

ANALYTICAL & ENVIRONMENTAL SERVICES

DIOXIN/FURAN
ANALYSIS REPORT
NUMBER D3224-3225

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This analysis is based on AES Organics Laboratory method O-55 which is accredited under the UKAS accreditation scheme.

This analysis was performed in accordance with BS EN 1448-2 : 1997 and BS EN 1448-3 :1997.

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SECTION 1

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SUMMARY

Two samples from TMS Environmental were analysed for dioxin and furan contamination. Analysis of the samples gave the following I-TEQ values (to 2 significant figures). Two values are quoted, the first taking any non-detects as zero and the second taking any non-detects as at the detection limit level: •

LAGAN CEMENT MAIN STACK	15 (27) pg ITEQ
LAGAN CEMENT MAIN STACK FIELD BLANK	0.25 (4.8) pg ITEQ

The total dioxin/furan content of the samples is indicated below (to 2 significant figures):-

LAGAN CEMENT MAIN STACK	1800 pg
LAGAN CEMENT MAIN STACK FIELD BLANK	39 pg

Full results for individual congeners and homologue group totals together with information on any deviations from methodology quality systems is shown in section 2.

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INTRODUCTION

Two samples were submitted to AES Ltd by TMS Environmental for analysis to determine the levels of polychlorinated dibenzo-p-dioxins (PCDD's) and polychlorinated dibenzofurans (PCDF's) present.

The analysis covered the 17 PCDD and PCDF congeners containing chlorine substitution at the 2,3,7 and 8 positions so that International Toxicity Equivalents could be calculated based on the NATO/CCMS system.

The samples were received on 1 1/2/05 and were stored in refrigerator HIN 286 at a temperature of 2.5°C ± 1°C. Details of the samples are shown below.

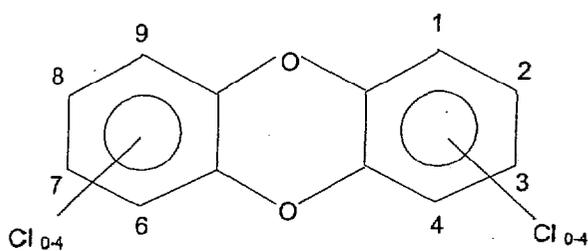
SITES SAMPLED -TMS ENVIRONMENTAL

DATE REC'D	SAMPLE	LAB N° R	E F
11/2/05	LAGAN CEMENT MAIN STACK	3037609	D3224
11/2/05	LAGAN CEMENT MAIN STACK FIELD BLANK	3037610	D3225

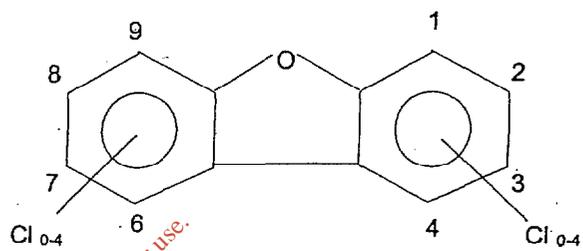
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DIOXINS AND FURANS

PCDDs and PCDFs form a group of 210 closely related substances. The structural formulae are shown below. A dioxin or furan molecule can have as few as one or as many as eight chlorine atoms attached to the molecule at any of eight locations. The combination of number and position of the chlorine atoms gives rise to 75 possible dioxins and 135 furans.

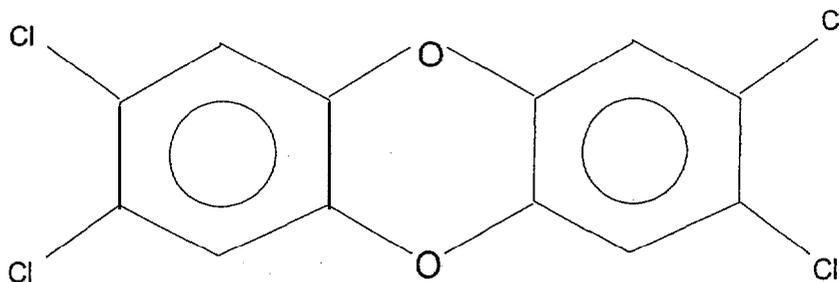


A Dioxin Molecule



A Furan Molecule

It is both the number of chlorine atoms and position in the molecule that determines the physical and chemical properties, as well as the toxicity of a given dioxin or furan. The most hazardous dioxin has chlorine substitution at the 2,3,7 and 8 positions and is therefore called 2,3,7,8-tetrachlorodibenzo-p-dioxin.



2,3,7,8-Tetrachlorodibenzo-p-dioxin

TOXIC EQUIVALENTS

In order to assess the toxicity of complex mixtures of PCDDs and PCDFs the concept of toxic equivalents was devised. International Toxicity Equivalent Factors are assigned to individual dioxins and furans on the basis of how toxic they are in comparison with 2,3,7,8-TCDD, the most potent dioxin which has been assigned a value of 1.0. By comparison, animal and cell tests show that 2,3,7,8-TCDF is approximately one-tenth as toxic as 2,3,7,8-TCDD. Consequently its toxic equivalent value is 0.1.

International Toxicity Equivalent Factors have been developed for those dioxins and furans that contribute most to the toxicity of a complex mixture which are those that have chlorine substitution in at least the 2,3,7 and 8 positions. Multiplication of the concentration of a particular PCDD or PCDF by its International Toxicity Equivalent Factor therefore gives a 2,3,7,8-TCDD Toxic Equivalent. The toxicity of any mixture, relative to 2,3,7,8-TCDD is therefore the sum of individual Toxic Equivalents.

Of the 210 dioxins and furans, 17 contribute most to the toxicity of a complex mixture and are of most concern. This does not mean that the remaining 193 dioxins and furans are not toxic but that they contribute comparatively little to the toxicity of a complex mixture.

The most widely accepted Toxic Equivalent system is the NATO/CCMS system and factors are shown in the table below.

NATO/CCMS TOXICITY EQUIVALENT FACTORS

COMPOUND	I-TEF
2,3,7,8-TCDF	0.100
2,3,7,8-TCDD	1.000
1,2,3,7,8-PeCDF	0.050
2,3,4,7,8-PeCDF	0.500
1,2,3,7,8-PeCDD	0.500
1,2,3,4,7,8-HxCDF	0.100
1,2,3,6,7,8-HxCDF	0.100
2,3,4,6,7,8-HxCDF	0.100
1,2,3,7,8,9-HxCDF	0.100
1,2,3,4,7,8-HxCDD	0.100
1,2,3,6,7,8-HxCDD	0.100
1,2,3,7,8,9-HxCDD	0.100
1,2,3,4,6,7,8-HpCDF	0.010
1,2,3,4,7,8,9-HpCDF	0.010
1,2,3,4,6,7,8-HpCDD	0.010
OCDF	0.001
OCDD	0.001

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METHOD

The analytical method used for the analysis is based on BS EN1948-2 & BS EN1948-3 1997

The sample is withdrawn isokinetically from the gas stream and collected in the sample probe, on a glass fibre filter and on a packed column of XAD-2 resin. The resin is spiked with a mixture of three stable isotopically labelled standards before sampling to give an indication of sampling efficiency and breakthrough. The filter is treated with 1ml of concentrated hydrochloric acid and dried. The resin/filter is spiked with 13 stable isotopically labelled standards before extraction to give an indication of extraction and clean-up efficiency. (The spiking scheme is illustrated on the next page). The filter and resin (after mixing with sodium sulphate for drying) are then combined with the solvent washes (after solvent exchange in toluene) and Soxhlet extracted for a minimum of 20 hours with toluene.

Impurities are removed from the extracts by acid/base back-extraction and column chromatography using silica and alumina absorbents, any or all of the techniques being used.

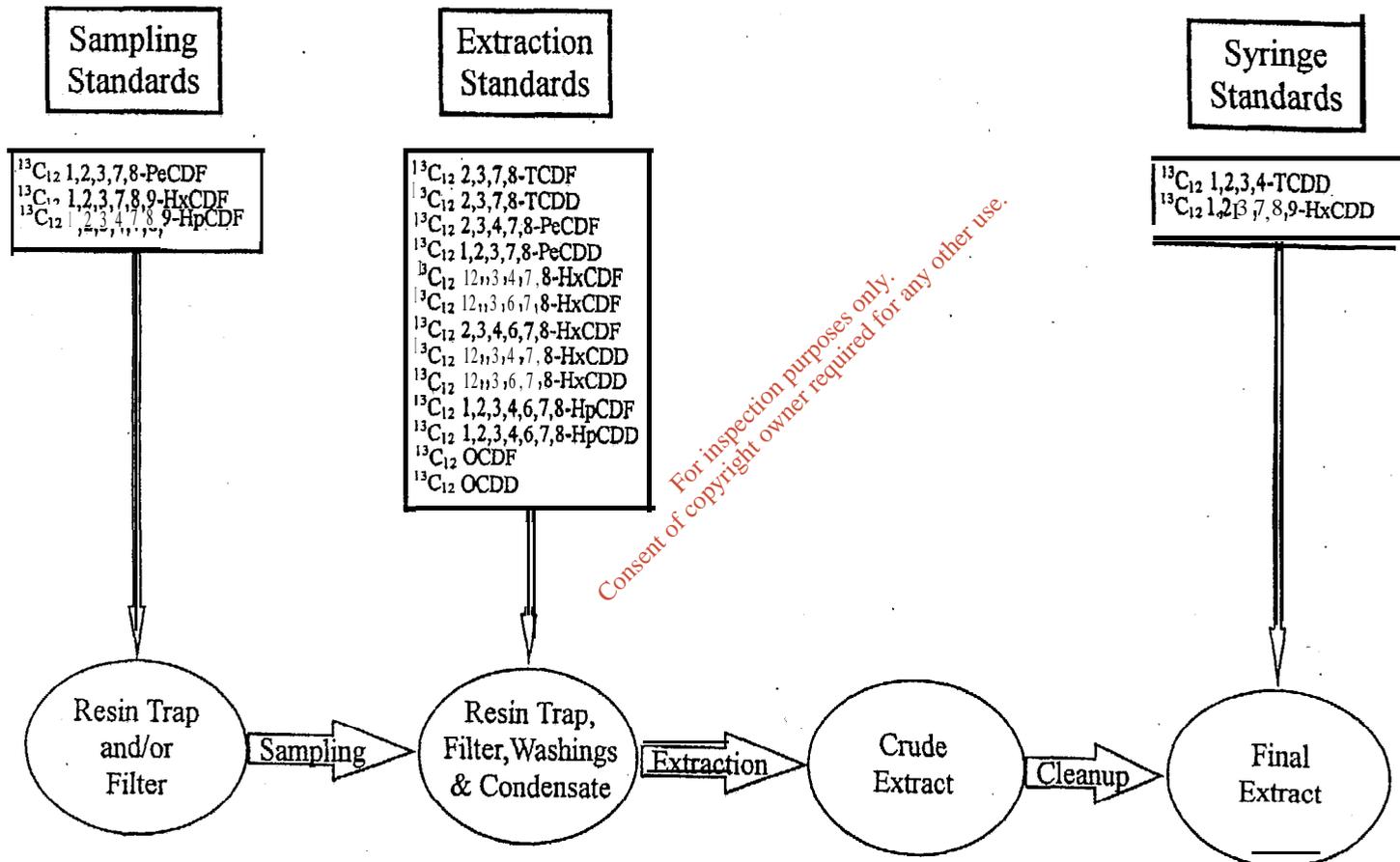
The resulting extracts are concentrated and solvent exchanged to give a final volume of 10 μ l in nonane.

Two isotopically labelled internal standards are added before analysis by high resolution gas chromatography- high resolution mass spectrometry (HRGC-HRMS) using a DB5-MS column. If any limiting value is exceeded for the sample then a confirmatory analysis is performed on an RTX 2330 column.

Identification of the dioxins and furans is based on comparison of GC retention time ranges and the ion abundance ratios of the m/z 's with the corresponding retention time ranges of authentic standards and the theoretical ion abundance ratios of the exact m/z 's.

If results for individual targeted dioxins/furans (i.e. 2,3,7,8 substituted) exceed the calibration range of the instrument then these results are flagged in the analytical report. The mass spectrometer is operated at a resolution of 10000 to minimize the potential for interference. Selected ions characteristic of the PCDD's and PCDF's are monitored together with ions characteristic of polychlorinated diphenyl ethers, which may interfere with the PCDF's. The mass spectrometer is continuously calibrated during acquisition to correct for any mass drift by allowing a reference compound FC43 to bleed into the system.

CEN 1948 Labelled Standard Spiking Scheme



SECTION 2

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RESULTS

The following pages contain the detailed analytical results for the isomer specific analysis for each sample and blank along with homologue group totals and recovery information for the labelled standards.

A matrix blank is analysed alongside the samples to show any possible contamination. This normally is a sample of XAD-2 resin from the same batch that was used to take the sample.

The following points should be noted.

Results have not been blank corrected. Results have not been rounded. This is to permit further processing if necessary and does not imply the level of accuracy. Summary results have been rounded to two significant figures.

N.D - Not Detected - Detection limits for the analysis are calculated on a sample specific basis by the GCMS software.

Results marked * are over the normal calibration limit of the method.

The total results for TCDD and TCDF homologue groups' do not include the 1,2,8,9 isomers due to the fact that these components elute prior to the first of the PeCDF's on the DB5-MS column used. Acquisition windows have been set up to acquire the first eluting PeCDF in preference to the two tetrachlorinated isomers identified above.

As part of the method validation the precision of the standard was assessed (including sampling and analysis) with the following results:-

The internal variability (corresponding to the repeatability in accordance with ISO 5725-2: 1994) is determined as the maximum difference to be expected with a 95 % statistical confidence between the results of one measurement institute measuring, and using the same laboratory facilities, in accordance with the requirements of this standard with two identical sampling trains and the same sample gas. The internal variability is expressed as the internal confidence interval with a 95 % statistical confidence.

The internal confidence interval for the filter/cooler method at a mean concentration of 0.040 ng I-TEQ/m³ was ± 0.060 ng I-TEQ /m³ and on a mean concentration of 0.030 ng I-TEQ/m³ ± 0.014 ng I-TEQ /m³.

The external variability (corresponding to the reproducibility according to ISO 5725-Z: 1994) is determined as the maximum difference to be expected with a 95 % statistical confidence between the results of several institutes measuring the same sample gas, each using their own individual sampling train and laboratory facilities and fulfilling the requirements of this standard.

The external confidence interval (with 95 % statistical confidence) at a mean concentration of 0.035 ng I-TEQ/m³ was ± 0.05 ng I-TEQ/m³.

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DIOXIN-FURAN RESULTS

CLIENT TMS ENVIRONMENTAL

CONTRACT TMSENVBO-9475

SAMPLE LAGAN CEMENT MA N- STACK

SITE TMS ENVIRONMENTAL

LAB NO 3037609

REF D3224

COMPOUND	pg in whole sample	I-TEF	I-TEQ(1) pg	I-TEQ(2) pg
2,3,7,8-TCDF	22.018	0.100	2.202	2.202
2,3,7,8-TCDD	N.D	1.000	N.D	5.105
1,2,3,7,8-PeCDF	N.D	0.050	N.D	0.461
2,3,4,7,8-PeCDF	16.600	0.500	8.300	8.300
1,2,3,7,8-PeCDD	N.D	0.500	N.D	5.372
1,2,3,4,7,8-HxCDF	5.637	0.100	0.564	0.564
1,2,3,6,7,8-HxCDF	6.461	0.100	0.646	0.646
2,3,4,6,7,8-HxCDF	7.082	0.100	0.708	0.708
1,2,3,7,8,9-HxCDF	1.285	0.100	0.128	0.128
1,2,3,4,7,8-HxCDD	6.955	0.100	0.695	0.695
1,2,3,6,7,8-HxCDD	N.D	0.100	N.D	1.864
1,2,3,7,8,9-HxCDD	7.360	0.100	0.736	0.736
1,2,3,4,6,7,8-HpCDF	11.480	0.010	0.115	0.115
1,2,3,4,7,8,9-HpCDF	N.D	0.010	N.D	0.019
1,2,3,4,6,7,8-HpCDD	41.650	0.010	0.416	0.416
OCDF	3.273	0.001	0.003	0.003
OCDD	19.183	0.001	0.019	0.019
			14.532	27.353

TOTALS	pg
TCDF's	841.860
TCDD's	161.980
PeCDF's	81.849
PeCDD's	229.359
HxCDF's	36.894
HxCDD's	311.945
HpCDF's	16.940
HpCDD's	63.215
OCDF	3.273
OCDD	19.183
TOTAL	1766.498

ITEQ (1) is taking any non-detects as zero. ITEQ (2) is taking any non-detects as at the detection limit level.

LABELLED STANDARD RECOVERIES

CLIENT TMS ENVIRONMENTAL

CONTRACT TMS ENWRO-9475

SAMPLE LAGAN CEMENT MAIN STACK

SITE TMS ENVIRONMENTAL

LAB NO 3037609

REF 2 2 4

SURROGATE STANDARDS	% RECOVERY
¹³ C ₁₂ 12378 PeCDF	108.7
¹³ C ₁₂ 123789 HxCDF	108.6
¹³ C ₁₂ 1234789 HpCDF	124.5

EXTRACTION STANDARDS.	% RECOVERY
¹³ C ₁₂ 2378 TCDF	61.1
¹³ C ₁₂ 2378 TCDD	64.3
¹³ C ₁₂ 23478 PeCDF	69.4
¹³ C ₁₂ 12378 PeCDD	58.2
¹³ C ₁₂ 123478 HxCDF	76.6
¹³ C ₁₂ 123678 HxCDF	72.7
¹³ C ₁₂ 234678 HxCDF	74.4
¹³ C ₁₂ 123478 HxCDD	73.0
¹³ C ₁₂ 123678 HxCDD	64.7
¹³ C ₁₂ 1234678 HpCDF	73.7
¹³ C ₁₂ 1234678 HpCDD	75.8
¹³ C ₁₂ OCDF	86.5
¹³ C ₁₂ OCDD	88.0

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DIOXIN-FURAN RESULTS

CLIENT TMS ENVIRONMENTAL

CONTRACT TMS ENVIRO-9475

SAMPLE LAGAN CEMENT MAIN STACK FIELD BLANK

SITE TMS ENVIRONMENTAL

LAB NO 3037610

REP D3225

COMPOUND	pg in whole sample	I - T E F	I-TEQ(1) pg	I-TEQ(2) pg
2,3,7,8-TCDF	N.D	0.100	N.D	0.188
2,3,7,8-TCDD	N.D	1.000	N.D	1.434
12,3,7,8-PeCDF	N.D	0.050	N.D	0.087
2,3,4,7,8-PeCDF	N.D	0.500	N.D	0.516
1,2,3,7,8-PeCDD	N.D	0.500	N.D	0.93 1
1,2,3,4,7,8-HxCDF	N.D	0.100	N.D	0.239
1,2,3,6,7,8-HxCDF	N.D	0.100	N.D	0.091
2,3,4,6,7,8-HxCDF	2.252	0.100	0.225	0.225
1,2,3,7,8,9-HxCDF	N.D	0.100	N.D	0.115
1,2,3,4,7,8-HxCDD	N.D	0.100	N.D	0.23 I
1,2,3,6,7,8-HxCDD	N.D	0.100	N.D	0.313
1,2,3,7,8,9-HxCDD	N.D	0.100	N.D	0.276
1,2,3,4,6,7,8-HpCDF	N.D	0.010	N.D	0.066
1,2,3,4,7,8,9-HpCDF	N.D	0.010	N.D	0.015
1,2,3,4,6,7,8-HpCDD	N.D	0.010	N.D	0.077
OCDF	N.D	0.001	N.D	0.001
OCDD	24.168	0.001	0.024	0.024
		TOTAL	0.249	4.829

TOTALS	pg
TCDF's	0.568
TCDD's	2.356
PeCDF's	N.D
PeCDD's	5.300
HxCDF's	2.252
HxCDD's	3.885
HpCDF's	0.430
HpCDD's	N.D
OCDF	N.D
OCDD	24.168
TOTAL	38.959

ITEQ (1) is taking any non-detects as zero. ITEQ (2) is taking any non-detects as at the detection limit level.

LABELLED STANDARD RECOVERIES

CLIENT TMS ENVIRONMENTAL

CONTRACT TMSENVIRO-9475

SAMPLE LAGAN CEMENT MAIN STACK FIELD BLANK

SITE TMS ENVIRONMENTAL

LAB NO 3037610

REFD3225

SURROGATE STANDARDS	% RECOVERY
¹³ C ₁₂ 12378 PeCDF	105.5
¹³ C ₁₂ 123789 HxCDF	108.9
¹³ C ₁₂ I234789 HpCDF	124.1

EXTRACTION STANDARDS	% RECOVERY
¹³ C ₁₂ 2378 TCDF	69.1
¹³ C ₁₂ 2378 TCDD	68.9
¹³ C ₁₂ 23478 PeCDF	74.4
¹³ C ₁₂ 12378 PeCDD	71.8
¹³ C ₁₂ 123478 HxCDF	87.7
¹³ C ₁₂ 123678 HxCDF	87.6
¹³ C ₁₂ 234678 HxCDF	79.2
¹³ C ₁₂ 123478 HxCDD	76.8
¹³ C ₁₂ 123678 HxCDD	79.2
¹³ C ₁₂ 1234678 HpCDF	77.9
¹³ C ₁₂ 1234678 HpCDD	84.9
¹³ C ₁₂ OCDF	89.3
¹³ C ₁₂ O C D D	100.9

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DIOXIN-FURAN RESULTS

CLIENT TMS ENVIRONMENTAL

CONTRACT TMSENVIRO-9475

SAMPLE BLANK EXTRACT -LAB

SITE TMS ENVIRONMENTAL

LAB NO

REF D3224-3225

COMPOUND	pg in whole sample	I-TEF	I-TEQ(1) pg	I-TEQ(2) pg
2,3,7,8-TCDF	N.D	0.100	N.D	0.105
2,3,7,8-TCDD	N.D	1.000	N.D	2.071
1,2,3,7,8-PeCDF	N.D	0.050	N.D	0.084
2,3,4,7,8-PeCDF	N.D	0.500	N.D	0.421
1,2,3,7,8-PeCDD	N.D	0.500	N.D	0.597
1,2,3,4,7,8-HxCDF	N.D	0.100	N.D	0.085
1,2,3,6,7,8-HxCDF	N.D	0.100	N.D	0.076
2,3,4,6,7,8-HxCDF	N . D	0.100	N.D	0.205
1,2,3,7,8,9-HxCDF	N.D	0.100	N.D	0.052
1,2,3,4,7,8-HxCDD	N.D	0.100	N.D	0.169
1,2,3,6,7,8-HxCDD	N.D	0.100	N.D	0.200
1,2,3,7,8,9-HxCDD	N.D	0.100	N.D	0.062
1,2,3,4,6,7,8-HpCDF	N.D	0.010	N.D	0.010
1,2,3,4,7,8,9-HpCDF	N.D	3.010	N.D	0.005
1,2,3,4,6,7,8-HpCDD	N.D	3.010	N.D	0.015
OCDF	N.D	0.001	N.D	0.001
OCDD	N.D	0.001	N.D	0.001
TOTAL			N.D	4.159

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TOTALS	pg
TCDF's	0.395
TCDD's	0.630
PeCDF's	0.611
PeCDD's	N.D
HxCDF's	N.D
HxCDD's	0.648
HpCDF's	0.353
HpCDD's	N.D
OCDF	N.D
OCDD	N.D
TOTAL	2.637

ITEQ (1) is taking any non-detects as zero. ITEQ (2) is taking any non-detects as at the detection limit level.

LABELLED STANDARD RECOVERIES

CLIENT TMS ENVIRONMENTAL

CONTRACT TMSENVIRO-9475

SAMPLE BLANK EXTRACT -LAB

SITE TMS ENVIRONMENTAL

LAB NO

REF D3224-3225

EXTRACTION STANDARDS	% RECOVERY
¹³ C ₁₂ 2378 TCDF	83.3
¹³ C ₁₂ 2378 TCDD	76.8
¹³ C ₁₂ 23478 PeCDF	78.7
¹³ C ₁₂ 12378 PeCDD	76.2
¹³ C ₁₂ 123478 HxCDF	87.6
¹³ C ₁₂ 123678 HxCDF	87.3
¹³ C ₁₂ 234678 HxCDF	90.1
¹³ C ₁₂ 123478 HxCDD	81.2
¹³ C ₁₂ 123678 HxCDD	82.5
¹³ C ₁₂ 1234678 HpCDF	83.5
¹³ C ₁₂ 1234678 HpCDD	82.6
¹³ C ₁₂ OCDF	92.1
¹³ C ₁₂ OCDD	105.4

All of the recoveries quoted above are within the acceptable limits quoted in BS EN 1948.

SECTION 3

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EXPLANATION OF APPENDICES

APPENDIX 1 CHAIN OF CUSTODY FORMS/EXTRACTION/AUTOSAMPLER LISTS

These pages show copies of forms that document the progress of the sample from the sampling stage through all analysis stages.

The chain of custody form documents the date that the sample was taken and contains sample identification information together with records of the transfer of the sample prior to analysis.

The extraction log shows the dates of all extraction and cleanup processes, including details of the spiking standards used for analysis. The final extract volume after addition of internal standards is also shown.

The autosampler list shows the run order of the samples GCMS analysis together with the datafile names under which data is stored.

APPENDIX 2 GLOSSARY

This is a list of abbreviations used in this report.