CONCENTRATION OF HYDROCARBONS ADSORBED ON SOIL AND ROCK SAMPLES BY SUPERCRITICAL FLUID CHROMATOGRAPHY

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ABSTRACT

A procedure for quantitatively extracting hydrocarbons ranging from C5 to C44 using carbon dioxide at supercritical conditions to yield a concentrated extract suitable for analysis by GC or GC-MS is described. Examples are presented of the application of this technique for the detection of petroleum hydrocarbons in samples from wells drilled with oil based mud and for the characterization of gasoline range contamination in water saturated soils.

INTRODUCTION

Isolation and concentration of hydrocarbons contained in soil and rock matrices by solvent extraction frequently results in the loss of low boiling components. Much of this loss results from the process of solvent removal by evaporation that must be performed in order to concentrate components prior to analysis. Also, presence of high concentrations of water in samples can interfere with the solvent extraction process. Supercritical fluid extraction (SFE) is the process by which a supercritical fluid removes analytes from a matrix and transfers them to a trap where the supercritical fluid is returned to a gaseous state and escapes, leaving the sample components behind. The sample is then rinsed from the trap with a small amount of solvent and transferred to output vials. A SFE procedure that overcomes difficulties of light end retention and water interference is described.

EXPERIMENTAL

A Hewlett Packard Model 7680T Supercritical Fluid Extractor was employed (1) using SFC grade carbon dioxide. The SFE trap was packed with a porous polymer selected to retain hydrocarbons while being inert to CO2. If samples were wet, desiccant was mixed with the sample prior to extraction. Extractions described here were performed in two steps as follows:

Step 1
Density = 0.25 g/cc, sample cell temperature = 40°C
Static (closed cell) extraction time = 1 minute
Dynamic (open cell) extraction time = 5 minutes (5.3 cell volumes)
Rinse trap to collection vial with 500 µl dichloromethane
Step 2
Density = 0.84 g/cc , sample cell temperature = 40°C
Static (closed cell) extraction time = 1 minute
Dynamic (open cell) extraction time = 10 minutes (3.1 cell volumes)
Rinse trap to collection vial with 500 µl dichloromethane

RESULTS AND DISCUSSION

As the use of oil based muds becomes more prevalent in drilling oil wells, detecting oil shows can be problematic. Hydrocarbons ranging from C5 to C44 can be readily extracted from rock samples (conventional cores, sidewall cores , or cuttings) using SFE and examined for non-mud hydrocarbon presence by gas chromatography of the extract.

The restricted boiling range of oil based muds, as shown in Figure 1, allows detection of hydrocarbons boiling at higher or lower temperatures than those of compounds present in the mud. Figure 2 contains expansions of gas chromatograms of supercritical fluid extracts of sidewall cores from a single well; one containing only oil based drilling mud and the other containing mud and hydrocarbons contributed from the core. A profile of the data down this well yielded the results in Figure 3, showing the presence of non-mud hydrocarbons at approximately 11,250 ft. Testing of this well from the interval identified by SFE produced oil with the composition shown in Figure 4. This oil likely could not have been detected using conventional solvent extraction methods as solvent evaporation would likely have resulted in loss of most of this particularly volatile oil.

Hydrocarbon contamination in soils can be very difficult to quantitatively extract and characterize, especially when water or low boiling components are present. Hydrocarbons ranging from C5 to C44 can be readily extracted from soil samples using SFE (even if the soils are wet) and the resulting extract characterized by gas chromatography.

Figure 5 is a chromatogram of a hydrocarbon "free product" collected from a severely contaminated site. The goal of this investigation was to evaluate soil core samples surrounding this free product accumulation to determine the extent of contamination and to ascertain if more than one source may have contributed to the main accumulation.

The character of the soil in this site was sandy with small pebbles. In order to test the effectiveness of the SFE method, a sample of clean sand was soaked with water and then spiked with the free product illustrated in Figure 5. A chromatogram of the resulting SFE extract, shown in Figure 6, is indistinguishable from the original material. Segments from multiple cores were extracted by SFE and analyzed by GC. Sample amounts, SFE and GC conditions were held constant. Figure 7 is an example a chromatogram of an actual core extract. Using the results of these analyses the extent of the contamination was clearly defined and significant differences in origin of material contributing to the free product were observed.

REFERENCES

(1) Hewlett Packard 7680A Supercritical Fluid Extractor Operational Manual: Part Number 07680-90320. Edition 2, November, 1991.

FIGURES

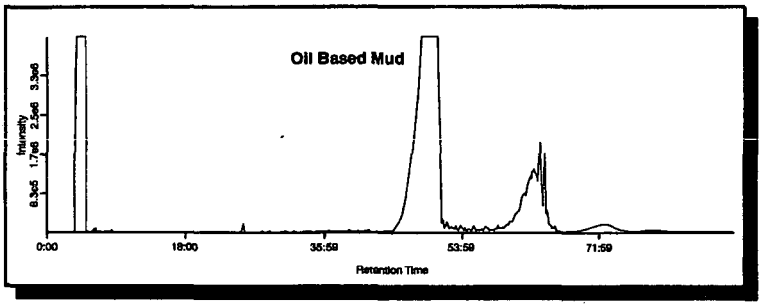

Figure 1 - Oil based Mud, Gulf of Mexico

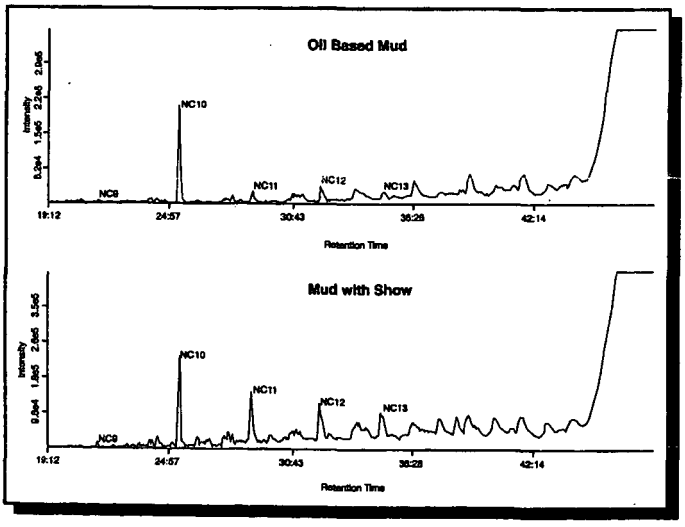

Figure 2 - Oil Based Mud and Mud with Show

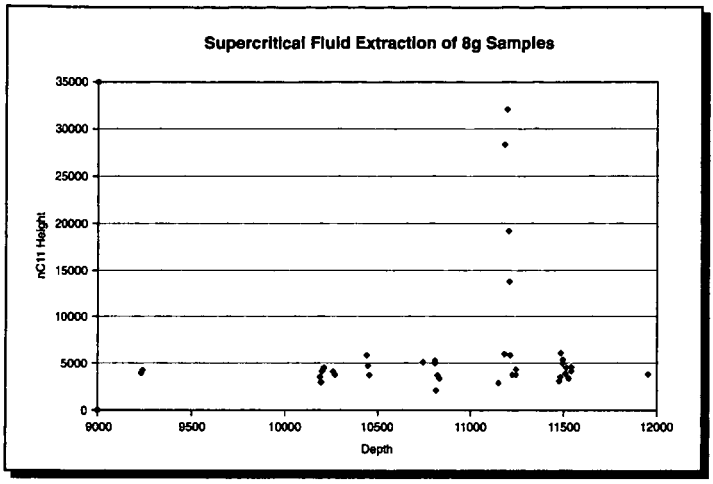

Figure 3 - Supercritical Fluid Extraction of 8 gram Core Samples

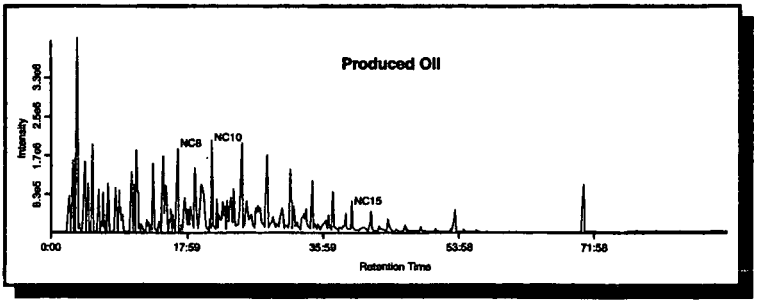

Figure 4 - Produced Oil

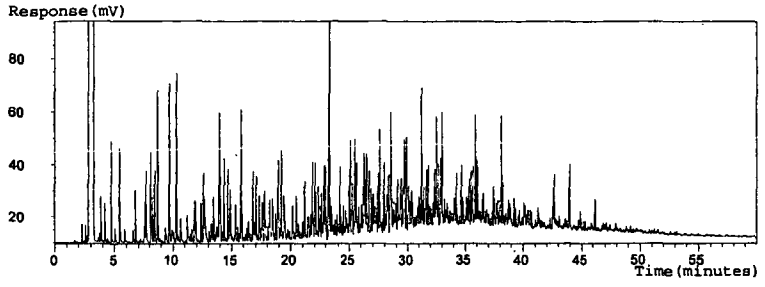

Figure 5 - Free Product

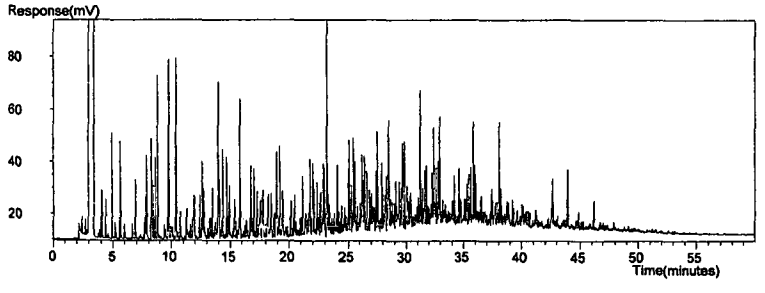

Figure 6 - Test of SFE Method to Remove Free Product From Similar Soil Matrix: 100ul Free Product on Water Saturated Sand

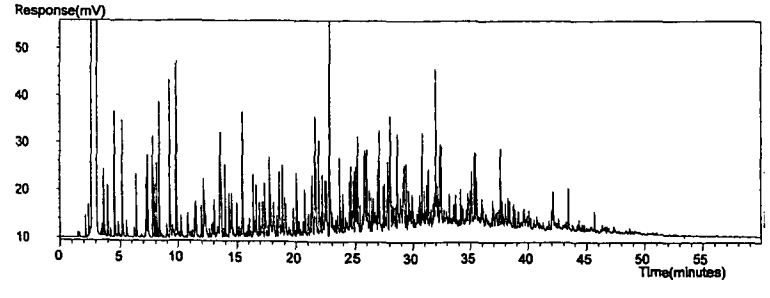

Figure 7 - Core Extract