

## Conclusion

The discovery of the effect of dissociation and excitation of high-lying vibrational states of polyatomic molecules by intense IR radiation has made it possible to investigate many hard-to-solve problems:

(1) Excitation of high vibrational levels with energies of several electron volts.<sup>3</sup> However, we have to devise some techniques for excitation of particular high vibrational levels without distributing the molecules over many vibrational levels. In principle, it is possible to solve this problem by combining the effects of triple rotational-vibrational resonance in comparatively weak fields with the influence of very strong IR pulses on excited molecules.

(2) Investigation of spontaneous transitions between highly excited vibrational states, in particular, collision-less intramolecular  $v-v$  relaxation. The first successful experiments of the kind have been conducted on  $\text{OsO}_4$  molecules.<sup>31</sup>

(3) The studies of transition paths between the vibrational levels higher than  $v = 1$ . The PQR transitions discussed above are, of course, the simplest transition of this type, and to get a full picture of the transitions one needs further theoretical investigations.

The investigation of stimulated transitions between highly excited vibrational levels makes it possible to obtain information about the absorption coefficients, transition cross sections, and level densities in the "vibrational quasi-continuum". The action of a two-frequency IR field on molecules is a standard method of such measurements.

(31) R. V. Ambartsumian, N. V. Chekalin, Yu. A. Gorokhov, V. S. Letokhov, G. N. Makarov, A. A. Puztzkii, and N. P. Furzikov, *Pis'ma Zh. Eksp. Teor. Fiz.*, **23**, 217 (1976); R. V. Ambartsumian, N. V. Chekalin, Yu. A. Gorokhov, V. S. Letokhov, G. N. Makarov, and E. A. Ryabov, *Laser Spectroscopy, Proceedings of the Second International Conference, Megeve, France, June 23-27, 1975 (Lect. Notes Phys., 43, 121 (1975))*.

(4) Excitation of molecular electronic states due to transfer of the vibrational energy of highly excited molecules in the ground electronic state to the energy of electronic excitation (V-E process) and further increase of molecular vibrational energy caused by stimulated transitions in the vibrational quasi-continuum of an excited electronic state and molecular absorption of energy which is much higher than that of molecular dissociation.

(5) Investigations of the ways how bonds are broken in polyatomics in strong IR fields and the composition of resultant fragments (the first experiments on IR photolysis show that its products differ essentially from those of UV photolysis)<sup>32</sup> and search for cases of dissociation into saturated simple molecules which are characterized by high selectivity of secondary photochemical processes. The full information about these processes can be obtained in experiments on molecular beams and from probing molecular fragments by laser radiation, as has been lately done on  $\text{NH}_3$  molecules<sup>33</sup> and  $\text{C}_2\text{H}_4$  molecules.<sup>34</sup>

(6) Study of other unimolecular processes with highly vibrationally excited molecules, in particular, the process of isomerization. Successful experiments on the trans-cis transition of  $\text{C}_2\text{H}_2\text{Cl}_2$  molecules have been performed.<sup>35</sup>

*We express our deep appreciation to our colleagues from the Institute of Spectroscopy, Academy of Sciences USSR, Dr. N. V. Chekalin, Dr. Yu. A. Gorokhov, N. P. Furzikov, A. A. Makarov, A. A. Puretsky, and E. A. Ryabov, who had obtained all the experimental results discussed above.*

(32) R. V. Ambartsumian, N. V. Chekalin, V. S. Letokhov, and E. A. Ryabov, *Chem. Phys. Lett.*, **36**, 301 (1975).

(33) J. D. Campbell, G. Hancock, J. B. Halpern, and K. H. Welge, *Opt. Commun.*, **17**, 38 (1976).

(34) N. V. Chekalin, V. S. Doljikov, V. S. Letokhov, V. N. Lokhman, and A. S. Shibanov, *Appl. Phys.*, in press.

(35) R. V. Ambartsumian, N. V. Chekalin, V. S. Doljikov, V. S. Letokhov, and V. N. Lokhman, *Opt. Commun.*, **18**, 400 (1976).

# Concentration of Solutes from Aqueous Solution

James S. Fritz

Ames Laboratory—ERDA and Department of Chemistry, Iowa State University, Ames, Iowa 50011

Received September 15, 1976

Drinking water is commonly analyzed for biological organisms, hardness, pH, etc., but until recently little has been known about soluble organic material in water. Organic contaminants can impart a bad taste and odor to water. The effect of organic impurities on health is largely unknown, although a statistical link with incidence of cancer has been established for New Orleans

water.<sup>1</sup> There is considerable interest in establishing what organic contaminants are actually present in various drinking water samples and in looking for ways to improve the quality of our drinking water with regard to organic impurities.

Analysis of waste water effluents for organic compounds is vital if industries are to meet environmental standards. There is also considerable interest in determining organic compounds in other types of aqueous samples. Groups such as those of Zlatkis at Houston<sup>2</sup>

James S. Fritz was born and educated in Illinois, receiving a Ph.D. from the University of Illinois in 1948. After 3 years at Wayne State University he moved to Iowa State University, where he is now Professor of Chemistry and Senior Chemist in the Ames Laboratory of ERDA. He is an analytical chemist, interested especially in methods of achieving chemical separations. The water analysis research group at Iowa State is headed jointly by the author and by Professor H. J. Svec.

(1) B. Dowty, D. Carlisle, and J. L. Laseter, *Science*, **187**, 75 (1974).

(2) A. Zlatkis, W. Bertsch, H. A. Lichtenstein, and F. Shunbo, *Anal. Chem.*, **45**, 763 (1973).

and Scott at Oak Ridge<sup>3</sup> are making a major effort to diagnose various diseases by noting variations in the chromatographic profile of organic substances in human urine. However, this Account will be concerned primarily with concentration and determination of organic substances in drinking water.

The analytical problem is formidable because of the extremely low concentrations of most organic impurities in drinking water. The general types and concentrations of organic matter that have been found thus far in water are: (1) nonvolatile organics, probably humic material, 1–5 mg/L; (2) gas chromatographable organic compounds, 0.5–3  $\mu\text{g/L}$ ; (3) chloroform and chlorobromohalocarbons, 1–300  $\mu\text{g/L}$ . It is likely that other kinds of organic material will be reported in the near future. For example, the widespread occurrence and relatively high concentration of chloroform and related halocarbons in chlorinated drinking water have only been known since about 1975.<sup>4</sup>

Humic material is naturally present in practically all water and should probably not be considered as a contaminant. Industrial pollutants and foreign organic substances that may be formed in the water during treatment (such as halocarbons resulting from chlorination of humic matter) are of greater interest. These substances are generally present in parts per billion or sub parts per billion concentrations. Analysis of water for such low concentrations is usually impossible without a preliminary concentration step. The magnitude of the analytical task might be dramatized by considering one way of preparing a solution of 1 ppb concentration. This would be to add 5 or 6 drops of an organic compound from a medicine dropper to the water in a swimming pool 30  $\times$  50 ft, 5 ft deep, and to mix well!

I was introduced to the problem of determining trace organic compounds in water by Dr. Vincent Calder in 1970. He was trying to identify the organic compounds responsible for occasional taste and odor problems with the drinking water of Ames, Iowa. Some of the wells supplying the city were believed to be contaminated by leaching residues from a coal gas plant that operated until the early 1920's. Positive colorimetric tests for phenols had been obtained, so phenols were believed to be the class of compounds causing the problem. My graduate student, Raymond Willis, was working on chromatographic separation of phenols using Rohm and Haas XAD-7, a macroporous polyacrylate resin, so we suggested the use of XAD-7 for concentrating phenols from the Ames water. Our collaboration with Calder and his student, Alan Burnham, produced a resin sorption method for concentrating organic impurities from water and a gas chromatographic procedure for separating the impurities from each other. Studies showed that the method worked well for several classes of organic compounds, not just for phenols.

Using this procedure, we concentrated and separated several odorous contaminants from the Ames wells. The pronounced odor of the separated substances emerging from the exit port of the gas chromatograph left no doubt that we had isolated the responsible materials. Attempts to identify these substances by

Table I  
Neutral Compounds Found in a  
Contaminated Ames, Iowa, Well

Acenaphthylene	Ethylbenzene
1-Methylnaphthalene	Naphthalene
Methylindenes (two isomers)	2,3-Dihydroindene
Indene	Alkyl-2,3-dihydroindene
Acenaphthene	Alkylbenzenes
Benzo[ <i>b</i> ]thiophene	Alkylbenzothiophenes
Isopropylbenzene	Alkyl-naphthalenes

fraction collection and examination by infrared or ultraviolet spectroscopy failed completely. We did not have enough sample, and there were too many possible organic compounds.

At this juncture we sought help from Dr. Harry Svec and Gregor Junk. In a short time they had identified the major water impurities by GC-mass spectroscopy. These are listed in Table I. It is interesting to note that no phenols were found in the water. The earlier colorimetric tests for phenols were apparently false. Our first paper containing these results and outlining an analytical procedure for concentrating and determining gas chromatographable organic compounds in water was published early in 1972.<sup>5</sup> Continuing work by our joint group at Iowa State, by several groups within the EPA, Grob and Grob in Switzerland, Hites at MIT, Rook in Rotterdam, and others have now provided data on organic substances in drinking water and working analytical procedures for their concentration and quantitative estimation.

This Account will review some of the major analytical approaches for concentrating trace organic substances from water prior to their separation by gas chromatography. For purposes of illustration a few (of many possible) results on analysis of drinking water will be included. This review is intended to be selective (rather than comprehensive) and emphasizes the author's own results and philosophy of analysis.

### Resin Sorption Method

The essential parts of this procedure for concentrating organic compounds from water are:<sup>6</sup>

(1) Sorption. A water sample ranging from 1 L up to 100 L or more is passed rapidly through a column containing a bed about 1 cm  $\times$  10 cm of XAD-2 macroporous resin.

(2) Elution. The sorbed organics are eluted with 25–30 mL of ethyl ether.

(3) Drying and evaporation. The water in the ether effluent is frozen out and the ether is evaporated carefully to 1 mL in a special apparatus.

(4) Separation. A 2- $\mu\text{L}$  aliquot of the ether is injected into a gas chromatograph and the individual organic solutes are separated.

(5) Identification. The solutes in an aliquot of the ether are identified by GC-mass spectroscopy.

This procedure has been thoroughly tested on nearly 100 model organic compounds added to water and has been found to give excellent recoveries of chromatographable compounds. Acidification of the water sample is necessary to convert carboxylic acids and

(3) C. D. Scott, *Science*, **186**, 226 (1974).

(4) U.S. Environmental Protection Agency, "Region V Joint Federal/State Survey of Organics and Inorganics in Selected Drinking Water Supplies", Government Printing Office, Washington, D.C., June 1975.

(5) A. K. Burnham, G. V. Calder, J. S. Fritz, G. A. Junk, H. J. Svec, and R. Willis, *Anal. Chem.*, **44**, 139 (1972).

(6) G. A. Junk, J. J. Richard, J. D. Grieser, D. Witiak, J. L. Witiak, M. D. Arguello, R. Vick, H. J. Svec, J. S. Fritz, and G. V. Calder, *J. Chromatogr.*, **99**, 745 (1974).

phenols to the molecular form and thus obtain good recoveries. The XAD-2 resin is nonionic and sorbs neutral organic compounds while allowing inorganic ions and ionized (or highly polar) organic substances to pass through the column.

For any satisfactory analysis at the trace level careful attention must be paid to experimental detail, and this procedure is no exception. First of all the XAD resin must be carefully purified to avoid an appreciable blank from naphthalene, ethylbenzene, benzoic acid, and other impurities that are initially in the resin itself. These are best removed by sequential Soxhlet extraction of the resin with methanol, acetonitrile, and ethyl ether. Once pure, the resin should be kept under methanol to avoid sorption of organic impurities from the atmosphere. (Also, if the resin becomes thoroughly dry, cracks and fissures can appear and allow more impurities to be leached out.)

Proper handling of water samples is also essential. Screw-capped glass bottles are satisfactory, but they must be thoroughly cleaned and free from grease; a few traces of grease on the bottle walls can sorb a significant percentage of the organic substances from the water. Some organic compounds (cumene, for example) added to water at the low parts per billion level form a surface film and may be lost by evaporation during the time it takes for the water to pass through the XAD-2 column. This error is avoided by capping the reservoir during the sorption step and using slight nitrogen pressure to force the water through the column.

Finally, the design of the glassware used in the ether evaporation step is critical. With some glassware losses of the order of 50% often occurred during the ether evaporation. To avoid loss the walls of the glassware must be continuously washed down by condensing ether vapor. At the end of the evaporation a final washdown is achieved by washing the outside of the apparatus with acetone and thus condensing the ether vapor inside.

The resin sorption procedure is dependable and gives good recovery of a large variety of organic compounds. A major drawback is that volatile organic compounds are partially or completely lost during the ether evaporation step. Another disadvantage is that only about  $1/500$ th of the ether concentrate is used for the actual gas chromatographic separation.

### Solvent Extraction

Extraction with an immiscible organic solvent such as pentane has been used for some years to concentrate organic solutes from water. Grob et al.<sup>7</sup> extract 1 L of water with only 200  $\mu$ L of pentane. This is carefully drawn off with a syringe and then shaken to separate the small amount of water that accompanies the pentane. The pentane extract is evaporated to 3  $\mu$ L, and this entire amount is injected into a gas chromatograph equipped with a capillary column.

Extraction has the virtue of simplicity. It works quite well for pesticides and aliphatic hydrocarbons, but only a low percentage of several classes of organic compounds are extracted. Losses of more volatile compounds occur during evaporation of the extracting solvent. For trace analysis impurities in the solvent itself can be a limiting factor.

Solvent extraction provides the basis of a very simple method of determining halocarbons in drinking water.<sup>8</sup> A 10-mL water sample is extracted with 1 mL of purified pentane. An aliquot of the pentane extract is then injected into a GC equipped with an electron-capture detector. Extraction of the various halocarbons ranges from about 80 to 96%, but the percentage of each substance extracted is reproducible over the concentration range usually encountered in drinking water.

### Water-Gas Distribution

The principle of this method is very simple: a water sample is shaken with a definite volume of a gas, and the solutes become distributed between the two phases. Helium, nitrogen, or even air can be used as the gaseous phase. High volatility and low water solubility cause solutes to strongly favor the gas phase.

In the method of McAuliffe<sup>9</sup> a water sample is shaken with nitrogen or helium in a glass syringe. Then a portion of the gas is injected into a gas chromatograph and the organic solutes are separated. Aliphatic hydrocarbons below about C<sub>10</sub> are >98% in the gaseous phase in a single equilibration. Aromatic hydrocarbons require several equilibrations for quantitative transfer to the gaseous phase; however, a linear plot of peak height vs. equilibration number can be extrapolated to calculate the amount of organic in the initial water sample.

An adaptation of this method<sup>10</sup> provides a convenient way to determine volatile halocarbons in water. After a single equilibration, an aliquot of the gas phase is injected into a gas chromatograph and the halocarbons are separated and detected with an electron-capture detector. Although transfer of the organic substances to the gas is far from quantitative, a reproducible percentage of each halocarbon is extracted into the gaseous phase.

### Gas Stripping

This is essentially a multiple equilibration technique in which a gas is bubbled continuously through the aqueous sample for a given period of time. The gas then passes through a sorbing material that retains the organic compounds but allows most of the water vapor to pass through. Zlatkis, who termed this technique "head-space" analysis, used a small tube filled with Tenax resin to sorb organics from the gas stream.<sup>11</sup> This resin has excellent sorbing ability for most organic compounds but is quite hydrophobic and thus has little affinity for water vapor. The Tenax tube is connected to a gas chromatograph and the organic substances are thermally desorbed over a time period of 15–20 min and collected in a cold trap. Then the cold is removed and the various substances are separated in the GC.

Grob et al.<sup>7</sup> developed a unique stripping system in which a small volume of gas is bubbled repeatedly through the water sample in a closed system. A bellows pump is used for the circulation. A small disk of activated carbon in the system sorbs the organics from the gas stream. Eventually the sorbed compounds are washed from the carbon pellet with a small amount of

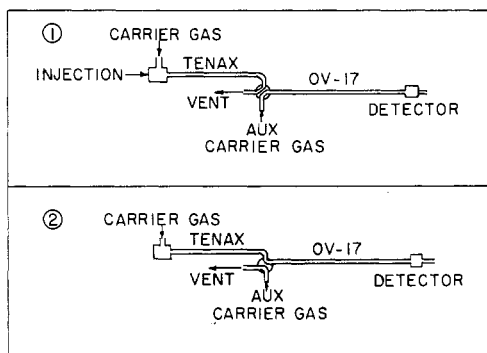
(8) J. J. Richard and G. A. Junk, *J. Am. Waterworks Assoc.*, submitted for publication.

(9) C. McAuliffe, *Chem. Technol.*, 1, 46 (1971).

(10) G. R. Umbreit, private communication, 1976.

(11) A. Zlatkis and H. A. Tishbee, *Chromatographia*, 6, 67 (1973).

(7) K. Grob, K. Grob, Jr., and G. Grob, *J. Chromatogr.*, 106, 299 (1975).



**Figure 1.** Switching valve arrangement for use with aqueous samples.

an organic solvent, and a portion of this solution is used for the gas chromatographic separation. When the water sample is heated to 75 °C and 2-h stripping is used, hydrocarbons up to C<sub>22</sub> can be volatilized from water with this technique.

Gas stripping has become very popular and works well for compounds that are somewhat volatile and are sparingly soluble in water. Low-boiling compounds that are very soluble in water may be incompletely volatilized. Low recoveries of such compounds may also be caused by incomplete retention by the Tenax tube. For example, one group of investigators obtained only about a 13% recovery for acetone.<sup>12</sup> Much of the work published using this technique has been mostly qualitative, so that the quantitiveness of the method is not clear for most organic compounds.

### Direct Injection

Water used to be considered as something that was best avoided in gas chromatography. Water tends to be adsorbed on many types of solid supports, resulting in large, tailed peaks. It can also cause stationary liquid phases to hydrolyze or bleed. However, several column packings have been developed that will tolerate small injections of aqueous samples. In principle direct injection of water samples is attractive because it is probably the simplest way to get *all* of a sample into the gas chromatograph. A limiting factor is the very small water sample (usually 1–3  $\mu$ L) that must be used.

In measuring the water solubility of a number of alkanes, alkenes, and aromatic hydrocarbons, McAuliffe<sup>13</sup> developed a unique chromatographic procedure. A "U" tube containing Ascarite is placed in the gas chromatograph between the injection port and the GC column. A rather large (50  $\mu$ L) water sample is injected. The Ascarite precolumn absorbs the water while allowing the hydrocarbons to pass rapidly onto the regular chromatographic column. The Ascarite has to be changed or regenerated after three 50- $\mu$ L injections. It is not known whether this technique would be applicable to other classes of organic compounds, or whether they would be sorbed or interact with the strong base in the Ascarite.

Our approach for direct injection of water samples has been to use a 4-port switching valve between a Tenax precolumn and a regular chromatographic column (Figure 1).<sup>14</sup> With the injection port at 200 °C

and the columns at room temperature a 50- $\mu$ L water sample is injected. After a 2-min wait another 50- $\mu$ L sample can be injected if desired. As many as six such injections have been used. There is an additional 5-min wait after the final injection to allow time for the rest of the water vapor to pass through the first Tenax column and through the vent. Then the switching valve is changed so that the two chromatographic columns are connected together and the oven temperature program is begun to effect a separation of the organic compounds. Good chromatograms were obtained with this procedure. Essentially quantitative recoveries were obtained for analysis of water containing 1.99 ppm of acetone and 9.0 ppm of benzaldehyde (50- $\mu$ L sample), and on a 300- $\mu$ L sample of water containing 3.0 ppb of carbon tetrachloride (electron-capture detector). This method is not sensitive enough for most analyses of drinking water for organic impurities, but it should be valuable for waste-water analysis.

### Resin Sorption–Pyridine Desorption

XAD resins provide a useful way to sorb organic solutes from extremely dilute aqueous solution, but a relatively large volume of organic solvent is needed to elute the organic compounds from the resin. The large solvent peak on the gas chromatogram often covers up or distorts some of the sample peaks. If an amine such as pyridine is used as the solvent, it is possible to avoid completely any solvent peak by use of a short abstractor column in the gas chromatograph. Chromosorb G coated with solid cupric chloride is very effective for removal of pyridine and other amines.<sup>15</sup> Removal is effective up to about 150 °C for most aliphatic amines and up to 180 °C for pyridine.

The effectiveness of the amine abstractor precolumn is shown in Figure 2 in which a mixture of aromatic hydrocarbons dissolved in pyridine is chromatographed with and without the abstractor. Tests on several classes of organic compounds showed that the abstractor column has very little effect on compounds other than amines. In water analysis this concept has been used in the determination of chloroform and other halocarbons.<sup>16</sup> A 250-mL water sample is passed through a small tube containing acetylated XAD-2 resin, and the sorbed organics are eluted with 2 mL of pyridine. An aliquot of the pyridine solution is injected into a gas chromatograph containing an abstractor precolumn and a  $m \times 4$  mm i.d. glass column packed with FFAP on Chromosorb W, electron-capture detector. Unlike some procedures, this method gives quantitative recovery of the halocarbons usually found in drinking water.

### Resin Sorption–Thermal Desorption

XAD resins are very effective in sorbing traces of organic solutes from drinking water. However, the earlier procedure<sup>6</sup> was deficient in that volatile compounds are lost during the ether evaporation, and only a small fraction of the ether extract can be injected into the GC. To avoid these drawbacks a procedure has been developed in which organic solutes which are sorbed on a resin are thermally desorbed directly into

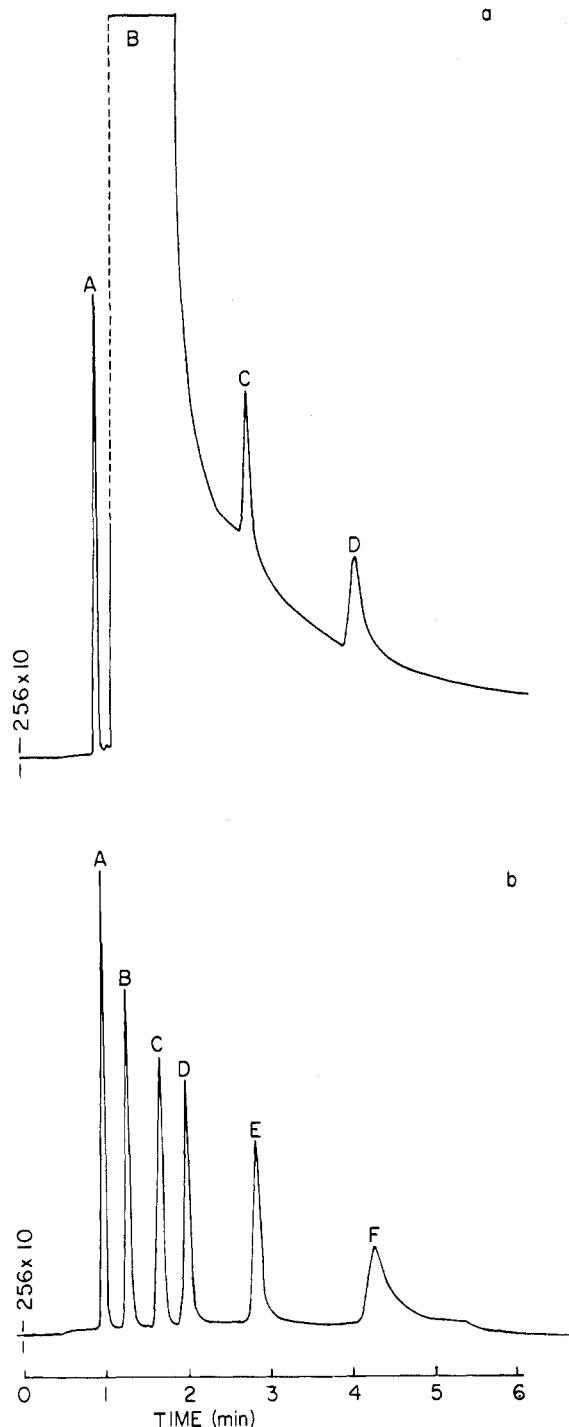
(12) W. Bertsch, E. Anderson, and G. Holzer, *J. Chromatogr.*, **112**, 701 (1975).

(13) C. McAuliffe, *J. Phys. Chem.*, **70**, 1267 (1966).

(14) R. C. Chang and J. S. Fritz, unpublished data, 1975.

(15) C. D. Chriswell, L. D. Kissinger, and J. S. Fritz, *Anal. Chem.*, **48**, 1123 (1976).

(16) L. D. Kissinger and J. S. Fritz, *J. Am. Waterworks Assoc.*, **68**, 435 (1976).



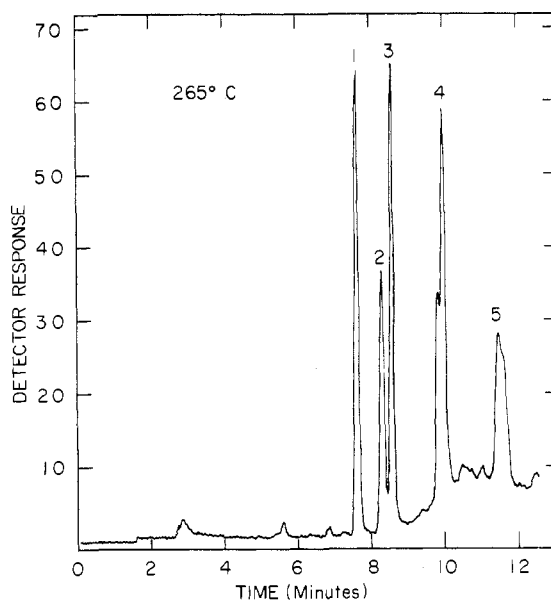
**Figure 2.** Chromatogram showing the effect of amine abstractor columns on the separation of aromatic compounds. (a) (A) benzene; (B) pyridine; (C) *n*-butylbenzene; (D) naphthalene. (b) (A) benzene; (B) toluene; (C) ethylbenzene; (D) isopropylbenzene; (E) *n*-butylbenzene; (F) naphthalene (from ref 15).

a GC. Such a method was suggested earlier by Mieure and Dietrich,<sup>17</sup> although they did not develop the method to any great extent.

The basic thermal desorption procedure<sup>18</sup> is outlined in Table II. Since all of the sorbed organic solutes from the water sample pass into the gas chromatograph, a much smaller water sample can be used than was feasible with the earlier procedure.<sup>6</sup> We force a 10- to 20-mL sample through the XAD-2 tube with a 20-mL

**Table II**  
Resin Sorption-Thermal Desorption Method

1. 10- to 20-ml water sample through XAD-2 tube (100 × 4 mm)
2. Desorb in heated injection port (15 min) onto Tenax tube
3. Insert Tenax tube into heated injection port. Separate organic compounds using 4 ft × 1/8 in. Tenax GC column. Temperature program: Room temperature, 5 min, heat to 90 °C and hold 1 min, 20 °C/min to 205 °C and hold



**Figure 3.** Gas chromatogram of model compounds by resin sorption-thermal desorption method. (1) Benzene, (2) *n*-octane, (3) toluene, (4) 2-octanone, (5) acetophenone.

glass syringe; this requires about 2 min. Desorption from the XAD tube onto the Tenax tube gets rid of most of the water entrained by the first tube because Tenax is known to have very little affinity for water vapor. (Attempts to dispense with the XAD tube and pass the water sample directly through a Tenax tube always gave low recoveries. XAD-2 appears to be superior to Tenax for sorption of organics from liquid water.)

The time and temperature required for desorption from the Tenax tube onto the GC column vary according to the volatility of the compound. For example, at 225 °C desorption of benzene is complete in about 2 min while naphthalene requires nearly 15 min. Desorption over several minutes is a long way from plug injection, which is supposed to be a cardinal requirement for gas chromatography. However, by having the GC column much cooler than the temperature of the Tenax tube and by using temperature programming, sharp, well-resolved peaks are obtained (see Figure 3).

A complete description of the resin sorption-thermal desorption method together with experimental results will appear in a forthcoming publication. In general very good quantitative recoveries have been obtained for several classes of organic compounds. Good recoveries are obtained for rather volatile hydrocarbons, chlorinated hydrocarbons and aromatic compounds, but lower molecular weight alcohols, ketones, and carboxylic acids are only partially retained by the resins and give lower recoveries. Compounds as high boiling as naphthalene give good results, but the method may not

(17) J. P. Mieure and M. W. Dietrich, *J. Chromatogr. Sci.*, 11, 559 (1973).

(18) R. C. Chang and J. S. Fritz, *Anal. Chem.*, submitted for publication.

Table III  
Ten Organic Compounds Found Most Frequently in the  
Drinking Water of Major U.S. Cities<sup>a</sup>

Diethyl phthalate	Butyl octyl maleate
Atrazine	Ionol
Naphthalene	Methyl benzoate
Dibutyl phthalate	Methylnaphthalene
Diisobutyl phthalate	Bis(2-ethylhexyl) phthalate

<sup>a</sup> Listed in order of frequency of occurrence.

be applicable to less volatile substances. Despite these limitations, this may be the most promising general procedure yet reported for concentrating and separating trace levels of organic compounds from water.

### Selected Results

In 1970 a tabulation showed only 66 neutral organic compounds that had been found in drinking water.<sup>19</sup> A survey of the literature made in 1975<sup>20</sup> listed around 400 organic compounds identified in drinking water, and the list seems destined to increase. From an extensive survey of the drinking water of U.S. cities,<sup>21</sup> the 10 most widely occurring impurities are listed in Table III.

The almost universal occurrence of chloroform and chlorobromomethanes in chlorinated drinking water has only been recognized since 1974 or 1975. An EPA survey of 79 cities conducted in 1975<sup>4</sup> found these chlorinated substances in every city surveyed. Furthermore, the concentrations reported ranged as high as ~300 ppb, which is more than 100 times the concentration of impurities of the type reported in Table III.

The likely source of chloroform and related compounds in water was shown by Rook<sup>22</sup> to be from chlorination of humic material that is naturally present in water. Rook's major experiments and conclusions may be summarized as follows:

- (1) Chlorine itself is not the source of halocarbons.
- (2) Chlorination of distilled water containing acetone or peat extract plus inorganic bromide produces chloroform and chlorobromomethanes.
- (3) Chlorine reacts with humic material to produce chloroform via the haloform reaction.
- (4) Inorganic bromide is oxidized by chlorine; the mixture of HOCl and HOBr acting on organic matter produces the compounds observed (CHCl<sub>3</sub>, CHCl<sub>2</sub>Br, CHClBr<sub>2</sub>, and CHBr<sub>3</sub>).

Work in the author's laboratory shows that many of the *quantitative* results reported for halocarbons in water<sup>16</sup> may have been considerably in error because the samples were not analyzed quickly enough. Our work shows that chlorinated water samples analyzed after 1 or 2 days storage always gave higher results for halocarbons than those that were analyzed immediately. A detailed study was performed in which samples of university tap water were stored for 7 days and analyzed daily for each of four halocarbons. The chloroform

(19) "Water Quality Criteria Data Book, Vol. 1, Organic Chemical Pollution of Fresh Water", U.S.E.P.A. Water Quality Office, Project No. 18010 DPV, December 1970.

(20) G. A. Junk and S. E. Stanley, "Organics in Drinking Water", IS-3671, July 1975.

(21) M. Avery, R. Vick, G. A. Junk, H. J. Svec, and J. S. Fritz, unpublished data, 1975.

(22) J. J. Rook, *Water Treat. Exam.*, **23**, 234 (1974).

Table IV  
Experiments on Haloform Production and  
Exchange Reactions<sup>a</sup>

Expt	Reactants	CH- Cl <sub>3</sub>	CH- BrCl <sub>2</sub>	CH- Br <sub>2</sub> Cl	CH- Br <sub>3</sub>
1	CHCl <sub>3</sub> , Br <sup>-</sup> , Cl <sub>2</sub>	+	+	+	+
2	CHCl <sub>3</sub> , Br <sub>2</sub>	+			
3	CHCl <sub>3</sub> , Br <sup>-</sup>	+			
4	CHCl <sub>3</sub> , Cl <sub>2</sub>	+			
5	CHBrCl <sub>2</sub> , Br <sup>-</sup> , Cl <sub>2</sub>		+	+	+
6	CHBrCl <sub>2</sub> , Br <sub>2</sub>		+		

<sup>a</sup> Concentration of reactants: Cl<sub>2</sub> and Br<sub>2</sub>, 5 ppm; Br<sup>-</sup>, 2 ppm; Cl<sup>-</sup>, 50 ppm; CHCl<sub>3</sub> and CHBrCl<sub>2</sub>, 5 ppb. Reaction time, 4 days.

concentration increased for 3 days to a maximum increase of 80% over the original, then decreased daily to about its original level. The two bromochloro-haloforms increased at first then gradually leveled off, but the concentration of bromoform increased steadily and had approximately tripled at the end of 7 days. A plot of the molar concentration of the total haloforms showed an initial increase in concentration, followed by a leveling and a slight decrease.

These results indicate a tendency for bromochloro or bromo compounds to be formed at the expense of chloroform. This is also supported by experiments with model compounds that showed that chloroform and bromodichloromethane can be converted slowly to more highly brominated haloforms under conditions similar to those existing in drinking water (Table IV).

### Future Developments

The compilation of even the *classes* of organic compounds in drinking water is certainly not complete. Although water has been chlorinated for years, the presence of chloroform and related compounds has been reported only recently. By reacting an extract with diazomethane to form methyl esters, we have found relatively high concentrations of several sulfonates and higher molecular weight carboxylic acids in river water.<sup>23</sup> It is likely that various amino acids, peptides, and carbohydrate compounds will soon be identified in river water and perhaps in drinking water.

Further improvement of analytical methodology will undoubtedly occur. Capillary GC columns are being used to obtain better resolution of the large numbers of organic compounds that are isolated by improved concentration techniques.<sup>7,12</sup> Improved sorbents are needed, especially resins that will sorb selectively various classes of organic compounds. Liquid chromatography may prove to have some advantages over gas chromatography, especially for less volatile compounds.

It is difficult to attack a problem intelligently until the problem itself has been clearly defined. The analytical methodology to do this is now available or should soon be available. Then the task will be to decide to what extent various organic impurities might be deleterious to health and what further steps should be taken to purify our water.

*This work was performed for the U.S. Energy Research and Development Administration under Contract No. W-7405-eng-82.*

(23) J. J. Richard and J. S. Fritz, unpublished work, 1976.