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TRACE ANALYSIS OF ORGANIC VOLATILES IN WATER BY GAS CHROMATOGRAPHY–MASS SPECTROMETRY WITH GLASS CAPILLARY COLUMNS

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SUMMARY

Traces of volatile organic materials in water have been concentrated by gas phase stripping and adsorption onto a porous polymer. A simple all-glass sampling device is proposed which allows efficient concentration at elevated temperatures. Sample transfer from adsorbent into a gas chromatographic column is effected by a simple one-step procedure involving heat desorption. The capacity of the adsorbent has been determined for a number of model substances which are found in water. Under the sampling conditions used, compounds being less volatile than benzene are usually quantitatively retained, with some exceptions.

Separations were effected with highly efficient glass capillary columns. Water samples, collected from a small number of locations, included both tap water and untreated waters. A number of volatiles have been determined by gas chromatography–mass spectrometry in drinking water and in a river which flows through an industrialized area. The drinking water examined contains a large number of chlorinated and brominated compounds whereas the river water is largely free from this class of substances. Derivatives of camphor and terpenes have been identified in this particular river.

INTRODUCTION

Increasing water usage in industrialized countries requires utilization of waters which have come into contact with man-made chemicals and effluents. Drinking water frequently has to be produced from heavily polluted streams, requiring extensive multistep treatment. Besides for human use, the quality of water has an important impact on all forms of life and needs to be monitored constantly.

Although complete analysis is desirable, limitations in analytical technology and economic considerations practically limit analysis to a few selected groups of substances and elements. The biochemist or bacteriologist has a different perspective

of water quality than the chemist or toxicologist, and all aspects have to be considered in the judgement of water for its fitness for various uses. In many cases, water analysis is limited to specific substances which have undesirable organoleptic properties or are contaminated by microorganisms. However, a growing list of industrial chemicals of confirmed or questionable pathological activity is constantly compiled and these compounds have to be considered in the analysis. Many efforts have been undertaken in the past to define the role of certain trace contaminants in the biosphere, but interest has mostly been focused on chemicals which persist in the environment.

Recently, halogenated hydrocarbons have been discovered in the drinking water supplies of many major U.S. cities. This incident has focused public attention on water quality. It can be assumed that the substances under discussion have been in the drinking water for some time, yet they have only recently been discovered and quantitated. The hypothesis has been put forward that these organohalogens are only formed during the chlorination process of water treatment.

The late discovery of these substances is somewhat surprising since their determination is relatively easy from an instrumental point of view, compared to most other substances at a comparable level. A relatively specific and very sensitive device suitable for their selective detection, the electron capture detector, has been described more than a decade ago. The reasons for the delay most likely have to be attributed to more than one factor, but the most important single contribution has been a lack of proper sampling procedures. We would like to provide a short review of current sampling procedures and discuss some of the options open to the analytical chemist.

Sampling methods

Sampling procedures and the preparation of a water sample for analysis depend on the concentration of the substances present and their chemical nature, *i.e.*, determination of dissolved gases certainly would call for a totally different approach than analysis of plasticizers. In almost any case however, some preconcentration step is necessary. Exceptions to this rule might only be applicable to some heavily polluted samples where only a few compounds are of interest or if specific detection methods for known or suspected compounds can be applied, such as selective ion monitoring by mass spectrometry (MS).

There are several reasons for sample preconcentration. In addition to the low inherent concentrations of the volatiles, it is also necessary to use instrumental methods which are only capable of accepting very small sample volumes, usually in the low microlitre range. In the following section, only sampling methods for substances will be discussed which can be subjected to gas phase methods.

Many different processes of various complexity have been applied for this purpose in the past, *i.e.*, liquid–solid adsorption, batchwise and continuous liquid–liquid extraction, freeze-drying, distillation, vacuum evaporation, gas-phase stripping, reverse electroosmosis, to name the most important ones. In most cases, combinations of these methods have been applied especially when samples having a wide range of different substances were to be analyzed.

Special problems have to be dealt with in trace analysis and ultratrace analysis. Kaiser[1] has pointed out that a very large number of substances can potentially be present in water at ultratrace levels and discussed a variety of systematic errors which

can easily be introduced into the sampling step. As an example, hydrocarbons were found to be adsorbed onto the walls of a glass container within a short time.

The materials which come into contact with the sample have to be chosen carefully from several points of view: sample alteration due to catalytic effects, contamination, and loss due to irreversible adsorption. Another point to be dealt with is the possible change of sample integrity during preparation, due to chemical and bacteriological action. This is especially important if samples are stored over prolonged periods of time or if large amounts of materials with high surface activity are involved, such as activated charcoal.

Various forms of charcoal have been used in the past to remove traces of organics from water, a process which is also sometimes used for municipal or industrial water purification. Adsorbed solutes can be recovered to various degrees by solvent extraction, which is mostly done with chloroform[2] (carbon chloroform extract, CCE) and subjected to chemical[3,4] or biological[5] testing.

Another principle with an equally long history is liquid–liquid extraction[6–13], done frequently in batchwise manner. The technique has mostly been applied to relatively concentrated samples, such as industrial effluents or treated sewage waters. The most common extraction solvents were methylene chloride, chloroform, hexane and carbon disulfide, but less volatile solvents such as hexadecane[14] also have been employed.

Extraction efficiencies and rates are determined by the distribution coefficient of the solute for the phase pair and the area of contact at which exchange occurs. Inherently, batchwise processes are not very efficient, even for solutes having relatively large distribution coefficients for the solvent and multiple extraction steps or a continuous process are required to effect complete extraction.

Some technical solutions which make use of these principles have been proposed, involving multiple stage[15] or continuous processes[16,17] with high yields of enrichment. An automated sampler based on similar principles and suitable for fieldwork has also been introduced[18]. In another approach liquefied butane[19] has been added under pressure to a container kept at room temperature and the organics extracted into the organic phase have then been recovered in a microcollector at low temperature.

Batchwise solvent extraction of water is a simple process which does not require expensive equipment. The purity of the solvent used, however, is an important factor and vigorous cleanup procedures are required[13]. Grob *et al.*[20] have shown that the choice of solvent and its amount are critical factors for successful extraction at ultratrace levels (parts per trillion range). Solvent miscibility with the water leads to decreased extraction efficiency and solvent impurities generate artifacts after its removal.

To concentrate the extracted organics from the solvent, the latter must be carefully removed. Vacuum distillation at room temperature or the use of a special evaporator (Kuderna-Danish or similar) have produced the best results, but some losses are inevitable, especially with low boiling substances.

Within the last few years, a number of synthetic organic polymers have been introduced for the concentration of organics, including pesticides[21–23], from both fresh water[4,24–33] and sea water[34,35]. The best known and most widely applied materials were macroreticular resins of fairly large surface areas (100–750 m^2/g), known under the tradename Amberlite XAD (Rohm and Haas, Philadelphia, Pa., U.S.A.). Other

polymers not based on copolymers of styrene–divinylbenzene were also used[36,37]. At this point, support-bonded silicones[38] should also be mentioned. In most applications, the polymer was simply packed into a conventional short column and the organics were concentrated by passing the water through its bed. Adsorbed solutes were regenerated by solvent extraction. Recoveries were excellent at ultratrace levels. As opposed to batchwise solvent extraction methods, the coefficient of adsorption of the solute for the polymer does not necessarily have to be large in order to ensure complete retention on the column since frontal development takes place. Adsorbent capacity, however, might be quite small for the more volatile components which are generally less well retained than higher-molecular-weight substances. The simplicity and economy of the approach are obvious, but the use of a solvent makes the method less attractive.

A method which lately has found widespread attention is based on gas phase stripping[1,10,39–48]. With this procedure, a gas is bubbled through the water and equilibrium is established between gas phase and liquid phase. Organic substances which partition into the gas phase are thus continuously removed from the water.

Recently an ingenious variation of the principle has been reported which employs recycling in a closed circuit[43,44]. This sytem also has been expanded to include substances in a volatility range, for which the technique is usually not applicable. This has been done by raising the temperature, thus modifying the stripping gas to approach the conditions of steam distillation. This principle is essentially adaptable to large sample volumes and therefore can approach ultimate sensitivity. Bergert *et al.*[45] have used drying agents to eliminate the moisture from the purge gas carrying the stripped organics. Electrolysis of the water itself[45] was also used to generate the stripping gas, in this case hydrogen.

The dynamic nature of the method allows very high enrichment factors at room temperature for substances having boiling points below 150°. Applications have been reported which reach down to the subpart per trillion level, making this procedure probably the most sensitive method available. There are only few drawbacks, such as a somewhat limited range. Purge-gas purity is very critical at such low levels and large volumes have to be avoided.

Contamination of water by mineral oils is often of concern and a special device, suitable for recovery of petroleum products and fatty acids from aqueous surface films has recently been introduced[47,48]. The sampler consists of a PTFE disc and organics adhering to its surface are washed off by a solvent. Obviously this device is limited to a special kind of sample and fairly high concentrations are required.

Analytical procedures

A review of analytical procedures on analysis of trace volatiles in drinking water has recently appeared in a series of three papers[20,43,44]. The conclusion of Grob and co-workers is that high-resolution capillary columns have to be used primarily because of two reasons, separation power and sensitivity. The limitations of gas chromatography (GC) were pointed out and it was suggested to extend the analytical procedures to include higher-molecular-weight substances or heat-labile compounds by the use of high-pressure liquid chromatography rather than by derivatization and high-temperature GC. It should be noted, however, that some types of samples frequently found in water, such as phenols[49] and acids[50–52], do require derivatization.

There cannot be any doubt about the need for high-resolution systems. Fortunately recent publications dealing with aspects of organic water pollution indicate a trend from packed columns to capillary columns. From a practical point of view, not even capillaries with the highest separation power can handle all the substances which might need to be resolved, in spite of the formidable state of art in column technology. A second approach open to the chromatographer is the use of multi-dimensional chromatography. The principle lies in the use of two or more chromatographic columns of different selectivities in series with intermittent heart-cutting techniques.

In principle, any chromatographic mixture which can be subjected to GC can be resolved, irrespectively of complexity, by selecting the right combination of GC phases and a narrow window for the cut. It is possible to use a combination of a packed column and a capillary column for such a purpose. This principle would be well applicable to a mixture as complex as organic volatiles in water at ultratrace levels. Unfortunately such instrumentation is not commercially available yet.

Significant advances have been made over the last few years in the design and operating characteristics of GC–MS instrumentation. This type of equipment is becoming more and more important in environmental trace analysis and is increasingly used for such purposes. The Environmental Protection Agency now has a large number of computerized GC–MS combinations in operation. Some of the procedures employed by this agency involving MS identification have been described[53].

EXPERIMENTAL

Sampling apparatus and procedure

The gas-phase stripping device basically consists of a source of pure purge gas, an elongated glass frit, condenser and tube holder. Fig. 1 shows a schematic drawing.

The sampler body was made by joining 70 mm O.D. glass tubing of 30–75 cm length to a 150-ml fritted-glass büchner funnel (fine porosity) capable of accom-

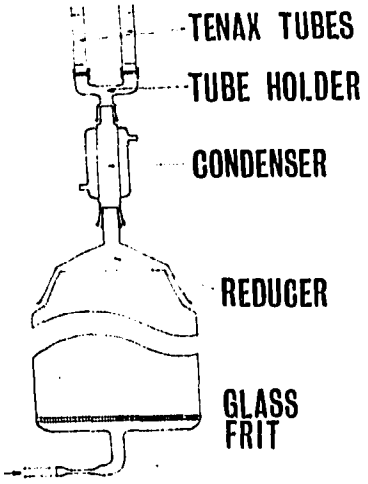

Fig. 1. Diagram of sampler. Dimensions not drawn to scale.

modating a sample of 1–2.5 l. The bottom part of the funnel was reinforced and joined with a 1/4-in. Kovar alloy to get an easy and leak-free connection to the gas source via a Swagelok reducing union. On top, a cap (45/50 glass joint) reduced the sampler body, connecting to a small condenser (length between 40 and 120 mm). A sample-tube holder was then placed on top of the condenser via a joint (all joints 10/30). Up to three samples could be collected in parallel. The connection to the adsorbent sampling tube was made by a short piece of shrinkable PTFE in such a way that the parts were in direct head-to-head contact with minimum exposure to the PTFE.

Purge gases were purified by the use of traps at cryogenic temperatures. Both helium and prepurified nitrogen were used. The traps combined layers of activated charcoal with Tenax GC, 60–80 mesh (Applied Science Labs., State College, Pa., U.S.A.). The use of liquid nitrogen for helium and of dry ice for nitrogen was found to eliminate background contribution to acceptable levels. Gas samples of up to 50 l were passed through Tenax and failed to produce significant interferences.

Purge-gas flow-rates were regulated by flow control with the aid of a valve (Nupro fine metering valve, Franklin Valve Co., Birmingham, Ala., U.S.A.) before the cryogenic traps. Flow-rates were measured directly at the sampling tubes with a bubble flow-meter and adjusted to values between 40 and 80 ml/min per adsorbent tube for most samples. Trapping time varied between 1 and 3 h, depending on flow-rate and size of container. The sampler body was externally heated prior to and during the concentration procedure. Heating tape was wrapped around the lower portion of the sampler and the variac was set to give a final temperature of approximately 70°. No attempt was made to control the temperature of the cooling water for the condenser.

Two sizes of adsorbent tubes were used, fitting into the inlet systems of the gas chromatographs and the GC–MS instrument. For the former, Pyrex tubes of 4 mm O.D. were cut to a length of 85 mm and both ends fire-polished. The tubes were filled with approximately 70 mg of Tenax GC 80–100 mesh. (This mesh size is not available commerically and was obtained through the courtesy of Tenax, Arnhem, The Netherlands.) Two small plugs of glass wool kept the adsorbent in place. For the GC–MS inlet system, the regular glass insert of the Perkin-Elmer 900 injector was replaced by a Pyrex tube, 145 × 5 mm O.D. and filled with up to 220 mg of the adsorbent.

Before the first use, the adsorbent tubes were conditioned for several hours in a specially built all-metal device at a temperature of 350° in a stream of nitrogen. The tubes were stored in PTFE-lined screw caps at room temperature. Water samples were stored in amber 1-gal. bottles with PFTE-lined screw caps and usually prepared within a few hours after collection. Except for the sampler body, all glassware was silanized, using standard procedures and kept in an oven at 200°.

Instrumentation

A Hewlett-Packard gas chromatograph, Model 5830A with single flame ionization detection was slightly modified to accommodate the adsorbent tubes and provide low dead volume connections for glass capillary columns. The inlet modifications consist of drilling out the top of the injector port to approximately 4.1 mm, exchanging the regular septum nut with a custom-made finned aluminum cap and positioning a precisely machined piece of PTFE or polyimide between septum and in-

jector body. A metal insert was dimensioned to accommodate the adsorbent tubes. Connections to the glass capillary columns were made with a 1/16-in. Swagelok union which is soldered to the bottom of the metal insert tube. At the detector inlet, the metal jet was replaced by a custom-made jet of a larger opening which allowed insertion of the glass capillaries to within a short distance of the burning tip. With this particular instrument, the hydrogen supplied to the flame also serves as makeup gas for the column outlet. The built-in integrator of the instrument was used for all quantitative determinations.

Another Hewlett-Packard gas chromatograph Model 5720 with single flame ionization detection was modified in the same way as described above. Carrier gas was purified by passing through a cylinder containing activated charcoal and molecular sieve 4A.

An LKB 9000 gas chromatograph–mass spectrometer combination was used for identifications. The chromatographic section of this instrument had previously been replaced with a Perkin-Elmer Model 9000 gas chromatograph. A single stage jet separator was used. Ionization voltage was 70 eV, and scan time for a mass range of 20–250 mass units was 1.0–3.5 sec. Scans were taken manually. Temperatures of ion source and separator were 220° and 230°, respectively.

Connection of the glass capillaries to the instrument was difficult due to the thin walls of the glass tubing. Only polyimide ferrules gave leak-free interfaces. The ferrules, 1/16-in. (Alltech, Arlington Heights, Ill., U.S.A.), were drilled out to accommodate the glass tubing within close tolerances. Chromatographic conditions were the same as used in the GC determinations.

Mass spectra were interpreted by comparison to a small library of spectra kept in files in our laboratory and with the use of tabulated data[54]. Identifications were confirmed for a number of substances by cochromatography (see Table IV).

Glass capillary columns

Glass capillary columns were drawn from both soft glass and Pyrex glass, using a Shimadzu glass drawing machine (Shimadzu, Silver Springs, Md., U.S.A.). Glass tubing of 8 mm O.D. was cleaned by rinsing with a series of common solvents and dried by either drawing air through it, or by slowly moving the tube through the flame of a bunsen burner. The drawn glass capillaries, having I.D.'s of 0.35–0.55 mm were immediately sealed after drawing, unless preparation of the column would commence on the same day.

Glass capillaries have been prepared with phases in a polarity range from OV 101 to Carbowax 20M and tested with the substances found in water and air pollutants. Analysis however was mostly done on Emulphor ON 870 (Applied Science Labs.), since this substrate elutes the compounds in the boiling-point range of interest conveniently and is relatively easy to coat. Also, as a matter of convenience, a large collection of retention data which has been accumulated in this laboratory with this phase, serves as an additional reference source.

Column pretreatment, described briefly in the following paragraph, refers to Emulphor or phases of similar polarity only. A more detailed description of the preparation and properties of these columns will be given elsewhere[55].

Column pretreatment essentially followed the methods suggested by German and Horning[56]. Instead of Silanox 101, a material of slightly more polar nature was

employed. This material was prepared by polymerizing a difunctional organosilicone (1-trimethoxysilyl-2-chloromethylphenylethane, Union Carbide reagent number Y5918) onto the surface of a fine microprecipitated silica, QUSO 32 (Philadelphia Quartz, Philadelphia, Pa., U.S.A.) with subsequent Soxhlet extraction. The silica contained between 2.9 and 9.5% (w/w) non-extractable polymer as determined by CNO analysis. A suspension was then made up, containing about 2% of the modified silica in tetrahydrofuran or chloroform. 2–3% (w/w) of Emulphor was then added, together with a trace of surfactant, benzyltriphenylphosphonium chloride (Aldrich, Milwaukee, Wisc., U.S.A.). The suspension is stable for about 1 h after the coarse particles which might have agglomerated during the polymerization process have been removed by sedimentation.

To introduce this suspension into the glass capillary, a plug of solvent must precede. If care is taken and air bubbles are excluded, the coating process proceeds smoothly. Velocity of the plug which should occupy approximately 10% of the total column length was adjusted to 2–4 cm/sec and maintained by readjustment of the pressure, if necessary.

Immediately after the solution left the column, the pressure was raised and the column dried for a few hours or overnight. During the drying process, tiny droplets could be seen in the glass capillary, periodically appearing and disappearing. Sometimes the glass capillary column had a slightly spotty appearance after drying which however did not affect performance. Before conditioning, the last 10–15 turns of the column were broken off and the ends straightened in a piece of metal tubing, heated over a bunsen burner. Columns were then recoated a second time, using a smaller and more concentrated coating solution (10 turns, filled with 5% phase in acetone). Occasionally columns have been etched in the gas phase by dry hydrogen chloride, but improvements were only moderate.

A column of 0.35 mm I.D. is judged to be satisfactory if 2000 theoretical plates per meter are obtained for standard compounds (substituted aromatic hydrocarbons) with partition ratios of 5–8. Occasionally columns have been prepared approaching 2500 theoretical plates per meter. Some of the glass capillaries have been in daily operation for months without signs of deterioration.

Chromatographic procedures

Sample transfer from the Tenax trap into the chromatographic column was done by a one-step elution process. One end of the glass capillary was straightened and bent with a match to U-shape, fitting into a small Dewar. Liquid nitrogen was used as a coolant.

To ensure optimal sample transfer, the head pressure on the column was reduced before introduction of the adsorbent tube into the desorption chamber. The pressure was then gradually increased. A trapping time of 15 min was chosen. During the transfer process, the GC detector or the total ion current monitor of the mass spectrometer was in operation to check for substances which might break through.

Adsorbent capacity determinations were made by connecting 3 tubes (small-size trap) in series and then directly injecting 1.0 μl of a standard into the plug of glass wool located in the first tube. The 1.0-μl volume contained 500 ng of each compound, dissolved in acetone or hexane. The tubes were then connected to a source of purified nitrogen or helium and purged at a flow-rate of 50 ml/min for 60 min.

Recoveries were determined by placing the same volume of standard into a previously calibrated piece of glass capillary. The capillary was slipped into an empty glass tube and introduced into the injector port without prior removal of solvent.

To check for losses due to irreversible absorption, some standards were successively diluted. A linear response resulted down to at least 5 ng. No attempt was made to determine the lower limit for quantitative recovery.

RESULTS AND DISCUSSION

Initial experiments

In the course of work on analysis of organic volatiles in air several years ago, involving a solid adsorbent, Tenax GC, we originally attempted to use the same polymer for drinking water samples. Water was passed directly through the tube followed by a drying process. It was possible to remove most of the water, but results were not well reproducible in our hands and the yields of recovery were generally low. Recently, polynuclear aromatic hydrocarbons and pesticides have been concentrated in this manner[68], however, larger quantities of Tenax were used and the sorbates were recovered by liquid extraction. In spite of limited reproducibility, some large peaks consistently appeared in the gas chromatograms. Identification by GC–MS[37] revealed the presence of a variety of chlorinated and brominated hydrocarbons which were well retained from the water by this direct adsorption method. The reasons for the unexpected behavior of this class of substances are not clear to us.

In the next step, an attempt was made to adapt the headspace technique described by Zlatkis *et al.*[57] for concentration of volatiles from body fluids. The yields were too low for drinking water analysis. A report on the successful application of a gas-phase stripping technique[43,44] prompted us to adapt this principle for an adsorbent, using only simple and readily available instrumentation and a low-cost sampler to be built from readily available materials.

Adsorbents for trace analysis

The use of adsorbents for concentration of organic substances in trace quantities from large sample sizes has some inherent disadvantages, compared to some other techniques available. Drawbacks are: limited sample capacity, especially for substances having low boiling points; some selectivity towards given classes of compounds; and possibly irreversible adsorption and sample alteration. With synthetic organic polymers, outgassing products, impurities trapped within the polymer, and oxidative or thermal degradation often produce high backgrounds. The temperature stability of a polymer is especially important if heat is used to regenerate the sample from the adsorbent rather than solvent extraction. It is well known that compounds are lost on adsorbents of high surface activity. In the case of activated charcoal, recoveries reported have been poor, even when vacuum-heat treatment was applied[58]. The alternatives for adsorbents at both ends of the scale are therefore to apply either solvent extraction for relatively active materials, or the use of adsorbents with only moderate surface area, when thermal desorption is to be applied. The need to limit the amount of highly active adsorbents, such as charcoal, even with solvent recovery procedures, has been pointed out. It is amazing to note that the amounts of activated charcoal reported for concentration of organic materials from water have been as little

as 20 mg[43] and as high as 70 g (ref. 3). Surface homogeneity of charcoal also seems to play an important role for preserving the identity of the more sensitive components of a sample. As a general rule, synthetic organic polymers, having only moderate surface areas are less able to retain low-molecular-weight substances, but become more quantitative as the molecular weight goes up. They also show selectivity, *i.e.*, alcohols are less retained than alkanes or aromatics. Taking these limitations into consideration, significant advantages, nevertheless, should result with direct heat desorption. Solvent extraction methods complicate analysis because of several reasons: artifacts can be introduced during concentration, inevitable losses occur and the solvent itself might obscure a part of the chromatogram. It also can be quite time consuming.

Most of these disadvantages can be overcome by the direct heat desorption procedure in which the sample is transferred from the adsorbent onto the chromatographic column in one step. Problems during regeneration of sample by heat might arise primarily from two sources: substances having a high affinity for the adsorbent might require temperatures of desorption high enough to cause decomposition of both sample and adsorbent, and impurities within the system itself are concentrated during the transfer step. On the other hand, an adsorbent giving off a small amount of degradation products or impurities might still be useful, if only the pattern is simple and reproducible. Advantages of the direct heat desorption method are its simplicity and speed, reduced losses during sample manipulation and ease of handling.

Since Hollis introduced polymers into chromatography in 1966, a limited number of applications have appeared in the literature, dealing with these materials as vehicles for concentration. Many workers have been discouraged by the fact that some of the polymers, primarily copolymers of styrene and divinylbenzene, do not have sufficient temperature stability to be used in conjunction with direct heat desorption methods. Elaborate cleanup procedures and conditioning steps, including Soxhlet extraction and vacuum–heat degassing methods[33], have been attempted for some of these adsorbents, but failed to produce satisfactory results.

In the last few years, a synthetic polymer has been introduced[59], which is not a copolymerization product of divinylbenzene and styrene. This material, Tenax GC, a linear polymer of 2,6-diphenyl-*p*-phenyleneoxide has some remarkable properties: excellent temperature stability (up to 380°) and virtual absence of volatile byproducts. Occasionally, minor traces of impurities have been found in some of the batches and it is necessary to test each new batch in this respect, but in general this polymer seems to lack low-molecular-weight components and gives exceptionally pure blanks. It is easily regenerated.

Unfortunately, the specific surface area of Tenax GC is relatively small (approx. 19 m^2/g, ref. 60) for the intended purpose. This fact somewhat limits its use to compounds of intermediate volatility. Nevertheless, a number of applications have been reported in which this material was used for the concentration of trace organics from dilute media[36,42,61–65]. The effect of water vapor on retention is negligible[66].

Adsorbent capacity and desorption

In order to explore the useful range of application, a number of model substances were tested at conditions similar to the ones to be used in obtaining actual water samples by gas-phase stripping techniques. At this point, it was of interest to

draw a line at which the method would become quantitative. Effects of flow-rate, temperature, particle size, length of adsorbent bed, sample size, packing density and moisture of carrier were briefly surveyed and found to influence the retention of a given substance on Tenax to various degrees. Except for the last two parameters, all factors play a significant role. As expected, frontal analysis and displacement occurs and the trap has to be treated as a short column. Data summarized in Table I have been collected at a fixed set of conditions which resemble the parameters applied for the actual sampling of water. As seen from Table I, aromatic hydrocarbons are well retained. Alcohols having boiling points in the same range are, however, less well retained. This behavior can be expected. Benzene is quantitatively adsorbed under these conditions. Water has little retention, but its amount is sufficient to interfere with MS analysis.

TABLE I

BREAKTHROUGH CAPACITIES OF TENAX ADSORBENT TUBES FOR VARIOUS SUBSTANCES

Conditions: nitrogen flow-rate, 50 ml/min; sampling time, 60 min; temperature, 20°. Tube dimensions, 85 × 3 mm I.D.

Substance	*Recovery (%)*		
	Tube 1	*Tube 2*	*Tube 3*
Acetone	12.0	13.0	13.0
Methanol	3.7	4.2	3.8
Benzene	86.5	12.5	1.0
Chloroform	99.0	0.6	0.4
Dimethyldisulfide	96.6	3.2	0.2
Toluene	91.8	7.4	0.8
Ethylbenzene	85.7	13.3	1.0
p-Xylene	88.0	11.3	0.7
m-Xylene	87.2	12.0	0.8
o-Xylene	88.7	10.6	0.7

Originally, a particle size of 30–60 mesh was used. Upon substitution with a 80–100 mesh range, retention was remarkably improved. Increasing the length of the sampling bed is the easiest way to increase the amount of substance which can be retained for a given amount of adsorbent. In some cases, when relatively large volumes of gas had to be passed through the adsorbent, up to 3 tubes were connected in series (total bed length 25.5 cm). Fig. 2 shows the effect for a gasoline standard. In this particular case, a considerable amount of the standard would have been lost if only one tube would have been used, but 2 tubes in series improved the results considerably. Because of these reasons we always adsorbed onto 2 or 3 tubes, connected in series.

Time requirement, minimum temperature needed to effect complete desorption, and the volume of gas necessary to flush the volatiles onto the cryogenically cooled column are of particular interest. The gas had to pass through the entire column since we found it difficult to make glass-to-glass connections (shrinkable PTFE in an appropriate size was not available). Using this arrangement it is easy to check, if components break through during the desorption process. Columns having good permeability had to be used.

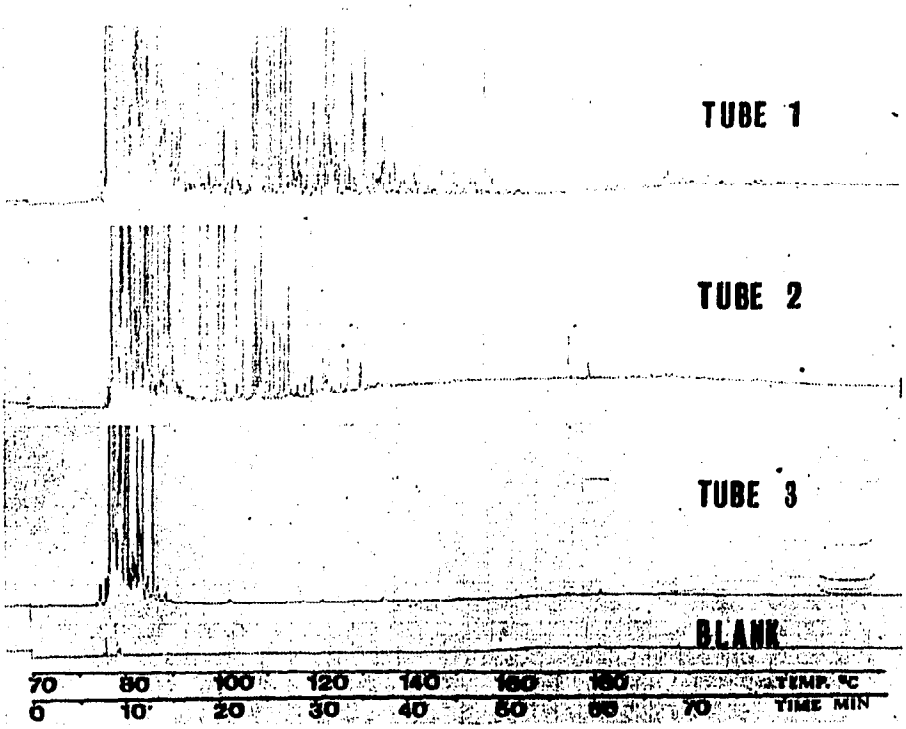

Fig. 2. Breakthrough capacity of a gasoline sample on 3 adsorbent tubes in series. Adsorbent tubes: 85 × 4 mm O.D., filled with 70 mg of Tenax GC, 80–100 mesh. Sample, 0.2 μl of gasoline, regular. Purge gas, helium, flow-rate, 60 ml/min; purge gas volume, 1.5 l. Glass capillary column, 41 m × 0.45 mm, Emulphor ON 870. Chromatographic conditions: cryogenic trapping (liquid nitrogen) for 15 min, carrier: helium at 5 p.s.i., temperature program: 70° for 10 min, 70°–180° at 2°/min.

If desorption is started at low flow-rates, breakthrough of components can be completely avoided. Desorption times are minimal if large inlet dead volumes are avoided. In an experiment, a set of 3 identical samples was desorbed, using desorption times of 2, 15 and 60 min. Transfer was almost complete after 2 min. The temperature used to effect desorption seems to be less critical. At a temperature of 250°, complete regeneration can be accomplished for all substances under investigation. If necessary, the temperature can easily be raised to 300° without generation of artifacts. Under these conditions, substances as involatile as tetrahydrocannabinol have been eluted[61].

Gas phase stripping

Trace amounts of organic materials cannot be concentrated from water by conventional extraction techniques[41] and gas-phase stripping is the method of choice. The key to efficiently remove traces of organics from water is an effective mass transfer into the gas phase. This can be accomplished by several means, most importantly a large area of contact of the stripping gas with the water, and elevated temperature. Experimentally, the use of fine glass frits yielding very fine bubbles, maximum time, and large area for equilibration, most easily insures rapid equilibrium. It has been shown that the use of a condenser does not noticeably affect the passage of trace amounts of organics, but holds back the bulk of water vapor[67].

Commercially available frit pore sizes range from coarse to ultrafine. Although ultrafine frits give extremely fine gas bubbles (the water looks "milky" and becomes intransparent), the pressure necessary to maintain adequate flow is too high and the frits are too thin and fragile to withstand the pressure difference. As a compromise, frits designated "fine" have been used. After prolonged use, the capability of a frit to generate fine gas bubbles decreases. Up to this time no satisfactory method was found to rejuvenate its surface and occasional replacement seems to be the only effective way to deal with this problem. Heating of the water sample can easily be done by wrapping heated tape around the sampler body. Convection within the sampler assures uniform heat distribution. If the water is heated to above 80°, large bubbles begin to form which cut down on the efficiency of sample transfer into the gas phase.

Careful preparation of the sampler before analysis is critical to avoid artifacts. It was found necessary to preheat the entire sampler with a heat gun prior to analysis, even when its parts are stored in a heated oven. The aspect of contamination after assembling and prior to analysis has caused many problems and is very difficult to deal with. Although the stripping gas inside the sampler is at a fairly high pressure, due to the restriction caused by the long adsorbent tubes, contamination from the surrounding air may occur. Results were only improved when the sampler was moved into a room free of organic solvents, and when the glass joints were wrapped with PTFE tape. Even after taking such precautions, frequent blank runs must be performed to ensure the absence of artifacts and background contamination. Fig. 3 gives an example of such an effect. The high peak on the right side of chromatograms B and C clearly has to be attributed to the background, since the size is almost constant and the substance was originally not present in the sample.

The rate of transfer of a compound from the aqueous matrix into the gas phase is determined by its equilibrium constant at the given temperature. It can be expected that substances of various functionality but similar boiling points are removed from water at different rates. Propanol, b.p. 97°, is more likely to remain in the aqueous phase than *n*-heptane, b.p. 98.4°. It is therefore important to determine the extraction efficiency for each particular substance for quantitative work. This is a formidable task for complex mixtures and only warranted for contaminants of

TABLE II

RATE OF RECOVERY FOR SUBSTANCES OF DIFFERENT FUNCTIONALITY FROM WATER

Conditions: helium flow-rate, 80 ml/min; sampling time, tube 1, 0–60 min, tube 2, 60–120 min, tube 3, 120–180 min, water temperature: 75°.

Substance	*Recovery (%)*		
	Tube 1	*Tube 2*	*Tube 3*
n-Decane	97.6	2.2	0.2
Decene-1	98.4	1.6	0
n-Butylbenzene	97.8	2.2	0
2-Decanone	65.5	28.2	6.3
1-Chlorodecane	98.5	1.5	0
Methyldecanoate	93.6	6.0	0.4
Decanol	58.1	30.5	11.4

critical importance which have to be determined with a high degree of accuracy. To a fair degree of approximation, it is sufficient to investigate the general behavior of a class of compounds such as alcohols or alkylated aromatics within a range, to estimate rates of recovery.

It can be predicted, that non-polar substances in general will be stripped more easily from water than polar ones, or compounds which are capable of hydrogen bonding. Table II summarizes the results for a standard containing substances with different functional groups. As expected, the rate of removal is lowest for the alcohol, followed by the ketone.

The substances to be dealt with are mostly in the volatility range of gasoline. Fig. 3 compares a gasoline standard obtained by direct injection (Chromatogram A) with a standard which has been recovered from a 2.5-l water sample. Most compounds are almost completely recovered after stripping for 80 min at 75°. It also can be seen that the ratio of the substances has largely been preserved, indicating non-discriminative extraction. This can be expected for a sample like gasoline, consisting mostly of aliphatic and aromatic hydrocarbons. Chromatogram C shows the substances left after purging with approximately 4 l of gas.

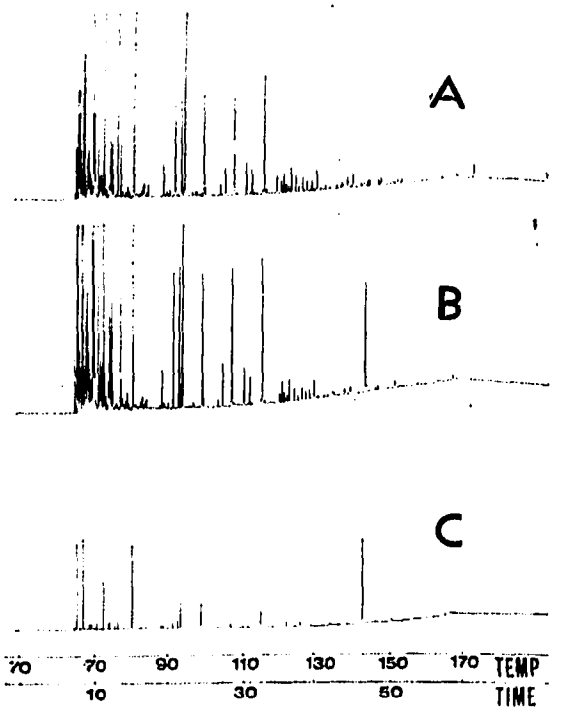

Fig. 3. Recovery of a gasoline standard from water. A: Gasoline standard, 0.7% in acetone, 0.4 µl injected onto 2 Tenax tubes in series and purged at a flow-rate of 50 ml/min for 7 min. B: Same gasoline standard, added to 2.5 l of water and recovered from one set of 2 parallel tubes. Sample size, 1.0 µl. Purge gas flow-rate, 50 ml/min per set of tubes. Sampling time, 80 min. Water temperature: 75°. C: As in B, except sample taken after B. Glass capillary column, 38 m × 0.35 mm, Emulphor ON 870. Chromatographic conditions: cryogenic trapping (liquid nitrogen) for 15 min, carrier: helium at 10 p.s.i., temperature program: 70° for 10 min, 70°–170° at 2°/min.

Practical applications

Some fifty different water samples have been collected in the vicinity of Tuscaloosa, Ala., and Houston, Texas, and were run by GC. These included tap water, samples taken from lakes and rivers, and a few effluents from plants. Total concentration varied over at least 5 orders of magnitude. Tuscaloosa drinking water had the lowest total concentration in volatile materials and a sample from Clear Lake, south of Houston, showed the largest amount. Clear Lake is used for recreational purposes and carries a large number of motorboats. A sample prepared from this water was so concentrated that it plugged the cryogenically cooled column. After heating the column for 12 h at maximum operating temperature, components were still eluting, giving a high background in the mass spectrometer.

Profiles obtained from rivers and lakes showed a relatively consistent pattern and variations in the absolute concentration of the volatiles were small, taking dilution factors into account. On the other hand, the picture was less consistent for the tap water samples and some large fluctuations were observed. The reasons are unclear and more samples need to be analyzed to get statistically significant data.

A small number of tap water samples were also subjected to analysis by GC–MS. Table III summarizes the substances identified in the drinking water of two different cities. Comparison with Table IV, which represents a similar list of an untreated water sample, reveals that a large number of halogenated hydrocarbons occur in drinking water which are absent in natural water. Some of these substances represent fairly large peaks in the chromatograms. This observation seems to confirm the hypothesis that these compounds are only introduced into the water during the water treatment process. Some of the components in the drinking water, having characteristic fragmentation patterns of halogenated hydrocarbons were of fairly high molecular weight and could not be identified at this time, due to a lack of references.

TABLE III

IDENTIFIED SUBSTANCES FOUND IN DRINKING WATER

Substance	*Sample**	*Substance*	*Sample**
Chloroform	A, B	Acetone	A
Carbon tetrachloride	A	Methyl ethyl ketone	A
Tetrachloroethylene	A	Benzene	A, B
Dichlorobromomethane	A	Toluene	A, B
Chlorodibromomethane	A	*m*-Xylene	A, B
Dichlorodibromomethane	B	*o*-Xylene	A, B
Bromoform	B	*p*-Xylene	A, B
Dichlorobenzene	A	Decahydronaphthalene	A
Dichlorotoluene	B	C_3 Benzenes	A, B

* Sources: A, Tuscaloosa, Ala., U.S.A.; B, Houston, Texas, U.S.A.

Mechanisms for the generation of organohalogens in drinking water are still discussed presently. It is possible that many more substances of this type are present at lower levels of concentration, escaping detection. It should be simple to obtain larger amounts of volatile material from tap water by a slight modification of the sampler design. Providing an inlet and outlet at the sampler body, water could be continually added and removed during the stripping process and large amounts of

TABLE IV

SUBSTANCES IDENTIFIED BY GC–MS IN THE WATER OF THE BLACK WARRIOR RIVER, TUSCALOOSA, ALA., U.S.A.

Peak No. in Fig. 4	*Compound*	*Peak No. in Fig. 4*	*Compound*
7	3-Methylpentane	33	Chloroheptane
8	2-Methylpentene	34	C_3 Benzene
9*	Acetone	36*	1-Chlorooctane
10	Methyl ethyl ketone	38	C_4 Benzene
11*	Benzene	42	Dichlorobenzene
13*	Chloroform + bromochloromethane	44	Indene
14*	Dimethyldisulfide	45	C_{13} Alkane
16*	Toluene	47	C_{14} Alkane
17	Hexanol	48*	Camphor
18*	α-Pinene	52	C_{15} Alkane
19	C_{10} Alkane	53*	Fenchyl alcohol
20*	Ethylbenzene	56*	Terpinene-4-ol
21*	*p*-Xylene	58	Anethole isomer
22*	*m*-Xylene	60	C_{16} Alkane
23	β-Pinene	61*	Naphthalene + borneol
24*	*o*-Xylene	63	α-Terpineol
27	C_{11} Alkane	65	Anethole isomer
29	C_3 Benzene	71	Anethole isomer
30*	Limonene	77	C_{18} Alkane
31	C_3 Benzene	79	C_{18} Alkane
32	C_3 Benzene		

* Substance confirmed by retention time.

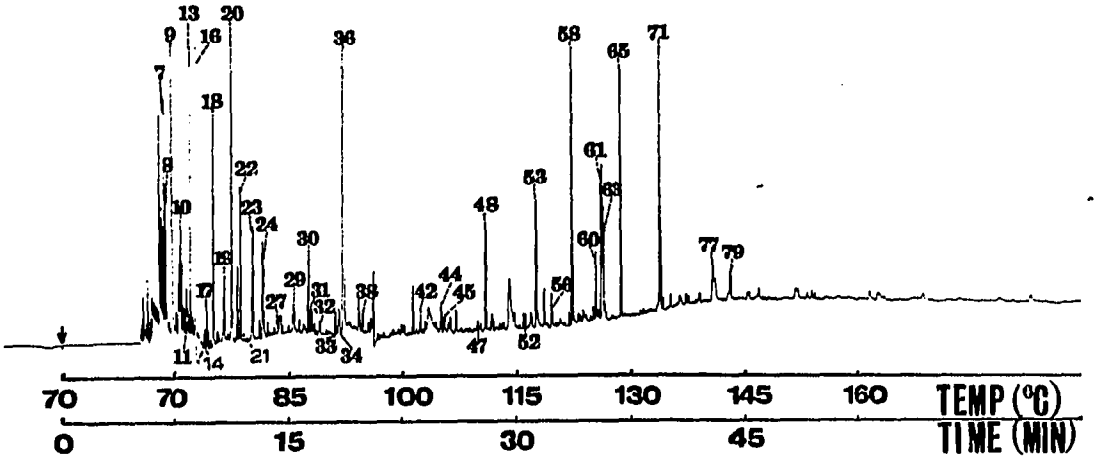

Fig. 4. Profile of volatiles from Black Warrior river, Ala. Sample size: 1.8 l. Date of sample: 5/6/75. Sample location: Tuscaloosa, Ala. Purge gas flow-rate: 60 ml/min. Purge gas volume: 7.2 l. Water temperature: 75°. Glass capillary column, 59 m × 0.45 mm, Emulphor ON 870. Chromatographic conditions: cryogenic trapping (liquid nitrogen) of one set of 2 tubes out of 2 sets for 15 min, carrier: helium at 5 p.s.i., temperature program: 70° for 8 min, 70°–160° at 2°/min.

water could be conveniently sampled. Work along this line is presently underway.

Samples taken from the Black Warrior river in Alabama were also analyzed by GC–MS and showed some unexpected compounds, camphor-related substances and terpene derivatives. The mass spectra of these classes of compounds are very characteristic, but large numbers of possible isomers exist. The only way to positively identify these substances is a combination of retention data and MS information. Some of the homologues have therefore only been tentatively assigned. Fig. 4 shows a representative profile and Table IV summarizes the substances identified.

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We have become aware of a sampling approach[69,70] similar to the the one described in this paper.

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