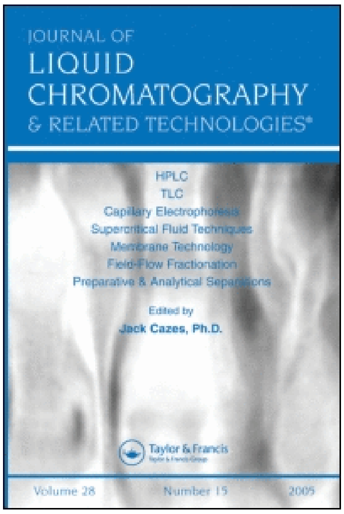

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DETERMINATION OF LOW MOLECULAR WEIGHT CARBOXYLIC ACIDS IN WATER BY HPLC WITH CONDUCTIVITY DETECTION

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ABSTRACT

Low molecular weight carboxylic acids (C_2-C_8) were measured in aqueous samples using reverse phase HPLC coupled with conductivity detection. The aqueous samples are adjusted to pH 2 with H_2SO_4 and extracted with diethyl ether. The ether is allowed to evaporate over distilled water. The acid concentrate is analysed using a Zorbax-ODS column (25 mm x 4.6 mm). The method is simple, fast, and because of the selectivity of the conductivity detector, is relatively free from interferences. Average precision is estimated to be approximately ± 13% for the overall method.

INTRODUCTION

The increasing concern with water quality protection has resulted in a proliferation of analytical methods for potentially hazardous water pollutants (1). Compounds such as phenols, pesticides, polycyclic aromatic hydrocarbons, and polychlorinated biphenyls have received much attention from the analytical community, because of inherent biological activity. All of these organic pollutants can be extracted from aqueous media and the extracts concentrated for subsequent measurement.

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A class of compounds which has been largely overlooked in the development of analytical methods for water quality is the low molecular weight carboxylic acids. While these compounds are generally considered to be interferences in the analysis of water samples, they are important constituents for several reasons. Carboxylic acids pose significant problems in standard wastewater treatment operations, such as solvent extraction, powdered activated carbon treatment, and biological treatment (2). The clean-up of wastewater containing these constituents requires expensive operations such as wet-air oxidation (3). Without such clean-up a high level of dissolved organic carbon may result in permit violation. In addition, the presence of these compounds may act to increase the water solubility of the nonpolar pollutants mentioned earlier, resulting in higher discharge levels and increased environmental mobility (4). These compounds have been shown to have biological activity in and of themselves, either by acting as a carbon source for microbial growth, or by exhibiting toxicity (5). Finally, the probability of finding these compounds in certain aqueous systems (e.g. coal conversion wastewaters and municipal waste leachate) is high (4,6).

Several methods exist for the determination of low molecular weight carboxylic acids in water, but all have limitations. Direct aqueous injection gas chromatography (6) is perhaps the most commonly used technique, but is limited in terms of selectivity and sensitivity. Isolation of the acids on diethylaminoethyl-Sephadex (7), followed by derivatization and gas chromatographic analysis (8), provides increased sensitivity and selectivity, but is tedious and requires a prior estimate of the level of acids present. Solvent partition followed by gas chromatographic analysis provides only limited improvement in terms of selectivity and sensitivity, and the analytical columns normally used are of limited durability (9).

In this paper, we discuss the applications of reverse-phase HPLC coupled with electroconductivity detection for the measurement of low molecular weight carboxylic acids in various fossil fuel process waters and municipal refuse leachates. The versatility of the conductivity detector coupled with HPLC for measuring organic acids has been demonstrated by Thurman (10,11). It would appear that this approach would have several advantages over commonly used methods for carboxylic acids in water (direct injection or derivatization - GC) and that due to the selectivity of the conductivity detector, the method would not be prone to interferences.

MATERIALS AND METHODS

Formic, acetic, propionic, butyric, valeric, hexanoic, heptanoic, and octanoic acids (C_1-C_8) were obtained from Aldrich Chemical Company and aqueous standards were prepared without further purification. Reagent grade diethylether (J. T. Baker Chemical Co.) was used for the extraction procedure.

Aqueous samples consisted of a sour waters collected from an operating coal liquefaction plant, a shale oil retort water, and municipal refuse leachates.

The liquid chromatographic components consisted of two Waters Associates (Milford, MA) Model 6000A chromatography pumps, a Waters Associates WISP 710A sample processor, - Waters Model 720 system controller. A Wescan Model 212 Conductivity Detector was used and the chromatograms were displayed on a Hewlett-Packard Model 7045-A X-Y recorder. Dupont Zorbax ODS columns (25 cm x 4.6 mm) were used. Distilled in glass methanol was obtained from Burdick & Jackson, Muskegon, MI. Doubly distilled water was used throughout.

The diethylether extraction/concentration was carried out by transferring an aliquot of the aqueous sample, usually 2 to 10 ml, to a 50 ml beaker and adjusting the pH to 2.0 ± 0.2 by the dropwise addition of 1 N H_2SO_4. The solution was transferred to a separatory funnel and extracted twice with 10-15 ml portions of ether. The mixture was shaken approximately four minutes for each extraction.

To the combined ether extracts contained in a 50 ml beaker, a 4 ml aliquot of doubly distilled water was added and the beaker placed in a ventilated hood to allow the ether to evaporate (∿25 mins) over the distilled water. The acid isolate was then adjusted to a known volume (usually 5.0 ml) and an aliquot was injected into the LC column. The recovery was measured by spiking authentic standards into distilled water and carrying the water through the extraction/ concentration step.

RESULTS AND DISCUSSION

The method presented in this paper involves a solvent partition extraction/concentration step followed by separation of the carboxylic acids by reverse-phase HPLC and conductivity detection. Initially, it was anticipated that aqueous samples could be analyzed directly. However, any aqueous sample containing inorganic salts produced a "solvent peak" which completely obscured the formic and acetic acid peaks. Therefore, solvent partition was used as a means of excluding these interferences, and in addition concentrating the aqueous sample prior to analysis. Diethyl ether was chosen as the organic solvent because of its high volatility, good partition characteristics and ability to exclude the inorganic interferences. Recovery of standard solutions of the various acids when carried through the extraction/concentration procedure are shown in Table 1. The recovery was measured by comparing the areas of the peaks to those of the standard compounds. The sensitivity of the method is approximately 10 µg/ml acetic acid and 100 µg/ml octanoic acid in the final isolate. In order to improve the accuracy of the analytical procedure, authentic standards were prepared to closely match the samples and carried through the same extraction/ concentration procedure as the samples. These extracted/ concentrated standards were then used for calibration (external standardization).

The chromatograms obtained from authentic standards of the C_1-C_8 carboxylic acids are shown in Figure 1. The C_1-C_4

TABLE 1

Efficiency of Diethylether Extraction

Analyte	Level(mM)	Recovery
formic acid	3	50
acetic acid	3	70
propionic acid	3	85
butyric acid	3	>90
pentanoic acid	6	>90
hexanoic acid	6	>90
heptanoic acid	6	>90
octanoic acid	6	>90

acids are eluted using water as the mobile phase. Even this weak mobile phase does not provide for retention of the formic acid, although an estimate of formic acid concentration can still be made. The retention times of the C_7 and C_8 acids are inordinately long using water, however, and it was more expedient to reinject the sample at a mobile phase strength of 50/50 water/methanol. Gradient elution was of limited utility because of the baseline drift of the conductivity detector as the mobile phase methanol concentration was varied. Depending on the specific analytes of interest, the mobile phase strength can be varied within these limits in order to achieve optimum resolution in a minimum time. Acids of higher molecular weight than C_8 show diminished response in conductivity detection. The asymetric peaks are due to the low capacity of the ODS column for such polar compounds, although this does not affect the precision of the determination.

Several aqueous matrices were analyzed for the C_1-C_8 acids, to evaluate the limitations of the method as well as to provide data on the levels of these compounds in the samples (Table 2). The analysis of a coal liquefaction process water indicated that the major component was acetic acid, with the higher homologs occurring at decreasing levels. This sample contained approximately 5 mg/ml total phenols (which would be carried through the

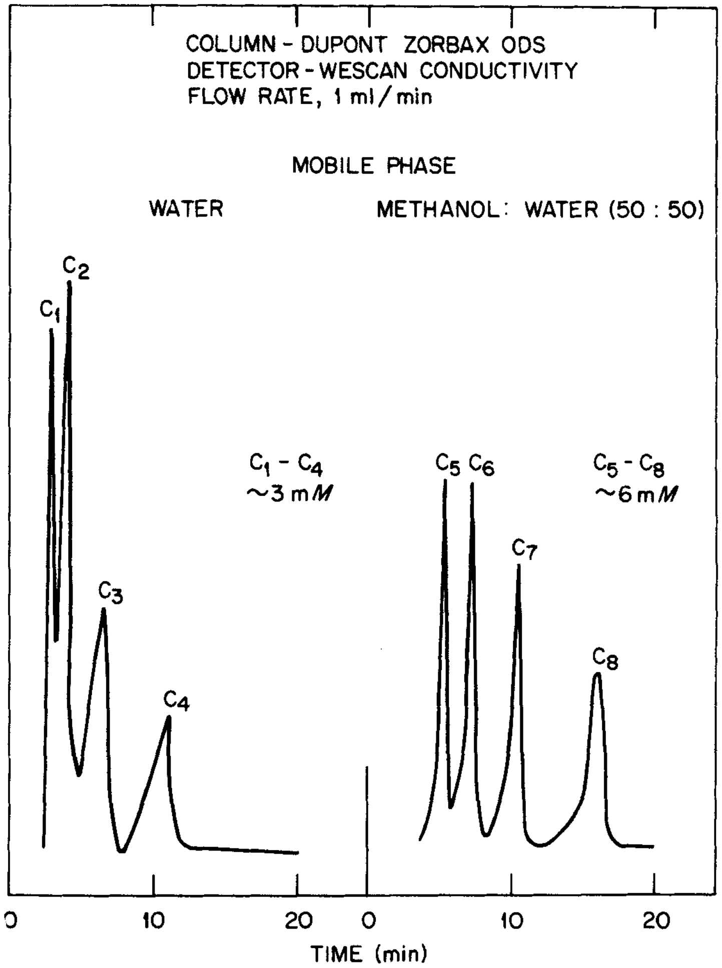

FIGURE 1. Separation of Carboxylic Acids

TABLE 2

Typical Carboxylic Acid Values for Various Aqueous Samples

Sample Type	Method	n		Concentration of Acid, mg/ml					
			C_2	C_3	C_4	C_5	C_6	C_7	C_8
Coal Liquefication Process Water	HPLC	1	0.09	0.05	0.03	0.02	0.01	--	--
Municipal Refuse Leachate	HPLC	1	0.06	0.05	0.24	0.33	0.77	0.15	0.40
Shale Process Water	HPLC	6	0.58 ± .05	0.15 ± .02	0.10 ± .01	0.13 ± .02	0.16 ± .03		--
Independent Analysis of Shale Process Water	GC [(a)]		0.60	0.21	0.13	0.20	0.25		--

(a) Reference 6

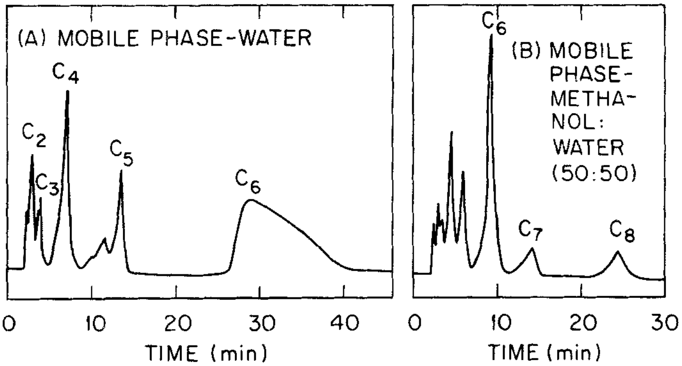

FIGURE 2. Carboxylic acid profile from municipal refuse leachate. Mobile phase flow rate 1 ml/min.

extraction/concentration step) yet no interference was noted. The weak mobile phase results in long retention times for phenols, which in any case do not produce a response with the conductivity detector.

The oil shale process water was chosen because comparative data on the levels of the acids had been generated by an independent method (6) which would serve as an evaluation of the accuracy of this method. As shown in Table 2, the agreement between the method developed here and direct-injection GC is reasonably good, although the levels of the acids in this sample were fairly high. Also as noted from the analysis of this sample, the precision of the method is best for the stronger (C_2, C_3, C_4) carboxylic acids for which the conductivity detector is most responsive. The average overall precision for the method, however, is about ± 13%. The analysis of the municipal refuse leachate (Figure 2) revealed that the levels of carboxylic acids increased with increasing carbon number up to C_6, with fairly high levels of C_8 as well. While this trend may be particular to this sample, the importance of the higher molecular weight acids in solublizing nonpolar landfill constituents (e.g. waste oils) cannot be overlooked. The samples examined here had relatively high levels of carboxylic acids. Lower levels could be detected by using larger amounts of water.

In conclusion, a method has been developed for the determination of C_1-C_8 carboxylic acids in water and wastewater which combines an extraction/concentration step with analysis by reverse phase HPLC and conductivity detection. The method has an overall precision of about ± 13%. The method is essentially free of conducting interferences (inorganic ions), by virtue of the extraction step, and is also free of weakly conducting interferences (organic compounds) by virtue of the relatively weak mobile phase system.

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