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## CONCENTRATION AND DETERMINATION OF ORGANIC ACIDS IN COMPLEX AQUEOUS SAMPLES

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### SUMMARY

The conventional "acid fraction" on aqueous samples obtained by solvent extraction fails to isolate many types of organic acids and acid anions. A new anion-exchange concentration method, coupled with subsequent formation of the methyl esters of acids and gas chromatographic (GC) analysis, is used to determine the acids in several actual water samples. Chromatograms are given and results discussed for analysis of river water samples, water from a large anaerobic digester facility and shale oil water. In some cases, acidic solutes have been identified by GC-mass spectrometry after concentration by the anion-exchange method. Neutral organic compounds can be successfully determined in the water after removal of the acidic components by anion exchange.

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### INTRODUCTION

In analyzing complex aqueous samples for organic solutes, it is customary to isolate an "acid fraction" by solvent extraction. However, this procedure either gives low recoveries or completely misses many types of organic acids and acid anions. In a recent publication<sup>1</sup>, a column containing a macroporous anion-exchange resin was used to concentrate selectively organic acids and acid anions from water samples. Excellent recoveries were obtained at the 10- or 100-ppb\*\* concentration levels for a wide variety of carboxylic acids ranging from acetic acid to stearic acid. Excellent recoveries were also obtained for a variety of organic sulfonates and phenols. This paper<sup>1</sup> and a subsequent publication dealing with the analysis of organic acids in water from a pesticide disposal pit<sup>2</sup> showed almost perfect selectivity of the anion-exchange column for acids over other types of organic solutes. Many acids isolated from the pit water by the ion-exchange method were not obtained by the conventional solvent extraction procedure.

In the present work concentration by anion-exchange with subsequent elution, esterification and gas chromatography (GC) is used to analyze water samples from a

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\*\* The American billion ( $10^9$ ) is meant here.

municipal anaerobic digester, river water and oil shale process water for acidic constituents. Gas chromatograms are shown and some of the acidic constituents are identified by GC-mass spectrometry (MS) and confirmed by the retention times of authentic samples. After extraction of the acidic sample solutes by anion exchange, neutral organic solutes can be concentrated and determined by use of conventional resin concentration-GC methods.

## EXPERIMENTAL

### *Anion-exchange column*

The anion-exchange resin was prepared by chloromethylation and subsequent alkylation of Rohm and Haas XAD-4 as described in an earlier publication<sup>1</sup>. The anion-exchange column was a glass tube (ca. 12 cm × 0.8 cm I.D.) with a standard taper joint on top for connection with a water sample reservoir. The column was filled with approximately 2-3 g of anion-exchange resin in the hydroxide form.

### *Reagents*

Diazomethane was prepared from Dizald (Aldrich, Milwaukee, MA, U.S.A.).

*Gas chromatography.* Most separations were performed on a 30-m glass capillary column coated with SE-54. Instrumentation and other columns were described in an earlier paper<sup>1</sup>.

### *Procedure*

(1) Pass a 200-ml sample of waste water or a 1-4-l sample of river water through the anion-exchange column at a flow-rate of 4-5 ml/min.

(2) Wash the column with 25 ml of diethyl ether to remove any sorbed neutral organic solutes. Then wash with 25 ml of methanol to remove residual water and with 25 ml of diethyl ether to remove residual methanol.

(3) Elute the sorbed acid anions from the column with 20 ml of diethyl ether saturated with hydrogen chloride. Pass this effluent through the column again and then wash the column with a fresh portion of HCl-ether.

(4) Evaporate the combined HCl-ether effluent (30 ml) to dryness. Use a stream of nitrogen to evaporate the last traces of liquid. Convert the organic acids to methyl esters by adding a solution of diazomethane until the yellow color persists (usually 2 to 3 ml). Dilute the solution to a definite volume with diethyl ether.

(5) Inject a portion of the esterified solution into a gas chromatograph (or a gas chromatograph-mass spectrometer for MS identification).

## RESULTS AND DISCUSSION

### *Anaerobic digester water*

This sample was obtained from an anaerobic digester used to produce methane gas from processed municipal refuse. Chromatograms obtained by the anion-exchange concentration procedure with capillary column GC analysis of the methyl esters resulted in the chromatograms in Figs. 1 and 2, using flame-ionization and electron-capture detectors, respectively. Analysis of a portion of the methyl ester

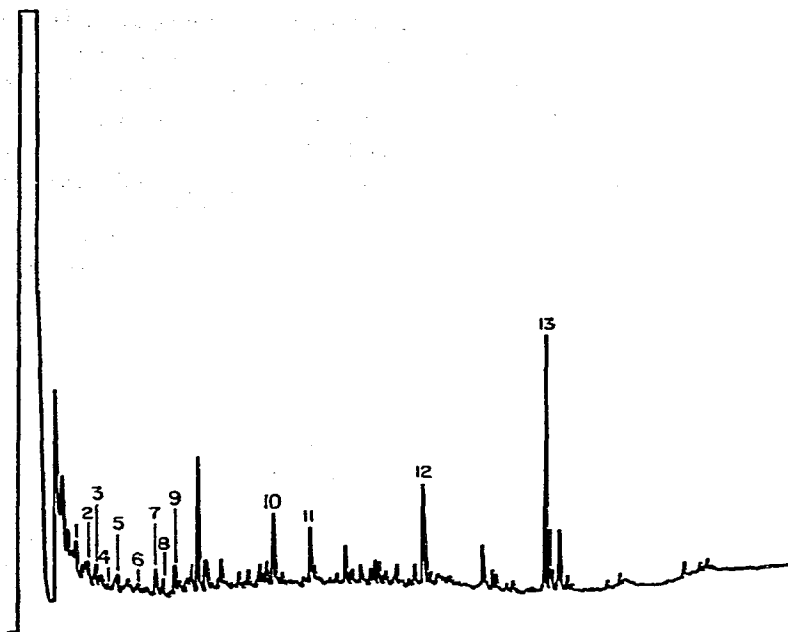


Fig. 1. Gas chromatogram of acids from anaerobic digester water, flame-ionization detector. 1 = benzoic acid; 2 = caprylic acid; 3 = *m*-toluic acid; 4 = phenylacetic acid; 5 = phenylpropionic acid; 6 = 3,5-dimethylbenzoic acid; 7 = capric acid; 8 =  $\beta,\beta$ -dimethylphenylacetic acid; 9 = phenylbutyric acid; 10 = MCP; 11 = myristic acid; 12 = palmitic acid; 13 = abietic acid. (Note: the actual peaks are the methyl esters, but it is likely that the original sample contained either the free acids or their salts.)

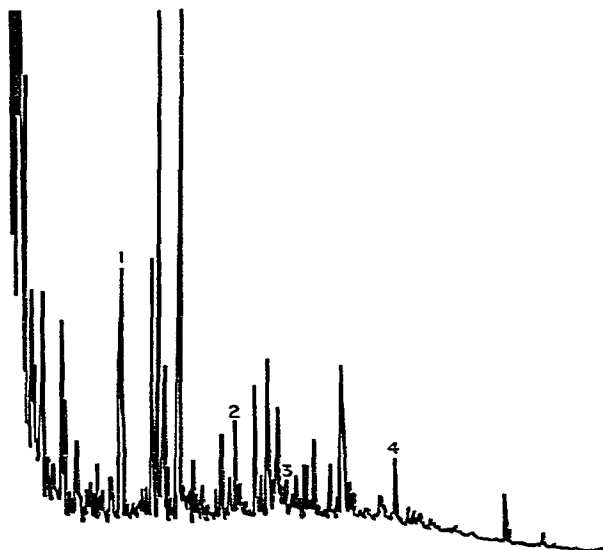


Fig. 2. Gas chromatogram of anaerobic digester water, electron-capture detector. Peaks: 1 = 2,4-dichlorophenol; 2 = MCP; 3 = 2,4-D; 4 = DCPA.

concentrate by GC-MS resulted in the tentative identification of more than thirty organic compounds. Then retention times for authentic pure compounds were obtained under the same chromatographic conditions. These retention data confirmed the identification of the peaks marked in the figures and listed in the figure legends. Additional pure compounds to check the identity of later-eluting peaks have not yet been received. Using anion-exchange preconcentration with different chromatographic conditions, acetic acid was also definitely identified in this water sample.

The actual water sample was murky and contained a great variety of organic substances. Attempts to isolate organic compounds by solvent extraction resulted in serious emulsion problems. However, the sample behaved well in the anion-exchange procedure with only a simple filtration beforehand.

#### *River water*

River water samples were collected on several occasions and the acidic solutes concentrated by the anion-exchange procedure. Fig. 3 is the chromatogram obtained for a sample taken during cold weather when the river flow was low. The major compounds identified were  $C_{12}$ - $C_{18}$  aliphatic carboxylic acids. For samples taken at times when the river flow was greater and there was significant surface run-off, additional peaks appeared in the gas chromatogram, as shown in Fig. 4. In addition to the compounds listed on the figures, the following compounds were identified: tetrachloroterephthalic acid, 2,4-dichlorophenoxyacetic acid, 2,4-dichlorophenol, bentazon, dimethylsulfide, dimethylsulfate, and trimethylphosphate. It is not clear whether the last three compounds existed in the original sample as the acid, acid anion or as a methyl ester.

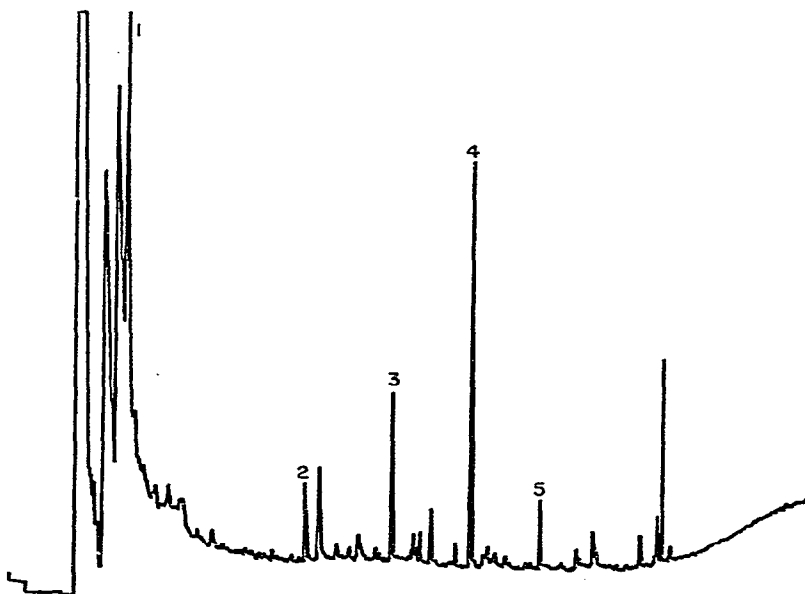


Fig. 3. Gas chromatogram of Skunk River water at low flow. Peaks: 1 = benzoic acid; 2 = lauric acid; 3 = myristic acid; 4 = palmitic acid; 5 = stearic acid.

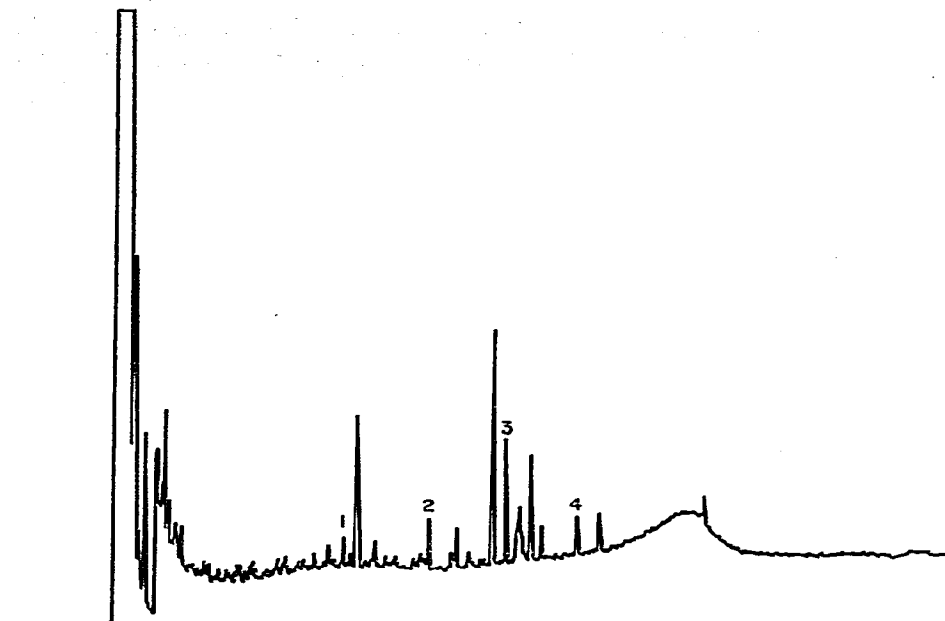


Fig. 4. Gas chromatogram of Skunk River water at higher flow and surface run-off. Peaks: 1 = lauric acid; 2 = myristic acid; 3 = palmitic acid; 4 = stearic acid.

Although identification of peaks in Figs. 3 and 4 is incomplete, the results are in accord with those of a recent publication<sup>3</sup> in which aliphatic carboxylic acids were the major acidic components found in Mississippi River water.

Humic and fulvic acids are concentrated from surface water using the anion-exchange procedure. These substances are fairly insoluble in diethyl ether but can be removed from the column by eluting with methanol saturated with hydrogen chloride gas. In addition to humic and fulvic acids, several gas chromatographable components were found in the methanol fraction, namely abietic acid and bentazon.

Neutral organic compounds either are not retained by the resin column or are washed from the column with 25 ml of diethyl ether. Thus, after removal of the acidic components by anion exchange, the neutral organic substances can be concentrated on a column containing XAD-2 resin and analyzed by GC<sup>4</sup>. Comparison of results obtained when identical surface water samples were passed through XAD-2 and anion-exchange column and then analyzed by GC gave identical results for atrazine, Sencor, alachlor and Bladex.

#### *Shale oil water*

Smelly, dark-colored water is produced when oil shale is heated to recover oil. The water has a high organic content and appears to contain a very large number of complex organic compounds. Fig. 5 shows a gas chromatogram of the methylated acidic compounds obtained by the anion-exchange procedure. The chromatogram obtained using the flame-photometric detector in the sulfur mode indicates that a considerable number of acidic sulfur compounds are in the shale oil water. The other major acidic components, indicated by the flame-ionization detector, appear to be

lower-molecular-weight carboxylic acids and aromatic acids. The chromatograms in Fig. 5 are remarkably simple to have been obtained from such a concentrated and complex mixture of organic substances in the water.

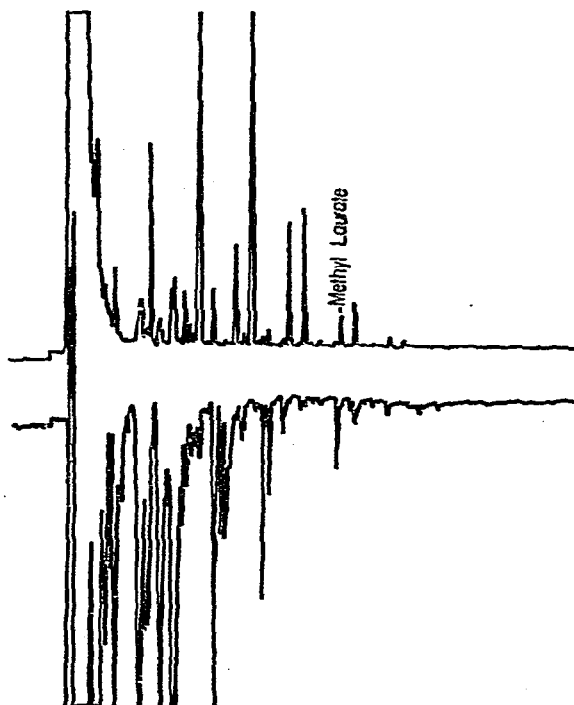


Fig. 5. Gas chromatogram of shale oil water. Top chromatogram is the flame-ionization detector and the bottom chromatogram is with the flame-ionization detector in the sulfur mode.

#### CONCLUSIONS

The anion-exchange preconcentration procedure, followed by esterification and GC analysis has been shown to work well for a variety of complex aqueous samples. The procedure is simple and reasonably quick to carry out. The evidence obtained in this work and in two preceding publications<sup>1,2</sup> indicates that the anion-exchange method is definitely preferable to solvent extraction for concentrating and measuring organic acidic components of water samples.

#### ACKNOWLEDGEMENT

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