UNDERSTANDING

DIOXIN

TESTING

BY

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UNDERSTANDING DIOXIN TESTING

INTRODUCTION

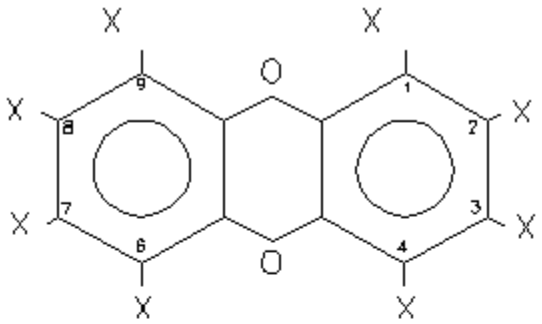
What are dioxins? The term dioxin or dioxins is generic. Used as such it typically refers to a compound or group of compounds from the dibenzodioxin or dibenzofuran classifications. The classification names suggest that the basic structure is of two benzene rings connected in one class by a dioxane structure and a furan structure in the other. Figure 1-1 contains examples of these structures. Thus, the basic structure is tricyclic or three-ringed. Further, the compounds generically referred to as dioxins have one or more chlorine or bromine atoms added to this basic structure. Many different numbers and configurations of these halogen atoms around the basic structure are possible. Those compounds with chlorine are referred to as polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). By chemical definition they are broadly classified as halogenated aromatic hydrocarbons. Structurally they are tricyclic aromatic compounds that are chlorinated or brominated.

One compound of the PCDD class is 2,3,7,8-tetrachlorodibenzo-p-dioxin. This compound has undergone extensive study and is sometimes called simply dioxin. The toxicity of this compound and those similar to it are of concern. To provide a way to measure the relative concern for those similar compounds this compound has been assigned a toxicity equivalence factor (TEF) of 1.0. This is based on laboratory studies which measured its toxic effect. It has thus become the reference compound for this class of compounds. The similar compounds which have been assigned a TEF value are those with chorines substituted in at least the 2,3,7, and 8 positions. Table 1-1 contains a list of these compounds and their TEF values. Additionally, the brominated dioxins and furans of the same substitution patterns and some polychlorinated biphenyls (PCB's) have sometimes been included in the definition of dioxin-like compounds.

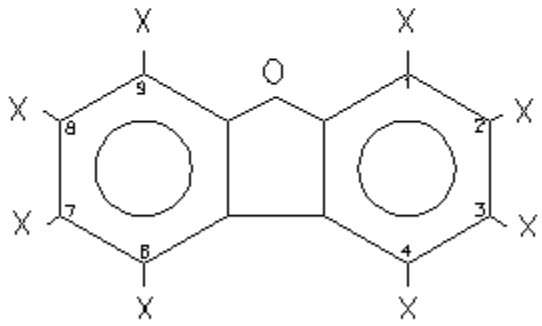
Sources of these compounds have been identified both in nature and industry. Much discussion and research is ongoing to further identify sources and to account for the amount of these compounds which are found in the environment. In recent reports on dioxins it has been stated that the trend since 1980 has been a decrease in the soil sediment concentrations of dioxins. However, further study will likely be required to confirm this and to provide an explanation for it.

Sources in nature include such things as forest fires and even some plants. The exact mechanisms are being discovered through research, however it is clear that both the basic ring structure and the necessary chlorine occur in nature. Industrial sources are more known and understood through studies that continue to help better understand mechanisms to develop controls. Manufacturing processes are one industrial source. Dioxin byproducts can result from the manufacturing of chlorine and chlorinated compounds such as chlorinated phenols, PCB's, phenoxy herbicides, chlorinated

benzenes, chlorinated aliphatics and other chlorinated compounds. Also the manufacturing of wood pulp and paper has resulted in the byproduct formation of dioxin. In this process the chlorine bleaching of wood pulp allows chlorine to interact with the natural occurring phenolic compounds in the wood pulp. Other industrial sources are combustion and incineration activities. The combustion sources included the operation of automobiles, trucks, and essentially any combustion device. Although improvements have been made, the fuels used and the presence of chlorine provide the ingredients. Incineration sources include various types of waste incineration such as municipal solid waste, sewage sludge, hospital waste, and hazardous waste. Also high temperature processes such as steel production, smelting, cement manufacturing, and the burning of coal, wood, and petroleum products for power or energy recovery can produce dioxins.



polychlorinated dibenzodioxin



polychlorinated dibenzofuran

Figure 1-1

Table 1-1
TEF Values

Compound	TEF
Mono-, Di-, and Tri-CDDs	0
2,3,7,8-TCDD	1
Other TCDDs	0
2,3,7,8-PeCDD	0.5
Other PeCDDs	0
2,3,7,8-HxCDD	0.1
Other HxCDDs	0
2,3,7,8-HpCDD	0.01
Other HpCDDs	0
OCDD	0.001
Mono-, Di-, and Tri-CDFs	0
2,3,7,8-TCDF	0.1
Other TCDFs	0
1,2,3,7,8-PeCDF	0.05
2,3,4,7,8-PeCDF	0.5
Other PeCDFs	0
2,3,7,8-HxCDF	0.1
Other HxCDFs	0
2,3,7,8-HpCDF	0.01
Other HpCDFs	0
OCDF	0.001

MEASUREMENT UNITS

Stack Emission Concentrations

Dioxin stack emission concentrations are usually reported as

PCDD/PCDF (ng/dscm @ 7% O_2)
or
TEQ (ng/dscm @ 7% O_2)

where ng/dscm = nanograms per dry standard cubic meter

@ 7% O_2 refers to a calculation performed to adjust the emisison concentration to a standard oxygen level.

In performing dioxin stack testing, it is prudent to insure that sufficient parameters are measured so that multiple comparisons can be determined. It is helpful to be able to determine mass emission rates, concentration emission rates, total PCDDs/PCDFs and toxic equivalency factors (TEQs). Along with the gas flow rates in the stack, oxygen should also be monitored during the stack testing, so that concentrations corrected to a specific oxygen level can be calculated.

For example, total dioxins and TEQs are not the same, nor is there a consistent ratio. According to the June 1994 draft USEPA dioxin reassessment, typical dioxin concentrations in cement plant stack emissions (14 kilns) range from 1.983E-09 to 1.998E-06 (0.000000001983 to 0.000001998). The toxicity equivalency (TEQ) for these same 14 kilns ranged from 1.750E-11 to 4.318E-08 (0.0000000000175 to 0.00000004318). While the lowest total PCDD/PCDF concentration did equate to the lowest TEQ, the highest total PCDD/PCDF concentration did not equate to the highest TEQ.

Process Sample Concentrations (solid matrix)

Dioxin concentrations are also determined in solid matrices such as soils and cement kiln dust (CKD). As an example, in the USEPA Report to Congress on Cement Kiln Dust (RTC), dioxin concentrations were analyzed and reported as total concentrations (μg/Kg) and TCLP concentrations (μg/L). PCDD/PCDF concentrations are often reported with laboratory notations indicating something other than detection at the value noted. Some of those notations are as follows:

< = not detected, the associated value is the detection limit
N.A. = detection limits are not available

B = the constituent was detected in an associated blank
J = the concentration is an estimate

The dioxin/furan constituent of most concern is 2,3,7,8-TCDF. Total 2,3,7,8-TCDF concentrations were reported for seven cement kilns in the RTC. Results for three of those kilns were reported below the analytical detection limit. Because of variations between runs, detection limits varied for all three of those kilns. The detection limits were 0.00065, 0.00087 and 0.00099 (μg/Kg) or micrograms per kilogram. The four facilities that reportedly did yield a measurable concentration ranged from 0.00039 to 0.038 μg/Kg. These are typical concentrations to target with appropriate analytical procedures.

TEQs

Often concentrations of dioxins are presented as toxicity equivalents (TEQ). TEQs are determined by summing the products of multiplying concentrations of individual dioxins times the corresponding TEF (See Table 1-1) for that compound [Section 4 Code of U.S. Federal Regulations (CFR) 266 Appendix IX].

Calculating TEQ's for PCDDs/PCDFs

Section 4.0 of Appendix IX, 40 CFR Part 266 does not state how to treat "non-detect" or less than detection limit values. Section 4.0 does reference USEPA document number USEPA/625/3-89/016 which has sample calculations. GCI obtained a copy of this document which is imposingly entitled "Interim Procedures for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-p-dioxins and Dibenzofurans (CDDs and CDFs) and 1989 Update." This document was published/released in March of 1989.

The sample calculations in this document have a number of instances where a value of zero is given for individual congener concentrations in real waste or real stack emissions. The subsequent Toxic Equivalent Quantity (TEQ) value that was calculated, based on the Toxicity Equivalency Factor (TEF) supplied by the USEPA, was also zero. There are a few instances where congener concentrations were listed as "<" a certain value. In these cases the TEQ value was listed as a zero or as a line, effectively a zero. There is one instance of a "ND" being listed as a value for a homologous group (A homologous group is not differentiated by isomer, in this case all TCDDs.) The subsequent TEQ calculated was listed as a short line, effectively zero. GCI, in examining these sample calculations, was careful to discount any source data for which the TEF was zero.

Based on this referenced document any PCDD/PCDF values that are below the analytical detection limit for the method should be listed as zeros or non-detects before calculating

the TEQ. GCI cautions that the sampling and analytical method QA/QC requirements must be met to demonstrate an adequate lower detection limit.

Sample PCDD and PCDFs Report

While report information and reporting format will vary between analytical labs and stack testing firms, Table 1-2 provides an example of what a PCDD/PCDF report might look like. Note that this particular report lists specific runs across the top to the columns, along with run start and stop times. Other information that is presented are gas conditions, volumetric flow rates, TEQs and total PCDFs & PCDDs. Averages of all the reported values are also provided.

Table 1-2
Sample Report

USEPA Methods 1-4 and 23
PCDDs and PCDFs

Stack

Run No.	1	2	3	Average
Date 1996	January 1	January 1	January 1	
Start Time (approx.)	08:00	11:10	14:20	
Stop Time (approx.)	11:10	14:20	17:28	
Gas Conditions				
T_s Temperature (°F)	236	228	234	232
B_{wo} Moisture (volume %)	13.41	13.43	13.23	13.36
O_2 Oxygen (dry volume %)	11.0	11.6	11.2	11.3
CO_2 Carbon dioxide (dry volume %)	16.4	15.5	16.6	16.2
Volumetric Flow Rate				
Q_a Actual conditions (acfm)	416,800	414,700	424,200	418,600
Q_{std} Standard conditions (dscfm)	270,700	272,300	276,900	273,300
2,3,7,8-TCDD Toxic Equivalent PCDDs & PCDFs (USEPA/87)				
C Concentration (ng/dscm)	43.0E-04	3.37E-04	36.0E-04	27.5E-04
C Corrected to 7% 0_2 (ng/dscm)	60.4E-04	5.03E-04	53.9E-04	39.8E-04
C Corrected to 12% CO_2 (ng/dscm)	31.5E-04	2.43E-04	26.1E-04	20.0E-04
E Emission rate (lb/hr)	4.36E-09	3.43E-10	37.4E-10	28.1E-10
Total PCDDS & Total PCDFs				
C Concentration (ng/dscm)	0.105	0.131	0.181	0.139
C Corrected to 7% O_2 (ng/dscm)	0.147	0.195	0.270	0.204
C Corrected to 12% CO_2 (ng/dscm)	0.077	0.094	0.131	0.101
E Emission rate (lb/hr)	1.06E-07	1.33E-07	1.87E-07	1.42E-07

C - Concentration
E - Emission Rate

Example Calculations

There is no standard reporting format for stack test data. Consequently, a review of the report format with a testing firm representative is recommended.

The following are things to look for when reviewing or comparing stack test data:

- Are the conditions "standard" as required by USEPA? That is at 25^{o}C?
  * Some reports will indicate that 0^{o}C was used rather than 25^{o}C. ("Standard" conditions for emission reports in Europe are different than the U.S. For this reason, emission results and regulatory limits cannot be directly compared.)

- Is the reported mass of the extract, in nanograms (ng), already divided by the sample volume or is it the mass of the total sample?

Dioxin samples are collected onto resin and then extracted. The testing company should report the dioxin that was present in the extract as a mass without a volume divisor.

Example 1: The stack sample reveals 0.190 ng TEQ for 4.23 dry standard cubic meters of sample,

0.190 ng/4.23 m^3, which can be written as 4.5E-02 ng/dscm.

In order to correct to 7% O_2, use the following correction calculation:

$\frac{(21-7)}{(21 - XO_2)}$ where 21 is the percentage of oxygen in the atmosphere, and

7% is the standard to which the value is to be corrected.
XO_2 is the actual stack gas oxygen concentration demonstrated during the test being corrected.

$$(\text{TEQ value in ng/dscm}) \times \frac{14}{(21 - XO_2)}$$

Example 2: the stack gas oxygen for example/sample 1 was 11.27%

$$4.5\text{E-}02 \text{ ng/dscm} \times \frac{14}{(21 - XO_2)} = 6.47\text{E-}02 \text{ ng/dscm TEQ @ 7\% } O_2$$

To convert concentration to a mass emission rate (e.g. grams per second), the flue gas flow rate at standard conditions must be known. Sometimes this is reported in dry standard cubic feet (dscf) rather than in metric units such as dry standard cubic meters (dscm). If the report provides:

Dioxin concentration (ng/dscm) 6.47E-2
Volumetric flow rate standard conditions (dscfm) 55,802

Per the following example of this conversion first coverting the flow rate from dscfm to dscm/min.

$$\frac{55{,}802 \text{ dscf}}{\text{minute}} \text{ (x) } \frac{1 \text{ dscm}}{35.31 \text{ dscf}} = 1580.4 \text{ dscm/min}$$

6.47E-02 ng/dscm (x) [kiln stack flow rate/minute] (x) 1 minute/60 seconds

$$6.47\text{E-}02 \text{ ng/dscm (x) } 1580.4 \text{ (x) } \frac{1}{60} = 1.7 \text{ ng/sec} = 1.7 \times 10^{-9} \text{ g/sec}$$

As an added note, GCI would point out that the current USEPA "Guidance on Structuring Trial Burns for Collection of Risk Assessment Data" released as an "Internal Review Draft" in May of 1997 discusses the use of the "full detection limit" value in calculation emissions of PICs for use in risk assessments "If the permit writer is setting an emission limit on the compound of concern..." Although this statement has been limited to PICs and PICs are discussed separately from PCDDs and PCDFs, a zealous permit writer may insert that the Dioxin TEQs be calculated in this manner. The permit writer is aided in being able to make this decision by the lack of a specified method of TEQ calculation. For BIF units, a specified TEQ calculation method is included in Appendix IX 40 CFR Part 266 which in turn references other USEPA documents that document the use of "Zeros" as the value for any non-detects (ND) in PCDD/PCDF emissions.

TEQ Calculation Considerations

Generally the stack testing firms will report the results of the USEPA Method 23 PCDD/PCDF analysis as total PCDD and PCDF concentration values (or as subtotals and totals of families of congener, i.e. tetra or penta) which are then converted to TEQ values and reported TEQ totals. In such cases, the individual congener are not reported and the owner/operator need not, and can not, calculate the TEQ values. However, if the individual congeners are reported, the worksheet (Appendix B, which may be copied) will aid in the calculation of the TEQ values. Please remember that in the past there have been a variety of toxic

equivalency factors (TEFs). As an example, the USEPA had a 1981 version as well as the currently accepted 1989 version. Ontario (Canada) and New York state have their own versions as do the FDA, the Swiss and Britain. It is possible that the USEPA will change the TEF values in the future based on continuing scientific research of the health effects of these compounds. Consequently, it is recommended that the analytical report include the concentrations for each of the congeners as well as the total PCDD/PCDF and total TEQ generally reported.

Oxygen Correction

In the USEPA Combustion Emission Technical Resource Document (CETRED), USEPA examined dioxin/furan emissions corrected to a stack gas oxygen level of 7%. This is also consistent with continuous emission monitoring required by the boiler and industrial furnace regulations (BIF). It is important to note that European guidelines require oxygen correction to 11% if you are comparing test results from European facilities.

STACK SAMPLING METHOD

Method Summary

The sampling method required in the United States is USEPA Method 23. It can be found in Appendix C of this document. The sample is withdrawn isokinetically and collected in the sample probe, on a glass fiber filter, and on a packed column of absorbent material. The PCDDs and PCDFs are extracted from the sample, separated by high resolution gas chromatography, and measured by high resolution mass spectrometry.

Prior to the actual sampling for dioxins certain preliminary determinations must be made. These preliminary determinations are common for several emissions stack sampling methods. The procedures described partially in USEPA Method 5 (Appendix D) for particulates are the same as for a number of emissions. Determinations for some other emissions have their own USEPA method number. They provide the basis for proper setup and selection of such things as: sampling site and number of sample points, sampling volume and time, size of nozzle and probe and the measuring of physical conditions of the stack gas which enable the proper calculation of emissions. USEPA Method 5 section 4.1.2 currently describes these determinations and references USEPA Methods 1-4 for more specific procedures.

The proper sample cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. The sampling components must have their external surfaces carefully wiped to prevent contamination of the final sample. Then the probes, filters, impingers, etc. must carefully have their contents rinsed or transferred to collection vessels for the analysis.

Detection Limits or Quantitation Limits

The detection limit for each isomer is determined by measuring the amount of analytical instrument response from the injection of calibration and internal standards. This determines the relative response factor. If a blank were injected into the analytical instrument, there would likely be some level of response, even though no actual analyte was injected. This is considered to be background noise. Using the response factor data and the background noise in the analyzer, a signal to noise ratio is calculated. The calculation includes ensuring that the ratio is greater than 2.5, which is required by the method. A minimum detection limit (MDL) is thus determined.
Determination of the amount of a given analyte would not be possible if the amount detected was below the minimum quantitation limit. In other words, quantitation

would not be possible because the amount detected would be below the analytical instrument quantitation limit and consequently could not be determined accurately. Analyte concentrations are often reported with laboratory notations reflecting some analytical limitation. Some of these notations sometimes used are as follows:

< = not detected, the associated value is the detection limit
N.A. = detection limits are not available
B = the constituent was detected in an associated blank
J = the concentration is an estimate, i.e. less than the quantitation limit but greater than the detection limit.

Sampling Checklist

(1) _____ Is the nozzle made of nickel, nickel-plated stainless steel, quartz, or borosilicate glass ?

(2) _____ Are sample transfer lines heated?

(3) _____ Is the filter support Teflon or Teflon-coated wire?

(4) _____ Do the number of sampling points add up to the minimum requirements of the method being used?

(5) _____ Were the sample trains assembled without the use of any sealing greases?

(6) _____ Were all leak checks performed as required?

(7) _____ Was a clean contaminant-free enclosed location provided for sample train breakdown and sample recovery operations?

(8) _____ Do field check sheets provide notes on observations as well as a record of all temperature and leak checks?

(9) _____ Do lab reports contain a narrative of any QA/QC observations during sample transportation, sample preparation, analysis, data reduction, or reporting?

(10) _____ Does the lab report contain all required maintenance and calibration documentation?

(11) _____ If an audit sample was required, was it run and was it an approved USEPA audit sample?

QA/QC

Sampling Train Collection Efficiency Check. An aliquot of the specified surrogate standard must be added to the sample train cartridges before collecting the field samples.

After the stack sample has been collected, USEPA SW846 analytical method 8290, section 6.0 Sample Collection, Preservation, and Handling, calls for stack samples to be extracted within 30 days and completely analyzed within 45 days of extraction.

Typical QA/QC Problems

- Breakage of sample train collection vessel. Recommend taking an extra run to cover breakage of at least one vessel.

- Failure of sample train to pass all leak check procedures.

- Plugging of the resin trap causing a build up of vacuum in the sampling train.

SAMPLE TESTING (ANALYSIS)

Method Summary

The complexity of USEPA Method 23 (Appendix C) is such that, in order to obtain reliable results, analysts should be trained and experienced with the analytical procedures. Normally, a stack testing contractor would have an experienced analytical lab which already does their work. If you have previously used an analytical lab which has given you good, reliable, defensible data, then it would be prudent to consider using them. Section numbers references are for USEPA Method 23 as published in 40 CFR Part 60, Appendix A (July 1, 1996 edition).

While method accuracy is the responsibility of the stack testing crew and the analytical laboratory, it may be helpful to have a basic understanding of the concerns involved. The accuracy of this method depends upon proper preparation of the sampling system and associated apparatus (Section 4.1.1). Also critical are the preliminary determinations (Section 4.1.2) and the sample recovery procedures (Section 4.1.3). The first phase of analysis is the extractions performed on the containers from the sample recovery (Section 4.2). These extractions are then cleaned up and fractionated (Section 5.2). From this point the next step is to inject an aliquot of the prepared extracts into a gas chromatograph/mass spectrophotometer (GC/MS), however, just prior to injection into the GC/MS, a known spike of a recovery solution is added to the prepared extract (Section 5.3). This is used with the quality control for the procedure.

Detection Limits

Every analytical method has a detection limit. The detection limit is dependent on a wide variety of factors including the analytical instrument, in this case a GC/MS. While normal method quality assurance/quality control (QA/QC), such as initial instrument calibration (Section 6.1.1) and daily performance checks (Section 6.1.2), helps to qualify method detection limits, it is an important issue that is sometimes confusing. For instance, in some cases, analytical results will indicate that there is a high likelihood that a substance has been detected but because of the limitations of the method/analytical instrument, it may not be possible to quantify how much of the substance was present. A particularly confusing issue can occasionally arise when a regulatory limit is lower than the detection limit of any known method or analytical instrumentation. Matrix specific interferences in any given run/sample exasorbate the problem. All of these issues should be addressed to some degree in the final analytical laboratory report.

Sample Matrix Issues

It is important to choose the appropriate analytical method. Just because a specific analytical method is designated does not necessarily mean that it is the best method for what you are trying to accomplish. For instance, USEPA initially used SW846 8280 (Appendix E) to analyze CKD samples for the CKD report to Congress. This method was debatably inappropriate based upon the sample matrix. The appropriateness of analytical methods was so noted in Section D of the Regulatory Determination on Cement Kiln Dust published in the 2-7-95 Federal Register. Make sure that the chosen analytical method is the most appropriate for what you are trying to accomplish.

USEPA SW-846 Method 8290

SW846 8290 (Appendix F) provides procedures for the detection and quantitative measurement of PCDDs and PCDFs in a variety of environmental matrices at part-per-trillion (ppt) to part-per-quadrillion (ppq) concentrations. The sensitivity of this method is dependent upon the level of interferences within the sample matrix.

This procedure uses matrix specific extraction, analyte specific cleanup, and GC/MS analysis techniques. The method also provides selected cleanup procedures to help eliminate encountered interferences. Quantitation of individual PCDD/PCDF congeners, total PCDDs and total PCDFs is achieved in conjunction with the establishment of a five point calibration curve for each homologue, during which each calibration solution is analyzed once.

Stack samples must be stored at 4° C in the dark, extracted within 30 days and completely analyzed within 45 days of extraction. Internal standards are used in this procedure and specific calibration procedures must be followed.

A gas chromatograph (GC) column performance check is only required at the beginning of each 12 hour period during which samples are analyzed. A method blank run is required between a calibration run and the first sample run. The same method blank extract may thus be analyzed more than once if the number of samples within a batch requires more than 12 hours of analyses.

Chromatography time for PCDDs and PCDFs exceeds the long term mass stability of the mass spectrometer (MS). Because the instrument is operated in the high resolution mode, mass drifts of a few ppm can have serious adverse effects on instrument performance. Therefore, a mass drift correction is mandatory, as described in the method.
A field blank is required for each batch of samples to be analyzed. Many times, a rinsate that was used to rinse the sampling equipment, is also included. Analysis of the rinsate helps to insure that the samples were not contaminated by the

sampling equipment. Duplicate analyses of some samples is also required as are matrix spikes and matrix spike duplicates.

Typical Checklist (Partial) for Sample/Analysis/Data Receiver

Apparatus (2.0):

(1) _____ Was all glassware cleaned and made free of silicone grease, especially on glass fittings?

(2) _____ Is the nozzle made of nickel, nickel-plated stainless steel, quartz or borosilicate glass?

(3) _____ Do sample transfer lines need to be heat traced?

(4) _____ Is the sample transfer line as short as possible?

(5) _____ Is the filter support made of Teflon or Teflon-coated wire?

(6) _____ Does the condenser conform to Figure 23.2?

(7) _____ Were the Section 3.0 reagent procedures followed?

(8) _____ Were traps loaded in a clean area, i.e., not in the field?

(9) _____ Were all samples sealed with aluminum foil or Teflon tape?

(10) _____ Were gas entry temperatures monitored and kept below 20°C for the XAD-2 resin?

(11) _____ Were all leak check procedures performed?

(12) _____ Was the proper cleanup procedure begun as soon as the probe was removed from the stack at the end of the sampling period?

(13) _____ Were all openings to sample trains, probes, etc. capped except when inserted or when sampling was underway?

Analysis(5.0):

(1) _____ Were appropriate sample extraction procedures followed?

2) _____

Were appropriate sample cleanup and fractionation procedures followed?

Quality Control (7.0):

(1) _____ Was the PCDD/PCDF internal standard added to every sample before extraction?

(2) _____ Were the surrogate compounds added to the resin absorbent sampling cartridge before the sample was collected?

(3) _____ Was the toluene QA rinse reported separately from the total sample catch?

Quality Assurance (8.0):

(1) _____ Were audit samples run along with the stack samples?

(2) _____ Were the surrogate recoveries between 70 and 130 percent?

(3) _____ Were all samples extracted within 30 days of collection?

(4) _____ Were all samples analyzed within 45 days of collection?

Glossary of Technical Terms

2,3,7,8-tetrachlorodibenzo-p-dioxin This compound is considered the most toxic of the chemical family of dioxins and furans. It is assigned the toxicity equivalent factor (TEF) of “1", and all other dioxins and furans are assigned a TEF value less than “1".

Adsorb To collect (a gas, etc.) in condensed form on a surface.

Aliquot An analytical chemistry term referring to a measured portion taken from a solution. When an aliquot of a sample solution is analyzed, the concentration of the targeted compound in the original solution can be calculated from those analysis results.

Analyte The targeted compound or element for which an analysis is being executed.

Background noise Electrical or chemical interferences with the signal coming from the detector of an analytical instrument. The analyte must create a signal in the detector which sufficiently overcomes these interferences in order to be detected. In the case of dioxin/furan analysis, the signal to noise ratio must be greater than 2.5 for all monitored analyte signals.

Blank A quality assurance sample which is analyzed to ensure that any contamination is known and can be accounted for. Contamination may occur before, during or after the sampling or analysis testing procedures. The primary contamination of concern is the analyte or analytes that are being tested for. In dioxin/furan testing, the method calls for a field blank because of the several different solutions and pieces of equipment used in the testing. As an example, a basic set of blanks normally analyzed in dioxin testing is the method blank, field blank and trip blank.

Calibration Procedures that are prescribed by the dioxin/furan test methods to check the performance of the analytical instrumentation. The procedures involve the running of standards at different concentrations and ensuring that the results are consistent with the predicted concentration value.

CFR Code of Federal Regulations.

Congener A generic name for one particular compound of the same chemical family; e.g. 2,3,7,8, tetrachlorodibenzo-p-dioxin is one congener of the 75 chlorinated dibenzo-p-dioxin congeners.

Daily performance checks A routine testing of the electronic lab equipment to confirm that the machines are properly calibrated and accurate. These are performed at routine

times each day and are recorded as part of the Quality Assurance/Quality Control (QA/QC) data for that equipment.

Detection limit A calculated value, the level at which a particular piece of analytical instrument can detect the presence of a specific compound above the background noise of the instrument detector. For dioxin/furan analysis, this value is determined by the signal to noise ratio which must be a minimum of 2.5.

Dry standard cubic feet (dscf) See dry standard cubic meters. The only difference between the two terms is the use of English units of measure rather than metric.

Dry standard cubic meters (dscm) Concentration of contaminants in gases emitted from sources (such as cement kilns) are generally expressed as a weight of that material per a volume of gas. Emissions from sources often contain water vapor from evaporation of water in the processed material or as water from combustion of hydrocarbons. This amount varies from source to source and at variable temperatures from source to source. To make an emission rate meaningful for comparison to another source or to a permit limit, the emission rate must be stated as a weight per (dry) gas at standard conditions. The specific standard conditions are set by the applicable authority, often a national laboratory group.

Duplicate analyses The sample is split and then each split is subjected to analysis.

Filter support A housing that holds the flimsy glass fiber filter in place in the sampling train.

Fractionated The second main step in the analysis of a dioxin/furan field sample. After the field sample has gone through extraction procedures, the dioxin/furans, if there are any, are put into a solution. The solution must be cleaned up and fractionated. This step is a series of procedures where the solution is passed through different columns of packed chemical material to purify the solution prior to injecting it into the analytical instrument.

Gas chromatograph/mass spectrometer (GC/MS) A gas chromatograph is an instrument where the sample gas passes through a carefully heated coiled metal, glass or silica tubing packed with a specially prepared media, or a glass or silica coil of a very precise bore measurement with an internal coating which causes the different compounds in the gas to separate based on their transport properties. Each compound exits the coil in a known sequence and at a predictable time. This permits identification of the compounds in the sample through the use of some type of detector at the exit of the coil.

The mass spectrometer is the detector that measures each of these compounds as they leave the coil. This is the most accurate device for identifying and determining the concentration of different organic compounds.

Glass fiber filter A special type of filter used in the Method 23 stack sampling train. It will not react to chlorinated hydrocarbons as some other mineral fiber or paper filter may.

High resolution gas chromatography (HRGC) A gas chromatograph especially configured to detect very low concentrations of hydrocarbon. The HRGC must be equipped with temperature programming, a high resolution capillary column for the separation, as well as other required accessories such as syringes, high purity gases and a data system to control operations, collect and process data. For dioxin/furan analysis of samples.

High resolution mass spectrometry (HRMS) A mass spectrometer which can identify a hydrocarbon by its very specific ion mass. The unit must be able to resolve each ion mass peak from another with a minimum of 10% difference between each mass peak. It also must have a data system to control and monitor the multiple ion monitoring process. The data system must also be able to acquire data at a minimum of ten ions in a single scan and be able to provide other details of the mass spectra for each hydrocarbon. For dioxin/furan analysis, the HRMS must be closely coupled with a HRGC to separate the individual hydrocarbons (dioxin or furan) before they enter the HRMS.

Homologous group All of the dioxins (or furans) of the same base grouping designated by the number of chlorine molecules in the compound. For example, all tetrachlorodibenzo-p-dioxins (TCDD) have four chlorine molecules and are a homologous group. 2,3,7,8-TCDD has four chlorine molecules, one each at the 2, 3, 7 and 8 positions, and is thus one member of the tetra group.

Impingers A glass tube containing a fluid that is part of a sample train. Gas from the source is passed through a dip leg (bend in the tubing) and then bubbles up through this fluid. The fluid may be water or a chemical that reacts with some constituent in the gas. The gas analytes of interest then remain in the fluid for subsequent analysis.

Initial instrument calibration The first calibration of an instrument, usually intended to achieve a gross, or rough, calibration that will be subsequently refined for accuracy.

Interferences Any substance or mechanism that compromises the accuracy of an analysis of another substance. Sample preparations and analyses must often be performed in certain steps to remove substances that would reduce the accuracy in determining the concentration of another substance.

Internal standards These are standards which are added to the sample to be analyzed prior to it being analyzed. For dioxin/furan analysis, they may be the same compounds as the analytes of interest, very similar or radioactively labeled. They are added to the sample in a quantitatively known manner. They are then analyzed for, just as are the analytes of interest. Results allow the analyst to be more precise in determining the concentration of the unknown analytes. Also, the results can indicate whether any portion of the sample was lost during the many steps of the analysis, therefore effecting the accuracy of the results.

Isokinetically A term which pertains to the sampling of stack gas. It means taking the sample under specific and relatively constant physical conditions such as gas flow rates, velocity, pressures, etc. The sampling of a stack requires several hours, movement of the sampling train between sample points on the stack and obtaining the required amount of gas sample. In order to extract a truly representative sample from a stack the sample must be withdrawn within 10% of isokinetic conditions. The sample probe nozzle is a key in achieving these monitored conditions. It should be selected and pre-tested to ensure its ability to maintain the isokinetic conditions while sampling gases moving through the stack.

Isomer In this case, one specific arrangement of chlorine molecules in a homologous group, e.g. 2,3,7,8-TCDD is one isomer of the TCDD group. 2,4,7,8-TCDD would be another isomer of the same group.

Kg Kilogram, or 10^3 grams, or 1000 grams.

Matrix spikes A quality control sample prepared and run during the analysis of the sample. It is prepared using the same media and chemical the field sample was taken in. It is split into two samples and spiked with internal standards. The two samples are then analyzed through the same steps as the field sample. The results are compared and for dioxin/furan testing should agree within 20% of each other.

mg Milligrams, or 10^{-3} grams, or 0.001 grams.

ng Nanogram, or 10^{-9} grams, or 0.000000001 grams.

ng/dscm Nanograms per dry standard cubic meter. See dry standard cubic meter.

Nozzle The tip of the sample probe inserted into the stack to sample the stack gas. These nozzles come in a number of opening sizes corresponding to the flow rate needed for the sampling period.

Packed column The metal or glass coil that has the precisely ground specially prepared media in it that the gas chromatograph carrier gas flows through. The sample

when injected into the carrier gas, flows through the media which separates compounds in the sample. See also gas chromatograph/mass spectrometer (GC/MS).

Products of Incomplete Combustion (PICs) Hazardous organic compound emissions which, in theory, result in complete combustion of fuels or other materials. Burning hydrocarbons breaks them down from more complex into more simple compounds. Burning that is not hot enough or long enough will result in some intermediately complex hydrocarbons. These intermediately complex hydrocarbons also routinely occur in nature for a wide variety of reasons. The EPA assumes that hydrocarbons volatized out of the raw feed in a cement kiln (or lime kiln, or aggregate kiln) comes only from incomplete combustion.

Quality Assurance/Quality Control (QA/QC) A set of procedures to ensure that analyses have been performed accurately. Some of these procedures precede the analysis and some follow the analysis.

Quantitation Limit A limit above the detection limit which, through calculation, meets certain statistical confidence criteria as defined by the test method, e.g. the confidence level for dioxin/furan analysis is 99%. The lowest possible level is also called the minimum quantitation limit (MQL).

Relative response factor This is a value calculated for each analyte of interest from calibration response factor data. These values are then used to determine the concentration of those analytes in the analysis of the test sample. This determination is made by comparing the responses of the known analytes to the responses of the unknown analytes.

Resin absorbent sampling cartridge This is a glass vial with a specially prepared resin that adsorbs organics out of the sample gas.

Response factor data This data is obtained during analytical instrument calibration procedures. In dioxin/furan testing, the data comes from analyzing a series of standards with the GC/MS and recording the detector response to the known concentration of the individual analytes in each standard. Calculations are then made using the detector response data and the known concentration of each analyte in the standard to determine the relative response factor.

Rinsate A solution used to wash across the inner surface of sampling equipment to ensure that all of the sample being analyzed will have all of the analyte.

Sample catch The actual amount of sample that the sampling equipment contains at the end of the sampling period.

Sample matrix The type of media (broadly; solid, liquid, or gas) that the analytes are found in, sampled in, or extracted to. For example, a stack gas may be sampled in the

gas phase by a bag or passed on to a sample train and captured in solid or liquid media. Within each of the broad categories there can be many more types of media or matrix. In dioxin/furan testing, quality control samples using the sample matrix must be tested to determine if they have an effect on the analysis results.

Sample probe The tubing (generally glass) that is inserted into the gas stream to extract a sample of the stream.

Sample recovery operations The activity to properly transfer the sample out of the sampling device into containers. This includes measurement of the fluids, rinsing and measurement of the rinsate, the addition of preservatives or reactants, etc.

Sample train breakdown The first steps in sample recovery. It involves very careful disassembly, rinsing and collection of sampling apparatus components and materials. For dioxin/furan testing, specific procedural steps are specified by the test method for all of these activities.

Sample transfer lines The tubing connecting different filters, impingers, etc. in a sample train through which the sample gas flows.

Sealing greases Greases used to create gas-tight connections between glass to glass connections or Teflon to glass connections. The test method for dioxin/furan emissions requires that no greases be used to prevent contamination of the sample.

Spike The addition of a compound of known composition and concentration to a material prior to analysis.

Standard See internal standards.

Surrogate compounds A substituted compound. When a compound is very hazardous or difficult to work with, it may be desirable to use a less hazardous material which has similar properties. A surrogate compound should be approved before it is used. In dioxin/furan testing a group of surrogate compounds are used as a part of the internal standards. The method specifies when and where these should be used.

Toluene QA rinse A quality control sample collected when testing stack gases for dioxin/furan emissions using method 23. After the stack sampling equipment has been cleaned and rinsed with acetone and methylene chloride as per the method, a final rinse is made with toluene. This rinse may be kept separate from the other cleaning rinses. If it is analyzed separately for dioxin/furan it can demonstrate that the prior cleaning and rinsing were effective in removing all the dioxin/furan from the sampling equipment. This rinse may be added to the other rinses and become part of that analysis.

Toxic Equivalent Quantity (TEQ) The quantity of each PCDD/PCDF emitted multiplied by its TEF. In this manner, devices that emit different relative quantities of the different PCDD/PCDF compounds can be compared to a standard limit.

Toxicity Equivalency Factor (TEF) An assignment of relative toxicity with 2,3,7,8-TCDD being "1".

µg Micrograms, or 10^{-6} grams, or 0.000001 grams.