

Gas Chromatographic Determination of Organic Compounds in River Water

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Introduction

There is interest in determining the concentrations of organic compounds in river water as is evidenced in a recent report in which a study on ninety-nine compounds is given (11). Our paper reports on the analysis of nine organic compounds in Embarrass River water samples taken at Lawrenceville, Illinois. The Embarrass River rises in Champaign County, Ill., and flows in a southerly direction to Newton. It then flows southeast to join the Wabash River near St. Francisville at the Indiana-Illinois border, about sixty miles north of the confluence of the Wabash and Ohio Rivers.

Experimental

Between fall 1975 and spring 1977, sixteen grab samples of 2.5 l each were collected from the central channel of the Embarrass River. The concentrations of nine organic compounds were determined in these samples using liquid-liquid extraction followed by gas chromatography.

Liquid-liquid extraction has been widely used with a variety of solvents. The choice of solvents used depends upon the type of organic compounds of interest. To extract petroleum products from natural water, Dell'Acqua *et al.*, (3, 4) and Garza and Muth (5) used hexane as the solvent. Adams (1) used a similar procedure with hexane to determine petroleum products in waste water. Jeltet (9) and Jeltet and Veldink (8) used nitrobenzene for the extraction of gasoline and diesel fuel from polluted ground water. They used carbon tetrachloride for extraction of heavier petroleum fractions. However, they found that carbon tetrachloride, ether, and carbon disulfide were not suitable for gasoline determinations. Novak *et al.* (10) reported that both carbon tetrachloride and nitrobenzene were not suitable to extract organic substances from polluted drinking water. Boylan and Tripp (2) used pentane in their determination of crude oil solubility in sea water. Pentane was also used by Grob *et al.*, (6) to analyze tap and natural water for a wide variety of organic compounds. Warner (12) has recently reported the use of ether extraction for the determination of petroleum components. To show the relationship between urban storm-water runoff and organic contaminants in river water, Hites and Biemann (7) used methylene chloride as a solvent. A wide variety of solvents have been and are being used for the extraction of organic compounds in water, as can be seen by the above examples.

Our choice for the extraction solvent was 1,2,3,4-tetrahydronaphthalene (tetralin). Samples collected from the surface of the central chan-

nel of the river were transferred immediately into clean glass bottles equipped with foil-lined caps. Samples were extracted in the glass bottles in which they had been obtained. Ten ml of tetralin was added to the sample along with 1 ml concentrated sulfuric acid and 5 g sodium chloride. Samples were shaken for 2 minutes. The two layers were separated by use of a separatory funnel. After the water had been drawn off, the tetralin layer was filtered through glass wool, previously washed with tetralin, into a separatory funnel. The glass wool was used to break the emulsion formed. The water was again placed in the bottle and an additional 10 ml of tetralin was added. The procedure was then repeated and the volume of the sample was measured after the second extraction. The tetralin portions were combined in the separatory funnel and any additional water separated was removed. The tetralin was then dried for 15 minutes over anhydrous calcium chloride and transferred to a 25 ml volumetric flask and diluted to 25 ml. Ten μ l of this sample was injected into a gas chromatograph for analysis. The tetralin used was Fisher purified, which had been dried and distilled twice. All other reagents were ACS grade.

Instrumentation

A model 5711-A Hewlett-Packard gas chromatograph was used. It was equipped with a dual flame ionization detector and a linear temperature programmer. The columns used were matched 12 ft. x $\frac{1}{4}$ in. O. D. stainless steel, packed with 5% of SE-30 (silicone gum rubber) on 80-100 mesh high performance acid-washed dimethyldichlorosilane treated chromosorb G. The recorder used was a Houston Instrument Omni-Scribe dual pen recorder with a built-in integrator. Gas flows were 60 ml/minute for hydrogen, 240 ml/minute for air, and 60 ml/minute for the carrier gas helium. Conditions used were as follows: column oven, initial temperature 40°C, final temperature 130°C; rate of heating 16°C/minute; initial time 8 minutes, final time 16 minutes; injection port temperature 150°C; and detector temperature 150°C.

Results and Discussion

The maximum concentration detected and the number of samples in which each of the compounds was detected are given in Table I. The compounds are listed according to the order of their retention times with toluene eluting last. Pentane and hexane were detected at the highest concentrations, and the average concentrations were calculated to be 1.3 and 1.7 ppb, respectively. In 15 samples, 1-hexene, 2-hexene, and cyclohexane were detected, and the averages were 0.5, 0.4, and 0.6 ppb, respectively. For the 14 samples where cyclohexene was detected, the average was 1.3 ppb. Averages for the five samples in which heptane, methylcyclohexane, and toluene were detected were 1.1, 1.1, and 1.4 ppb, respectively.

Nine organic compounds were readily detected and quantitated by our methods. The Embarrass River drains much of an area in southern Illinois having crude oil production. The possible sources for these compounds could be runoff from numerous oil wells in the area and

possibly biological activity or other natural sources. The results obtained indicated that our analytical methods and techniques are useful for determining concentrations as low as 0.1 ppb.

TABLE 1. *Maximum concentrations in parts per billion of nine selected organic compounds in Embarrass River water samples and number of samples in which the compounds were detected.*

Compounds	Max. concn ppb	No. of samples detected in (16 possible)
pentane	4.7	16
1-hexene	2.6	15
hexane	7.7	16
2-hexene	1.6	15
cyclohexane	2.3	15
cyclohexene	2.8	14
heptane	3.6	5
methylcyclohexane	3.0	5
toluene	2.5	5

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