 10,000-11,000 ($M/\Delta M$, 10 percent valley definition). Operating parameters for the HRGC/HRMS analyses are summarized in Table 1. The data were acquired by selected-ion-recording (SIR), monitoring a group of ion masses as described in EPA Method 1613. Two ion masses were monitored for each native and $^{13}\text{C}_{12}$ -labeled class so that the ratio between the low and high ion masses could be compared to the expected theoretical value (0.77). The actual ion masses monitored are listed below.

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HRGC/HRMS Analyses (Continued)

	<u>Native TCDD</u>	<u>¹³C₁₂-labeled TCDD</u>
Ion Masses	319.8965	331.9367
	321.8936	333.9338

A lock mass was used by the data system to automatically correct the mass focus of the instrument. Most modern mass spectrometers are stable on a short term basis (1 - 10 minutes); however, they can drift from the center of the mass peak during the course of a 30 - 60 minute analysis. The data system determined the centroid of the lock mass during each data acquisition cycle and corrected the mass focus of the analyte and internal standard ion masses to assure that the centers of the mass peaks were monitored.

The criteria used to judge positive responses for the 2,3,7,8-TCDD included:

- Simultaneous response at both ion masses
- Signal to noise ratio equal to or greater than 2.5:1.0 for both ion masses
- Chlorine isotope ratio within 15 percent of the theoretical value
- Chromatographic retention times within +/- 2 seconds of the expected retention time

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Quantification and Calculations

The 2,3,7,8-TCDD was quantified by comparison of its responses to the responses of the labeled internal standard. Relative response factors were calculated from analyses of standard mixtures containing the natives at five concentration levels, and the internal standards at fixed concentration levels, as shown in Table 2. The response factors were calculated by comparing the sum of the responses from the two ion masses monitored for the native compound to the sum of the responses from the two ion masses of the isotopically labeled internal standard. The formula for the response factor calculation is:

$$R_f = \frac{A_n \times Q_{is}}{A_{is} \times Q_n}$$

where:

- Rf = Response factor
- An = Sum of integrated areas for analyte
- Qis = Quantity of internal standard
- Ais = Sum of integrated areas for internal standard
- Qn = Quantity of analyte

The level of 2,3,7,8-TCDD in each sample was quantified using the following equation:

$$C = \frac{A_n \times Q_{is}}{A_{is} \times W \times R_f}$$

where:

- C = Concentration of 2,3,7,8-TCDD
- An = Sum of integrated areas for 2,3,7,8-TCDD
- Qis = Quantity of labeled internal standard added to the sample
- Ais = Sum of integrated areas for the labeled internal standard
- W = Sample amount
- Rf = Response factor

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Quantification and Calculations (Continued)

The Pace Reporting Limit (PRL), equivalent to the practical quantitation limit, was determined based on the sample aliquot weight that was extracted, the volume of the final extract, and the concentration of the lowest level in the standard curve. A PRL was calculated using the following equation:

$$PRL = \frac{(C \times V)}{W}$$

where:

- PRL = Pace Reporting Limit
- C = Concentration of Lowest Level Standard
- V = Volume of Final Extract
- W = Initial Sample Amount

The recoveries of the 2,3,7,8-TCDD-¹³C₁₂, relative to 1,2,3,4-TCDD-¹³C₁₂, were calculated using the following equation:

$$\%R = \frac{Ais \times Qrs \times 100\%}{Rfr \times Ars \times Qis}$$

where:

- %R = Percent recovery of the labeled internal standard
- Ais = Sum of integrated areas of labeled internal standard
- Qrs = Quantity of recovery standard
- Ars = Sum of integrated areas of recovery standard
- Rfr = Response factor of the labeled internal standard relative to the recovery standard
- Qis = Quantity of the labeled internal standard added to the sample

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Quality Control

The performance of the sample processing steps and the instrumentation are monitored on a routine basis. The procedures and criteria are summarized below.

One method blank and one laboratory spike sample are typically prepared with each ten samples of any given matrix. Recoveries of the native analytes in the laboratory spike samples generally range from 70 to 130%. Recoveries of selected analytes outside this range do not invalidate the data but provide information which is used by the laboratory to monitor recovery trends and to assure optimization of the method.

Internal standards are spiked into each sample prior to extraction in order to monitor the level of recovery which is achieved for each individual sample. Acceptable recoveries range from 25 to 150 percent unless a deviation is due to variation in instrument response as a result of analytical interferences.

The resolution of the mass spectrometer is verified prior to each analysis to be 10,000 or greater. Hardcopies of the reference peaks are printed at the beginning and end of each analysis day. The resolving power of the DB-5MS chromatographic column is checked daily by analyzing a standard solution containing 2,3,7,8-TCDD and the adjacent TCDD isomers. Acceptable performance is achieved when 2,3,7,8-TCDD is resolved from the adjacent isomers by a valley of 25% or less.

Initial calibrations are generated by analyzing standard solutions (see Table 2) containing target native and labeled compounds. Response factors are calculated and averaged for each compound. These averages are used for quantification and for comparison to the daily continuing calibration. The relative standard deviation for each native compound must be 20% or less (\pm 30% or less for the labeled compounds) as specified in Method 8290. A continuing calibration standard is analyzed at the beginning of each 12-hour shift on days when initial calibrations are not performed. The initial calibration is considered to be valid when the values obtained from the continuing calibration analyses fall to within the ranges specified in Method 1613.

RESULTS

The results from the 2,3,7,8-TCDD analyses are summarized in the following:

- Appendix A - Chain of Custody Documentation
- Appendix B - 2,3,7,8-TCDD Analysis Results

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DISCUSSION

The isotopically-labeled 2,3,7,8-TCDD internal standard in the extracts were recovered at 70%, indicating a level of efficiency through the extraction and enrichment steps that is considered typical for this matrix. All of the labeled internal standard recoveries obtained for this project were within the target range specified in Method 1613. Since the quantification of the native 2,3,7,8-TCDD is based on isotope dilution, the data are automatically corrected for recovery and accurate values are obtained.

A laboratory method blank was prepared and analyzed with the sample batch as part of our routine quality control procedures. The results, included at the beginning of Appendix B, show that 2,3,7,8-TCDD was not detected at the reported limit of detection. This indicates that the sample processing steps were free of background levels of this isomer.

A laboratory quality control spike sample was also prepared with the sample batch by extracting clean sand that had been fortified with native standard material. The results, included at the end of Appendix B, show that the spiked native 2,3,7,8-TCDD was recovered at 98%. This indicates a high degree of accuracy for these determinations.

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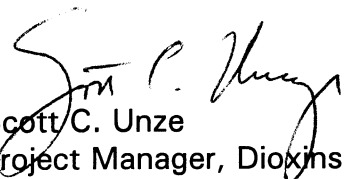
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REMARKS

The sample extracts will be retained for a period of 30 days from the date of this report and then discarded unless other arrangements are made. The raw mass spectral data will be archived on magnetic tape for a period of not less than one year. Questions regarding the data contained in this report may be directed to the authors at the numbers provided below.

Pace Analytical Services, Inc.



Scott C. Unze
Project Manager, Dioxins
(612) 607-6383

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TABLE 1. HRGC/HRMS Operating Parameters

Mass Resolution	10,000-11,000 (M/ Δ M, 10% valley)
Instrument	VG 70SE
Electron Energy	32 electron volts
Accelerating Voltage	8,000 volts
Source Temperature	275°C
Preamplifier Gain	10 ⁻⁶ amp/volt
Electron Multiplier Gain	~10 ⁵
Chromatographic Column	60M DB-5MS
Transfer Line Temperature	260°C
Injection Mode	Splitless
Carrier Gas	Helium
Carrier Flow Velocity	~30 cm/sec

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TABLE 2. High Resolution TCDD Calibration Solutions

Solution#	TCT#	Concentration (pg/uL)		
		2,3,7,8-TCDD	1,2,3,4-TCDD- ¹³ C ₁₂	2,3,7,8-TCDD- ¹³ C ₁₂
1	CS1	0.5	100	100
2	CS2	2.0	100	100
3	CS3	10	100	100
4	CS4	40	100	100
5	CS5	200	100	100

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www.pacelabs.com

Pace Analytical Services, Inc.

1700 Elm Street, Suite 200
Minneapolis, MN 55414

Phone: 612.607.1700

Fax: 612.607.6444

APPENDIX A

REPORT OF LABORATORY ANALYSIS

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Attn: Richard Lacey

1060110

FAXED

Project: WJ366
Laboratory: AgriQuality

Pattle Delamore Partners Ltd
Wellington

REQUEST FOR ANALYSES / CHAIN OF CUSTODY

SHEET 1 of 2

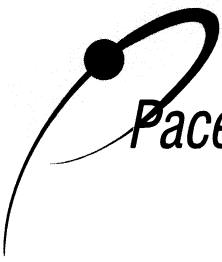
REQUEST FOR ANALYSES						
Sample I.D.	Date	Lab ID	Container	Sample Type	Analyses Requested	
SS#1	31-5-2002	188-1	280ml Glass	Soil	2378-TCOD	
SS#1G	"	2				
SS#2	30/May	3				
X SS#2-GX	"	Not Received				
SS#2-75mm	"	4				
SS#4-9	30/May	5				
SS#4-75mm	"	7				
SS#5	30/May	8				
SS#6	31/May	9				
SS#7	29/May	10				
SS#8	28/May	11				
SS#9	29/May	12				
SS#9-G	"	13			103695664	
SS#9-75mm	"	14				
SS#10	30/May	15				
SS#11	31/May	16				
SS#11-75mm	"	17				
SS#12	28/May	18				
SS#12-G	"	19				
SS#13	30/May	20				
SS#13-G	"	21				
SS#4-G	30 May	6				

CHAIN OF CUSTODY			
Signature	Affiliation	Date	Time
<i>[Signature]</i>	Pattle Delamore Partners Ltd	31-5-2002	6pm
<i>[Signature]</i>	AgriQuality	4-6-2002	8pm
<i>[Signature]</i>	Price	7-5-04	10:30

Quote Details: 20 Samples will be reported today 19/6
Remainer will be reported 6/6
early next week

NOTE: Please acknowledge receipt of these samples by signing this form and faxing it to: Pattle Delamore Partners Ltd, Wellington. Fax number 04 - 472 1958

T-222



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www.pacelabs.com

Pace Analytical Services, Inc.

1700 Elm Street, Suite 200
Minneapolis, MN 55414

Phone: 612.607.1700

Fax: 612.607.6444

APPENDIX B

REPORT OF LABORATORY ANALYSIS

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Method 1613B Blank Analysis Results

Client - PATTLE

Lab Sample ID	BLANK-1942	Matrix	SOLID
Filename	F20728A_04	Dilution	NA
Total Amount Extracted	10.2 g	Extracted	07/24/2002
ICAL Date	05/04/2002	Analyzed	07/28/2002 20:17
CCal Filename(s)	F20728A_01	Injected By	BAL

Native Isomers	Conc ng/Kg	EMPC ng/Kg	PRL ng/Kg	Internal Standards	ng's Added	Percent Recovery
2,3,7,8-TCDD	ND	-----	0.98	2,3,7,8-TCDD-13C	2.00	75
				Recovery Standard 1,2,3,4-TCDD-13C	2.00	NA
				Cleanup Standard 2,3,7,8-TCDD-37Cl4	0.20	83

Conc = Concentration
EMPC = Estimated Maximum Possible Concentration
PRL = Pace Analytical Reporting Limit.
I = Interference
P = Recovery outside of method 1613 control limits
ND = Not Detected
NA = Not Applicable
NC = Not Calculated
* = See Discussion

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Method 1613B Analysis Results

Client - PATTLE

Client's Sample ID	SS#2 188-3		
Lab Sample ID	103695656		
Filename	U20729B_08		
Injected By	CVS		
Total Amount Extracted	11.57 g	Matrix	SOLID
% Moisture	11.7	Dilution	NA
Dry Weight Extracted	10.2 g	Collected	05/30/2002
ICAL Date	07/28/2002	Received	07/05/2002
CCal Filename(s)	U20729A_17	Extracted	07/24/2002
Method Blank ID	BLANK-1942	Analyzed	07/30/2002 07:11

Native Isomers	Conc ng/Kg	EMPC ng/Kg	LOD ng/Kg	Internal Standards	ng's Added	Percent Recovery
2,3,7,8-TCDD	3.9	-----	0.14	2,3,7,8-TCDD-13C	2.00	70
				Recovery Standard 1,2,3,4-TCDD-13C	2.00	NA
				Cleanup Standard 2,3,7,8-TCDD-37Cl4	0.20	75

Results reported on a dry weight basis

Conc = Concentration (Totals include 2,3,7,8-substituted isomers).
 EMPC = Estimated Maximum Possible Concentration
 LOD = Limit of Detection. Totals are averages of individual isomer LODs.
 D = Result obtained from analysis of diluted sample
 B = Less than 10 times higher than method blank level
 P = Recovery outside of method 1613 control limits
 J = Concentration detected is below the calibration range
 Nn = Value obtained from additional analysis

I = Interference
 E = PCDE Interference
 ND = Not Detected
 NA = Not Applicable
 NC = Not Calculated
 * = See Discussion

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Method 1613B Analysis Results

Client - PATTLE

Client's Sample ID	SS#5 188-8		
Lab Sample ID	103695664		
Filename	U20729B_09		
Injected By	CVS		
Total Amount Extracted	13.59 g	Matrix	SOLID
% Moisture	26.1	Dilution	NA
Dry Weight Extracted	10.0 g	Collected	05/30/2002
ICAL Date	07/28/2002	Received	07/05/2002
CCal Filename(s)	U20729A_17	Extracted	07/24/2002
Method Blank ID	BLANK-1942	Analyzed	07/30/2002 08:00

Native Isomers	Conc ng/Kg	EMPC ng/Kg	LOD ng/Kg	Internal Standards	ng's Added	Percent Recovery
2,3,7,8-TCDD	94	-----	0.28	2,3,7,8-TCDD-13C	2.00	70
				Recovery Standard 1,2,3,4-TCDD-13C	2.00	NA
				Cleanup Standard 2,3,7,8-TCDD-37Cl4	0.20	87

Results reported on a dry weight basis

Conc = Concentration (Totals include 2,3,7,8-substituted isomers).
 EMPC = Estimated Maximum Possible Concentration
 LOD = Limit of Detection. Totals are averages of individual isomer LODs.
 D = Result obtained from analysis of diluted sample
 B = Less than 10 times higher than method blank level
 P = Recovery outside of method 1613 control limits
 J = Concentration detected is below the calibration range
 Nn = Value obtained from additional analysis

I = Interference
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 ND = Not Detected
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 NC = Not Calculated
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Method 1613B Laboratory Control Spike Results

Client - PATTLE

Lab Sample ID	SPIKE-1943	Matrix	SOLID
Filename	F20728A_02	Dilution	NA
Total Amount Extracted	10.42 g	Extracted	07/24/2002
ICAL Date	05/04/2002	Analyzed	07/28/2002 18:09
CCal Filename	F20728A_01	Injected By	BAL
Method Blank ID	BLANK-1942		

Compound	Cs	Cr	Lower Limit	Upper Limit	% Rec.
2,3,7,8-TCDD	10	9.8	7.3	14.6	98
2,3,7,8-TCDD-37Cl4	10	8.5	3.7	15.8	85
2,3,7,8-TCDD-13C	100	65.6	25.0	141.0	66

Cs = Concentration Spiked (ng/mL)
Cr = Concentration Recovered (ng/mL)
Rec. = Recovery (Expressed as Percent)
Control Limit Reference: Method 1613, Table 6a, 10/94 Revision
X = Background subtracted value
P = Recovery outside of control limits
* = See Discussion

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