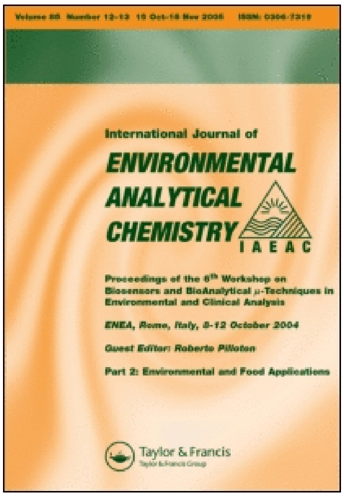

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Characterization of Discharge Water from Hydrostatic Testing of Natural Gas Pipelines Using High Resolution Gas Chromatography/Mass Spectrometry

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Hydrostatic testing of natural gas pipelines may lead to production of water which is contaminated with organic compounds in a highly complex mixture. Present in this complex mixture are benzene, C_1 to C_5 alkylated benzenes, dimethyl disulfide, C_3 to C_5 alkylated disulfides, saturated alkanes, and branched/unsaturated alkanes. Estimated minimum concentrations of benzene were 25 to 38 mg/L. Composition of discharge water was not uniform throughout the dewatering process but varied as a function of extent of discharge. While chemical oxygen demand decreased uniformly in discharge water with increased extent of dewatering, selected toxic organic compounds showed less consistent variations. Other similar examinations of discharge waters from natural gas pipelines have not been previously reported.

KEY WORDS: Discharge Water, Pipelines, Natural Gas, Hydrostatic Testing, Organic Compounds.

INTRODUCTION

Hydrostatic testing of natural gas pipelines is commonly practiced for testing physical integrity of new pipelines or of existing pipelines scheduled for use at increased pressure. Testing with hydrostatic pressure is accomplished by filling pipelines with water drawn from local water sources such as rivers and lakes. Then, pipelines are pressurized using air or natural gas. After these tests, lines are emptied (dewatered) using a metal or plastic plug which is pneumatically forced through the pipeline so as to remove water, unwanted deposits, and residues. Test waters in the U.S. Southwest are typically released into rivers directly or into stock ponds for treatment even though such discharge waters may contain high concentrations of organic compounds. For example, in portions of discharge waters the chemical oxygen demand may be as large or larger than 63,000 mg/L depending upon age and history of use for a particular pipeline.[1] While discharge waters from hydrostatic testing (DWHT) are often released into public water supplies such as rivers, little or no information exists in public domain regarding detailed composition of toxic organic compounds in DWHT. Results from preliminary analysis in our laboratory showed that a very complex hydrocarbon mixture including several toxic organic compounds was present in DWHT from an old natural gas pipeline and further more detailed examination of DWHT samples was warranted.

One objective of this work was preliminary characterization of volatile organic compounds on several samples drawn throughout dewatering operation on a single pipeline. A second objective, in light of the complexity of DWHT, was to evaluate and modify if necessary, procedures for determination of trace amounts of organic compounds in such aqueous solutions. Since analyses for DHWT from only two pipelines are included here, results should not be misconstrued as representative for discharge waters from all natural gas pipelines, but rather what might be encountered with DWHT of old or heavily-used pipelines.

EXPERIMENTAL

Samples

Grab samples were taken during discharge of two pipelines in the U.S. Southwest. Samples were taken near the start of dewatering procedures and at 10 min intervals thereafter. Samples were stored in glass bottles at 1°C. Additionally, a sample of fill-water was collected to determine background contribution to organic compounds from the water supply. Visual inspection of DWHT samples showed color and texture from a dark oily fluid to a light yellow-brown solution. All samples had pungent unpleasant odors. For pipeline A, sample numbers, volume percent of discharge at time of sampling and chemical oxygen demand (COD) were: (no. 1) 0%, >100 mg/L; (no. 2) 21%, 19,000 mg/L; (no. 3) 43%, 11,000 mg/L; and (no. 4) 84%, 5,400 mg/L Total volume of discharge was 665,327 L of wastewater. Only one sample (no. 1) from pipeline B was included for analyses here. Percent of discharge at time of sampling was 54% and COD was 2,100 mg/L. Total volume of aqueous discharge was 1.4×10^6 L.

Procedures

Samples were analyzed using purge and trap methods.[2] Conditions for purging were: sample size, 10 mL; flow rate of purge gas (N_2), 40 mL/min; time of purge, 12 min; and size of Tenax-GC sorbent trap, 100 mg. Contents of traps were then analyzed using high resolution gas chromatography and gas chromatography/mass spectrometry using direct thermal desorption of Tenax-GC traps.[3] Conditions for desorption were: temperature of desorption, 180°C; time of desorption 1.75 min after a 0.25 min period of preheating; and switching valve temperature, 160°C.

Instrumentation

Gas Chromatography: A Hewlett-Packard model 5721A gas chromatography (GC) was equipped with flame ionization detector (FID), splitless injection port, 20 m OV-1 fused silica capillary column, and model 3390A reporting integrator. Conditions of analyses were: intitial temperature, 0°C; initial time, 1.75 min; oven temperature program rate, 6°C/min; final temperature, 120°C; injection port temperature, 250°C; FID temperature, 250°C; carrier gas, nitrogen at 20 cm/s average linear velocity; time for splitless injection 2 min; chart speed, 1 cm/min; area reject, 1000 counts; and threshold, 2.

Gas Chromatography/Mass Spectrometry: A Hewlett-Packard model 5992A gas chromatograph/mass spectrometer (GC/MS) was equipped with jet separator, model 9885M disk drive, model 7225B X-Y plotter, splitless injection port and 20 m OV-1 fused silica capillary column. Chromatographic conditions were identical for scanning GC/MS techniques and GC-FID analyses. Mass spectrometer conditions for scanning analyses were: lower mass, 45 amu; upper mass, 600 amu, scan rate, 690 amu/s; delay between scans; 0.5 s; electron multiplier voltage, 1600 V; and MS detection threshold, 10 linear counts. Concentrations of benzene, toluene and disulfides were too large for selected ion monitoring analyses and were estimated using results from GC-FID analyses. Standards for GC and GC/MS analysis were prepared for as many compounds as available to support identifications based on mass spectra. Procedure blanks were free of detectable levels of contamination from glassware, procedures or instrumentation.

RESULTS AND DISCUSSION

Chromatographic analysis

Results from GC-FID analyses of five samples of DWHT are summarized as GCPLOTS[4] of percent full scale values versus retention time in Figure 1. Although these plots are from purge and trap procedures where samples were partially prefractionated on basis of vapor pressure, results were still very complex with over 22 to 40 major and minor components detected per sample. During discharge of pipeline A, the COD decreased uniformly from $>100{,}000$ mg/L to 2,100 mg/L. Correspondingly, visual inspection of these samples also showed a decrease in color and viscosity with trends similar to COD. However, concentrations of the bulk of volatile organic compounds which eluted between 2 min to 20 min did not follow this pattern and trends in distributions of these organic compounds showed non-trivial variations in change with extent of dewatering. For example, the initial discharge of pipeline A had viscosity similar to motor oil, very dark brown appearance and complex chromatographic profile (Figure 1B) typical for petroleum samples. Numerous components, only partially resolved, were evident.

Results from GC analysis of samples A2 to A4 (representing discharge throughout dewatering of a single pipeline) are shown in Figures 1C to D. While trends in changes of total concentration (see full scale values) were not evident in samples taken during

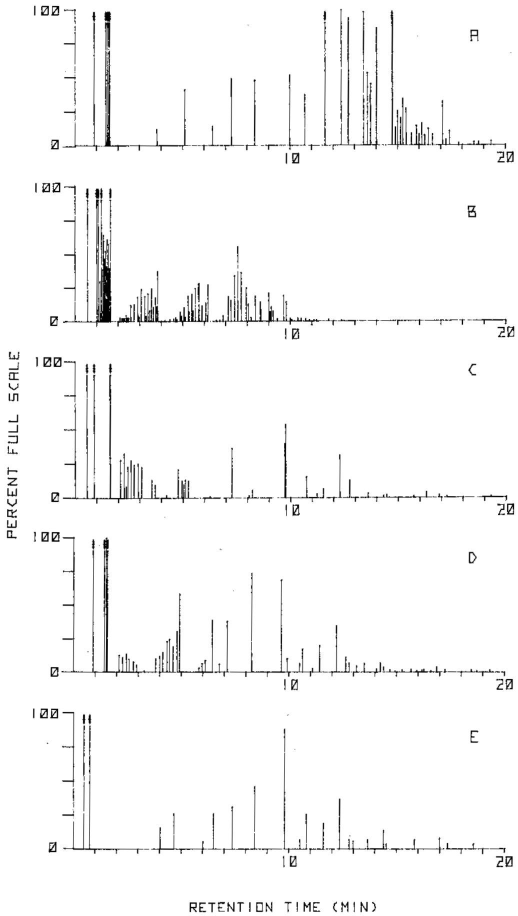

FIGURE 1 Bar graph plot of results from GC analyses of DWHT samples from natural gas pipelines. Full scale values were: (A) Sample B1, 220,000; (B) sample A1, 100,000; (C) Sample A2, 150,000; (D) Sample A3, 200,000; and (E) Sample A4, 150,000. Full scale values are measure of relative concentrations. Chemical oxygen demand, extent of discharge at time of sampling, and estimated total organic mass from purge and trap methods are given in text. Stars above lines are printed when abundance exceeds full scale value.

dewatering operations, an increase in presense of later eluting compounds was seen in Figures 1B to E. Since the direction of discharge was identical to direction of filling which followed an initial dry pigging of pipeline A, these results showed an increase in residue of a broad range of molecular weights during later stages of dry pigging. This pattern is consistant with decreased cleaning efficiency of the pig during dry pigging of the pipeline toward the last portion of the pipeline. But since results for only one discharge test are reported here, few general conclusions can be made. Nevertheless, DWHT for old pipelines may be very complex with regard to just volatile organic compounds with semi-volatile and non-volatile species aside. Baseline data for fill water showed no detectable contamination between 0 to 15 min retention time and minor ($<10\,\mu$g/L) amounts of three to four components at rentention time of 15 to 20 min.

Initial comparison of results from GC-FID analysis for DWHT sample B1 showed suprising differences from samples A2 to A4 especially since pipeline B was located near pipeline A and carried similar feedstock. Although a few early eluting components were present in sample B1 (Figure 1A), a large number of major components eluted between 10 to 17 min unlike samples from pipeline A (Figures 1B to E) where very few major components were seen at retention times greater than 10–12 min. Causes for these differences are unknown but preliminarily suggest a need for caution in extrapolation of data between pipelines. Further information on detailed history or use of these pipelines was unavailable, but these results suggest large variations in water quality may be exhibited with DWHT for other pipelines and support the need for extensive survey analyses. Concentrations of total volatile organic compound mass based on FID average response factor of 100,000 area counts/μg showed the following values A1, 150 mg/L; A2, 20 mg/L; A3, 13 mg/L; A4, 10 mg/L and B1, 7 mg/L. Since these samples were not analyzed immediately after sampling and since recovery efficiencies were not accurately determined for each compound in each sample (with a complex matrix) these total concentrations and all further cited specific concentrations may be considered only minimum values and actual values in fresh discharges may be expected to be larger.

Results for scanning GC/MS analyses for DWHT sample B1 are

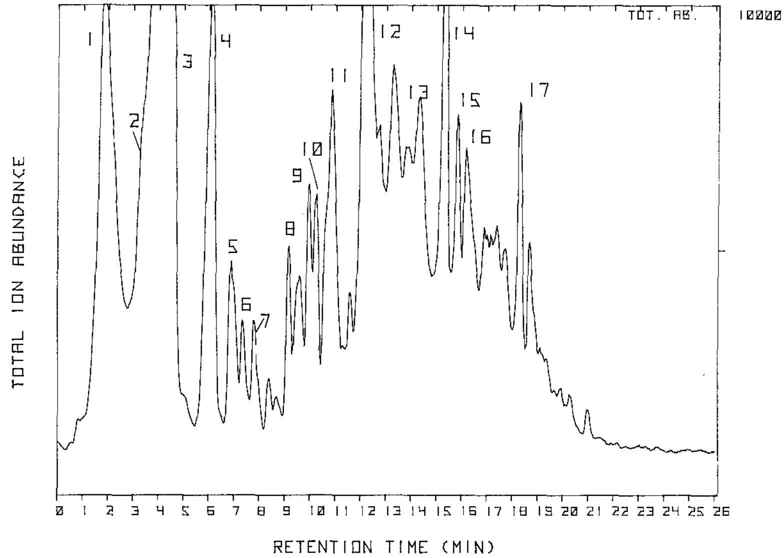

FIGURE 2 Total ion chromatogram from scanning GC/MS analysis of DWHT sample No. B1. Conditions of analysis are in text.

shown in Figure 2 as in plot of total ion current versus time. While a loss in resolution occurred in part from overloading the capillary column and from the computer/plotter smoothing algorithm, still more than 40 partially resolved volatile organic components were detected. Nevertheless, in other analysis where columns were not heavily overloaded, coelution of individual peaks on a curved baseline between 10 to 21 min was evidence that a 20 m capillary column with 45,100 theoretical plates (based on major peak at 18.4 min) was insufficient for resolution of all major components in sample B1. Thus, even for the volatile species which were already prefractioned from the remaining hydrocarbons in aqueous solution fused silica capillary columns did not provide complete resolution. Compounds which are numbered were identified by using mass spectra and are listed in Table 1. When standards were available, mass spectra and GC retention times were matched with the unknowns.

Included as major components in these samples were three classes of organic compounds based on benzene, disulfides, and alkanes.

TABLE I

Compounds identified in DWHT sample B2.

Peak no. on Figure 2	Compound	Techniques for identification[a]
1	Benzene	RT, MS
2	Dimethyl disulfide	MS(I)
3	Toluene	RT, MS
4	Methyl Ethyl Disulfide	MS(I)
5	C_4H_{10} Disulfide	MS(I)
6	Xylenes	RT, MS
7	Methyl Propyl Disulfide	MS(I)
8	Dimethyl Trisulfide	MS(I)
9	Ethyl Propyl Disulfide	MS(I)
10	Ethyl Propyl Disulfide	MS(I)
11	$C_5H_{11}S_2+C_3$ Benzene	MS(I)
12	n-$C_{10}H_{22}$	RT, MS
13	$C_{11}H_{22}$ isomer	MS(I)
14	n-$C_{11}H_{24}$	RT, MS
15	$C_{11}H_{22}$ isomer	MS(I)
16	$+C_{12}H_{24}$ isomer	MS
17	$C_{12}H_{26}$	RT, MS

[a] RT = retention time matched to authentic standard.
MS = mass spectra matched to authentic standard.
MS(I) = mass spectra matched to Index.

While benzene and toluene were defined as priority pollutants by the U.S. Environmental Protection Agency[2] and were present at large relative and absolute concentration, another major class of compounds found in DWHT, alkyl disulfides, are relatively unusual, little studied, and unregulated compounds. Additional details on the complexity of the volatile fraction from DWHT may be seen in Figures 3 and 4 which are mass chromatograms using ions characteristic for benzene and alkylated benzenes and alkylated disulfides. In Figure 3, ions for benzene (78 amu), toluene (91 amu) and higher alkylated benzenes (105, 119, and 133 amu) are plotted from stored scanning MS data. Mass chromatograms for benzene and toluene are distinct being free of interferences. However, higher alkylated benzenes between C_2 and C_5 showed mass chromatograms which were made complex through presence of ions from fragmentation of higher alkylated benzenes. For example, C_2

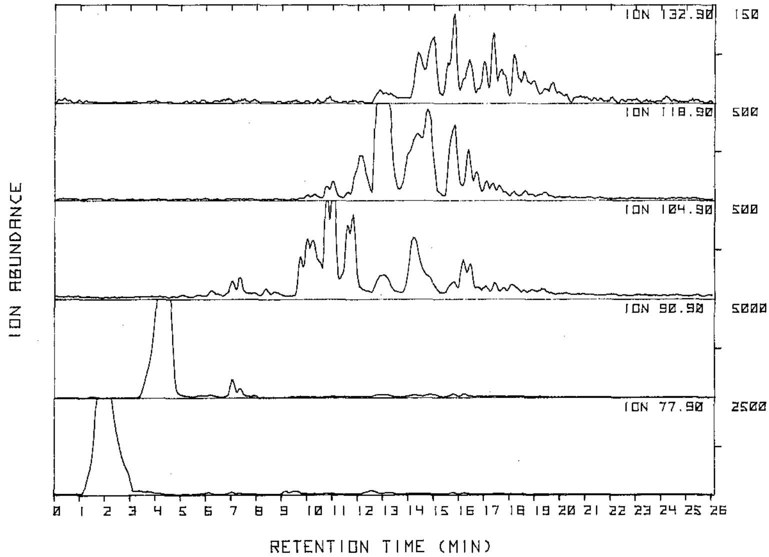

FIGURE 3 Mass chromatograms for benzene (77.9 amu), and C_1 to C_5 alkyl substituted benzenes in DWHT sample B1. Note full scale values on right side of each plot.

benzenes which show a significant 91 amu (M-15) and 105 amu (M-1) peak in the MS appear in the mass chromatogram at both 105 amu and 91 amu with retention time of 7 to 7.5 min. Also, present in the mass chromatogram of 105 amu are C_3 substituted benzenes at retention times 9.5 to 12 min. The C_3 substituted benzenes also showed significant M-1 peaks in MS and the M-1 peaks are visible in the 119 amu mass chromatogram at the same retention times. The absence of significant m/z of 91 amu at retention times of 9 to 15 min even when corrected for differences in abundances between classes is evidence for multi alkyl substitutions on the benzene ring. These results illustrate both the complexity of DWHT and the limitations of mass chromatography or selected ion monitoring as an aid to high resolution GC in complete resolution and quantification of DWHT particularly for these aromatic compounds. Mass chromatography was used with better success toward the homologous series of disulfides as shown in Figure 4. Each member of the series, separated by units of 14 amu, may be seen at ion

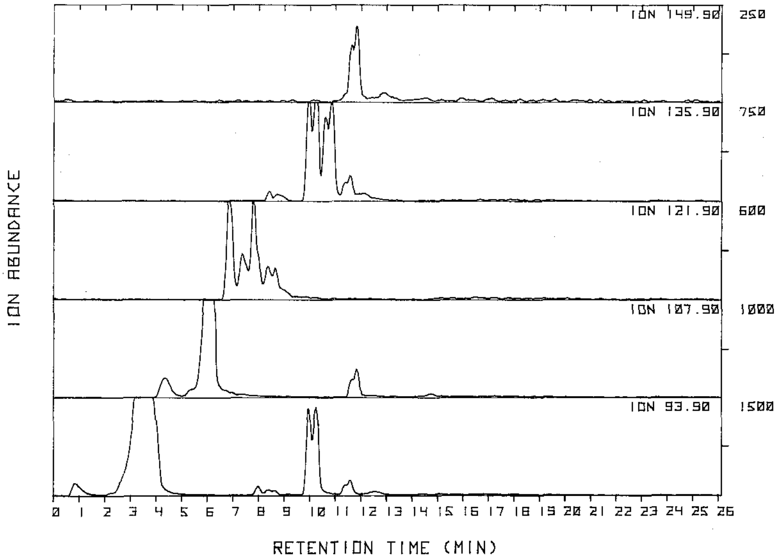

FIGURE 4 Mass chromatograms for dimethyl disulfide (93.9 amu) and higher alkylated disulfides in DWHT sample B1. Note full scale values on right side of each plot.

masses of 94, 108, 122, 136 and 150 amu starting with dimethyl disulfide at 94 amu and retention time of 3.2 min. Since many of the alkylated disulfides of greater molecular weight were major species as seen in Figure 2, clean mass spectra were collected and were used to confirm the identity of selected components in Figure 4. The characteristic elution pattern for a homologous series and the simple MS fragmentation patterns of alkylated disulfides make selected ion monitoring or mass chromatography a satisfactory tool for use in monitoring or survey procedures. Possible interferrences could be alkylated phenols but phenols showed very poor purge and trap efficiencies and should not present major limitations. The decreasing full scale values seen in Figure 4 and in Figure 3 with increased molecular weight could have been due to actual sample content, but more likely was due to decreasing recovery efficiency with decreasing vapor pressure of higher molecular weight compounds in purge and trap methods. These differences of course must be corrected in future development of refined or quantitative methods for use with DWHT.

In the preliminary study only benzene was quantified in order to access the potential for environmental impact. For these DWHT samples, benzene concentrations (mg/L) were: A1, 37; A2, 26; A3, 38; A4, 25 and B1, 10. No significant trends in benzene content were observed from discharge of pipeline A. Furthermore, the values were very large but could have been much larger in fresh samples. Content of toluene was estimated at greater than 50 mg/L in all samples. Comparison of other peaks in Figure 2 to benzene peak size may be used to give a very rough estimate of concentrations of other components in sample B1 which was after 54% discharge. Since pipeline A was dry pigged to remove the bulk of residue before hydrostatic testing, potential for impact on surface water or underground water systems must be considered as serious.

Technical Analysis: The presence of organic compounds other than C_1 to C_6 alkanes in natural gas, has been recognized for many years. But, the general practice has been to label such residues as the Heptane+ (C_7+) fraction and little additional attention has been given to the detailed composition of this fraction. Similarly, information on the composition of this fraction in pipelines is unavailable. An exception is work on the presence of aromatic hydrocarbons in natural gas condensate.[5]

Rough calculations were made using known content of natural gas to determine if deposition processes from natural gas could theoretically account for bulk of organic mass in DWHT. Results shown below support a mass balance argument. Treated natural gas contains up to 0.01 or greater mole percent of C_7+ compounds.[5] Wellhead gas before treatment actually contains greater percentages of C_7+compounds. Volume percents may be less than 1% of mole percents for C_7+ compounds including aromatic compounds. A conservative estimate in volume percent may be $1 \times 10^{-5}\%$ for C_7+ species. Assuming retrograde condensation efficiency of only 1% for pipeline A carrying 2×10^{12} L of gas/decade, total volume of C_7+ (average density 0.85 g/ml) would be 2×10^5 L or 1.7×10^8 g of C_7+ material. In a hydrostatic test where all the deposit would be removed for discharge and the volume of test water was 1.4×10^6 L (pipeline A), the total organic carbon would be 100 g/L or 100,000 mg/L. Since a bulk of C_7+ material was removed in the dry pigging step and considering all the variables of this complex system and approximations used above, these values are reasonable. This conclusion and differences of over 1500 in values for gas–liquid equilibrium constants between methane and heptane provide support for theory of deposition of C_7+ hydrocarbons in pipelines from the natural gas.

CONCLUSIONS

Characterization of volatile organic compounds in several samples of DWHT showed a complex mixture including benzene and alkylated disulfides at minimum estimated concentration levels of 10 to 30 mg/L. While these results are for a small number of samples, developing this cursory understanding of water contamination was necessary for design of future analytical schemes. Clearly, not all DWHT samples will be as contaminated as these,[1] but some samples as shown here may be very complex even though prefractionated in purge and trap techniques. Direct discharge of DWHT into streams or ground water may present an environmental threat to fish life from dilsulfide content and humans through content of benzene. Since these results which are the first in public domain showed the presence of benzene in alkylated disulfides in DWHT of natural gas pipelines, further studies on possible environmental impact of these industrial practices are needed.

Acknowledgement

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