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STACK CONTAMINATION EFFECTS DURING SMALL-SCALE COMBUSTION TESTING OF SYNTHETIC FUELS

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ABSTRACT

The Analytical Chemistry Branch at the Pittsburgh Energy Technology Center has undertaken the assessment of the possible environmental impact of substituting synfuels for petroleum-based fuels in utility and industrial boilers. The assessment is based on a study of results obtained from the analysis of trace organic compounds present in the exhaust gases of a fully instrumented 20-hp firetube boiler.

The stack gases from petroleum-based fuels, synfuels, and methanol combustion tests have been sampled and analyzed by combined gas chromatography/mass spectrometry. The stack gas sampled during the combustion of methanol showed the presence of saturated and aromatic hydrocarbons as well as detectable amounts of organic sulfur compounds, such as dibenzothiophene. The presence of these compounds could not be explained on the basis of methanol combustion but suggests contamination of the 20-hp combustor-exhaust system from earlier tests using petroleum or coal-derived fuels.

The previously established exhaust stack cleanup protocol was reviewed by the Combustion Technology Branch and the Analytical Chemistry Branch. It was decided that a more exhaustive protocol was required. When this revised protocol was instituted, cross-contamination and memory effects disappeared, and sampling integrity was reestablished, thus allowing the analytical data to be properly interpreted.

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INTRODUCTION

The Analytical Chemistry Branch at the Pittsburgh Energy Technology Center has undertaken the assessment of the possible environmental impact of substituting synfuels for petroleum fuels in utility and industrial boilers. The assessment is based on a study of results obtained from the analysis of trace organic compounds present in the exhaust duct of a fully instrumented 20-hp firetube boiler. Earlier work on this synfuel combustion test program is summarized in the technical progress report "Small-Scale Combustion Testing of Synthetic Fuels."¹ The above report gives complete details of the fully instrumented 20-hp boiler operation. Also included in this report are the specific sampling procedures and the analytical methodology necessary for the determination of trace organics present in the combustion effluents.

Petroleum-based fuels and synthetic fuels were individually burned, and their stack gases were analyzed according to the previously referenced protocol. When methanol was burned to verify the sampling and analytical procedures, unexpected results were obtained: the stack gases showed the presence of saturated and aromatic hydrocarbons as well as detectable amounts of organic sulfur compounds, such as dibenzothiophene. The presence of these compounds could not be explained on the basis of methanol combustion.

It is suggested that these components are the result of contamination from earlier tests using petroleum or coal-derived fuels. Cross-contamination, or "memory effect," is here defined as the carry-over of some or all of the components of one sample to a subsequent sample or samples. In order to test the validity of this cross-contamination hypothesis, the following series of experiments was designed and performed.

A fuel, whose combustion characteristics are well documented, is burned, and its combustion gases are analyzed in order to establish a reference data bank. In the next experiment, the reference fuel containing a selected additive is burned. The nature of the additive is such that it is not naturally a component of the reference fuel and such that measurable amounts survive combustion in the 20-hp boiler so as to exist as a combustion marker. It is desirable that this tracer be readily available in bulk amounts at reasonable costs. In the final step in this experimental series, the reference fuel is again burned without the presence of the additive, and the analytical results obtained by analysis of the combustion effluents from the three consecutive burns are compared.

The fuel chosen was No. 2 fuel oil, whose combustion characteristics are well documented. The additive chosen for this study was diisopropylnaphthalene (DIPN) because it is not a component in No. 2 fuel oil, and it meets all other stipulated criteria of a tracer.

The results of this series of experiments are summarized as follows:

1. The initial combustion experiment of No. 2 fuel oil without DIPN added showed no DIPN detected in the combustion effluent.

2. The second combustion of No. 2 fuel oil with DIPN added showed significant amounts of DIPN in the combustion effluent.
3. The third experiment, combustion of No. 2 fuel oil without DIPN added, showed detectable quantities of DIPN in the combustion effluent. It should be emphasized that neither the combustor nor the exhaust duct was cleaned during these experiments. However, the fuel storage and handling system leading up to the boiler was thoroughly cleaned. Since DIPN was detected in the third burn, this confirms the hypothesis of cross-contamination, or memory effect, in the exhaust duct.

It was necessary to scrutinize all materials, procedures, and cleanup protocols in order to evaluate possible sources of cross-contamination. Since all glassware and materials associated with sampling and analysis were scrupulously cleaned, the boiler system was next investigated as a possible source of cross-contamination.

"Operating Procedure Number 19"2 for the 20-hp boiler does not contain a written protocol for cleaning of the exhaust ducts. Scrutinizing of the cleanup regime employed when new fuels are combusted revealed that the horizontal exhaust duct was cleaned, whereas the vertical exhaust duct, where the sampling ports were mounted, was not cleaned. Soot deposited from previous combustions still remained on the duct wall.

When studying the combustion parameters of different fuel oils in the 20-hp boiler system, the established cleanup regime was adequate for measuring the combustion performance and monitoring combustion product gases on line at the parts per million level; however, this clean-up procedure was apparently inadequate for sampling stack gases for trace organics at the nanogram and picogram levels. The sampling methodologies developed for detecting trace organics in stack gases necessitated additional duct cleaning.

With the cooperation and assistance of the PETC Combustion Technology Division staff, the cleanup protocol was expanded to include cleanup of the vertical exhaust duct. A series of methanol combustion tests was consecutively performed after a series of No. 2 fuel oil tests. When the cleanup of the vertical duct was included in the cleaning protocol, the products of the methanol combustion did not contain detectable amounts of saturated or aromatic hydrocarbons. This is in contrast to the situation when the vertical ducts were not cleaned between each test and supports the assumption that the source of cross-contamination was the vertical exhaust duct system. It is postulated that the trace organics from petroleum and synfuel combustion were sorbed on the soot on these duct walls, and then if the soot was not removed by thorough cleaning, some of these trace organics were desorbed into the stack gases during subsequent combustions.

EXPERIMENTAL DETAILS

The stack gases were sampled from each combustion experiment using the modified sampling train shown in Figure 1 under the conditions listed in Table 1. The two modifications made to the original sampling train were

the addition of an ice trap prior to the gas meter to prevent corrosion problems; and the addition of an air-bleed valve on the vacuum pump for better control of the flow rate. Sampling was initiated only after the 20-hp boiler system was operating stably at full-load conditions. The same boiler conditions preestablished for optimum combustion of No. 2 fuel oil were set and maintained for all combustion tests.

The stack gases are first drawn through a particulate knockout trap (Figure 2) heated at 150°C. The gases then pass through a modified Jones adsorbent sampler^{3,4} that is filled with the polystyrene resin XAD-2* (mesh size 20/60) used for the collection of organic vapors in hot gas streams.⁵ Immediately prior to sampling, the XAD-2 resin was cleaned by continuous Soxhlet extraction, employing the solvent regime listed in Table 2. After methylene chloride extraction, the resin was thermally desorbed of solvent at 150°C for 30 minutes under a helium flow of 30 cc/min. After thermal desorption, the XAD-2 was packed into the Jones adsorbent sampler (Figure 3), and the sampler was immediately attached to the sampling train mounted on the vertical exhaust duct of the 20-hp boiler.

After sampling the combustion effluent for 6 hours, the sampler was dismounted from the stack; the XAD-2 was removed and the resin was immediately Soxhlet-extracted for 24 hours using approximately 200 mL of methylene chloride. The resulting extract was concentrated to 1 mL using a Kuderna-Danish evaporative concentrator. The concentrate was stored in a Teflon-sealed "REACTI-VIAL" and analyzed using a Hewlett-Packard Model 5985 combined gas chromatograph/mass spectrometer (GC/MS) under the conditions listed in Table 3.

To acquire DIPN GC/MS calibration data, a sample of DIPN was analyzed under the analytical conditions given in Table 3. Figure 4 illustrates the total ion chromatogram as well as the mass chromatogram of DIPN's molecular ion at m/z 212.

The capillary column separates four isomers of DIPN, detected at 30.9, 31.1, 32.1, and 32.3 minutes. The predominant isomers observed at 32.1 and 32.3 minutes were used as markers for detecting and quantifying trace DIPN in all subsequent analyses. The area under the mass peaks of these isomers was computed, and the GC/MS response for DIPN was calculated to be 117 area counts per nanogram. The mass spectrum of the DIPN isomer eluting at 32.3 minutes is presented in Table 4. The four principal fragment ions at m/z 197, m/z 212, m/z 155, and m/z 198 were used to confirm the presence of DIPN in the analyzed stack gases.

The 20-hp boiler combustor duct was sampled during the three test burns. The three fuels were combusted in the following order: No. 2 fuel oil; No. 2 fuel oil spiked with 1.5 v/v % DIPN; and No. 2 fuel oil. The commercial DIPN was graded at a purity of 96% 2,6-diisopropylnaphthalene; however, combined GC/MS analysis showed the DIPN to be an isomeric mixture.

*Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

After the series of experiments, the boiler system, including both the vertical and the horizontal ducts, was cleaned. Then, the effluent gases of two consecutive methanol combustions were sampled and the concentrated extracts were analyzed for the presence of previously noted saturated and aromatic hydrocarbons.

RESULTS AND DISCUSSION

Individually, the concentrated trace organics from the three combustion burns were analyzed by GC/MS to verify the presence or absence of DIPN.

No detectable ions at m/z 212 were observed between the retention times of 32 and 33 minutes during GC/MS analysis of the combustion effluent from the first burn. This verified that DIPN is not a detectable volatile organic in the combustion products of No. 2 fuel oil.

The GC/MS analysis of combustion gases from the second experiment, where No. 2 fuel oil was spiked with 1.5% DIPN, readily confirmed the presence of DIPN. A mass chromatogram of m/z 212 (Figure 5) shows the presence of the four isomers of DIPN; the identifications of these isomers are confirmed by the GC relative retention times and individual mass spectra. This proves conclusively that under the conditions of the experiment, some DIPN survives combustion, and a significant amount is detected in the combustion effluent.

The GC/MS analysis of the combustion effluent from the third experiment, where No. 2 fuel oil without additive was combusted after the combustion of the spiked No. 2 fuel oil, still showed the presence of DIPN in the stack effluent. Figure 6 presents a mass chromatogram at m/z 212 obtained from analysis of the combustion effluent from the third burn. Due to the low concentration, only the predominant isomers present in the DIPN used for spiking were observed. The relative gas chromatographic retention times and mass spectra of these components confirmed the presence of DIPN in the combustion effluent of burn #3.

The DIPN recovered from burns #2 and #3 was calculated (Table 5) on the basis of nanograms recovered in each cubic foot of stack gas sampled. Although approximately 0.1 nanogram of DIPN per cubic foot in burn #3 is a small amount, this represents the cross-contamination of an organic compound not present in the combustion fuel. The presence of DIPN in the combustion effluent during burn #3 clearly demonstrates a stack memory effect for organic compounds in consecutive burns.

After cleanup of the boiler system, which included cleaning the vertical ducts, GC/MS analysis of the effluent gases from two consecutive methanol burns resulted only in a background chromatogram. Aliphatic and aromatic components, if present, were at less than detectable quantities. This is in contrast to the original methanol burns, where the quantities of the aliphatic, aromatic, and sulfur-containing compounds were sufficient to be easily detected.

This contrast is readily seen in the Total Ion Chromatograms (TIC) presented in Figure 7. The TIC of the stack gases sampled from a methanol burn

when there was no cleanup of the vertical ducts is chromatogram A; B is the TIC of sampled stack gases from a methanol burn when there was cleanup of the vertical ducts; C is the background TIC, resulting from analysis of a blank. The blank was a methylene chloride extract of the XAD-2 resin after solvent cleaning. Compounds identified by number in chromatogram C consist of phthalates (1), possibly originating from the resin, and silicone compounds (2), possibly originating from the stationary phase of the GC column. Compounds identified in A were aliphatics (3), aromatics (4), and sulfur compounds (5). In contrast, in B, no detectable amounts of these components were found. The components common to A and B are the phthalates (1) and silicones (2) found in C, the blank.

Since the cross-contamination, or memory effect, was lost with cleaning of all ducts, sample integrity is reestablished when proper analytical protocols are observed.

CONCLUSIONS

Even under optimum combustion conditions, small amounts of organic constituents of the fuel are incompletely combusted and result in trace organics being present in stack gases. Appreciable portions of these trace organics are sorbed on the soot deposited on the duct walls during the combustion process. In subsequent combustion tests, portions of the sorbed trace organics are desorbed in sufficient amounts to be detected in stack gas effluents. This results in cross-contamination or what might be referred to as a memory effect.

When both the horizontal and vertical duct systems are cleaned between combustion tests, and normal analytical techniques are observed, cross-contamination was not observed. Methodologies for detecting trace organics in the exhaust gases require more stringent cleaning procedures between fuel tests than normally are required when typical combustion parameters are being studied. Thus, a written protocol detailing the procedure needed for a complete cleanup that avoids cross-contamination is mandatory when stack gases of utility boilers are being monitored for trace organics.

Stack gas sampling integrity is imperative if proper interpretation of the analytical data in regard to environmental impact is to be achieved. This study established a cleanup procedure that achieves sample integrity.

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REFERENCES

1. Gibbon, G.A., Ekmann, J.M., White, C.M., Navadauskas, R.J., Joubert, J.I., Retcofsky, H.L., Small-Scale Combustion Testing of Synthetic Fuels, DOE/PETC/TR-82/1, available at Technical Information Center, P.O. Box 62, Oak Ridge, TN 37830.
2. "Operating Procedure Number 19: Cleaning Boiler Firebox, Punching Tubes and Cleaning Firetube," Contract No. DE-AC22-78ET13011, p. 4, prepared by General Electric, Management & Technical Services Company, Pittsburgh, PA 15236, June 1982.
3. Jones, P.W., Giammar, R.D., Strup, P.E., and Stanford, T.B. Efficient Collection of Polycyclic Aromatic Hydrocarbons from Combustion Effluents. Environmental Sci. Technol., 10, 806 (1976).
4. Strup, P.E., Wilkenson, J.E., and Jones, P.W., "Trace Analysis of Polycyclic Aromatic Hydrocarbons in Aqueous Systems Using XAD-2 Resin and Capillary Column Gas Chromatography-Mass Spectrometry Analysis," in Carcinogenesis. Vol. III, edited by P.W. Jones and R.I. Freudenthal, Raven Press, New York, 1978.
5. Sonnichsen, T.W., McElroy, M.W., and Bjorseth, A., "Use of PAH Tracers During Sampling of Coal Fired Boilers," in Polycyclic Aromatic Hydrocarbons, edited by A. Bjorseth and A.J. Dennis, pp. 617-632, Battelle Press, Columbus, Ohio, 1980.

TABLE 1. Exhaust Duct Sampling Conditions

1. Sorbent Bed Temperature	70°C
2. Duct Temperature	210°C-249°C
3. Flow Rate	25 Lpm
4. Sampling Time	5-6 hours
5. Volume of Sample Taken	150-180 cu. ft.
6. Particulate Knockout Trap Temperature	140°C-150°C

TABLE 2. XAD-2 Cleanup Solvent Scheme

<u>Solvent</u>	<u>Soxhlet Extraction Time</u>
Water, Distilled	2 hours
Methanol, High Purity Grade ^a	24 hours
Diethyl Ether, Nanograde ^b	24 hours
Pentane, Nanograde ^b	24 hours
Methylene Chloride, High Purity Grade ^a	24 hours

^aBurdick and Jackson Laboratories, Inc.

^bMallinckrodt, Inc.

TABLE 3. Analytical Conditions for GC/MS

Fused-Silica Capillary Column	19 m x 0.30 mm, SE-52, 0.25- μ m film
Injector Temperature	275°C
He Flow Rate	1-2 mL/min
Injection Conditions	Inject 1-2 μ L; Split 15:1
Temperature Program	3-min hold at 30°C; 30°-300°C @ 4°C/min
PT/IR Transfer Line Temperature	275°C
Quadrupole Scan Rate	2 scans/sec
Masses Scanned	40-300 amu
Source Temperature	200°C
Electron Multiplier Voltage	2400 volts

TABLE 4. Mass Spectrum of DIPN

M/Z	ABUNDANCE	M/Z	ABUNDANCE	M/Z	ABUNDANCE
40.2	0.7	115.1	3.6	168.0	1.5
42.0	0.6	116.1	0.6	169.1	9.3
42.3	0.6	126.1	1.0	170.1	1.5
43.3	0.7	127.1	2.2	176.0	0.7
44.0	0.6	128.0	4.8	177.0	1.0
46.8	0.6	129.0	3.6	178.1	2.3
50.2	0.6	130.2	0.6	179.1	1.4
51.4	0.6	133.0	1.0	180.1	0.8
63.2	0.7	139.0	1.5	181.0	3.3
71.1	0.6	141.0	9.2	182.1	1.0
73.0	1.0	142.0	1.4	183.0	1.4
74.8	0.6	147.0	0.7	191.0	0.6
76.0	1.3	150.0	0.8	193.1	0.6
77.0	1.3	151.1	2.7	195.0	0.8
81.1	0.6	151.9	9.5	197.0	100.0
82.1	0.7	153.0	14.5	198.0	15.7
83.1	1.2	154.0	7.0	199.0	1.3
84.0	1.1	155.0	32.4	206.9	4.8
85.1	0.6	156.0	4.3	208.0	1.2
89.1	1.0	156.9	0.6	208.8	0.8
90.9	2.8	163.0	0.7	212.0	54.5
95.0	0.6	164.1	1.0	213.0	9.0
96.1	0.7	165.0	8.4	214.1	0.7
98.5	0.8	166.0	3.1	266.8	0.8
103.1	0.6	167.1	3.9	281.0	1.1
111.1	0.6				

TABLE 5. Recovered DIPN Stack Vapors

	<u>ng DIPN/mL CH₂Cl₂</u> <u>Extract</u>	<u>ng DIPN/cu ft</u> <u>Stack Gas</u>
Burn #1 Unspiked Fuel	0	0
Burn #2 DIPN-Spiked Fuel	3400	27
Burn #3 Unspiked Fuel	20	0.1

FIGURE 1. SAMPLING TRAIN

BSI/3502

Figure 2. Particulate Trap

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Figure 3. Adsorbent Sampler

Figure 4. Total ion chromatogram and mass chromatogram of DIPN at m/z 212.

Figure 5. Mass chromatogram at m/z 212 of stack gases sampled from Burn no. 2.

Figure 6. Mass chromatogram at m/z 212 of stack gases from Burn no. 3.

Figure 7. Total ion chromatograms: A. stack gases from methanol burn, partial cleanup; B. stack gases from methanol burn after complete cleanup; C. background. Legend of components: 1. phthalates; 2. silicones; 3. aliphatics; 4. aromatics; 5. sulfur compounds.