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A LABORATORY METHOD FOR COLLECTING VOLATILE EMISSIONS FROM SPENT SHALE RETORTED BY THE FISCHER ASSAY METHOD

By
Robert B. Carroll
Jeff Clark
Kimberly Raska

January 1986

Work Performed Under Contract No. FC21-83FE60177

For
U. S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Laramie Project Office
Laramie, Wyoming

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Western Research Institute
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SUMMARY

Organic compounds not removed in the oil shale retorting process are likely to remain with the retorted shale and may volatilize after the shale's removal from the retort.

The purpose of the study was to determine if volatile organic emissions from the retorted oil shale were present in sufficient quantities to be detected in the laboratory. This study demonstrated that measurable quantities of volatile organic emissions are evolved from retorted shale and can be detected in the laboratory. Alkanes and alkenes were the primary compounds identified, although other organic compounds were detected.

INTRODUCTION

The commercial retorting of oil shale will produce vast quantities of waste, the greatest portion of which will be the actual shale refuse left after retorting. This refuse may contain volatile organic compounds that will contribute to atmospheric pollution and cause unfavorable impact on humans or the environment (Perry and Gratt 1984). It is important to determine whether these compounds are present and, if they are, to identify them.

Atmospheric pollution caused by the compounds left in the retorted shale will likely occur during two stages of the disposal process. The first stage is during removal of the retorted shale from the retort. At that point the greatest concentration of lighter volatile organics remaining on the retort, and some from the retorted shale, will escape to the atmosphere. Fortunately, release of these compounds will be of short duration and they will dissipate fairly rapidly. The second stage of atmospheric pollution will occur after disposal of the retorted shale. During this stage, significant quantities of volatile organic compounds will be released, but they will be released very slowly. Pollution from this source, unless monitored, is not likely to be noticed until some damage has occurred.

There may be an immediate hazard posed by volatile organic compounds remaining in or on the retorted shale. Spontaneous combustion may cause refuse pile fires and contribute to atmospheric pollution.

The source of these second-stage releases is the organic compounds not removed during the retorting process. Degradation of these compounds--caused by solar radiation, oxidation-reduction reactions, microbial activity, or a combination of these and other processes--is likely to increase volatile emissions during this stage. This activity will take place at or near ambient temperature, and weather may play a key role in the timing and quantity of these releases.

The purpose of this study was to determine whether volatile organic emissions from the retorted shale could be detected in the laboratory. Laboratory methods were developed in order to quantify organic emissions from retorted oil shale piles.

MATERIALS

All chemicals used were the appropriate reagent grade, and normal laboratory procedures were adhered to throughout this study. All stainless steel and brass apparatus, with the exception of the vessel, were refluxed in methylene chloride for 48 hours before use. The vessel was washed three times with methylene chloride and heated at 350°C for 24 hours before its initial use. A blank sample run was made to insure that no detectable organics were retained on or in the vessel. After each use, the apparatus was cleaned with methylene chloride and heated to remove all traces of organic compounds.

Gas Chromatograph

The gas chromatographic analyses were performed using a flame ionization detector (FID) on a Hewlett-Packard 5840A gas chromatograph (GC). The GC was equipped with a 15 m X 0.25 mm (1.0-μ film thickness) DB5 Durabond fused silica capillary column. This capillary column is capable of detecting both polar and non-polar compounds.

Sample injections were made with a Hamilton 5.0-μL syringe. The samples were injected at 0°C and held at that temperature for 5 minutes. After the initial holding period, the column was heated at 10°/min to 200°C and held at that temperature for 5 minutes.

Vessel

A stainless steel vessel was constructed for this study (Figure 1). The body of the vessel was cut from a 10-inch-long section of stainless steel pipe 1/4-inch thick with a 6-inch outside diameter. The bottom was cut from a 1/4-inch thick stainless steel plate that was welded to one end of the body.

The removable stainless steel lid was cut from a 1/4-inch stainless steel plate. The lid was held in place with 16 bolts screwed directly into a stainless steel flange welded to the top of the vessel. The lid can be sealed with either an aluminum gasket or a Teflon "O" ring. The vessel was designed so that modifications could be made by altering or replacing just the lid.

The vessel was the only piece of custom equipment made for this study. It could be replaced by any reaction vessel which can be sealed and will accommodate temperatures of approximately 500°C. All other specialized equipment, e.g., volatile emission collectors, was made from materials usually found in the laboratory or local hardware stores.

The carrier gas, used to remove the volatile organic emissions from the vessel, enters through a quick-connect assembly attached to a stainless steel tube which extends 8 inches into the vessel. The carrier gas leaves the inlet tube approximately 1 inch above the retorted shale inside the vessel. Another stainless steel tube in the center of the lid extends from 1 inch inside the vessel, through the lid, to 1 inch above the vessel. It serves as the outlet for the carrier gas and volatile organic emissions. Connected to this outlet, and running horizontally above it, is an 8-inch stainless steel tube that carries the gases to the volatile emission collectors.

A thermocouple well in the lid extends 1 inch into the vessel and monitors the exit gas temperature. Another thermocouple well, located 1 inch above the bottom of the vessel, extends through the side of the vessel inward to its center. This thermocouple monitors the cooling rate of the retorted shale.

While the sample was retorting, the vessel was heated to approximately 350°C. After retorting, the hot retorted shale was

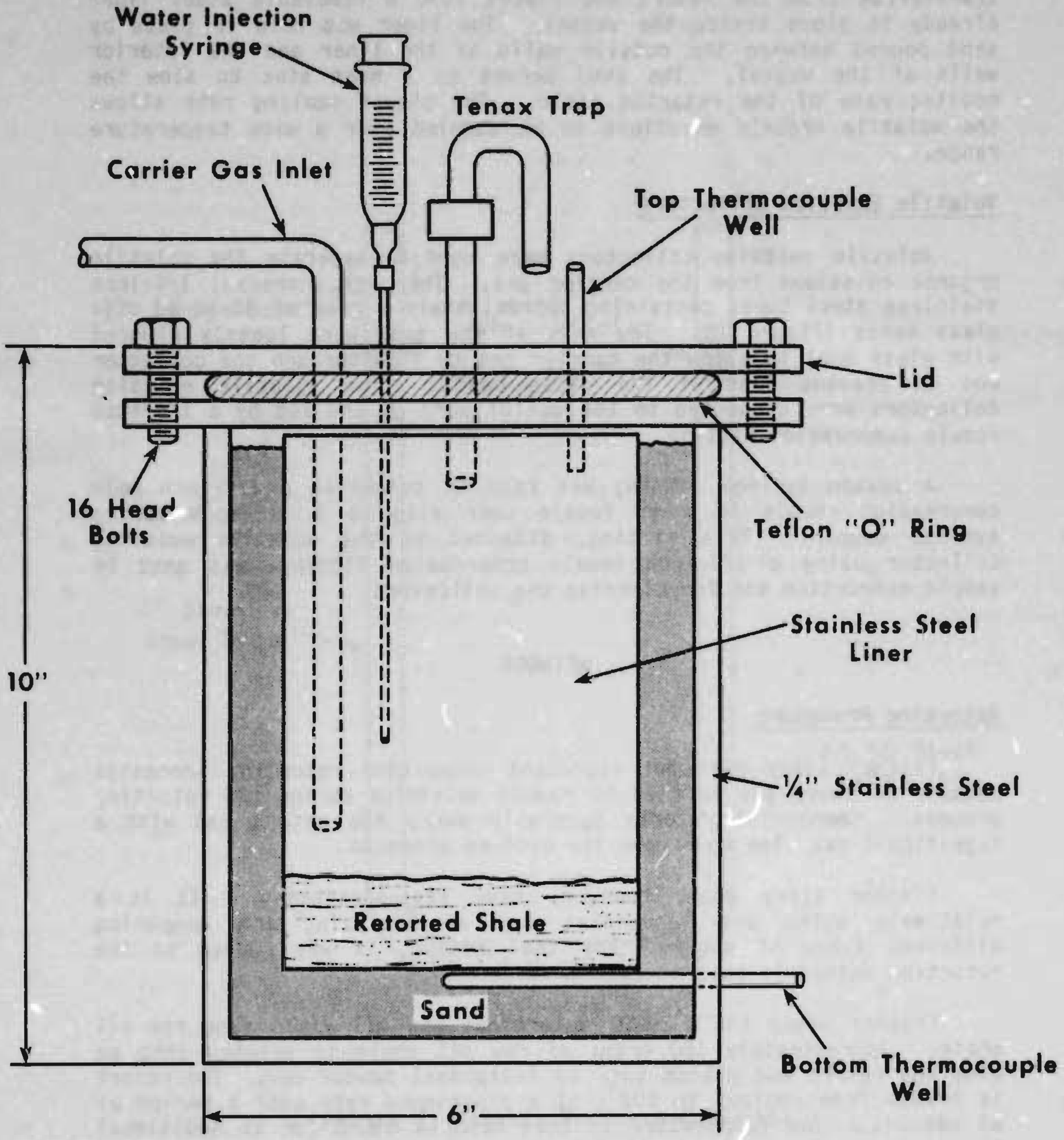

Figure 1. The Vessel

transferred from the retort and placed into a removable steel liner already in place inside the vessel. The liner was held in place by sand poured between the outside walls of the liner and the interior walls of the vessel. The sand serves as a heat sink to slow the cooling rate of the retorted shale. The slower cooling rate allows the volatile organic emissions to be sampled over a wide temperature range.

Volatile Emission Collectors

Volatile emission collectors were used to separate the volatile organic emissions from the carrier gas. They are u-shaped, 1/4-inch stainless steel tubes containing approximately 1 gram of 60 to 80 mesh glass beads (Figure 2). The ends of the tube were loosely plugged with glass wool to allow the carrier gas to flow through the collector and to prevent loss of the glass beads. The volatile emission collectors were connected to the outlet port on the lid by a 1/4-inch female compression fitting.

A custom syringe fitting was made by soldering a 1/4-inch male compression couple to a BD female Luer slip to a 1/8-inch tubing syringe couple. This fitting, attached to the volatile emission collector using a 1/4-inch female compression fitting, was used in sample extraction and for cleaning the collectors.

METHODS

Retorting Procedure

Fischer assay does not represent commercial retorting processes because no sweep gas is used to remove volatiles during the retorting process. Commercial retorts generally sweep the retort bed with a significant gas flow to remove the evolved products.

Fischer assay does, however, have its advantages. It is a relatively quick and convenient way of analyzing and comparing different types of shale. For that reason, it was chosen as the retorting method in this study.

Fischer assay (ASTM 1980) determines the oil yield from raw oil shale. Approximately 100 grams of raw oil shale is weighed into an aluminum retort and placed into an individual heater box. The retort is heated from ambient to 500°C at a programmed rate over a period of 45 minutes. The temperature is then held at 500°C for an additional 45 minutes. The evolved oil is condensed and collected as it comes out of the retort. At the end of the retorting run, the heater cuts off automatically, and the retort is allowed to cool to ambient temperature before the retorted shale is removed.

The standard Fischer assay method was modified so all products evolved could be collected and a mass balance calculated. The retort products (including the oil, water vapor, condensate, and cooled shale) were weighed, and the various percentages of each component were calculated (Table 1).

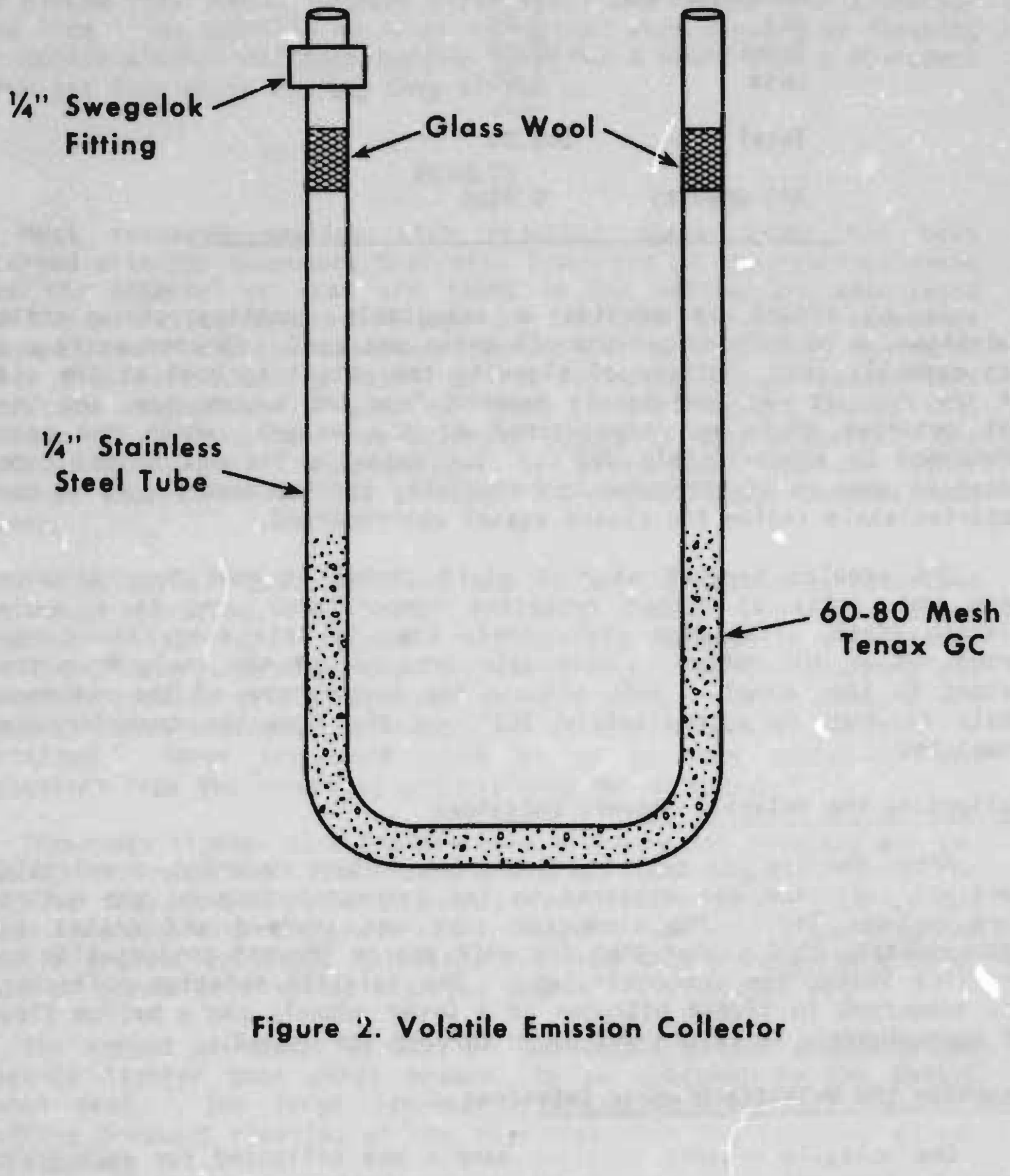

Figure 2. Volatile Emission Collector

Table 1. Fischer Assay Analysis of Oil Shale Used

Material	Weight Percent	
Oil	28.87	(76.6 gal/ton)
Water	2.35	
Cold Trap Oil	1.74	
Gas	3.81	
Spent	63.18	
Loss	0.05	

Total	100.00	
API Gravity	0.9028	

In an effort to provide a detectable quantity of volatile emissions, a 76 gallons-per-ton oil shale was used. Fischer assay was run normally, but, instead of allowing the retort to cool at the end of the run, it was immediately removed from the heater box, and the hot retorted shale was transferred to the vessel, which had been preheated to approximately 350°C. The vessel's lid was bolted into place as soon as the transfer was complete, and the temperature of the retorted shale inside the closed vessel was recorded.

One problem typical of high yield shales is that they tend to coke and, while at higher retorting temperatures, are in a semi-plastic state. The high yield shale used in this study had to be pried out of the retort, slowing the transfer of the shale from the retort to the vessel. This allowed the temperature of the retorted shale to drop to approximately 350°C by the time the transfer was completed.

Collecting the Volatile Organic Emissions

After the lid was sealed and the temperature recorded, a volatile emission collector was attached to the connector tube on the outlet port on the lid. The connector tube was wrapped and heated to approximately 20°C higher than the exit gas to prevent condensation of organics inside the connector tube. The volatile emission collector was submerged in liquid nitrogen in a Dewar vessel, and a helium flow of approximately 50 cc/min was begun through the vessel.

Sampling the Volatile Organic Emissions

One volatile organic emission sample was collected for each 50°C drop in temperature, as measured by the bottom thermocouple, until ambient temperature was reached. A final sample was collected for 12 hours after ambient temperature was maintained. The sample was removed at the proper sample interval by stopping the carrier gas flow, detaching the outlet connector tube from the vessel, and removing the volatile emission collector from the liquid nitrogen Dewar vessel. A new volatile emission collector was immediately attached to the vessel, and the carrier gas flow was resumed.

The volatile organic emissions were removed from the collector by attaching the syringe adaptor and injecting 5 mL of HPLC grade methyl alcohol into the collector. In an effort to reduce sample dilution, only the first 2 mL of this wash was collected. The sample washings were placed into small, labeled glass vials and capped with aluminum-lined lids. The volatile emission collectors were cleaned by flushing with methyl alcohol and then purging them for 4 hours with a 60-cc/min helium gas flow while heating them at 300°C.

RESULTS

Most research dealing with retorted shale waste has been concerned with the compounds that will leach out of the retorted shale after its disposal or that are found in the wastewaters associated with the retorting process. Some of the more prevalent compounds reported in oil shale wastewaters (Persoff et al. 1984 and Hawthorne et al. 1985) are shown in Table 2. It is reasonable to assume that these same compounds will also be found in the retorted shale, and, based on this assumption, two separate standards were prepared. One consisted of alkanes from pentane to octadecane, and the other contained those alkanes plus benzene, iso-octane, ethyl benzene, and xylenes.

The volatile organic emission samples were collected as described above and extracted with methyl alcohol within 5 minutes after collection (Figure 3). Alkanes, ranging from heptane to octadecane, were the primary compounds detected using the cryogenic trapping and solvent extraction method employed in this study. Ethyl benzene was detected, as were alkenes, although the alkenes were not specifically identified. Other compounds known to be in both shale oil and wastewaters from the retorting process were not detected.

Compounds lighter than heptane were probably not detected for two reasons. First, when the methyl alcohol was injected into the cryogenic trap, the lighter compounds were likely volatilized by the sudden increase in temperature Second, the small quantity of volatile organic emissions collected required that a relatively large amount of sample (4.0 μL) be injected for analysis (Figure 4).

The amount of methyl alcohol in the sample caused unvolatilized compounds lighter than ethyl benzene to be obscured by the methyl alcohol peak. The large samples also caused column overloading, requiring frequent cleaning of the injection port and frequent column conditioning.

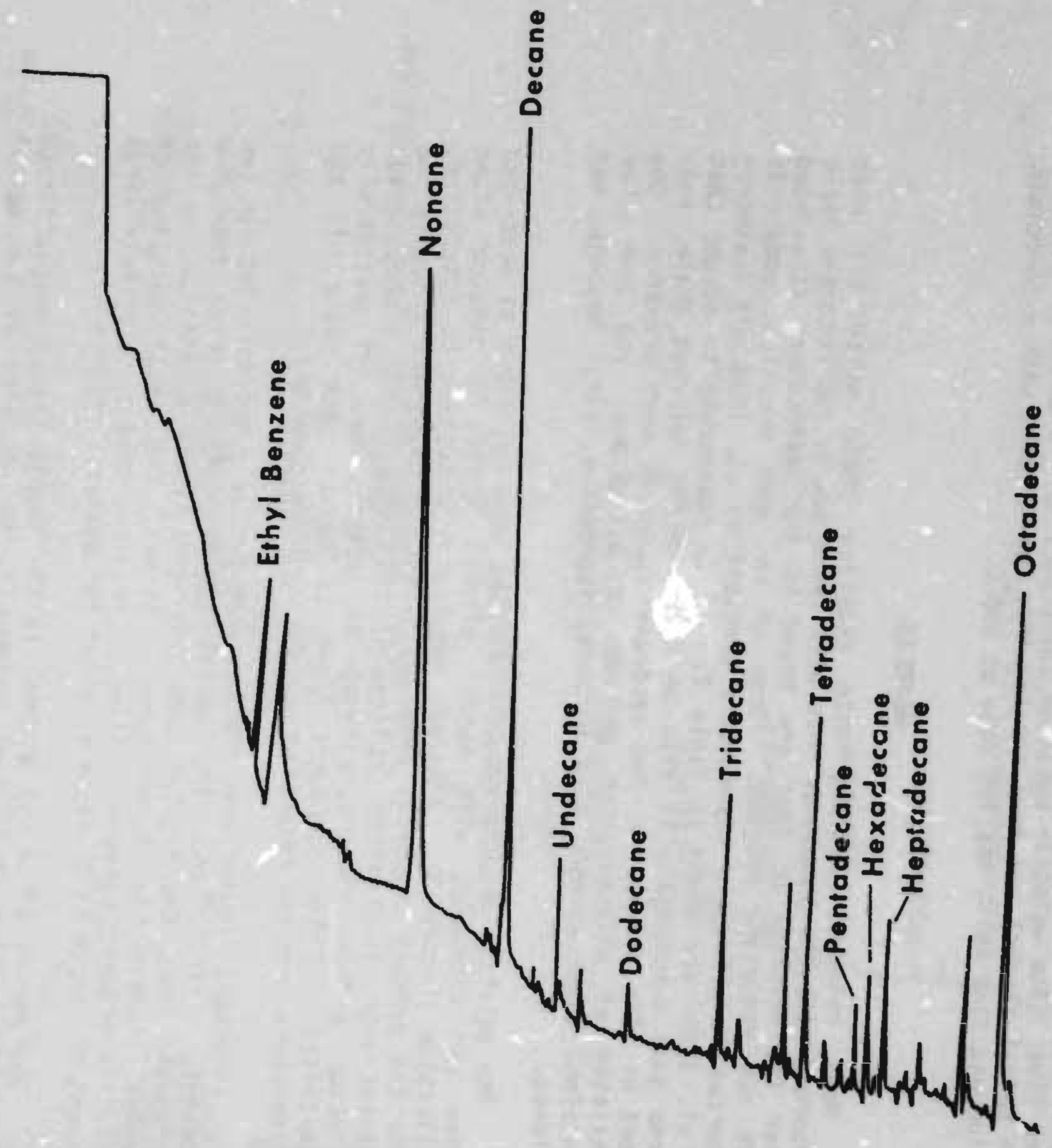

Figure 3. Sample Collected Between 350°C and 300°C (2 µL Injection)

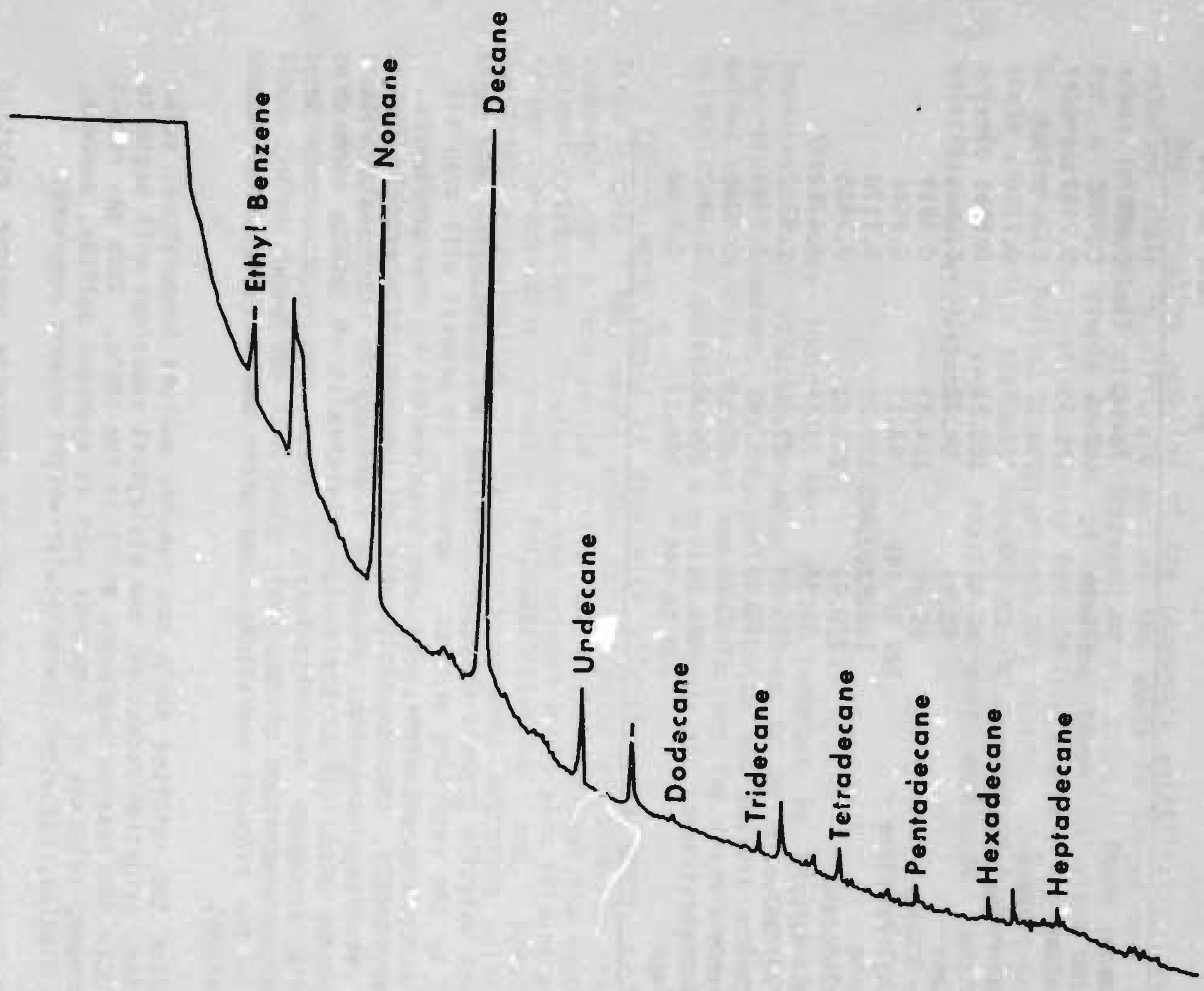

Figure 4. Sample Collected for 12 Hours at Ambient Temperature (4 μL Injection)

Table 2. Organic Compounds Reported in Oil Shale Wastewaters

Compound	Boiling Point °C	Molecular Weight gr.	Density Rel. to H_2O
Benzene	80.10	78.12	0.8787
Decane	174.10	142.29	0.7300
Dodecane	216.30	170.34	0.7487
Ethyl benzene	136.20	106.17	0.8670
Ethyl-Methyl-Pyridine	160 to 198	121.18	0.9286
Heptane	98.42	100.21	0.6838
Hexane	68.95	86.18	0.6603
Iso-Octane	99.24	114.23	0.6919
Methyl-Pyridine	129 to 145	93.13	0.9566
Nonane	150.80	128.26	0.7176
Pentadecane	270.63	212.42	0.7685
Pentane	36.07	72.15	0.6262
Pyridine	115.50	79.10	0.9819
Pyrrole	130.00	67.09	0.9691
Toluene	110.60	92.15	0.8669
Undecane	195.90	156.32	0.7402
Xylene	138 to 144	106.17	0.8802

DISCUSSION

Most volatile organic emissions released during retorting will be trapped by the retorting process. However, no process will trap all volatile organic emissions, and some will escape to the atmosphere. More importantly, the raw shale will not be completely organic free after retorting, and the compounds remaining in the shale will continue to volatilize as the shale cools (Fox et al. 1984). One of the more immediate manifestations of these organic compounds is spontaneous combustion of the shale pile. It may occur during any phase of the disposal operations, even after ambient temperature has been reached.

After the retorted shale has reached ambient temperature, solar radiation, oxidation-reduction, and biological reactions will begin to break down the heavier compounds still in the shale. This may result in secondary releases of compounds such as hydrogen sulfide, ammonia, carbon dioxide. and other low-molecular-weight organic compounds.

The object of this study was to determine whether volatile organic emissions from the retorted shale were present in sufficient quantities to be detected in the laboratory. For that reason, the hot retorted shale was transferred to another vessel to insure that there was no carryover from oil or other compounds trapped in the retort.

The currently accepted model of volatilization of organics incorporated into soils assumes that volatilization of near-surface compounds will cause migration of subsurface compounds to the surface (Jury et al. 1980). This migration may continue until there are no compounds left to volatilize.

Representative sampling of the compounds volatilizing from the retorted shale is difficult because the shale is spread over large areas in its final disposal (Persoff et al. 1984). There is a need for a quick, simple method of sampling these emissions in the laboratory. The best opportunity for sampling the retorted shale will be during its initial discharge from the retort. The hot retorted shale will contain the most concentrated mixture of lighter volatile organic emissions and the heavier organic compounds that will volatilize after disposal.

CONCLUSIONS

This study indicates that shale retorted by Fischer assay produces enough volatile organic emissions to be detected in the laboratory. However, the cryogenic trapping and solvent extraction method used in this study was not satisfactory for transferring the volatile organic emissions to a medium adequate for identifying them.

Future work should be done with effective gas traps, such as Tenax traps. They would allow for trapping of volatile organic compounds over a long period of time and would eliminate the need for solvent extraction. Eliminating the solvent would also eliminate the column overloading problem. Identification and, possibly, quantitative evaluation of the volatile organic emissions collected might also be possible with the Tenax traps.

The long-term volatile organic emissions from disposal piles are probably degradation products of larger compounds. Quantities of these compounds are likely to be minuscule and not detectable by the collection method used in this study. Tenax traps would allow for sampling these compounds over long periods of time. Longer collection times could be used to concentrate and identify the volatile organic compounds remaining with the retorted shale.

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DISCLAIMER

REFERENCES

American Society for Testing Materials. ASTM Standard D 3904-80, 1980.

Fox, J. P., P. Persoff, A. Newton, and R. N. Heistand. "The Mobility of Organic Compounds in a Codisposal System," 17th Oil Shale Symposium Proceedings, Colo. School of Mines, Golden, CO, 1984.

Hawthorne, S. B., R. E. Sievers, and R. M. Barkley. "Organic Emissions from Shale Oil Wastewaters and Their Implications for Air Quality," Environ. Sci. Technol., 1985, 19, 992-997.

Jury, W. A., R. Grover, W. F. Spencer, and W. J. Farmer. "Modeling Vapor Losses of Soil-Incorporated Triallate," Soil Sci. Soc. Am. J., 1980, 44, 445-450.

Perry, B. W., and L. B. Gratt. "Public Health Risks from an Oil Shale Industry," 17th Oil Shale Symposium Proceedings, Colo. School of Mines, Golden, CO, 1984.

Persoff, P., L. Hunter, J. F. Thomas, and C. G. Daughton. "Prediction of Atmospheric Emissions Resulting from Codisposal of Oil Shale Waste," in Applied Science Division 1983 Annual Report, Lawrence Berkeley Laboratory Report LBL-17073, 1984.

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