



Project Summary

Volatile Organic Sampling Train—Soot Interference Report

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Boiler performance studies sponsored by the U.S. Environmental Protection Agency (EPA) have shown that industrial boilers co-firing hazardous waste are capable of achieving destruction and removal efficiencies (DREs) of 99.99 % for Resource Conservation and Recovery Act (RCRA) Appendix VIII compounds designated as principal organic hazardous constituents. Evaluation of boiler DREs for volatile organic compounds (VOCs) is accomplished in part by sampling those compounds as described in EPA Method 0030, the Volatile Organic Sampling Train (VOST). A hysteresis effect, resulting from soot deposits on boiler surfaces, has been observed in previous studies and is the subject of several related reports. Sorption behavior of organic compounds on deposits of soot in boilers, as demonstrated by these hysteresis studies, has led to concern that similar sorption effects from soot captured by the particulate filter of the VOST might cause a low bias in measurement results. It seemed prudent, then, to determine if such an effect is measurable, to investigate the magnitude of any observed effect on VOST sampling, and, as appropriate, to also determine whether the effect is greater for higher boiling point VOCs as expected.

This study examined the effects of soot deposits within the sampling apparatus upon levels of VOCs recovered. Specifically, collection efficiency was evaluated by comparing VOC levels collected in a control VOST, when a soot-free particulate filter (i.e., glass

wool plug) was used in the sampling probe, to VOC levels recovered while using a soot-laden particulate filter in the VOST probe. Samples were collected at routine VOST sampling rates and analyzed by gas chromatography and mass spectrometry (GC/MS) as described in EPA Methods 0030, 5040, and 8240. Because of time and cost considerations, the soot was generated only from No. 2 fuel oil, as opposed to that produced from hazardous waste. Soot deposition on the filters varied from 4 to 70 mg.

Volatile organic compounds evaluated were selected to span the range of boiling points covered by VOST methodology. Emphasis was directed to substances in the upper range of VOC boiling points (i.e., 120 to 130 °C), because sorption phenomena often correlate with boiling points, and thus the higher boiling point compounds were deemed more likely to be seriously affected.

The data collected were subjected to descriptive and pattern recognition techniques (i.e., percent difference and rotated principal component analysis). Results of these statistical analyses indicated that at least two of the higher boiling point VOCs appear to be negatively biased by the presence of soot on the glass wool filter. However, it is not likely that these findings would have a major impact on previously collected hazardous waste incinerator data, since the VOST-Soot effect was determined at moderately high soot loadings, which are atypical of properly operating haz-



ardous waste incinerators. Also, a level of soot where the effect ceases to cause significant deterioration of the data was not established in this study. Consequently, the data gathered in this study was not totally conclusive in determining whether soot may impact DRE determinations from boilers using the VOST methodology.

This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

EPA-sponsored studies of boiler performance under both normal and transient conditions have shown that the boilers can achieve a destruction and removal efficiency (DRE) of at least 99.99% for Resource Conservation and Recovery Act (RCRA) Appendix VIII compounds (40 CFR 261) that are principal organic hazardous constituents (POHCs). However, the DRE measurements made during some of the earlier EPA studies could have been affected by the presence of deposits of unburned, carbonaceous material (i.e., soot) either (1) on cold boiler surfaces or (2) within the organic sampling system. The first concern deals with a phenomenon referred to as hysteresis. The second concern, however, is the primary focus of this project. Specifically, the quality of data on volatile organic concentrations in boiler stack gases may be impacted by the presence of soot if the soot is trapped on the glass wool plug (i.e., particulate filter) typically used in the probe of a volatile organic sampling train (VOST) and if the soot functions as an active sorbent. If sufficient effect is present, the current VOST sampling technique may not be appropriate for certain boiler applications.

Experimental Procedure

The primary objective of this project was to determine if combustion-generated soot will sorb a sufficient quantity of volatile organic compounds (VOCs) to cause an erroneously low measurement of VOCs by the VOST method. The type of soot, that is, its source and conditions of formation, may affect its propensity to sorb VOCs. Thus, soot generated by actual mixtures of hazardous waste and fuel may differ from soot generated by hydrocarbon fuels alone in its effect upon VOST mea-

surements. However, for the initial "range-finding" experiments described herein, soot was generated in only one way, by No. 2 fuel oil combustion only, without any hazardous waste constituents present (i.e., no RCRA Appendix VIII compounds).

These experiments followed a two-step format. In the first step, the soot deposition step, the soot was collected upon the glass wool plug of a VOST system probe by withdrawing soot-laden gas through the probe of the experimental VOST system at a flow rate of 0.5 L/min. (The mass of soot deposited was controlled by adjusting the deposition time, ranging from 6 to 9 min for Experiments 14-16 and from 10 to 18 min for Experiments 17-19.) During the second step, which was sampling, glass wool doped with soot was used in the experimental probes, but a clean glass wool filter was used in the control probe. (The control probe was positioned in the VOST adapter after the soot deposition step.)

A mixture of target VOCs was introduced downstream of the flame zone following soot deposition, and the test VOST and a control VOST were operated concurrently. The target VOCs are shown in Table 1. The VOCs in Table 1 were selected by EPA personnel to span the range of boiling points covered by the VOST method and also to concentrate on the upper range of boiling points (approximately 120 to 130 °C) associated with the VOST method. All compounds except octane are Appendix VIII compounds that could be used as POHCs for DRE determination.

Sampling procedures followed EPA Method 0030, sample preparation procedures followed Method 5040 (thermal desorption), and analysis procedures incorporating gas chromatography/mass spectrometry (GC/MS) followed Method 8240. In the next phase of the experiment, a well-mixed, diluted VOC mixture was injected directly into the VOST probes, instead of being injected into the middle of the quartz flow tube of the soot generator, as was the case during Phase 2.

Table 1. Volatile Organic Compounds Injected During Phase 2 Testing

Compound Name	Boiling Point (°C)
Chloroform	61
Carbon tetrachloride	77
Toluene	111
Tetrachloroethene	121
Octane	126
Chlorobenzene	131
1,1,1,2-Tetrachloroethane	131

A mixing chamber was designed and installed to improve the mixing of the VOC mixture (from the diluent bag) with air. A VOC mixture was introduced at the inlet of the mixing chamber, and air was introduced at the outlet of the chamber at near-sonic velocity. The entire chamber and the inlet and outlet lines were electrically heated. The combined mixture, diluted with air and well mixed, then entered the VOST adapter through a small tube that passed through a port. The gases then passed into a large stationary section of glass tubing (electrically heated), into which the VOST probes were inserted. A sliding section of slightly larger tubing (also electrically heated) was used to help contain the gases and prevent contamination by residual organic material in the combustion system. A nominal flow of 6 L/min (dry, standard basis) was used, of which only 1 L/min was withdrawn by the two VOST systems during the sampling step of each experiment.

As in Phase 2, only one type of soot was tested during Phase 3; that is, only soot generated from No. 2 fuel oil was used. To deposit soot on the filter, the soot-laden gas was withdrawn through the probe of the experimental VOST system at a flow rate of 0.5 L/min; the mass of soot deposited was controlled by adjusting the deposition time (ranging from 6 to 9 min for Experiments 14 to 16 [filter type B] and from 10 to 18 min for Experiments 17 to 19 [filter type A]). The deposition time was limited by the ability of the sampling pump to accommodate the pressure drop across the filter. Baseline experiments, in which no soot was generated, were run for comparison to experiments involving soot generation. The soot mass deposited on the glass wool plugs ranged from 3.5 to 70 mg.

Results and Discussion

Analytical and Quality Control Results

All VOST samples were analyzed within 2 weeks after collection. Percent differences between the control and experimental VOST samples were calculated to determine if any bias between the two VOST systems existed.

Quality assurance/quality control (QA/QC) results for Phase 3 were generally very good. A performance audit (PA) sample was prepared by the Midwest Research Institute (MRI) Quality Assurance Department and submitted for analysis. The PA sample was analyzed by GC/MS with the same instrumental parameters planned for use with the VOST samples.

Four of the eight target compounds were identified and quantified in the PA sample, and the remaining four were not found. Results were then reported to the project QA Coordinator prior to analysis of actual project samples. All target compounds present in the PA sample were correctly identified and were quantified with recoveries of 100% to 108%, based upon the actual concentrations.

The percent differences for the injected VOCs were less than 10% (with one exception) in the baseline experiments. This suggests that the VOC mixture was more homogeneous in the vicinity of the VOST probes. The high reproducibility shown by the two VOSTs allows more confidence in assessing any soot effects observed.

The percent differences for both octane and chlorobenzene indicated a clear reduction with soot on the filter. In addition, a positive bias was observed in the case of benzene, which was monitored as a residual product of incomplete combustion (PIC).

Statistical Analysis

The concentration data generated in this phase of the program were subjected to rotated principal component analysis (RPCA). In brief, RPCA reduces the dimensionality of the data set by creating composite variables that are linear functions of the original variables. This reduction in dimension is based upon the observed correlations between the original variables. The correlation coefficients obtained by this technique are shown in Table 2.

The RPCA results indicate that the measured variability in concentration among the eight variables in the experiments can be compactly expressed in terms of three composite variables:

- Variable 1 is principally a weighted function of the compounds toluene,

octane, tetrachloroethene, and chlorobenzene; 1,1,1,2-tetrachloroethane also figures into this composite, although it is apparent that its intercorrelations with other high boiling point compounds are not as strong as those exhibited between toluene, octane, tetrachloroethene, and chlorobenzene.

- Variable 2 is dominated by benzene, although some contribution from 1,1,1,2-tetrachloroethane also is indicated.

- Variable 3 is a weighted function of chloroform and carbon tetrachloride.

RPCA analyses indicated a tendency for low boiling point compounds to behave differently from compounds with relatively high boiling points. Differences in standard scores between the control and experimental trains are far more pronounced for the high boiling point composite variable than for the low boiling point variable.

Conclusions

The presence of soot on the glass wool particulate filter within a VOST probe appears to have the potential to bias the amount of certain VOCs collected in the VOST traps, in particular, octane and chlorobenzene. The extent of the bias does generally correlate with the amount of soot on the filter. There is some evidence that the higher boiling point compounds are more likely to be biased by the presence of soot, but other chemical or physical properties may also be involved. The cause of the negative bias is not known for certain; it could be at least partially based upon pressure differences in the test VOST console as compared to a control VOST (due to a soot-based pressure drop in the probe), in addition to a potential sorption of the VOC upon the soot. Loss of VOCs due to soot on the appara-

tus surfaces was carefully controlled, which thus clarified the effect of soot in the particulate filter. Also, a high degree of sampling reproducibility was achieved in the experiments, and this strengthened the above conclusions.

In addition to a negative bias (i.e., loss of VOCs known to be present in the gas phase), a positive bias (i.e., desorption of VOCs from the soot into the gas phase) may be indicated so that compounds that may not always be present in the sampled gases may show up in the VOST analysis. A positive bias was observed for benzene, which was presumably formed as a PIC during soot generation and temporarily trapped in the soot. (Alternatively, the soot may have partially decomposed, emitting benzene as a by-product.)

If the presence of soot in the filter of the VOST probe does affect the VOCs with boiling points above 120° C, as this study indicates, it is highly unlikely that the effect would have a major impact on previous hazardous waste incinerator data. This study examined moderately heavy soot loadings, which are not typical of properly operating hazardous waste incinerators. Also, only two VOCs (octane and chlorobenzene) showed a significant effect from the soot loadings. Both of these VOCs have boiling points above 120° C, indicating that only VOCs with boiling points above that level would be affected.

Since more than one POHC is chosen for DRE determinations and four nines (99.99%) must be achieved for all POHCs, it is not likely that the VOST-Soot effect on this one POHC (chlorobenzene) would have any impact on permitting decisions. However, this study does indicate that caution should be exercised in future VOST sampling when potentially sooty conditions are present or are expected in incinerator emissions.

Table 2. Pearson Correlation Coefficients Between Test Compounds for Phase 3

	CHCl ₃	CCl ₄	C ₆ H ₅ CH ₃	C ₈ H ₁₀	CCl ₂ CCl ₂	C ₆ H ₅ Cl	CCl ₃ CH ₂ Cl	C ₆ H ₆
CHCl ₃	1.000							
CCl ₄	0.775	1.000						
C ₆ H ₅ CH ₃	0.001	0.001	1.000					
C ₈ H ₁₀	0.001	0.090	0.817	1.000				
CCl ₂ CCl ₂	0.250	0.056	0.865	0.557	1.000			
C ₆ H ₅ Cl	0.055	0.131	0.874	0.969	0.669	1.000		
CCl ₃ CH ₂ Cl	0.518	0.142	0.535	0.268	0.852	0.360	1.000	
C ₆ H ₆	0.239	-0.031	-0.164	-0.401	0.053	-0.266	0.206	1.000

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The complete report, entitled "Volatile Organic Sampling Train—Soot Interference Report," (Order No. PB93-144145; Cost: \$19.50; subject to change) will be available only from

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