An Assessment of Test Methods Designed to Accurately Quantify PCDDs/PCDFs in Stack Gas Emissions

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Abstract

The EPA stack test method currently used by facilities quantifying dioxin/furan (PCDD/PCDF) emissions is Method 23. Cement kilns burning hazardous waste are scrutinized for emitting hazardous constituents, some of which are PCDDs/PCDFs. Because PCDDs/PCDFs have been a key focus point by the EPA for proposed emissions reductions requirements, accurate quantification is important. PCDD/PCDF formation mechanisms continue to be theorized, but remain unresolved. However, the D/F formation rate appears to be a strong function of temperature and catalytic activity. The EPA Resource Conservation and Recovery Act (RCRA) Boiler and Industrial Furnace (BIF) regulations promulgated under 40 CFR Part 266 have attempted to limit PCDD/PCDF formation by controlling the inlet temperature to the dry air pollution control device (APCD). Optimum temperatures for D/F formation are believed to be between 450 and 750 °F. Cement kilns normally use electrostatic precipitators (ESPs) or bag houses (BHs) for particulate matter (PM) control and limit temperatures accordingly following confirmatory testing. This paper investigated the potential for PCDD/PCDF formation within the filter holder of EPA Test Method 23 when flue gas temperatures are within 450 to 750 °F. Preliminary results are inconclusive, but suggest that the EPA Test Method 23 should be further evaluated and potentially modified.

Theory

Hazardous waste burning cement kilns are federally regulated under the Boiler and Industrial Furnace (BIF) regulations promulgated by the EPA under the Resource Conservation and Recovery Act (RCRA). 40 CFR Part 266.104 provides hydrocarbon emissions and related operating requirements, which also includes provisions designed to limit dioxin/furan (PCDD/PCDF) emissions. Facilities operating a dry air pollution control device (APCD) with an inlet temperature between 450 and 750 °F are required to quantify PCDD/PCDF emissions using EPA Test Method 23, which is described in Appendix IX of Part 266. Following quantitation, facilities are required to insure compliance with the acceptable ambient air concentration limit derived by the EPA using a direct pathway risk assessment.

The recently proposed Hazardous Waste Combustor (HWC) Maximum Achievable Control Technology (MACT) rule has established a more stringent PCDD/PCDF emissions concentration standard with additional APCD inlet temperature control requirements. PCDD/PCDF formation inhibitor and system removal activities were also incorporated in the proposed regulatory requirements. More specifically, the proposed MACT rule focused on temperature control to the dry APCD and monitoring requirements for potential PCDD/PCDF promoters or inhibitors, including precursor compounds, competing reactions and catalysts.

In general, cement kilns normally use either electrostatic precipitator (ESP) or bag house (BH) APCD equipment to control particulate matter (PM) emissions. Depending on operating conditions such as rapping frequencies of the ESPs or cleaning cycles of the BH, optimum reactive conditions for PCDD/PCDF formation can occur within the APCD equipment. Also, depending on the actual PCDD/PCDF formation mechanism, the APCD may provide for an ideal reactive environment for potential heterogeneous catalysis in addition to gas-phase reactions. As long as flue gas temperatures are between 450 and 750 °F, the collected PM and associated extended residence times created with APCD cleaning cycles allow for optimum PCDD/PCDF formation conditions to exist.

PCDD/PCDF Stack Test Methods

Stack gas sampling trains designed to collect representative flue gas samples for PCDD/PCDF analysis are also equipped with a filter device similar in design to a cement kiln dry APCD. Because the sampling train is exposed to flue gases passing a filter collector with PM for approximately two to four hours, precautions should be taken to limit filter temperatures to less than 450 °F, the temperature at which PCDD/PCDF formation is thought to be thermodynamically favored.

EPA Test Method 23

Figure I depicts the Method 5 sampling train referred to by Method 23 to condition stack samples prior to collection. Although the oven temperature is monitored and controlled to 248± 25 °F, the filter temperature is not. As a result, flue gas with temperatures exceeding 450°F may enter the filter box at elevated temperatures if heat transfer rates through the sampling probe and/or oven box are not sufficient to allow for reduced filter holder temperatures below 450 °F.

European Test Method prEN 1948-1

Figure II depicts the European Test Method prEN 1948-1 which differs from the EPA test method by requiring temperature control at the filter holder. Depending on the waste gas temperature, the probe is equipped with a heating or cooling device to bring the temperature of the gas sampled at less than 257 °F. In addition, the temperature in the filter casing shall be at least 50 °F above the dew point.

Results

A preliminary test at a wet cement kiln in Missouri supports the theory that PCDDs/PCDFs may be formed in the stack sampling train filter box and subsequently overestimate flue gas PCDD/PCDF emission rates. Table I summarizes toxicity equivalent (TEQ) and total PCDD/PCDF analyses for EPA Test Method 23 versus a Modified EPA Test Method 23 which utilized a flue gas temperature conditioning system similar to that described for the European Test Method prEN 1948-1.

Table I. PCDD/PCDF emissions quantified using EPA Test Method 23 versus a Modified EPA Test Method 23

	PCDD/PCDF TEQ (ng/dscm)	PCDD/PCDF Total (ng/dscm)
EPA Test Method 23	1.05	91.1
Modified Method 23	0.785	76.1

Conclusions

Further analysis is required and is currently being conducted to test theories proposed in this paper. However, the potential for significant PCDD/PCDF formation in the filter box of EPA Test Method 23 is theoretically possible. Flue gas temperature conditioning may be required to eliminate the potential for PCDD/PCDF formation in the sampling train. In addition, filter box temperature monitoring may be required to assess the potential for a favorable PCDD/PCDF reactive environment.

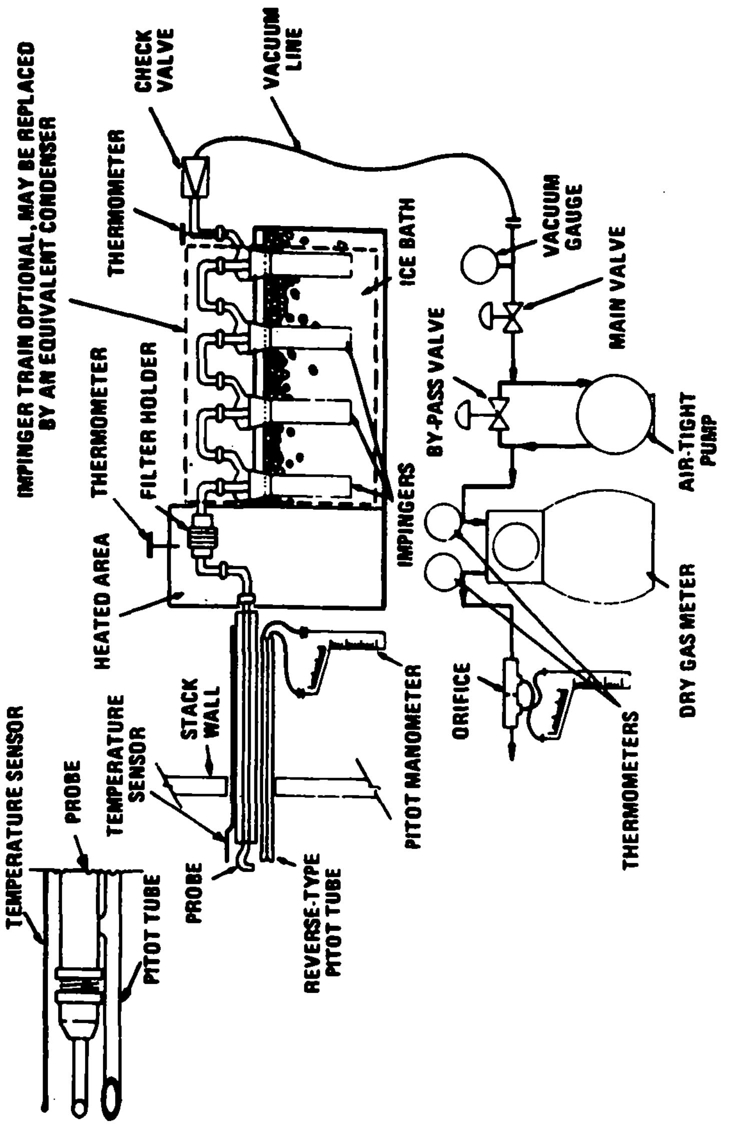
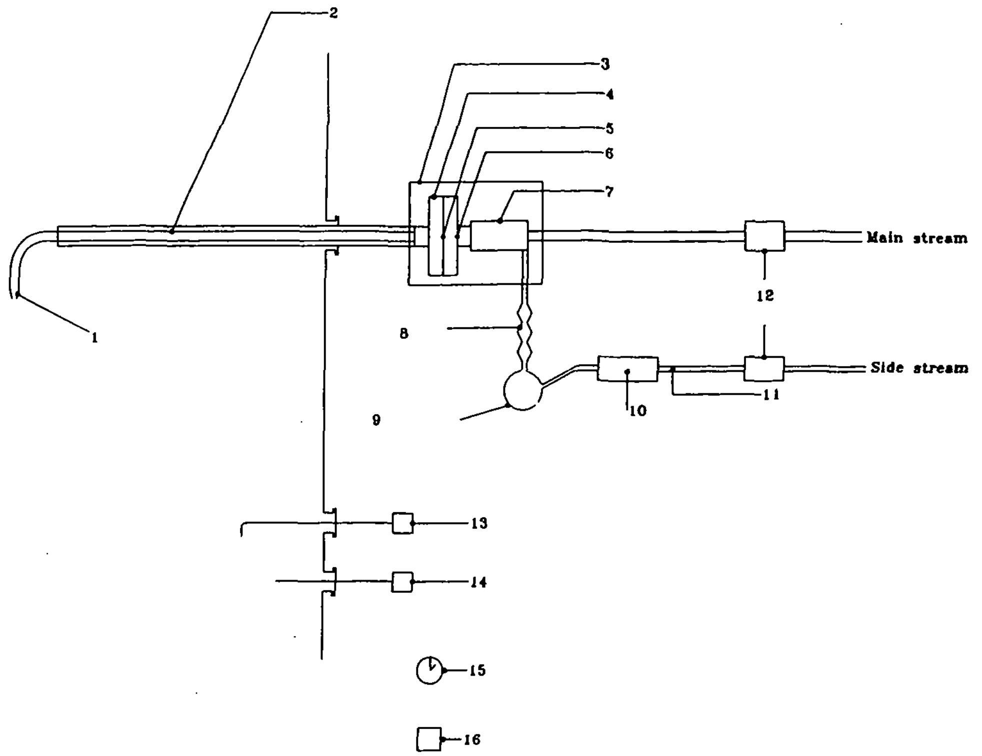


Figure I. Method 5 Sampling Train (Referenced by Method 23).



1 Sampling Nozzle
2 Probe (eventually heated)(790 to 1190 mm)
3 Temperature regulated casing (box) (T<125C)
4 Filter holder
5 Filter (diameter = 125 mm)
6 Temperature
7 Flow divider
8 Condenser
9 Condensate bottle (1 litre)
10 Solid adsorber and/or impinger unit
11 Suction device main stream 15 l/min. max.
12 Suction device main stream 120 l/min. max.
13 Gas velocity and pressure
14 Gas temperature
15 Time
16 Atmospheric pressure

Figure II. European Filter/condenser Method with Flow Division.