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**CALCINING PROCESS EMISSION SCREENING TEST FOR
POLYCHLORINATED DIBENZODIOXINS**

S. D. Hartenstein

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Steven D. Hartenstein

INTRODUCTION

Since 1963, the Idaho Chemical Processing Plant (ICPP) at the Idaho National Engineering Laboratory has been using fluidized-bed technology to convert high-level radioactive liquid waste into a granular solid for interim storage before eventual long-term storage. The calcining process (Figure 1) uses kerosene, oxygen, air, and a cooling jacket to maintain the temperature of the fluidized bed at approximately 400°C. The solids are moved to storage bins and the combustion gases and fine particles are swept from the bed to an atmospheric protection system. This atmospheric protection system includes a cyclone to collect larger particles; a nitric acid scrubber to cool gases and collect small particles; a condenser to reduce water content; silica gel beds to adsorb volatile ruthenium, water, and hydrocarbons; and a series of high efficiency particulate air (HEPA) filters to collect minute particles. After passing through this system, the gas is mixed with 40 times its volume of exhaust from other ICPP facilities, passed through another series of HEPA filters, and released to the environment via a 75 m stack. The exiting gas is approximately 50°C and contains 500 ppm NO_x.

The calcination process solidifies waste solutions containing molar levels of acid, nitrate, fluoride, zirconium, aluminum, iron, boron, and cadmium; minor levels (<0.1%) of various fission products and organics; and trace levels (<50 ppm) of chloride and sulfate. Because the process burns kerosene in the presence of other organics and chloride salts; the calciner was considered a potential production source of polychlorinated dibenzo-p-dioxins (PCDD). Therefore, it was necessary to determine if PCDD were being released from the calcination process. Because a gas chromatograph mass spectrometer (GC-MS) and PCDD standards were not available, a screening procedure using two gas chromatographs with electron capture detectors and no PCDD calibration standards was developed. The general approach follows the procedures described in a draft of EPA Method 23¹ and other reports²⁻⁴; with modifications to accommodate the unique nature of the sample source and availability of instrumentation and standards.

EXPERIMENTAL

Reagents: All reagents were as prescribed in draft EPA Method 23, except for the following: glassware, sample bottles, and the sampling train were cleaned with methanol and methylene chloride rather than hexane and the pre-cleaned XAD-2 resin was not tested for residual methylene chloride.

Gas Sampling Train: The sampling train (Figure 2) consisted of a glass fiber filter (EPA-selected, Whatman EPM 2000 high-volume air sampling filter) in series with a 500-mL impinger containing 0.1 M

ferrous ammonium sulfate, a 500-mL impinger containing 1 M sodium hydroxide, a trapping column containing 50 g of XAD-2 resin, and a pump drawing sample at 0.1 L/min. Connections between all sampling train components were glass or stainless steel. The connection from the sampling port to the sampling train was made with 2 m of 0.25 in ID Teflon tubing. The sampler arrangement of the XAD-2 column and water-filled impingers in the sampler recommended in draft EPA Method 23 was not used, because direct contact of NO_x with XAD-2 resin discolors the resin. The combination of the ferrous ammonium sulfate and sodium hydroxide impingers used in the sampling train effectively removed all NO_x from gases reaching the XAD-2 column.

Stack Sample: One stack sample was drawn from the ICPP stack after gases from the calcination process had passed through the entire atmospheric protection system and half-way up the stack to the release point. The stack sample was collected at a rate of 0.1 L/min for 24 hours under ambient conditions (0°C and 640 torr).

Sample Preparation Procedure: After collecting a sample, the impinger solutions and XAD-2 resin were removed from the sampling train and the sampling train components were rinsed with hexane. The impinger solutions, resin, and rinse hexane were stored in FEP bottles under ambient conditions. Within 48 hours of collecting a sample, the filter paper and XAD-2 resin were extracted with 350 mL of toluene in a soxhlet extractor for 16 hours and the aqueous impinger solutions were extracted three times with hexane for 5 minutes in a separatory funnel. The hexane from the sampling train rinses and impinger solution extractions (600 mL) was combined with

the toluene from the soxhlet extractor. The resulting solution was then evaporated to 1 mL by passing nitrogen over the mixture while it was warmed in a water bath at 42°C. The concentrate was washed with 90 mL of hexane through a glass column (20 cm long x 3 cm ID) containing a glass wool plug, 1.5 g of silica gel, 3 g of silica gel impregnated with sodium hydroxide, 1.5 g of silica gel, 6 g of silica gel impregnated with sulfuric acid, and 1.5 g of silica gel. The effluent hexane was evaporated 1 mL, and then loaded onto a glass column (25 cm long x 0.8 cm ID) containing a glass wool plug and 8 g of basic alumina. This column was rinsed with 80 mL of 0.5% methylene chloride in hexane and the sample was eluted with 80 mL of 35% methylene chloride in hexane. The eluate was concentrated to 0.1 mL and processed through smaller versions of the silica gel and alumina columns in which the quantities of adsorbents and volumes of solutions were reduced by two-thirds. The resulting sample was then evaporated to 0.1 mL and stored in the dark at 4°C until analysis.

The Celite 545/activated charcoal column clean-up procedure described in draft EPA Method 23 was not used. If a sample had indicated the possible presence of a PCDD, this procedure would have been added in the preparing of the sample to verify the observation.

GC Screening for PCDD: Two Varian 3700 gas chromatographs (GC) with electron capture detectors (ECD), equipped respectively with a J&W DB-5 (60 m long, 0.25 mm i.d.) and a Supelco SP-2331 (60 m long, 0.32 mm i.d.) chromatographic column, were used to screen for PCDD. The GC with the DB-5 column was operated in the splitless mode under the following conditions: helium carrier gas at 30 psi (22 cm/sec

flow rate); injector temperature of 350°C; ECD temperature of 350°C; column temperature program of 140°C for 5 minutes, followed by a 4°C/min ramp to 300°C; nitrogen make-up gas to the ECD at 40 mL/minute; sample injections containing 1 microliter of sample sandwiched between 0.5 microliter aliquots of isooctane and decane. The GC with the SP-2331 column was operated under the following conditions: helium carrier gas at 24 psi (30 cm/sec flow rate); injector temperature of 270°C; ECD temperature of 300°C; column temperature program of 200°C for 1 minute, followed by a 3°C/min ramp to 250°C; nitrogen make-up gas to the ECD at 40 mL/minute; sample injections containing 3 microliters of sample sandwiched between 0.5 microliter aliquots of isooctane and dodecane.

Calibration: A National Institute of Standards and Technology standard reference material SRM 1614, which contains 70 ng/mL of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), was used to identify the retention time of 2,3,7,8-TCDD for each column. The standard provided a response which was approximately 10-fold above the detection limit (7 pg) for the DB-5 column and near the detection limit (50 pg) for the SP-2331 column. The retention time for 2,3,7,8-TCDD was 39.1 minutes for the DB-5 column and 15.7 minutes for the SP-2331 column. The retention times of 2,3,7,8-TCDD was verified by: 1) altering the injected volume of SRM 1614 and observing the expected change in the size of the chromatographic peak; 2) evaporating 0.05 mL of SRM 1614 to 0.01 mL and observing the expected change in the size of the chromatographic peak, and 3) matching conditions of the GC with the SP-2331 column to those

presented in commercial literature provided by Supelco⁵ and observing the retention time for a chromatographic peak representative of 2,3,7,8-TCDD.

Method Verification: Two independent GC's with different types of columns were used so that: 1) any chromatographic peak which appeared on both columns with a retention time equivalent to a specific PCDD could be identified with a high degree of certainty to be a PCDD and 2) any chromatographic peak which appeared on only one of the columns with a retention time equivalent to a specific PCDD could be identified with a high degree of certainty to be a non-PCDD contaminant. The method was evaluated prior to collecting a stack sample by processing a blank and a spike sample. The blank was prepared by passing laboratory room air through the sampling train for approximately 24 hours. The spike sample was prepared by placing a 0.5 mL aliquot of SRM 1614 inside the Teflon tubing at the sampling train inlet and passing laboratory room air through the sampling train for 24 hours. The blank and spike sample were processed through the sample preparation procedure and the GC-ECD analysis. The 2,3,7,8-TCDD peak area (retention time = 39.14 minutes) for the spike sample indicated that the method has a recovery efficiency of 80%.

RESULTS

The chromatograms for the stack sample and a concentrate of the stack sample prepared by evaporating the final extract from 0.1 mL to 0.01 mL showed no 2,3,7,8-TCDD peak. Also, because all peaks in

the stack sample chromatogram could be identified with peaks in the blank and spike sample, no other PCDD were detected in the stack sample. Based on the size of the stack sample (corrected to 120 L at 760 torr, 0°C), the sample preparation recovery efficiency (80%), and the sensitivity of the GC-ECD detection, the amount of 2,3,7,8-TCDD in the stack sample is estimated to be less than 1 pg/L of air.

CONCLUSIONS

This screening procedure is a means of testing for the presence of 2,3,7,8-TCDD in air samples without using a GC-MS and PCDD standards. The sample preparation procedure achieves adequate recovery of 2,3,7,8-TCDD and removes most interfering impurities. The use of a second GC-ECD system to verify the presence of 2,3,7,8-TCDD improves the ability to eliminate "suspect" peaks recorded by one of the GC-ECD systems. The absence of any 2,3,7,8-TCDD in the stack sample is an indication that there are no PCDD released to the environment from the ICPP stack with a possibility that the atmospheric protection system traps any PCDD that may be formed or liberated during the calcination process. However, since the calcination process is operated continuously for periods greater than four months and all scrubbing solutions, condensates, and collection beds are recycled; the entire process is in an equilibrium state. Therefore, any PCDD's produced in the process should be detectable in the off-gas. Since no PCDD's were detected, it can be concluded that no PCDD's are generated.

REFERENCES

1. Federal Register Volume 54, No. 243, Wednesday, December 20, 1989, pp. 52190-52207, a proposed amendment to Appendix A of 40 CFR Part 60 "Standards of Performance for New Stationary Sources: Appendix A - Addition of Methods for Measurement of Polychlorinated Dibenzo-p-Dioxins, Polychlorinated Dibenzofurans, and Hydrogen Chloride Emissions From Stationary Sources".
2. Lamparski, L. L.; Nestruck, T. J.; R. H. Stehl, Anal. Chem. 1979, 51, 1353.
3. Nestruck, T. J.; Lamparski, L. L.; Anal. Chem. 1980, 52, 1865.
4. EPA Method 625, "Base/Neutrals and Acids", 40 CFR Part 136, Appendix A, Method 625, July 1, 1987 Edition.
5. Supelco Chromatography Products Catalog 29, 1991 (Supelco, Inc., Bellefonte, PA), p. 24.

FIGURE CAPTIONS

Figure 1 Schematic flowsheet of the New Waste Calcining Facility at the Idaho Chemical Processing Plant

Figure 2 Schematic of the sampling train: A) ICPP stack wall sampling port, B) existing ICPP stack sampling system, C) tubing connecting sampling train to existing stack sampling system, D) high air flow particle filter, E) 0.5 L impinger containing 0.1 M ferrous ammonium sulfate, F) 0.5 L impinger containing 1 M sodium hydroxide, G) trapping column containing 50 g XAD-2 resin, H) rotameter, I) pump operating at 0.1 L/min, and J) tubing returning exhausted air to ICPP stack sampling system.

Schematic Flowsheet of the New Waste Calcining Facility

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Figure 1

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Figure 2

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