

## **Analysis of Organic Compounds in Water Samples by Gas Chromatography—Mass Spectrometry**

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### **Introduction**

Steadily rising industrial output and rapid population growth have deteriorated the quality of the water environment in many of the nation's lakes, rivers and ground water. In recent years widespread interest has been focused on the determination of trace organic compounds in water. This is primarily due to the evidence that some of the organic compounds that are continuously being discharged into the nation's streams and rivers are harmful.

The purpose of this study was to determine the presence of volatile organic compounds in selected water samples. Samples were collected from places where a certain degree of water pollution was suspected. These samples included well water from several places in Indiana; Wabash River water; Deming, Dobbs, and Fowler Park lake water; Sewage Treatment Plant water; and tap water.

### **Experimental**

Water samples were analyzed for volatile organic compounds by a purge and trap method. This method utilizes gas bubbles to transfer organic compounds from the aqueous phase to gaseous phase by bubbling helium gas through the water samples. These organic compounds are then transported by the helium gas into a porous polymeric trap where the trap adsorbent retards and concentrates the purged compounds while the helium gas is vented. The compounds are then transferred into the gas chromatograph for analysis by backflushing the trap at elevated temperature (180°C).

The purge and trap equipment consisted of a purging device, trap column, and desorber. The purging device was a 500 ml gas-washing bottle equipped with a ground glass joint and a 20 mm medium fritted disc at the end of the glass tube to disperse the purging gas. The inlet and exit ports were made of a 1/4" O.D. glass tubing which permitted leak-free removable connection with tygon tubing. At the inlet end, the tygon tubing was connected to the helium gas line by a 1/4" O.D. copper tubing. At the exit end, the tubing was attached to a trap column.

The trap columns were made of 1/4" O.D. stainless steel tubing of about 140 mm length. These columns were also provided with exchangeable Swagelok fittings, enabling the columns to be connected to gas line copper tubing during thermal desorption and conditioning of the traps. These trap columns were packed with glass wool at both ends. The central portion contained Tenax-GC (2,6-diphenylene oxide) and silica gel packings.

The desorber consisted of a heating mantle which was regulated by a temperature controller unit. Optimum heating setting of this controller was found by experimentation. For quantitative desorption it was necessary to heat the trap column as quickly as possible to 180°C without exceeding the thermal stability limit of the column packing.

The GC-MS system consisted of a Hewlett-Packard model 5712A gas liquid

chromatograph and HP 5930A quadrupole mass spectrometer. The gas chromatograph was equipped with a model 5705A thermal conductivity detector and a 5702A model temperature controller. The columns used were matched 6 ft x 1/8 in. O.D. stainless steel, packed with methyl vinyl siloxane, UCW-98, on 80-100 mesh Chromosorb G acid washed with dimethyl dichlorosilane. The recorder used was a Hewlett-Packard 7127A recorder set at 1 inch/min.

The gas chromatograph operating conditions were as follows:

Helium -- 40 psi	Column Oven Temperature:
Nitrogen -- 50 psi	Initial -- 60°C for 2 min
Injection Port Temperature--250°C	Rate -- 8°C/min
Detector Temperature --250°C	Final --200°C for 16 min
Sensitivity -- 5	
Attenuation -- 2	

The molecular separator used in this system between the gas chromatograph and mass spectrometer was a silicone semi-permeable membrane.

The mass spectrometer operating parameters were as follows:

Electron Energy -- 70V	Gain	-- 3
Emission Current -- .3 mA	Mass Filter Temperature	-- 100°C
Ion Focus -- 40 V	Ion Source Temperature	-- 250°C
Repeller Potential -- 28 V	Scan Speed	-- 20
Analyzer Pressure -- $1.2 \times 10^{-6}$	Bandwidth	-- 73
Mass Range Setting -- 30-250	Volt/Div	-- 0.2

Prior to daily use, the Tenax traps were conditioned by placing the trap inside a heating mantle that was regulated to heat constantly at 180°C. The exit end of the trap was connected to the helium gas line by a Swagelok teflon fitting and a 1/4" O.D. copper tubing. The traps were conditioned for 30 minutes with 10 psi helium passing through. The traps were cooled and were ready for purging and trapping. A 300 ml sample was poured into the purging device. The Tenax trap inlet was attached directly to the purging device exit using tygon tubing. The helium gas line was connected to the device inlet using Swagelok nylon fittings, 1/4" copper tubing, and tygon tubing. 20 psi helium gas was bubbled through the sample for 15 minutes to transfer the volatile organics from the sample to the trap, where the organics were adsorbed by the trap packing. The trap was then removed from the device, sealed with caps, and placed in a 4°C cooler until it was used.

The next step was desorption and analysis. The gas chromatograph was cooled to 30°C by leaving the oven door open. The caps were removed from the Tenax trap containing the sample, and a 22 gauge needle was attached to the end of the trap. The trap was then inserted into a heating mantle that had been preheated to 180°C and regulated to stay at that temperature. The other end of the trap was connected to the helium gas line by a nylon Swagelok fitting. The trap needle was immediately inserted into the injection port septum of the gas chromatograph and the hot trap was backflushed with 40 psi helium for 3 minutes.

After desorption and sample transfer was complete, the needle was removed from the injection port, the oven door was closed, and the gas chromatograph column oven was rapidly heated to the initial operating temperature of 60°C. This temperature was maintained for 2 minutes; then the oven was heated at a rate of 8°C per minute to a final temperature of 200°C. The oven was kept isothermally at 200°C for 16 minutes. As each organic compound was eluted from the column, a mass spectrum was taken.

### Results and Discussion

Some well water samples were taken from Seymour, Indiana. For a period of twelve years, more than 60,000 drums of chemical wastes were stored in Seymour's Freeman Field Industrial Park by the Seymour Recycling Corporation. Most of these drums were rusty, and chemical wastes leaked out of the corroded drums. Some residents feared that chemicals might have seeped through the ground to pollute the ground water beneath the park and to contaminate nearby private wells as well (2). Removal of the drums was proceeding during 1982(1).

During 1980 and 1981, samples were collected from wells within one to two miles of the dump site. A definitive spectrum for toluene was obtained from some of the samples. Other spectra gave no definite results although 1-methyl naphthalene, 1,2-dimethyl naphthalene, and 1-1-biphenyl were possibly indicated. Other spectra obtained from the samples could not be matched with reference spectra.

During 1981, Deming Park Lake, Dobbs Park Lake, and Fowler Park Lake—all in the Terre Haute area—were sampled. Toluene and 1,2-dichloropropene were found to be present in the Deming Park Lake sample. Benzeneacetonitrile methylene was indicated in a Dobbs Park Lake sample. Other spectra could not be matched with reference spectra.

The mass spectra from some samples of Wabash River water showed the presence of 1-ethyl-3-methyl-benzene. Other spectra obtained from Wabash River water could not be matched with reference spectra.

Samples from the Terre Haute Wastewater Plant gave spectra indicative of 3,3-dichloropropene, 1,2-dichlorobenzene, toluene, 1,4-dimethylbenzene, tetrachloroethane, 1-(1-propynyl)-cyclohexane, and other compounds that could not be identified.

Terre Haute tap water was also sampled. Most of the samples gave a few spectra with small peaks that could not be identified. However, one sample gave spectra quite indicative of dibromomethane and dibromochloromethane.

The conclusion was reached that this method allows detection of volatile organic compounds in water samples at the parts-per-billion level, but that matching of spectra with reference spectra is difficult and may sometimes be complicated because two or more compounds may elute from the gas chromatograph at nearly the same time. Nevertheless, the method is very sensitive and some spectra are quite definitive.

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