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ORGANIC SUBSTANCES IN POTABLE WATER AND IN ITS PRECURSOR PART I. METHODS FOR THEIR DETERMINATION BY GAS-LIQUID CHROMATOGRAPHY

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SUMMARY

Organic substances are liberated from potable water and transferred to a very small amount of charcoal in a hermetically closed circuit system, in which the carrier may be an inert gas or water vapour (yielding complementary results). The organic substances are dissolved from the charcoal, separated by capillary gas-liquid chromatography and identified by gas-liquid chromatography-mass spectrometry. In unpolluted water, hundreds of substances up to C₂₄ are detected at concentrations down to 1 in 10¹³ (w/w). Equipment and methods are discussed in detail.

INTRODUCTION

After analyzing trace organic substances in the atmosphere¹, we have tried to carry out corresponding work on water. Whereas the total organic constituents of air can usually be analysed both quantitatively and qualitatively, this is not necessarily true for water. It is extremely difficult to separate trace amounts of polar substances such as humic acids from water. By means of the present methods, only some of the whole range of substances can be handled, and it is difficult to judge the importance of this restricted selection.

In this work, the number of analyzed substances is arbitrarily limited by the principle that gas-liquid chromatography (GLC) was used as the fundamental method of separation and that derivatives of polar components of the samples were not produced. This means that only substances with sufficient volatility were included, but fortunately the experimental results showed that this limitation was less serious than expected.

After working on polluted water (an example is given in ref. 2), we concentrated our efforts on drinking water for the following reasons. We realized that only a knowledge of the composition of "pure" water would enable us to judge whether or not the presence of a given substance should be considered as pollution, and, even more important, to detect experimental contaminants. This led, for instance, to several of the major peaks in the chromatograms shown in ref. 2 being traced back to the equipment (PTFE). It is obvious, furthermore, that a technique that permits the or-

ganic content of drinking water to be determined is automatically capable of analysing contaminated water.

This paper describes several procedures, *e.g.*, the handling of charcoal and the principle of using a closed circuit system, that are not confined to water analysis but are applicable to any kind of head-space analysis.

EXTRACTION OF ORGANIC SUBSTANCES FROM WATER

Extraction with organic solvents

Extraction by shaking with solvents is the simplest and most rapid method. Of the numerous applications, we cite here only a few of the more recent papers³⁻⁷. A technically outstanding version, called pressure distillation, has recently been developed^{8,9}. In agreement with Novák *et al.*¹⁰, we found that trace amounts of organic substances such as alkanes cannot be determined in this way much below concentrations of 1 ppm. In contrast, single substances in lake or river water are normally present at the ppb* level and in drinking water at the ppt* level. Although the extraction itself can be rendered very efficient by using a counter-current system and a large volume of solvent, the final result is impaired by large losses during the evaporation of excess of solvent and by the simultaneous concentration of impurities present in the solvent. There are, however, favourable circumstances (*e.g.*, easily extractable and selectively detectable substances such as halogenated hydrocarbons) under which determinations down to the level of 1 ppb are feasible. For drinking water, in any case, liquid extraction fails by several orders of magnitude.

Adsorption on solids

Extraction by adsorption has gained in interest in recent years and seems to be replacing liquid extraction, especially for routine work. Charcoal¹¹⁻¹³ has been widely used, and the influence of particle diameter, contact time, temperature, pH and other factors has been studied thoroughly¹³. Recently, better results have been obtained by replacing charcoal with an organic resin such as Amberlite XAD-2^{14,15} or Amberlite XAD-4¹⁶. Similar improvements by using support-bonded silicones¹⁷ have been reported. Specific procedures have been developed, *e.g.*, very efficient adsorption of acids on anion-exchange resins¹⁸.

According to our experience, these recent developments are very valuable for the determination of specific organic substances. With halogenated hydrocarbons, for instance, relatively large volumes of adsorbent, subsequently extracted with even larger volumes of solvent, can be used. The resulting large volumes of very dilute organic solutions of pesticides or chlorinated biphenyls do not present serious problems because of the high sensitivity and selectivity of the electron capture detector. If, however, organic substances are to be determined, the volume of adsorbent has to be greatly reduced, with the aim of obtaining a more concentrated organic solution.

In our experiments, the adsorption efficiency of reasonably small amounts of adsorbent (*e.g.*, 1 ml for 10 l of water) was far from adequate for analyzing drinking water. The only means of increasing the efficiency was to decrease the particle size. This resulted, however, in excessive flow resistances of the filters, or, when the ad-

* The American billion and trillion are used: 1 ppb = 1 in 10⁹; 1 ppt = 1 in 10¹² (w/w).

sorbent was agitated directly in the water sample, it became impossible to recover the loaded adsorbent quantitatively from the water.

In another series of experiments, with the adsorbent suspended directly in the water sample, we observed a greatly increased adsorption efficiency when the motion of the adsorbent particles in the water was intensified. We concluded that adequate efficiency might be obtained by using ultrasonic vibration. Unfortunately, the particles of charcoal or Amberlite were comminuted under these conditions and therefore could not be recovered for extraction.

Extraction by evaporation

The third possibility, stripping the organic substances from the water by contact with a gas, has attracted much less interest in the past. Swinnerton and Linnemborn¹⁹ were the first to determine C_1 - C_4 hydrocarbons by stripping them from water by a stream of helium. Desbaumes and Imhoff²⁰ extended the method to include substances such as benzene and toluene. They bubbled a stream of purified air through the water sample and then passed it immediately into a hydrocarbon analyzer.

The most recent application was reported by Novák *et al.*¹⁰. Helium is purified by passing it through a cold trap, bubbled through the water sample and dried over magnesium perchlorate. The stripped organic vapour is retained in a second cold trap, from which it is passed into a gas chromatograph. The extraction is enhanced by adding a salting-out agent. Organic substances in trace amounts down to the ppt and sub-ppt levels are determined. The authors reported, however, that their method is limited to substances with boiling-points that are not substantially above 100°.

We have independently followed a similar line and have recently presented the first results²¹. In general, we agree completely with Novák *et al.*¹⁰ that the stripping method is several times more efficient than any other extraction method. We did not, on the other hand, observe any serious boiling-point limitation. At present we have examined substances up to C_{24} , but we believe that the analysis can be extended far beyond this limit without the need to modify the method fundamentally.

We feel that the difference between the findings of Novák *et al.* and ourselves stems primarily from two technical aspects. The lower the vapour pressure of the substances to be stripped from the water, the larger is the gas volume necessary for complete extraction. This calls for a very high flow-rate of the gas stream, the purification of which is hardly possible with a cold trap. Similarly, the complete trapping of trace amounts of organic substances from this gas stream is very difficult when a cold trap is used. The second problem derives from the high moisture content of the gas stream leaving the water sample. We assume that the above boiling-point limitation is caused at least partly by the loss of less volatile substances on the drying agent. Naturally, the problem of drying would be greatly increased with a higher flow-rate of the gas stream.

Our solutions to these problems are firstly, the use of a closed circuit system, and second, the use of charcoal, which selectively adsorbs organic substances from a very moist gas stream. We have confined our report to the analysis of drinking water with extraction by evaporation, followed by trapping of the organic substances on charcoal.

PRINCIPLES OF TRACE ANALYSIS WITH ADSORPTION ON CHARCOAL

Charcoal versus other adsorbents

In trace analysis, there is a basic interest in lowering the bed volume of the adsorbent to the minimum. The smaller the bed volume, the less solvent is needed for the complete extraction of adsorbed material. This is important, as concentration of the solution by evaporating the solvent to a small volume should be avoided. This is the main reason why, in many comparative experiments, we could not find any reasonable alternative to charcoal, which offers by far the greatest specific adsorption capacity.

A second advantage of charcoal, especially in comparison with synthetic adsorbents, is its absolute chemical stability. Under no conceivable conditions does it release substances that would result in contamination. A further advantage is its thermal stability. As shown below, we have to make our adsorption filters at temperatures of *ca.* 700°, and these filters could not be prepared from any existing synthetic adsorbent.

In many laboratories, the use of charcoal has been discontinued because certain adsorbed substances were recovered incompletely or with some structural modification. After many years of continuous work with charcoal, we can make the following observations on this aspect. Incomplete recovery from any adsorbent is observed if an unsuitable ratio between the adsorbent and adsorbed material has been selected, *i.e.*, if the amount of adsorbed material is too low in comparison with the active adsorbent surface. Because of the extremely high specific surface area of high-quality charcoal, in most applications excessive amounts of charcoal are used, thus causing the problems mentioned above. As a consequence of the much lower specific surface area, the corresponding mistake with organic adsorbents is hardly ever made and the corresponding difficulty is therefore almost unknown.

Structural modifications on the charcoal surface may occur if the adsorbent has been activated by the addition of certain inorganic salts²², which act as catalysts. The selection of pure charcoal is, therefore, of primary importance. According to our experience, commercially available activated carbons show surprisingly large differences in quality. The product we use has been developed after many years of work by the laboratories of F. J. Burrus & Cie (Boncourt, Switzerland) for use in cigarette filters. For scientific purposes, it is available with different particle sizes*.

A further reason for structural changes may be the use of an unsuitable method of desorption, *e.g.*, the use of heat instead of a solvent. Corresponding studies have been published by Palamand *et al.*²³.

Amounts and concentrations in water analysis

In order to plan the individual stages of the analysis, as well as to design the components of the equipment, it is important to survey the quantitative aspects. We have tried to present the situation schematically in Fig. 1.

In 5 l of unpolluted water (tapwater from the Zürich supply, sampled from a continuously running tap), 20 ng ($2 \cdot 10^{-8}$ g), corresponding to 4 ppt, represent an average amount of a single organic constituent among the 50 or so major constitu-

* Bender-Hobein AG, Riedtlistr., 8006 Zürich, Switzerland.

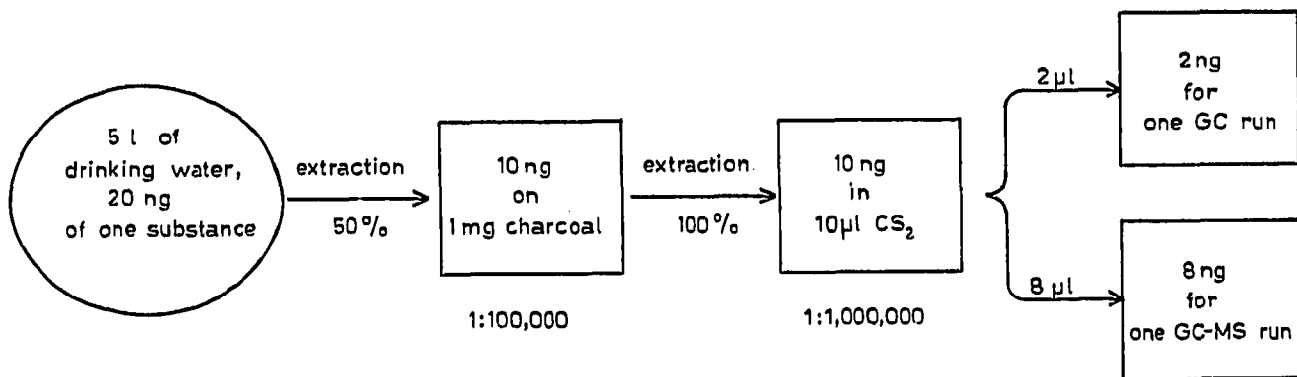


Fig. 1. Scheme of the analysis, illustrating the practical limitations and problems deriving from the given quantitative conditions.

ents. If the evaporation works with 50% efficiency, 10 ng of this substance are deposited on the adsorbent filter containing 1 mg of charcoal, yielding an adsorbate to adsorbent ratio of 1:100,000. According to our experience, a ratio of 1:10,000 should not be exceeded. Hence, for ideal conditions, the filters should be prepared with 0.1 mg of charcoal or the sample volume should be increased to 50 l. Both modifications are excluded for technical reasons. We stress these relationships because normally one would tend to use a much larger carbon filter.

Complete extraction of the loaded filter is possible with 10 μl of solvent, without subsequent concentration of the solution. Hence the solute to solvent ratio is 1:1,000,000. High-resolution GC analysis of this solution, by injection of 2 μl on a suitable column without splitting, is well within the ideal chromatographic conditions. The remainder of the sample may be used for a single GC-MS run. In this procedure, at least for substances that yield complex spectra, the lower limit of sample size is involved. It should be emphasized that the total extracts from 5 l of water are consumed in two chromatographic runs.

The closed circuit system

The stripping and trapping, as discussed above, are successfully achieved only by using a closed circuit. We are not able to avoid, on a thin filter disc prepared from 1 mg of charcoal and at gas flow-rates of 2–3 l/min, small areas where, because of unfavourable particle distribution, the retention of organic substances is incomplete. This could be prevented only by increasing considerably the amount of adsorbent, with all of the attendant serious drawbacks discussed already. In a closed circuit, in contrast, substances that break through the filter are automatically recycled and therefore only the closed circuit offers the conditions under which very small adsorbent filters can be used.

The principle of the closed circuit is important for a second reason. As discussed under extraction by evaporation, relatively large gas volumes (e.g., a flow-rate of 2 l/min for 20 h, totalling 2400 l) must be bubbled through the water if less volatile substances are to be stripped. The complete elimination of contaminants from this gas volume would be a very difficult task. This problem does not exist in the closed circuit, where 0.5 l of gas is recycled continuously.

We should emphasize that, in head-space analyses, the closed circuit is very helpful for a third reason. During the trapping of head-space vapour from materials such as fruit, vegetables, meat and bread, there is the risk that the sample may become dry, thereby losing its normal properties. In the closed circuit, constant sample conditions are maintained without additional care as the evaporated moisture is recycled. Obviously, this is true only if adsorbent filters instead of cold traps are used.

Selection of carrier material

Up to now, only inert gases or purified air have been mentioned as carrier materials for the stripping procedure. As reported elsewhere²¹, the stripping stage can be considerably influenced by modifying the carrier. Carrying out the analysis at an elevated temperature (the whole circuit, including the pump, has to be heated so as to prevent condensation) results in inclusion in the stripped substances of those of lower volatility. Whereas at room temperature reasonable stripping is possible for substances up to *ca.* C₁₈, C₂₄ substances are stripped at 80° with comparable efficiency. With heating, the composition of the carrier is shifted continuously from inert gas to water vapour. It may be argued that the increase in the molecular weight of the stripped substances is caused by the higher temperature of the water, rather than by the modified composition of the carrier. We have observed, however, that a comparable effect can be obtained at room temperature by adding 10% of methanol to the water sample. Unfortunately, we have not been able to purify methanol sufficiently to allow its regular use. Similar effects can probably be obtained with other additives. Very interesting selective effects can be expected from the addition of substances such as ammonia or formic acid for the stripping of basic or acidic substances, respectively. Unfortunately, all of these useful modifications are encumbered with the almost inevitable side-effect of introducing foreign trace substances or other artifacts (see below).

There is one important modification that is free from this drawback, namely replacing the carrier gas by pure water vapour by means of a closed circuit steam distillation with the water in the sample acting as its own carrier, with the following advantages. Firstly, no foreign material is introduced. Secondly, no side-effects from the equipment (pump, tubing, etc.) are to be expected as all-glass apparatus is used. Thirdly, an important inclusion in the stripped materials of polar substances is observed. Fourthly, there is virtually no molecular weight limitation on the stripped material. The serious drawback of the method is the virtually complete loss of low-molecular-weight substances up to about C₁₄. At the present time, we feel that in order to obtain the maximum amount of information, the two methods, stripping with an inert gas at room temperature and stripping with water vapour, should be used complementarily.

Influence of equipment materials

The selection of the appropriate materials for the equipment is of primary importance. Obviously, any rubber or plastic material that releases or absorbs organic substances must not be used. It may be less obvious that PTFE also must not be used, at least for all parts of equipment where the released organic substances are continuously trapped and, therefore, concentrated. There are a few exceptions to the positions where we use, with strict precautions, small PTFE parts, but the most severe

restriction is that PTFE must not be used to prepare fittings (*e.g.*, sealing the adsorbent filter) or to construct even small parts of the pump.

Glass and metal equipment can be used without restriction. Even so, some precautions must be observed, and a number of possible influences have still to be studied.

For stripping with an inert gas at room temperature, for instance, we use a circuit with the tubing and pump made from stainless steel. At present, we are not sure whether or not certain substances (*e.g.*, phenols) are lost by adsorption on the steel surface. We have observed another difficulty caused by glass surfaces. After a number of steam distillations with neutral water, we rinsed the apparatus thoroughly and then analyzed a slightly basic water sample of pH \approx 10. This run yielded several major constituents (10–50 ppt) that were not derived from the water sample being analyzed. Our explanation of this surprising result is that these substances had been trapped, during numerous preceding runs at a pH of *ca.* 7, on the glass surface, which acted as an ion exchanger, and were released under basic conditions. We conclude that any glass apparatus should be used exclusively for water samples of a single pH. We may add that we have never observed a similar effect with stripping at room temperature.

A comprehensive survey on possible background contaminations has recently been published by Giam and Wong²⁴.

PRACTICAL PROCEDURES

Preparation of adsorbent filters

Some guidelines for the preparation of charcoal filters have already been discussed earlier¹. The following parameters must be considered.

Amount of charcoal. As discussed above, this amount should bear a reasonable relationship to the amount of adsorbed material. Also, it should be as small as possible so as to permit extraction with a small volume of solvent. We found the optimum amount to be in the range of 1–2 mg. Smaller filters would be desirable, but we are not able to make them of sufficient quality.

Particle size. In general, very small carbon particles should be selected. With decreasing particle size, both the rate of adsorption and the ease of liquid extraction are increased, and the influence on the second variable is the more important. The diffusion of liquids through intact charcoal is very slow, and we assume that difficulties with incomplete recovery in many laboratories were caused by the use of too large particles. The lower size limit is given by the flow resistance of the filter disc. It is desirable for this resistance to be low so as to prevent large pressure differences in the closed circuit. A hermetically air-tight circuit is most easily obtained when the internal pressure at any point is as close as possible to the ambient pressure. Reconciling these contradictory interests led us to use particle diameters of 0.05–0.1 mm.

Filter geometry. The flow resistance of a filter is determined by its geometry if the amount and particle size of the charcoal are fixed. As a result of extended trials, we actually use filter discs with a diameter of 3–4 mm, which are *ca.* 0.5 mm thick. Thinner discs are highly desirable but are very difficult to prepare with a homogeneous particle distribution.

We prepare our filters (see Fig. 2) as follows. The glass tube is constricted at one end and the first stainless-steel screen disc is introduced. The constricted end is connected to the water pump and a weighed amount of charcoal is slowly

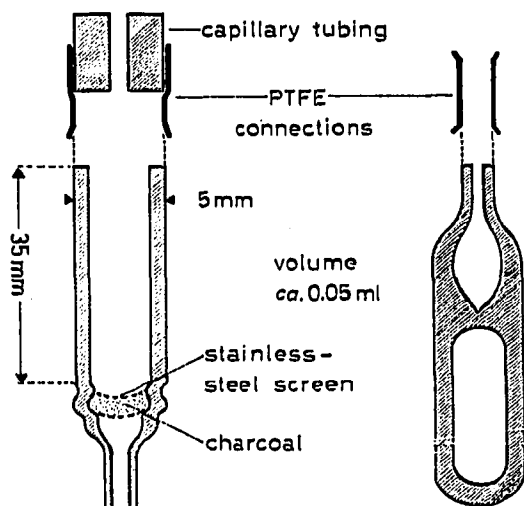


Fig. 2. Left: charcoal filter tube with cap reducing solvent evaporation during extraction. Right: sample tube in which the batches of carbon disulphide solution are collected, with PTFE tubing providing a tight connection to the filter tube.

sucked into the tube. Without disconnecting the vacuum (which holds the particles in a good distribution on the first screen), the second screen is added and the open end of the tube is then stoppered. The vacuum produced is necessary in order to allow heating without burning the carbon and screens. The tube is then turned over a small flame, the tip of which is directed exactly on to the edge of the filter disc. When the glass starts to soften, the external pressure causes the tube to become constricted above and below the filter disc, thus holding the latter firmly in position (this is a delicate procedure and many trials may be necessary).

The freshly prepared filter is rinsed with dilute nitric acid so as to dissolve the metal oxides produced during heating, and is then thoroughly rinsed with water, methanol and chloroform. After being immersed in carbon disulphide overnight, it is ready for use and no further activation is necessary. The filters are stored immersed in an organic solvent. From time to time, deposited lime is dissolved with dilute acid and the filters are washed with water and methanol. We have used the filters continuously for almost 2 years and their lifetime seems to be unlimited.

As PTFE must not be used in the stripping equipment, we are unable to find means of fitting the filters hermetically into a closed circuit. We place them in a glass tube or cylindrical bore the diameter of which leaves very little clearance (Figs. 4 and 6) along a tube length of 3–4 cm. Exact flow measurements have shown that it is not difficult to have 95–98% of the circuit stream passing through the filter, while 2–5% pass between the filter and filter holder.

Extraction of loaded filters

The direct transfer of adsorbed material from the filter on to the capillary column is feasible, as described earlier²⁵, but the procedure is recommended only for the most volatile substances. Its advantage is that no solvent will interfere with the determination of C₃–C₆ compounds.

For most substances, liquid extraction is necessary²³ in order to avoid qualitative changes. We have found carbon disulphide to be the best solvent for this procedure. While for larger filters we use a continuous extraction procedure¹, the small filters are treated as follows. If there is any chance that the charcoal might have a considerable moisture content, we keep the filter in a small glass tube together with a few grains of dry silica gel for 2–5 min under the vacuum of a water pump. In order to prevent rapid evaporation of the solvent, the upper end of the filter is covered with a short piece of capillary tubing. The filter is then connected by its constricted end to the sample tube using a suitable piece of PTFE tubing (all parts depicted in Fig. 2). These are the only PTFE parts that are used in the entire equipment, in a position where no concentration of organic substances occurs. Nevertheless, we store both of these PTFE connections under trichloroethylene when not in use. The two restricted ends of the filter and sample tube should be in direct contact.

For extraction, we introduce 5 μl of carbon disulphide with a syringe on to the filter disc. By periodically moving the connected tubes between a warm and a cool air stream (which are always available in the vicinity of a gas chromatograph and a fume hood), we force the small volume of liquid to move up and down through the charcoal layer. Between two short mixing periods brought about in this manner, we let the filter stand for *ca.* 1 min so as to permit diffusion within the carbon particles. After a total time of *ca.* 5 min, we dip the sample tube into cool water (*ca.* 10°), thus transferring the liquid down into the cavity of the sample tube. This procedure is then repeated three times, using 3 μl of carbon disulphide each time. Owing to evaporation during the standing time, the combined extract has a volume of *ca.* 10 μl . Further repetitions of the extraction procedure yield pure solvent. We stopper the sample tubes with a piece of glass rod of the same diameter as the open end of the tubes and a hermetic connection is obtained in the same way as for connecting the filter and sample tube.

Normally, the internal standard is required to undergo the same treatment as the adsorbed substances as far as the extraction is concerned. Depending on the nature of the water sample, we add 1–10 μl of a 1:50,000 solution of the standard substance directly on to the filter disc. After waiting 1–2 min so as to allow evaporation of the solvent (hexane), the capillary cap is pushed on to the filter tube and extraction is carried out as described.

Stripping with inert gas at room temperature

The equipment used is shown schematically in Fig. 3. As far as we know, only two types of pump completely fulfil our requirements of being strictly gas-tight and working without any plastic or lubricated parts. One type, MB 110–10*, works with stainless-steel bellows. Its output cannot be controlled mechanically. Under the flow resistance conditions used, however, it automatically yields an ideal flow-rate of 2–3 l/min. The manufacturer also offers a type designed for continuous work at elevated temperature. The essential part of the second pump (Sera, MV 1181) is a stainless-steel membrane**. This pump has a variable speed gear, and offers much less

* Metal Bellows Corp., Sharon, Mass., U.S.A.; distributor for Europe: Registra Trust Reg., P.O. Box 34605, Vaduz, Liechtenstein.

** Scybert & Rahier, 3524 Immenhausen, G.F.R.

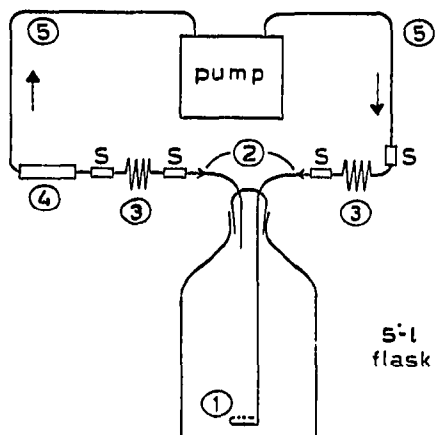


Fig. 3. Closed circuit for stripping with inert gas. 1 = Coarse glass frit; 2 = fused glass-metal connections; 3 = coiled steel tubing; 4 = filter holder (for details see Fig. 4); 5 = stainless-steel tubing, 3.2/2.0 mm; S = Swagelok fittings.

dead volume and less metallic surface than the bellows pump. On the other hand, it is considerably more delicate and more expensive. Both pumps work perfectly during continuous 24-h operation. We have had, however, no long-term experience with them.

The 5-l sample flask is stoppered with a ground-glass joint and both glass tubes leaving the ground-glass cap carry fused glass-metal connections. The circuit is essentially constructed with stainless-steel tubing of 2 mm I.D. and 3.2 mm O.D. The parts adjacent to the sample flask are spirally rolled in order to protect the glass-metal connections (which are mechanically delicate) during manipulations.

The circuit must be absolutely gas-tight, as 1–2 l of ambient air entering the circuit during a 24-h run will yield at least as much organic material as 5 l of drinking water. Fortunately, every laboratory atmosphere has its characteristic organic components, of which at least part is not present in water. The amount of these substances trapped therefore offers a direct measure of the leakage of the circuit. While it is not difficult to obtain gas-tight metallic connections, the ground-glass joint on the sample flask is a critical part of the circuit. We can reduce the leakage of this joint virtually to zero by adopting the following two measures. We balance the two major flow resistances, the fritted glass disc in the sample flask and the adsorbent filter, in such a way that the pressure between them, *i.e.*, inside the ground-glass joint, is virtually identical with the ambient pressure. Furthermore, before closing the sample flask, we wet the ground-glass surfaces with sample water. After setting the joint firmly, we cover the upper edges of the ground-glass parts with pure glycerin.

The filter holder, made of stainless steel, contains a 3 cm long bore in which the filter tube fits with a small clearance (Fig. 4), thus yielding 95–98% seal (see above). During operation, the filter holder together with the spiral tube preceding it are maintained, by means of an infrared lamp, at a surface temperature of *ca.* 35°. Under these conditions, the water, introduced from the sample flask in dust particles, is evaporated continuously.

We prepare each analytical run in the following way. The sample flask is

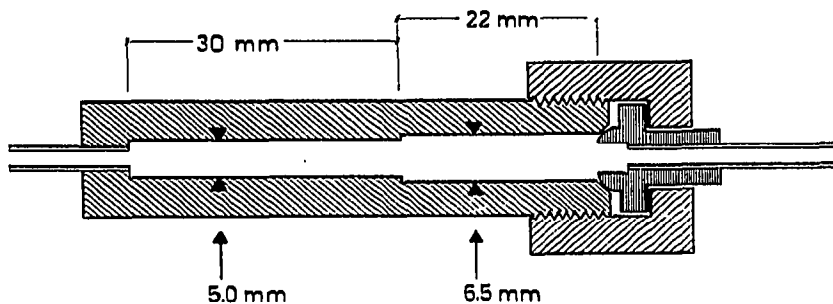


Fig. 4. Filter holder made from stainless steel, closed with a circular joint.

thoroughly rinsed with the water to be analyzed. During filling to a free volume of *ca.* 0.5 l, we carefully avoid unnecessary turbulence or bubbling that would facilitate the dissolution of atmospheric substances in the water. The hermetic stripping circuit is then established with an auxiliary adsorbent filter in the filter holder. The pump is turned on for *ca.* 1 min, which is sufficient to purify the air remaining over the water sample. The auxiliary filter is then replaced with the freshly cleaned analytical filter, and the run is started.

The stripping process is strongly intensified when the entire circuit is in a thermostatic oven, provided that the pump is built to withstand the elevated temperature. We have observed that in an oven without forced ventilation, the upper part is sufficiently warmer than the bottom to ensure that the steel tubing and filter are dry. As the temperature in the pump is automatically above ambient temperature, there is no risk of condensation in this part of the circuit. We have found, however, that sealing the circuit at elevated temperature is considerably more difficult.

Between runs, the spiral tube at the outlet of the flask is rinsed periodically with dilute acid and water so as to dissolve deposited lime or salt.

Stripping with water vapour

The closed circuit apparatus for continuous steam distillation is shown in Fig. 5. The 6-l round-bottomed flask, normally filled with 5 l of water, is heated with a 1000-W heating mantle (not shown in Fig. 5) so as to reach the boiling-point within reasonable time. The water is then kept boiling by means of a cartridge heater inserted in the bottom of the flask. In this manner, the best pre-conditions for quiet and continuous boiling (which is, nevertheless, not assured) are created. Under the conditions used (heat insulation of the flask), the heater is operated at 80–100 W for continuous stripping.

The filter holder is depicted in more detail in Fig. 6. The essential part is the 4 cm long central glass tube, in which the filter tube leaves almost no clearance. A platinum wire ring prevents the filter tube from being pushed to the left-hand side, and the charcoal filter disc itself remains *ca.* 5 mm outside the filter holder on the right-hand side. During operation it is located, therefore, in the outlet part of the tube numbered 2 in Fig. 5. The final 4 cm of this tube is wound with a heater band, which is used to slightly overheat the circulating steam and also to heat, by radiation, the filter disc. The latter function is of primary importance, because the least condensation of water in the filter disc will increase the flow resistance to such an extent that most

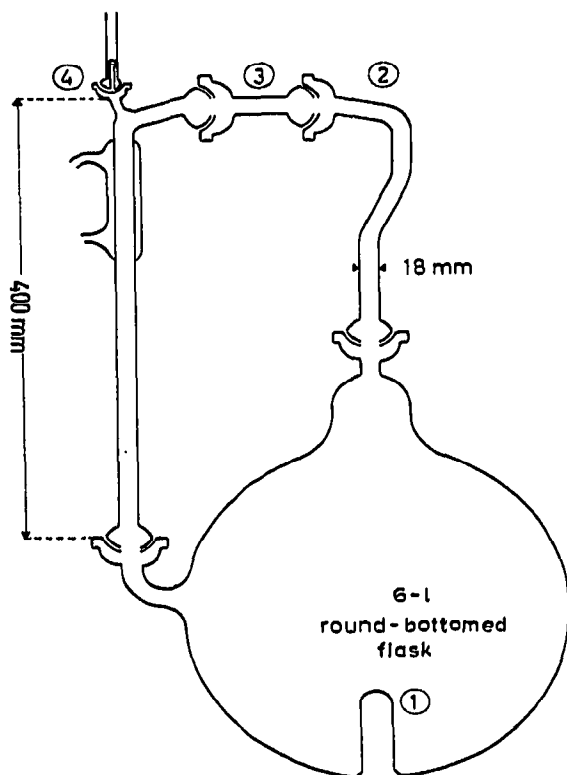


Fig. 5. Glass apparatus for stripping with water vapour. 1 = 24 mm I.D. glass tube receiving cartridge heater; 2 = externally heated section; 3 = filter holder (for details see Fig. 6); 4 = back-flow valve.

of the water sample will be driven out of the apparatus through the back-pressure valve (4).

A further essential detail of the apparatus is the free height above the surface of the water sample. During operation, a head of water is built up in the vertical tube on the left-hand side and the height of this column of water determines the pressure over the water sample and, therefore, the flow-rate in the circuit. The 40-cm dimension shown relates only to our equipment; it can be increased to give a greater excess of pressure over ambient.

An important advantage of this circuit system is that the entire circuit operates constantly with an internal pressure slightly above ambient pressure. Therefore,

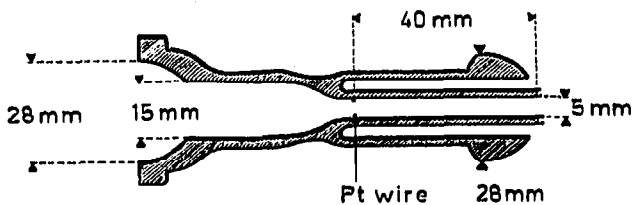


Fig. 6. Filter holder (Pyrex glass) for stripping with water vapour.

provided that the ground-glass joints are of good quality, negligible losses, but no artifacts from the ambient air, are to be expected. During prolonged use, the sample flask becomes considerably corroded, which may produce problems of interferences from the glass surface. We believe that a sample flask should be reserved for a given type of sample in which the inorganic content and acidity are virtually constant.

When starting a run, twice the normal power is applied to the heated section (2) in order to keep the charcoal dry. It is important, furthermore, that boiling should start slowly, *i.e.*, the heating mantle should be turned off early. During the whole of the heating period, air from the sample flask is transferred through the filter and is periodically released through the back-pressure valve (4). In order to avoid sudden outlet of relatively large volumes of air, we apply a water column of *ca.* 5 cm above the valve, followed by a volume of *ca.* 20 ml of air, with a needle valve acting as a pressure regulator. It takes 3–4 h to reach final equilibrium. All of the air has then been expelled, and the upper surface of the water column, equalling the pressure drop through the filter, remains in the lower part of the water cooler. This equilibrium depends, of course, on the power applied to the cartridge heater in the sample flask. The power applied to the heating of the filter area is lowered to a minimum that has to be found experimentally. Heating that is too intense will impair the adsorption and increase the losses of relatively volatile substances, while insufficient heating will completely disturb the run by sudden overpressure. Once equilibrium is established, the equipment can be left unattended for several days.

It should be noted that continuous steam distillation is much more delicate and complicated to operate than a circuit working with a pump.

As a modification, we have tried to carry out the procedure under vacuum. The water vapour leaving the filter was conducted directly to the water pump, the principle of a closed circuit thus being abolished. Operation under these conditions is very simple. A run is automatically terminated when almost all of the water has been evaporated. In addition to the problems created by operating without a closed circuit, the main problem with this procedure is the important pressure drop acting on the ground-glass joints. We have not been able to design an apparatus that would eliminate the ingress of relatively large volumes of ambient air containing serious artifacts.

GLC and GLC-MS analysis

The organic material trapped from water has a very complex composition, for which reasonably high-resolution GC is indispensable. Many workers seem to have wasted their efforts by using a clearly insufficient resolution. As an example of the analysis of water pollution by capillary column GC, Adlard *et al.*²⁶ examined the resolution of alkanes up to C₃₈. In drinking water, an extremely broad molecular-weight range of organic substances was found, at least when intensified stripping, *e.g.*, by steam distillation, was used. Complete analysis, therefore, necessitates separate runs on a regular and on a high-temperature column. We shall report on this aspect in Part II of this work. The examples described in this paper were examined with one column only. In order to broaden the volatility range of the resolved material, we selected a short column (a glass capillary, 20 m × 0.28 mm I.D., coated with Emulphor O), which for detailed analysis does not give an adequate separation.

As all samples are obtained as very dilute solutions (diluted 1:10⁶ to 1:10⁷), sufficient material can be introduced on to the column only by directly injecting 1–3

μ l. We have described the corresponding technique in an earlier paper²⁷. All GC analyses were carried out on gas chromatographs from Carlo Erba, Milan, Models GI and 2400 T.

For mass spectrometric identification, severe pre-conditions have to be observed. In order to introduce the substances in as pure a state as possible, at least the same chromatographic resolution in GC-MS as in GC alone has to be assured. Because of the very small amounts of single substances involved, any loss caused by the GC-MS interface has to be avoided. For the same reason, the coupled capillary column must have a very low bleed rate. We use a Model CH5 mass spectrometer from Varian-Mat. We have recently given details of the coupling technique²⁸. An important feature of this technique is the possibility of using the same capillary column for GC as for GC-MS, with negligible loss of time and effort. Hence, identical resolution patterns can be obtained from both applications. At first, this may seem to be illusory, with respect to the very different flow conditions (He instead of H₂ as carrier gas; high vacuum instead of ambient pressure at the column exit), but it is our long experience that identical elution sequences are observed, provided that the temperature programme for the GC-MS run is set in such a way that a given substance is eluted at exactly the same temperature as in GC alone. This procedure greatly facilitates the interpretation of gas chromatograms.

Examples of water analyses

Fig. 7 shows analyses of the drinking water from the Zürich supply and of the surface water of Lake Zürich. The reason for comparing the two samples is that *ca.* 60% of the drinking water originates from Lake Zürich, the remainder being ground water. Sampling for both analyses was carried out on the same day.

For the semi-quantitative interpretation, one has to remember that in the case of lake water, 2.5 times as much internal standard (peak No. 50) has been added. Taking into account the different heights of the standard peaks, one realizes that the peak heights in the chromatogram of the lake water must be multiplied *ca.* 8 times in order to allow a direct comparison of both chromatograms. The essential results of this comparison are then as follows. Qualitatively, the same substances are found in both samples, with 5-10 times lower concentrations in the drinking water. For single substances, this relationship does not occur proportionately. Nos. 38 and 62, for instance, appear in virtually the same concentrations in lake and drinking water. The most striking difference occurs with the low-molecular-weight substances, for which the concentrations in lake water exceed those in drinking water by 15-20 times. It was found that these substances are almost exclusively derived from automobile fuel. We have sampled lake water at the surface of the lake, which is in equilibrium with the atmosphere, and it is known that most of the organic substances in the atmosphere are constituents of automobile fuel^{1,29}. In the production of drinking water, in contrast, lake water is pumped from a depth of some 100 m.

Table I presents some preliminary identifications of the numbered peaks in Fig. 7. The nature of the individual substances will be discussed in more detail in Part II of this work. At present, we may state that numerous substances in unpolluted water yield mass spectra that are not easily interpreted. The substances are, therefore not of a simple nature.

While these analyses have been carried out by stripping with air at room

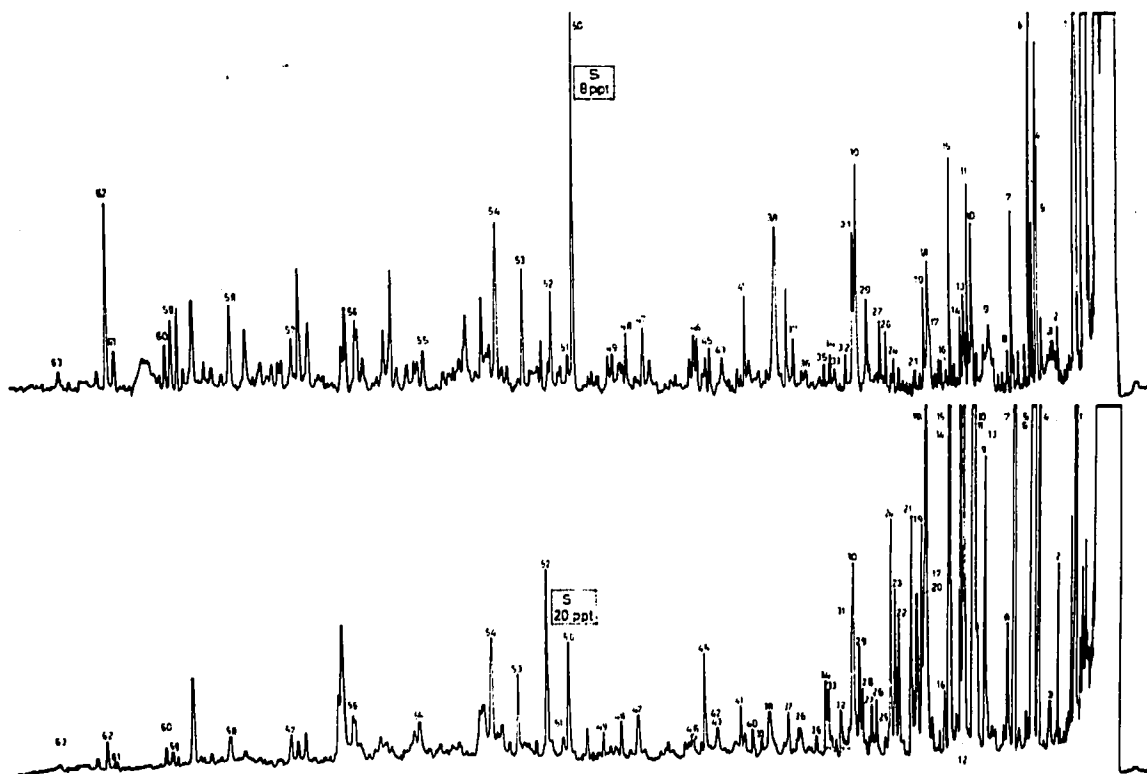


Fig. 7. Organic substances stripped with inert gas from drinking water (upper chromatogram), and from surface water of Lake Zürich (lower chromatogram). For direct quantitative comparison, peaks in the lower chromatogram must be multiplied 8 times in height (see text). A 2.0- μ l volume of CS_2 solution was injected without splitting on to a glass capillary 20 m \times 0.28 mm I.D., coated with Emulphor; carrier gas, H_2 , 2.5 ml/min; temperature programmed at 3.0 $^\circ$ /min from 25 $^\circ$ to 185 $^\circ$; attenuation 1 \times 4.

temperature, Fig. 8 shows an analysis of the same drinking water run with continuous steam distillation. The striking difference is the almost complete loss of more volatile substances, which is not surprising as the charcoal filters used for purifying industrial exhaust gases are regenerated by purging with steam. This result demonstrates, however, the great importance of any measure (*e.g.*, the use of a vacuum) that permits the temperature of the adsorbent filter to be reduced during stripping. The advantage of this procedure is the efficient stripping of high-molecular-weight and more polar substances, as will be shown more clearly in the next section.

Stripping efficiency and recovery under different analytical conditions

In order to evaluate the efficiency of our procedures, we have developed the following recovery test. To a water sample from which the organic components had been previously stripped, we added the substances indicated in Fig. 9 and Table II. The substances were selected to represent various functional groups as well as to match the ideal working range of a short Emulphor capillary. We prepared a solution containing each substance at a concentration of 1 in 50,000 in acetone. In the example

TABLE I
LIST OF SUBSTANCES IDENTIFIED

Numbers correspond to peaks in Fig. 7.

| No. | Substance | No. | Substance | No. | Substance |
|-----|------------------------|--------|--------------------------|--------|--|
| 1 | Toluene | 20 | Indane | 46 | Trichlorobenzene |
| 2 | <i>n</i> -Nonane | 21-24 | C ₄ -benzenes | 47 | Pentadecane |
| 3 | Isodecane | 25 | Methylindane | 48, 49 | Methylnaphthalenes |
| 4 | Ethylbenzene | 26 | Dichlorobenzene | 50 | Hexamethylbenzene (internal standard) |
| 5 | 1,4-Dimethylbenzene | 27 | <i>n</i> -Dodecane | 51 | Hexadecane |
| 6 | 1,3-Dimethylbenzene | 28 | Indene | 52 | C ₁₃ H ₂₂ O |
| 7 | 1,2-Dimethylbenzene | 29, 30 | C ₄ -benzenes | 53 | Diphenyl ether |
| 8 | <i>n</i> -Decane | 31 | Dichlorobenzene | 54 | Heptadecane |
| 9 | Propylbenzene | 32, 33 | Methylindanes | 55 | Octadecane |
| 10 | 4-Ethyltoluene | 34 | C ₄ -benzene | 56 | Nonadecane |
| 11 | 3-Ethyltoluene | 35 | Ethylindane | 57 | Eicosane |
| 12 | Isoundecene | 36, 37 | C ₅ -benzenes | 58 | C ₂₁ -alkane |
| 13 | Trimethylbenzene | 38 | Paraldehyde | 59 | C ₂₂ -alkane |
| 14 | 2-Ethyltoluene | 39 | C ₆ -benzene | 60 | <i>o</i> -Terphenyl |
| 15 | 1,2,4-Trimethylbenzene | 40 | C ₅ -benzene | 61 | C ₂₃ -alkane |
| 16 | <i>n</i> -Undecane | 41 | Trichlorobenzene | 62 | Dialkyl phthalate |
| 17 | Propyltoluene | 42 | C ₅ -benzene | 63 | C ₂₄ -alkane |
| 18 | 1,2,3-Trimethylbenzene | 43 | Tetradecane | | |
| 19 | Isooctenone | 45 | Naphthalene | | |

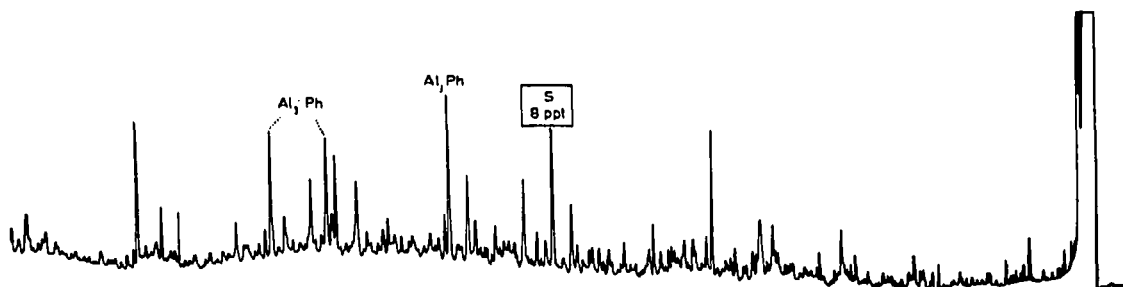


Fig. 8. Organic substances stripped from drinking water with water vapour (closed steam distillation). Many substances are qualitatively identical with those indicated in Table I. Al₃Ph = trialkylphosphates (3 peaks), not detectable by stripping with inert gas.

depicted in Fig. 9 (stripping with air at room temperature), 2 μ l of this solution were added with a syringe to 50 ml of drinking water. We know from many previous tests that, under these conditions, even long-chain alkanes are completely dissolved in water. In the stripping circuit (Fig. 3) used to purify the water sample, we now opened a Swagelok fitting on the output side of the pump, and replaced the tubing from the pump with a rectangular piece of steel tubing. We immersed the vertical end of the latter in the water containing the test substances. Turning on the pump for *ca.* 2 sec was just sufficient to suck the water into the sample flask without simultaneously introducing ambient air. The procedure was repeated with several 50-ml volumes of water to rinse the beaker and the tube. We then introduced the fresh adsorbent filter, closed the circuit and started the stripping operation. Before extracting the filter,

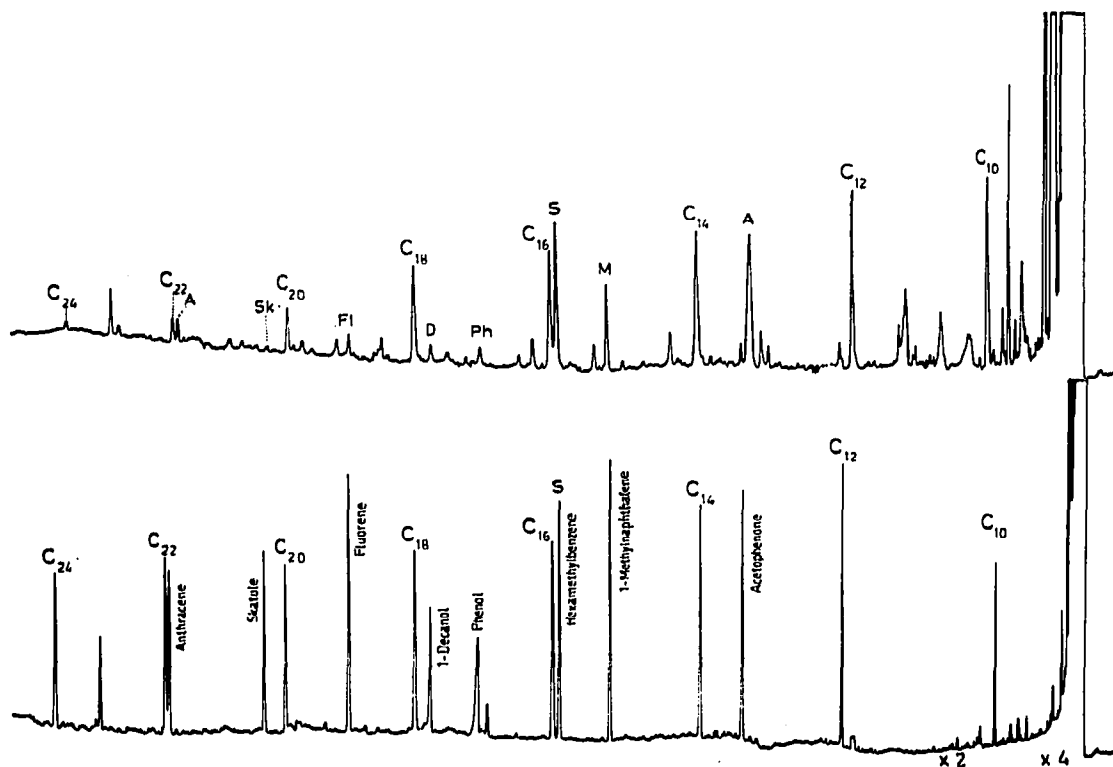


Fig. 9. Recovery test. Upper chromatogram: test substances added to purified water to yield 8 ppt per single substance. Same amount of internal standard (S) added to filter after stripping. Stripping with inert gas, 20 h at 25°. Lower chromatogram: direct separation of a mixture of test substances with the same amount of internal standard. Chromatographic conditions as for Fig. 7.

we added, directly on to the filter disc, 2 μ l of a hexane solution containing hexamethylbenzene (the internal standard) at a concentration of 1 in 50,000. The solution obtained by extracting the filter produced the upper chromatogram in Fig. 9. The lower chromatogram was obtained from a mixture of equal amounts of both of the above 1 in 50,000 solutions in carbon disulphide. For 100% recovery, therefore, both chromatograms should be identical, *i.e.*, with identical peak height ratios of the test substance to the internal standard. By comparing these ratios, it is easy to calculate the actual recoveries.

Table II gives the recoveries calculated from Fig. 9 and the corresponding figures obtained with prolonged stripping. The third column of figures in Table II shows the recoveries obtained by prolonged stripping from a more concentrated sample (corresponding to lake water rather than to drinking water). Finally, the figures for a relatively short extraction with water vapour (steam distillation) are given. From these results, the following simplified rules can be deduced.

From drinking water (with a concentration of major constituents of *ca.* 5 ppt), the alkanes can be extracted and determined with losses less than 25% up to C_{20} by simple stripping with air at room temperature. For lightly polluted water, as found in lakes and rivers, the corresponding limit is C_{22} . For aromatic as well as

TABLE II
RECOVERY OF TEST SUBSTANCES (%) UNDER DIFFERENT STRIPPING AND CONCENTRATION CONDITIONS

| Substance | Air, 2.5 l/min, 25° | | Steam distillation, | |
|-------------------------|---------------------|-------|---------------------|--------|
| | 20 h, | 44 h | 20 h, 100 W, | |
| | 8 ppt | 8 ppt | 8 ppt | 20 ppt |
| C ₁₀ -alkane | 91 | 86 | 92 | — |
| C ₁₂ | 102 | 97 | 98 | 16 |
| Acetophenone | 85 | 90 | 88 | 62 |
| C ₁₄ | 92 | 101 | 96 | 48 |
| Methylnaphthalene | 49 | 62 | 92 | 50 |
| C ₁₆ | 96 | 102 | 97 | 71 |
| Phenol | — | — | 5 (?) | 67 |
| 1-Decanol | 21 | 36 | 62 | 102 |
| C ₁₈ | 86 | 97 | 101 | 72 |
| Fluorene | 13 | 21 | 47 | 42 |
| C ₂₀ | 43 | 78 | 94 | 68 |
| Skatole | 3 | 4 | 11 | 23 |
| Anthracene | 21 | 32 | 57 | 82 |
| C ₂₂ | 21 | 45 | 84 | 67 |
| C ₂₄ | 7 | 16 | 47 | 74 |

for oxygenated and nitrogenated substances, the limits are shifted to much lower molecular weights and must be checked individually.

Stripping with water vapour shifts the corresponding limits towards much higher molecular weights and yields much better efficiencies for polar materials. Simultaneously, low-molecular-weight substances are lost (alkanes up to C₁₆).

These results may seem to be very modest with respect to recovery as well as concerning structural limitations. We stress, however, that no other procedure has shown comparable potentialities. This holds with the exception of certain substances, the analytical conditions for which are especially favourable, e.g., halogenated hydrocarbons.

Semi-quantitative determinations

The only reliable way to determine a given constituent in water is as follows. After qualitative identification, an additional run is made with water to which a known amount of the same substance has been added so as to give a concentration as close as possible to that in the fresh sample. A chromatographic run is also made under identical conditions with a sample containing the required substances together with an internal standard in a known proportion. From these runs, the result obtained from the fresh sample can easily be corrected for 100% recovery. The major source of errors in this procedure are substances being accidentally eluted together with the substance to be determined, or together with the internal standard. This risk is best minimized by using high-resolution separations.

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