

STUDIES OF SOLUBLE ORGANICS IN SIMULATED IN SITU OIL-SHALE RETORT WATER
BY ELECTRON IMPACT AND CHEMICAL IONIZATION FROM A COMBINED GAS CHROMATOGRAPH-
MASS SPECTROMETER SYSTEM

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INTRODUCTION

Research on the development of in-situ oil shale processes has recently accelerated into a nation-wide program. This technique of in-place underground retorting of oil shale deposits virtually eliminates the environmental problems posed by the conventional mining of oil shale and the disposal of resulting spent materials. However, the in-situ process also presents a serious disposal problem, namely the co-production of vast amounts of process water along with the oil shale.

The composition and properties of the retort water produced usually depends upon the technique and operating conditions employed in the retorting process as well as the location and nature of the oil shale. Generally, the retort water is loaded with considerable quantities of soluble organic and inorganic materials. The presence of carboxylic acids (from acetic to caprylic acid) has been noted earlier by Cook (1) in TOSCO oil shale retort water; but, the presence of phenols in retort water from the Green River Oil Shales has been doubted for several years (2). In addition to these acidic organic compounds, substituted benzenes and nitrogen bases are present since these too, exist abundantly in shale oils (3,4). Untreated retort water effluents contain varying quantities of organics which could seriously impair the quality of ground water. This would pose a health hazard to humans due to the presence of certain phenolic and toxic components in the retort water.

A number of processes have been suggested for retort water treatment. The objective of this work is aimed not at a discussion of the purification of organic components present in retort water; but rather to provide an identification of the organic compounds found in the benzene soluble fraction of retort water, including carboxylic acids, phenols, nitrogen bases, and substituted benzenes, from gas chromatography-mass spectrometry (GC-MS) data.

EXPERIMENTAL

A. Sampling and Extraction Procedures

The retort water samples formed from Green River Oil Shale of either the Utah or Colorado region were all collected from the Laramie 10-ton simulated in-situ retorting process. A homogeneous representative sample of retort water was obtained by filtration through a Nalge 0.2 micron filter unit for removal of oily particulate prior to sampling. To avoid biological and physical degradative effects, all samples were kept under refrigeration. A 200 ml aliquot of retort water was taken and poured into a 500 ml lyophilizing container. This was then allowed to freeze-dry at a low temperature. The extraction method chosen was Soxhlet extraction using benzene as the solvent over an 8-10 hour period. The extracts were then adjusted to the desired concentration for GC-MS injection by evaporating the benzene solvent with a purified

nitrogen stream. A portion of the extract was methylated by BF_3 esterification in methanol, followed by subsequent extraction of the ester by heptane for analysis.

B. Gas Chromatograph-Mass Spectrometer Analysis

Gas chromatography is often employed in the analysis of complex mixtures of organic compounds. Through gas chromatography, it is possible to separate an organic mixture into its various fractions on the basis of volatility. Each fraction will be composed of constituents having similar boiling points, with the lower boiling compounds being vaporized and recorded by the detector before the higher boiling components. The advantages of the gas chromatograph lie in its speed and convenience of operation as well as the relatively few instruments required as basic apparatus, its high degree of sensitivity in determining the composition of the gas effluent, and its capability of producing both qualitative and quantitative data.

When a mass spectrometer is attached to a gas chromatograph, even more specific results are obtained. The combination of a gas chromatograph with a mass spectrometer (with the aid of a computer) allows the detection of two or more components belonging to a single gas chromatograph peak. GC-MS works on the principle of either chemical or electron impact ionization of organic compounds. Chemical ionization (CI)-mass spectrometry involves a much milder ionization process than electron impact (EI) and thus improves the chances of detecting molecular ions for labile compounds. The mass spectral data of an unknown compound can be compared against reference EI or CI spectra to aid in the identification of the unknown compound. However, EI mass spectrometry cannot be used alone since some molecular ions (M^+) produce weak signals and therefore go undetected. This is especially true of some alcohols, amines, ethers, esters, and other labile molecules. The absence of these molecular ions makes the interpretation of unknown mass spectra extremely difficult if not impossible.

C. Conditions

1. Column: $\frac{3}{8}$ OV-17 on 80/100 mesh Gas Chrom Q, 6 ft x 2 mm ID
2. Column temp: 60-250°C programmed at 8°/min
3. Carrier Gas: Helium (methane) at a flow of 18 cc/min
4. Injection temp: 250°C
5. Ion source pressure: 1.0×10^{-5} torr (1.0 torr)
6. Electron energy: 70 eV (120 eV)
7. Filament current: 500 microamps
8. Ion source temp: 180°C
9. Scan speed: 2.5 sec
10. Mass Range: 34-350 (60-350)
11. GC-MS Interface temp: 260°C

(The CI conditions, when different from EI, are in parenthesis.)

The GC-MS interface for EI analysis was a single stage glass jet separator. For CI analysis, the GC column was connected directly to MS ion source via an isolation valve. The mass spectrometer used was a Finnigan Model 3300 interfaced to a Finnigan Model 9500 gas chromatograph. Data collection and output was done using a Finnigan Model 6000 GC-MS data system.

RESULTS AND DISCUSSION

The examination of the methylated benzene-soluble fraction shows that the normal carboxylic acids do exist in retort water; however, these carboxylic acids represent only the minor portion in the methylated fraction. As shown in Figure 1, there are two series of these acids presented. One has carbon numbers below C_{11} (undecanoic acid) which could come directly from the pyrolysis of retorting. Another series have carbon numbers above C_{16} (palmitic acid) which has been found in the original oil shale sediment (5). The even normal carboxylic acids are dominant in this series. However, the C_{12} to C_{15} acids are entirely absent. An example of the search for methyl palmitate (C_{16}) is shown in Figure 2 in which a weak peak of m/e 270 in EI (electron impact) spectrum can be enlarged and identified certainly by the chemical ionization (CI) mass spectrometer.

Phenols from shale oil have been identified by various investigators (3,6), but their presence in the Green River retort water was doubtful (2). Figure 3a represents the gas chromatographic peak of m/e 94. It was confirmed by the mass spectrum of the odd-electron $66(M-CO)^+$ peak accompanied by $65(M-CHO)^+$ to recognize the phenol functionality (7) in the retort water (Figure 3b). Additionally, cresols have also been found in retort waters. The mass spectrum of the methylated fraction also indicates a trace amount of long-chain alkanes. Their presence is not surprising since they exist abundantly in shale oils.

Compounds of the C_nH_{2n-6} substituted benzene series consist of xylenes (C_8H_{10}) and ethyltoluene (C_9H_{12}). The most prominent M-15 ion peak in the spectra of these two types of compounds indicates a methyl substituent with the benzene ring. In addition to the above substituted benzene series, biphenyl ($C_{12}H_{10}$) has also been identified in the benzene soluble fraction of retort water. Figure 4 represents the identification of the parent molecular ion peak M^+ 154 and the isolated GC peak of biphenyl.

Two types of oxygen-containing nitrogenous compounds, $C_nH_{2n-5}NO_2$ and $C_nH_{2n-3}NO_2$, have been identified from benzene extracts of retort waters. Recently, in a comprehensive study on polar constituents of Green River oil shale by Anders et al. (8), $C_nH_{2n-5}NO_2$ has been listed among the identified nitrogen compounds. Figure 5 represents the mass spectrum and possible structures of this compound ($C_7H_9NO_2$). The experimental mass of the fragment ions appearing at nominal masses 53, 67, 81, 96, 106, 110, 111, 121, 124, and M^+ 139 all correspond closely to that reported by Anders et al. (8) in which M-15, M-18, M-28, and M-29 fragment ions indicate a loss of CH_3 , H_2O , CO, and CHO from the parent structure. The mass spectrum of other oxygenated nitrogen compounds, $C_5H_7NO_2$ (n-methylsuccinimide), are shown in Figure 6. These two compounds could be derived partly from the oxidation products after cleaving the amide C-C bond to the C=O group in the original kerogen matrix, and partly from the dehydration of dicarboxylic acids with amines. The organic sulfur compound has also been searched by the chemical ionization mass spectrometer in which the major representative falls into a M+1, mass number of 128. However, not enough information is available to speculate about this sulfur compound.

The above preliminary report constitutes the initial investigation of the organic components in retort waters. The major results of the investigation can be summarized as follows:

1. There are two series of long-chain normal carboxylic acids existing in retort waters which could come partly from the pyrolysis of retorting, and partly from the original oil shale sediment.
2. Phenolic compounds have been found in the retort water which may be formed from the thermal decomposition under retorting conditions.
3. Long-chain normal alkanes and substituted benzenes were identified in retort waters, since they exist abundantly in shale oils.
4. Spectral analysis of nitrogen compounds showed that two types of oxygenated nitrogen components (maleimides and succinimide) can be identified from the benzene extract of retort waters. Maleimides have been found in the polar fraction of Green River oil shale (8). The amide oxidation as well as the dehydration between dicarboxylic acids and amides will all cause the formation of these two nitrogen compounds.

Further experiments to characterize and isolate retort water into acid, base, and neutral fractions are in progress. The present method of the combination of electron impact and chemical ionization MS in conjunction with GC offers the inherent advantages for the analysis of the vast number of organic components in retort waters.

ACKNOWLEDGEMENT

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Fig. 1.

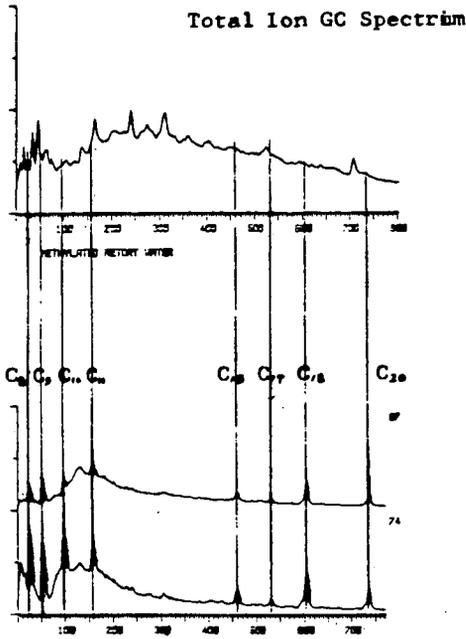


Fig. 2 METHYLATED RETORT WATER SAMPLE BY EI

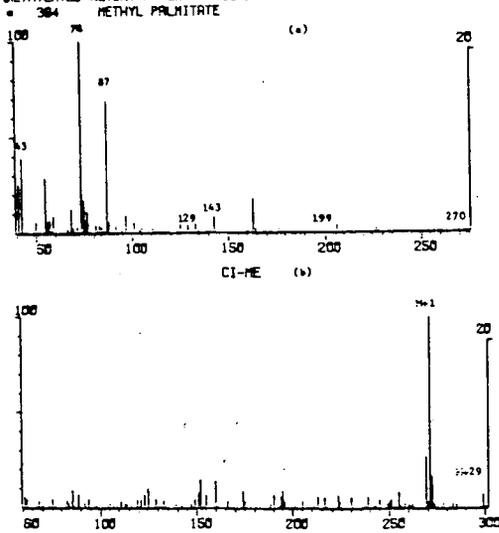


Fig. 3... RETORT WATER ELECTRON IMPACT
M/E94

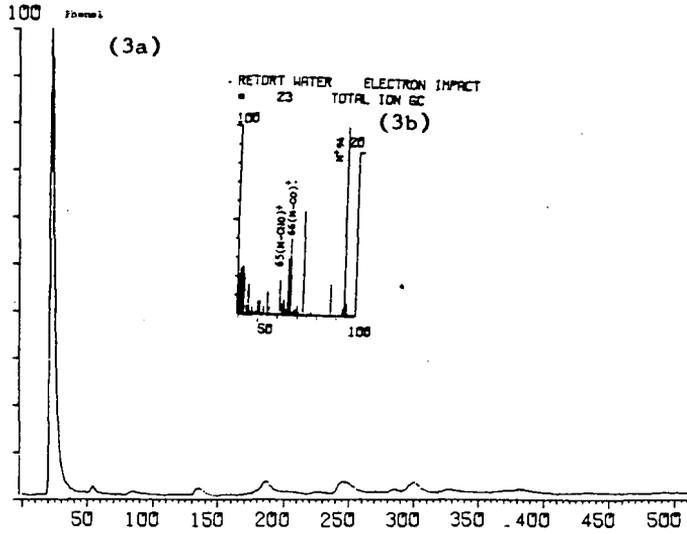


Fig. 4. RETORT WATER ELECTRON IMPACT
M/E 154

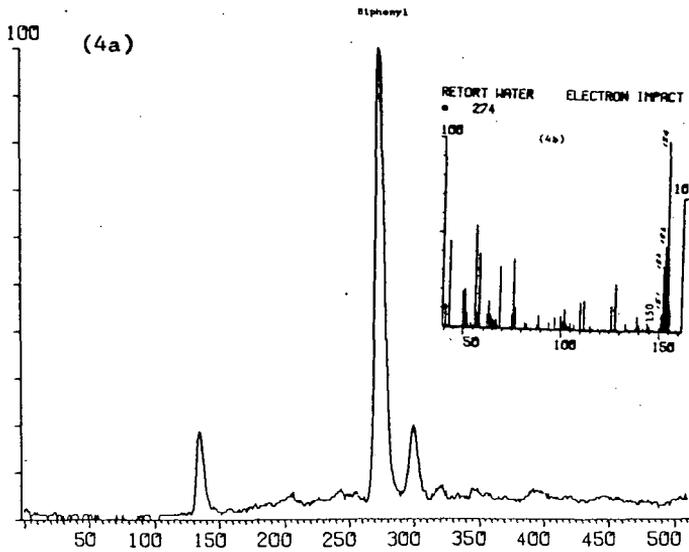


Fig. 5. RETORT WATER ELECTRON IMPACT
* 186

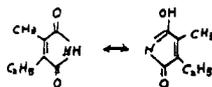
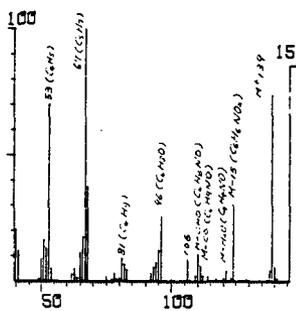


Fig. 6 RETORT WATER

