

Analysis of Water Extracts of Hydrocarbon Mixtures

S. Wasik and Robert L. Brown

Institute for Materials Research
National Bureau of Standards
Washington, D. C. 20234

INTRODUCTION

Concern over the pollution of water systems by oil has generated a desire for improved methods of analyzing water for dissolved hydrocarbons (1). The complexity of crude oil and oil products makes the analysis of their water extracts difficult. It can be simplified by physically or chemically separating the components of the extract into hydrocarbon groups such as saturated hydrocarbons, olefins, aromatics, and polar hydrocarbons. One approach to this separation problem involves the analysis of hydrocarbons in a gas which has passed through the extract. Elution times for the various hydrocarbons will depend on their partition coefficients; e.g., the slightly soluble aliphatic compounds will be removed far more rapidly than the more soluble aromatic hydrocarbons. Group separations can thus be based on group elution times.

In the present work, helium was used as the stripping gas and its hydrocarbon content was determined by gas chromatography. For group separation it is not essential to achieve an equilibrium distribution of the hydrocarbons between the two phases, although this gives the highest sensitivity. If equilibrium can be approximated, however, the method yields a direct determination of the partition coefficients from the elution times. In practice, it is not difficult to approach equilibrium closely. Under such conditions, plots of the log of the chromatographic peak area against the volume of helium passed through the extract will be linear, and the slopes of the plots will depend only on the volume of the extract and the partition coefficients of the solutes. Partition coefficients for members of a group, and thus the slopes of the log plots can be drastically changed by the addition of complexing agents. This greatly facilitates group identification. The method is similar to the multiple phase-equilibrium scheme described by McAullife (2). It differs, however, in that it is a continuous process and that it utilizes group complexing agents.

EXPERIMENTAL

Apparatus

The extract was contained in a vertically-mounted glass tube 50 cm long and 1 cm in diameter. Bubbles of helium were injected into the bottom of this cell from a very small opening in the end of a 1/16-inch stainless steel tube. This orifice was made by pinching off the end of the tube and reopening it slightly with a file. A pressure head of 80 psig across this hole produced a helium flow of 1 ml/min in the form of small bubbles averaging approximately 0.1 mm in diameter. The outlet of the cell was connected to a gas sampling valve with 1/16-inch stainless steel tubing. The extract was introduced into the cell from a pipette, with the amount chosen to bring the liquid level almost to the top of the cell thereby minimizing the dead volume in the gas phase. A dye experiment showed that the rising bubbles kept the liquid phase well stirred. The cell was immersed in a water bath whose temperature was controlled to $\pm 0.1^\circ\text{C}$.

The chromatographic column was a 1/4-inch by 12-foot length of stainless steel tubing packed with 60-80 mesh glass beads that had been coated with 1.0% w/w of an aqueous solution of 6.0 M silver nitrate. The column was used at room temperature. An electronic integrator was used to measure peak areas.

Analysis of Data

Assume that the concentration of a particular hydrocarbon in the helium leaving the cell is proportional to its concentration in the extract at that moment. One then has the relation $C = C_s/K$, where C is the hydrocarbon concentration in the helium, C_s is its concentration in the water extract, and $1/K$ is the proportionality factor. If there were equilibrium, K would be equal to the partition coefficient. If V is the volume of helium which has been passed through the extract, one can show that the ratio of C to its value, C_0 , at zero helium volume is given by the expression

$$-\log_e(C/C_0) = K^{-1}(V/V_s), \quad (1)$$

where V is the volume of the extract. A plot of \log_e of this ratio or $\log C$ versus V/V_s or V should be linear if K is constant, and the slope will give its value. Having determined K , one can calculate C_s provided C is known. In particular, the initial amount of hydrocarbon in the extract can be determined from C_s and K .

A series of experiments with benzene, for which extensive solubility data are available (3), gave linear log plots and a value of K close to the equilibrium value. This technique should thus provide a convenient means for determining partition coefficients even though more work is necessary to learn how to discover and correct for non-equilibrium effects.

The log plots can be used to identify chromatographic peaks as to hydrocarbon group. For example, saturated hydrocarbons may be identified by the low K values they have in aqueous solution. The concentration of saturated hydrocarbons will diminish to approximately 97% of their original concentration when V is equal to V_s . This very sharp decrease in peak area with helium volume is the same for all saturated hydrocarbons and can be used to identify this group. This also provides a way of quickly eliminating the saturated hydrocarbons from the analysis thereby simplifying the identification of other types of hydrocarbons. The polar hydrocarbons have a much larger value of K and can easily be identified by means of the log plots.

Peaks may also be identified as to hydrocarbon group by the addition of reagents to the extract, thus changing the value of K in equation 1 (4). Mercuric ions complex very strongly with olefins ($K = 10,000$) but not with the aromatics. Addition of mercuric ions lowers the partial pressure of the olefins so much that their peak area is reduced practically to zero. The olefins may thus be identified as those peaks that disappear after the addition of mercuric ions to the extract. The same procedure may be used for the identification of aromatic compounds by the addition of silver ions to the extract. Although the silver-aromatic complex is not as strong as the mercuric-olefin complex the effect is sufficient for identification purposes.

A water extract containing a normal paraffin (decane), an olefin (octene-1), and aromatic (ethylbenzene), and a polar compound (ethylacetate) was used to illustrate the identification of peaks as to hydrocarbon group. The procedure is shown graphically in Fig. 1 as semi-log plots of the peak area versus helium volume for each component in the water extract. The large difference in K values of the saturated hydrocarbons compared to the polar hydrocarbons is illustrated by the difference in slopes of the two compounds. The plots also show the large effects that mercuric and silver ions have on the olefinic and aromatic compounds, respectively. In the olefinic case the peak area went to zero whereas in the aromatic case the peak area was reduced to a much lower value followed by a linear plot with a reduced slope. For this latter case, the lowering of the peak area and the value of the resulting slope depends upon the concentration of the silver ion, the stability constant of the silver-aromatic complex, and the volume of the water extract.

There are solutes whose peaks overlap for the particular chromatographic column being used but which happen to belong to different hydrocarbon groups. The use of the log plots and mercuric and silver ion additions can be very helpful both in recognition of the overlap condition and in the identification of the peak

components. For example, consider the case of a saturated hydrocarbon peak overlapping a peak from any other group. Passage through the cell of a volume of helium equal to that of the extract would so reduce the concentration of the saturated hydrocarbon in the helium stream, that essentially only one peak would remain.

Analysis Time

In order for the analytical scheme presented in this paper to be practical, it is essential that the chromatography be capable of quick analyses. Columns packed with glass beads coated with aqueous silver nitrate were found to be ideal for this work. We achieved a complete separation of meta- from para-xylene in less than two minutes and an almost complete separation of sec-butylbenzene from iso-butylbenzene in six minutes. These two separations have been achieved (5) on a 100,000 plate capillary column in 60 and 120 minutes, respectively.

CONCLUSIONS

The method of analysis presented in this paper is restricted to systems in which the solute molecules are fairly insoluble in the solvent. Water extracts of crude and processed oils are ideal because at equilibrium, from 75 to 98% of the hydrocarbons are in the vapor phase. There is little loss in sensitivity because the vapor is injected directly into the analytical column. The big advantage is the ease with which the analysis can be divided into hydrocarbon groups. For instance, if only the aromatic fraction of the water extract were of interest, the saturated hydrocarbons could be blown out with the helium and the olefins taken out by complexing with mercuric ions, leaving only the aromatics and the polar hydrocarbons. The aromatic "fingerprint" could then be obtained by comparing the chromatograms before and after silver ions were added to the cell. This analysis by groups could be important in toxicity studies or oil identification.

LITERATURE CITED

- 1) Boylan, D. B. and Tripp, B. W., *Nature* **230**, 44 (1971).
- 2) McAullife, C., *Chemical Technology*, January 1971, (American Chemical Society, Washington, D. C.), p. 46.
- 3) Arnold, D. S., Plank, C. A., Erickson, E. E., and Pike, F. P., *Chem. Eng. Data Ser.* **3**, 253 (1958).
- 4) Sillen, L. G. and Martell, A. E., Stability Constants of Metal-Ion Complexes, (Special Publication No. 17, The Chemical Society, London 1964).
- 5) Schwartz, R. D., Mathews, R. G., and Brasseaux, D. J., *J. Gas Chromatog.* **5**, 251 (1967).

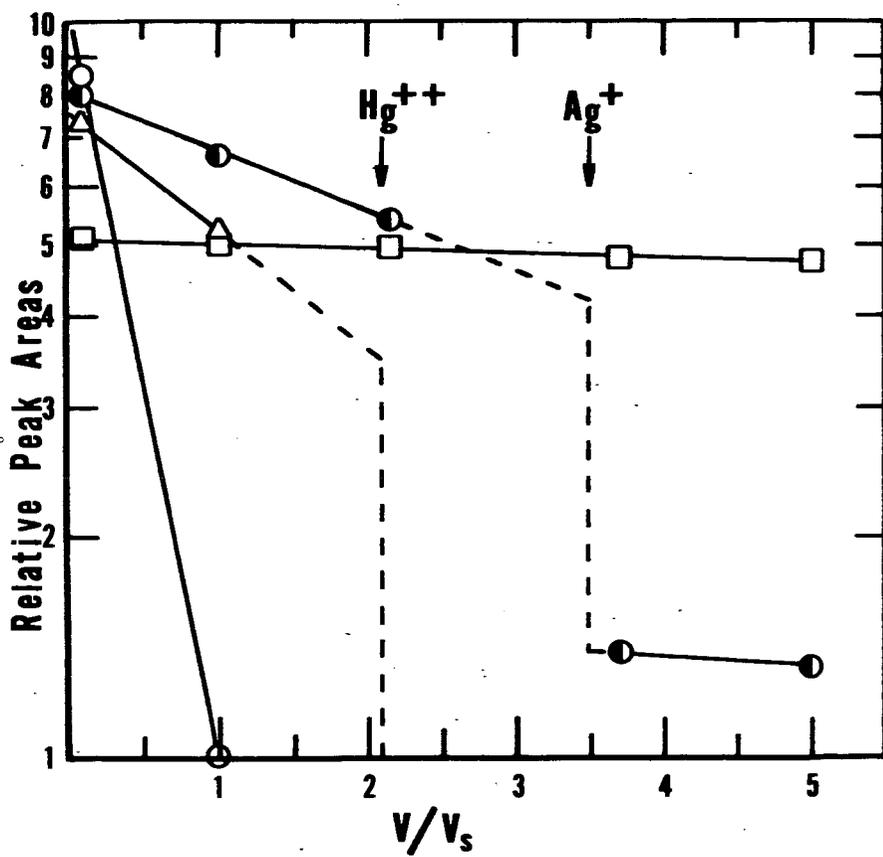


FIGURE CAPTION

Hydrocarbon group-identification scheme. Open circles indicate peak areas for n-decane; half-filled circles, ethylbenzene; triangles; octene-1; and squares, ethylacetate. V is the volume of helium passed through the cell and V_g is the volume of the aqueous extract. The arrows indicate the values of V/V_g at which H_g^{++} and A_g^+ ions were added to the extract.