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Project Summary

On-Site GC/MS Analysis of Chapman Gasification Separator Liquor

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This report gives results of a study to characterize a wastewater stream from a coal gasification facility using on-site extraction and GC/MS analysis. Objectives of the program were to:

- **Characterize the wastewater organic components primarily for selected Priority Pollutants, Appendix C, and synfuels compounds.**
- **Investigate the stability of these compounds under refrigeration and ambient storage.**
- **Evaluate the removal of organics by diisopropyl ether extraction and wet oxidation.**

Extractable material in the wastewater consisted primarily of phenols and alkylphenols. These compounds account for about 99 percent of the total mass identified. Several polynuclear aromatic (PNA) compounds were also identified. Deterioration in the composition of the sample was observed even though the water was held in amber bottles at 4°C. This was most evident in the concentration of dimethylphenols which dropped approximately 75 percent during 2 weeks of refrigerated storage. Ambient sample storage produced a greater decrease in the concentration of phenol but did not appear to affect the alkylphenols or the base/neutral compounds as much. It is expected that the observed changes in composition would hamper any off-site wastewater treatability studies with waters of this type. The diisopropyl ether (DIPE) extraction confirmed the 99+ percent removal efficiency of phenol which had been demonstrated in previous studies. Wet oxidation removed organics almost as efficiently as DIPE extraction but may have limited use due to its high cost of operation.

This Project Summary was developed by EPA's Industrial Environmental Research 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

Radian Corporation has been conducting environmental assessment studies of low- and medium-Btu coal conversion facilities under contract to the Environmental Protection Agency over the past 5 years. A Chapman-Wilputte coal gasification facility was the first source characterized in such an assessment. The plant, in continuous operation and in the U.S., is an easily accessible source of coal gasification wastewater. Three previous studies examined this water as part of an environmental data base for coal conversion technologies. This data base will provide input to the planning and design of future gasification facilities and formulation of regulations for water discharges. This program characterized the separator liquor and aqueous process condensate from the Holston plant under conditions which minimized

sample deterioration. This allowed a more accurate determination of the composition of the waste stream. Hewlett-Packard provided a Model HP-5993B GC/MS for use on the program and technical support for maintenance of the instrument.

Objectives

Primary objectives of the program were to:

- Characterize the separator liquor. This included sampling over a 100-hour monitoring period to determine the average composition and variability of the identified compounds.
- Determine sample stability by monitoring one sample for a month for deterioration of identified compounds.
- Investigate methods for reducing the levels of organic materials in the wastewater by wet oxidation and diisopropyl ether (DIPE) extraction.

In addition to these objectives, the feasibility and utility of the operation of a GC/MS system installed in a mobile laboratory designed for field use was evaluated.

Conclusions

The mobile GC/MS program provided a more accurate characterization of the separator liquor than had been previously achieved. EPA Priority Pollutant Appendix A base/neutral, acid extractable, and volatile organic compounds, Appendix C compounds, and 57 organic species of environmental interest were quantitated. Of these, the Consent Decree Appendix A volatile (purgeable) organic compounds, the Appendix C compounds, and the 57 additional organics had not been quantitated during previous studies. Phenolic compounds appear to represent essentially all of the total chromatographable organic (TCO) material in the acid fractions and most of the material in the base/neutral fractions.

Using a methylene chloride/diethyl ether extraction procedure for base/neutral and acidic compounds, it was observed that a high percentage of the phenolic compounds (usually found only in the acid fraction) were extracted into the base/neutral fraction. Therefore, in order to obtain more accurate values for the concentrations of phenolic compounds in the separator liquor, both the acid and base/neutral fractions were analyzed and the values for phenolic compound concentrations in each fraction were added to give the value for total phenolic compound concentration.

Extractions of aliquots taken periodically from the same water sample indicate some loss of organic material over a period of time. This is especially true of the alkylphenols. This observation is corroborated by a comparison of mobile GC/MS data with similar data from previous wastewater studies. Such a comparison shows that the immediate extraction and analysis of the wastewater on-site yielded higher concentrations of phenolic, as well as base/neutral extractable, compounds. It is believed that the observed changes in composition imply degradation that would hamper any off-site wastewater treatability studies with waters of this type.

Results from this program confirm the 99 percent removal efficiency of phenols by diisopropyl ether extraction found in previous work and also show a 90 percent removal efficiency of phenol and alkylphenols by wet oxidation. Wet oxidation demonstrated a potential advantage over biological treatment of wastewater: it can reduce the levels of many organic compounds which are resistant or moderately resistant to biodegradation. Wet oxidation is expensive and has been used only on a very limited basis. Therefore, it may not be economically feasible on an industry-wide basis.

Recommendations

The recommendations below are given for two major categories:

- Analytical methodologies.
- Additional studies which would provide complementary data to this study.

Analytical Methodologies

Recommendations for analytical methodologies relate to some of the difficulties encountered during sample analysis and data reduction.

The major analytical difficulty was associated with the extraction of the phenols into the base/neutral fraction. Due to the high concentration of phenolic compounds, better partitioning of acid and base/neutral compounds is required. This might be achieved by:

- An acid/neutral followed by a basic extraction, then separation of acid and neutral compounds.
- Less vigorous extraction of base/neutral compounds, using only methylene chloride for the base/neutral compounds, but continuing with methylene chloride/diethyl ether extraction for the acidic compounds.

For each suggested procedure modification, extraction efficiencies must be determined by performing the separation procedure with controls consisting of known quantities of standard compounds added to samples of the separator liquor as well as water blanks.

The procedure for analysis of a sample of this complexity should be refined to provide a more cost effective approach. The necessity of using GC/MS for every analysis has not been established; these analyses might be performed as accurately with a gas chromatograph equipped with a flame ionization detector and capillary column. The capillary column would provide better separation and detection of the compounds than packed columns. Once retention times are determined adequately for compounds of interest, GC will be more cost effective than GC/MS. Periodic confirmation of compound identifications by GC/MS would still be required.

Future studies should also incorporate an experimental determination and documentation of the variability associated with the sampling and analytical procedures.

The necessity of on-site extraction and analysis versus on-site extraction followed by off-site analysis should also be investigated. The stability of the extracted samples should be evaluated by analysis of the extract immediately after extraction and at predetermined intervals following the extraction in order to monitor any decrease in the concentration of one or more compounds. If the stability of extracted samples is adequate to allow transport and storage, the expense of providing on-site analytical capabilities could be avoided.

Additional Studies

During this program the separator liquor from the plant was characterized for organic content:

- Immediately following collection.
- Periodically over a period of a month under refrigerated storage.
- After a period of 3 weeks at room temperature storage.
- Following DIPE extraction performed immediately after collection.
- Following wet oxidation performed immediately after collection.

Additional studies which characterize the wastewater after biological treat-

ment would supplement the information already obtained. A more complete set of data would then be available when water treatment information is required for selection of treatment schemes for wastewater streams of similar composition.

The feasibility of operating a GC/MS in a mobile laboratory was successfully demonstrated in this program. The HP-5993B has a data processing software package capable of identifying and quantitating compounds in conventional samples in 10 to 15 minutes. This feature makes a field GC/MS invaluable when results are required quickly. However, the sample matrix of the separator liquor was a complex mixture of many isomers. The resolution provided by the packed column was not sufficient to allow the software to distinguish the quantitating ions for each isomer. Consequently, extensive manual data interpretation was required. If adequate separation of the isomers could be achieved, as with a capillary column, then the software package should be able to function as designed, providing identification and quantitation of compounds in a short amount of time.

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The complete report, entitled "On-Site GC/MS Analysis of Chapman Gasification Separator Liquor," (Order No. PB 82-107 285; Cost: $6.50, subject to change) will be available only from:
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