

EVALUATION OF MODIFICATIONS TO EPA METHOD 23 FOR MEASURING DIOXINS IN FLUE GAS FROM COAL-FIRED POWER PLANTS

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Introduction

Between 1993 and 2000, EPRI, the U.S. Department of Energy (DOE) and other organizations conducted a series of dioxin stack tests at coal-fired power plants using U.S. EPA Method 23. These tests detected extremely low levels of PCDDs/PCDFs (averaging about 2 pg TEQ/dscm). However, the data include significant dioxin contamination originating not from the flue gas but from the sampling apparatus, laboratory, or field procedures. EPRI's analysis of the data indicates that, based on the results of field and method blanks, almost half of the observed "emissions" may come not from the stack gas but from these extraneous sources (Figure 1). The octachlorodibenzodioxin (OCDD) and octachlorodibenzofuran (OCDF) congeners had the highest blank levels in relation to the reported concentrations. These two congeners were also the most frequently detected in stack gas from coal-fired power plants.

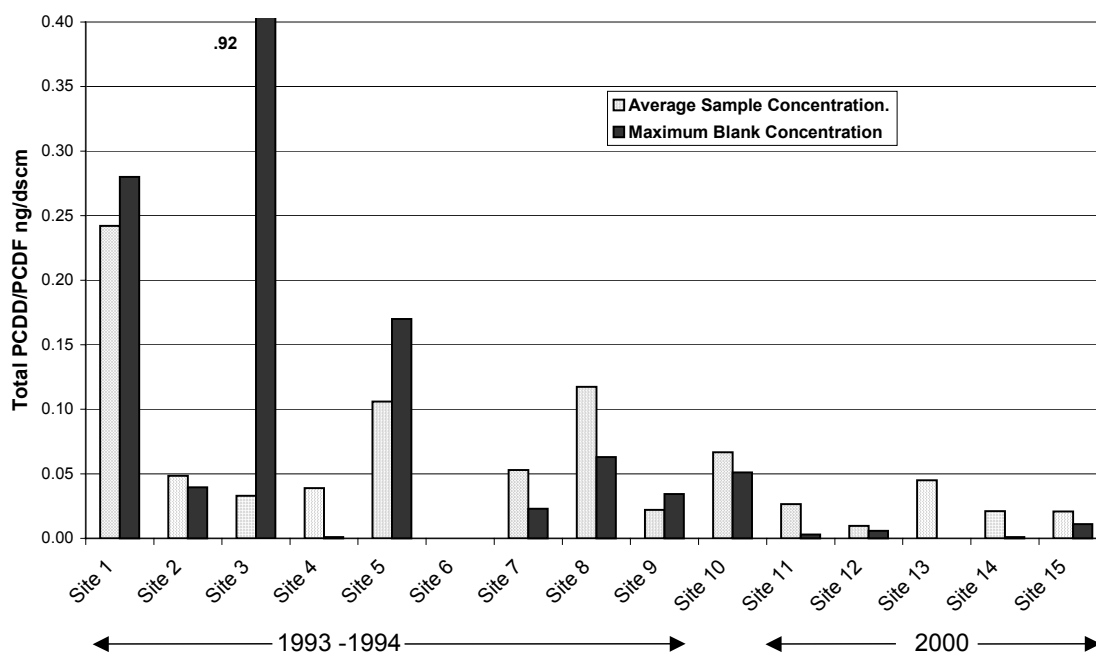


Figure 1. Background Contributions to PCDDs/PCDFs Measured in Flue Gas from Coal-Fired Power Plants

It is apparent that background sources of dioxin are ubiquitous and have the potential to bias the reporting of emissions from power plants and other low-level sources. One approach to obtaining a more accurate estimate is to correct the measured emission rates for the levels observed in the blanks. EPA Method 23 does not address blank correction¹, but EPA's policy is to forbid blank correction if an analytical method does not specifically allow the practice. EPA explicitly rejected blank correction for related Method 0023A in the context of compliance monitoring². This policy is highly problematic when a contaminant is ubiquitous and present at significant levels in blanks.

The quality of the coal-fired power plant data is also impacted by the sensitivity of the method. Many of the PCDD/PCDF detections in the 1993-2000 data set described above were at concentrations close to the method detection limits. This suggests that Method 23, as it is usually performed, is not sensitive enough to accurately measure power plant dioxin emissions.

Under the EPA Toxics Release Inventory program (EPCRA), industrial facilities are required to report dioxin releases that exceed 0.1 gram total dioxins and dioxin-like compounds per year³. For a large power plant, detection of even a few picograms of dioxin in a sample can trigger the reporting requirement. To address industry concerns on this issue, EPRI evaluated modifications to EPA Method 23 with the goal that the improved method could be used in the future to improve the emissions inventory.

Methods and Materials

Previous research has evaluated modifications to EPA Method 23, but was targeted at higher stack gas concentrations⁴. In 2002, EPRI conducted a field test program to explore modifications to EPA Method 23 that could reduce blank contamination and improve method sensitivity. The method modifications were designed to reduce blank levels and increase the ratio of sample mass to blank mass.

A second objective of this program was to evaluate the practicality of possible method modifications and their approximate cost when applied to a routine stack test program. Dioxin tests are already quite expensive, as a single laboratory analysis can cost \$1000 to \$1500 (U.S.). An arbitrary target was set for this program of keeping cost increases for the modifications to no more than 25% of a standard three-run dioxin stack test.

The field tests were conducted in September 2002 at a 100MW coal-fired power plant. The plant burns eastern bituminous coal, cofired with up to 8 percent natural gas during the ozone season. Cofiring was in effect during the tests. The test unit is a tangentially-fired boiler, equipped with a cold-side electrostatic precipitator (ESP) and a flue gas desulfurization (FGD) system. Isokinetic flue gas samples were collected from four ports on the stack.

Stack gas samples were collected for three consecutive days using dual Method 23 sampling trains (six samples). The operation of dual trains was intended to allow estimation of method precision at the levels of interest. Stack gas samples were collected using EPA Method 23, using a number of modifications to the method designed to increase sensitivity:

- Employ extended sampling periods of up to 12 hours.
- Reduce the level of ³⁷Cl₄-TCDD spiked into each sample as a surrogate standard, to avoid positive bias from an interfering M+2 ion that can interfere with quantitation of native 2,3,7,8-TCDD

- Use a newest-generation high resolution gas chromatograph /high resolution mass spectrometer (HRGC/HRMS)
- Calibrate the mass spectrometer using a lower low-level standard

In addition to the method modifications, the program employed a series of improved work practices designed to reduce positive bias:

- Precertify XAD resin and solvents.
- Use the same XAD resin lot for all samples and blanks.
- Use a lot of XAD resin with known low dioxin content.
- Pre-extract XAD resin with solvent prior to use.
- Extract samples in area of lab dedicated to low-level dioxin analysis
- Use virgin (new, unused) glassware for a majority of sampling train components.
- Test sampling glassware for contamination before use (pre-proofing) and after cleaning (for reused glassware).
- Recover PCDDs/PCDFs from sampling train components at the laboratory in lieu of the test site.
- Maintain a no-smoking zone in all sample-handling areas.
- Collect one train blank per test day.

Results and Discussion

All stack gas samples were reported as not detected (ND), with the exception of a single detection of OCDD at 8.7 pg/sample (0.00068 ng/Nm³) in one stack gas sample from the first day of testing. OCDD was not detected in the sample from the second sample train. Each test run was 11 hours in duration. One sample was lost when the sampling train failed a leak check. Results for all quality assurance/quality control (QA/QC) samples (field blanks, trip blank, glassware pre-proof, glassware cleaning verification, XAD and solvent precertification samples) were ND for all PCDDs/PCDFs.

Detection limits for individual congeners ranged from 2 pg/sample (0.15 pg/Nm³) for 2,3,7,8-TCDD to 6 pg/sample (0.5 pg/Nm³) for OCDD. Method detection limits were lower than the historical tests that used standard procedures. The effective stack gas detection limits were lower than the historical data due to the longer sampling duration. Method precision could not be evaluated because most sample values were nondetects.

The extended sampling duration did not cause problems with sample collection (e.g., filter clogging), but may have contributed to the loss of one sample that failed a leak check. Recoveries of surrogate standards were within limits for all samples except two: recovery of the hepta-CDF isotopically labelled standard fell below the acceptable range of 70% - 130% in one train blank and one field sample. This result indicates that no systematic loss of surrogates from the XAD resin occurred over the extended sampling period.

Conclusions

Certain method modifications and work practice improvements were judged to be practical and cost-effective measures to reduce blank contamination and enhance method sensitivity. Other modifications were judged to be too expensive for routine stack test studies or unnecessary for improved method performance. Table 1 summarizes the project conclusions for each of the method modifications and work practice improvements.

| Modification or Work Practice Change | Indicated for Routine Use? | | Comment |
|---|----------------------------|----|--|
| | Yes | No | |
| Extended sampling duration | ✓ | ✓ | Depends on project objectives |
| Use newest generation HRGC/HRMS | ✓ | | Improves method sensitivity |
| Calibrate HRGC/HRMS with lower low-level standard | ✓ | | Improves method sensitivity |
| Reduce surrogate spike of ³⁷ Cl ₄ -TCDD | ✓ | | Improves method sensitivity |
| Extract samples in lab area dedicated to low-level samples | ✓ | | Minimizes likelihood of sample contamination |
| XAD and solvent certification analysis | ✓ | | Minimizes likelihood of sample contamination |
| Use single XAD lot for all samples and blanks | ✓ | | Minimizes likelihood of sample contamination |
| Use virgin glassware for front end of sampling train | | ✓ | High cost. Not required if glassware preproofed |
| Conduct pre-proof sample train glassware rinse analyses | ✓ | | Minimizes likelihood of sample contamination |
| Conduct post-proof sample train glassware rinse analyses | | ✓ | Unnecessary if pre-proof used |
| Recover non-probe sampling train components at laboratory | ✓ | | Minimizes likelihood of sample contamination |
| Recover probe liner at laboratory | | ✓ | Risk of breakage in shipping |
| Maintain no smoking zone in sample handling areas | ✓ | | Minimizes likelihood of sample contamination |
| Collect one daily train blank | | ✓ | Gives information on blank variability - too expensive for routine application |

Table 1. Evaluation of Modifications to EPA Method 23

The recommended method modifications and work practice improvements would increase the cost of a routine three-run dioxin stack test by approximately 44%, which does not meet the project target of less than 25% additional cost. However, much of this increase is due to use of a longer sampling duration. If a standard 3 to 4-hour sample is taken, the cost increase is under 20%. The need for the lower stack gas detection limits provided by the longer sampling period depends on the objectives of each project, and should be evaluated carefully in that context.

Because PCDDs/PCDFs were below detection limits for all target parameters and all samples excluding the one OCDD detection, the evaluation of method modifications is based solely on practicality, cost and effectiveness at lowering method detection limits. Further work is required to demonstrate that these modifications are able to improve method sensitivity and reduce blank contributions in the presence of detectable levels of dioxins in flue gas. In addition, to apply the Method 23 to extremely low-level sources it will be necessary to establish the performance characteristics of the modified method at the target concentrations.

References

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2. Federal Register, 64:189 Sept. 30,1999, p. 52957.
3. U.S. Environmental Protection Agency (2000). EPA-745-B-00-021.
4. Davis, L.C, Wood, M.W., and B. Maisel. Proceedings of the Air and Waste Management Association 90th Annual Meeting, June 8-13, 1997, Toronto, Canada.