**Note**

# Simple method for concentrating volatiles in water for gas chromatographic analysis by vacuum distillation

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In order to obtain mass spectrograms of the less concentrated contaminants in drinking water, a gas chromatographic–mass spectrometric (GC–MS) technique, capable of concentrating volatiles from large volumes of water, is required[1]. Likewise there is a similar need if extremely low levels of trace contaminants are to be analyzed by the purge-and-trap technique using more conventional detectors.

The purge-and-trap techniques that are capable of handling liter-size water samples are either inefficient, involve the expense of constructing specialized equipment, or require long purge times or heating the water which can cause chemical changes to occur[1-6]. The vacuum distillation apparatus described here is easily constructed and readily coupled to commercial purge-and-trap systems. The distillate of a 1-l water sample is condensed in a liquid nitrogen trap over a period of about 13 min. The purgeable components in the distillate are then transferred to a gas chromatograph by conventional gas purging. The losses of volatiles due to the formation of mists in the cryogenic trap is largely avoided by the formation of a closed system when an ice plug forms in the trap shortly after distillation begins.

EXPERIMENTAL

*Purging system*

A schematic diagram of the purging system is shown in Fig. 1. The purging vessel was a 1-l Pyrex ⚎ 24/40 short-necked round-bottom boiling flask (1) with a 2 × 3/8 in. magnetic stirring bar (Cole-Parmer, Chicago, IL, U.S.A.) with hemispherical ends. The contents of the flask were stirred with a Thermolyne stirrer hot plate, Model SPA 1025B (2). A ⚎ 20/40 JA-2790 adaptor (3) (SGA, Bloomfield, NJ, U.S.A.) connected the flask to the system. Only a small amount of silicone vacuum grease was used on the upper portion of the adaptor to reduce any possible adsorption of the volatiles. All tubing connections in the system were made with 1/4 in. I.D. polyethylene tubing (1/16 in. wall), which was softened with a heat gun for ease in making the connections. A 15-cm length of 0.7 cm O.D. glass tubing (4) connected the adaptor to the U-tube trap (5). The lower portion of the U-tube trap was 18.5 cm high and had arms of 1 cm O.D. glass tubing spaced 2.5 cm apart (center to center). The upper section of the U-tube trap was of 10 cm lengths of 0.7-cm tubing bent at right angles to the plane of the U-tube (shown on opposite sides and in the plane of the
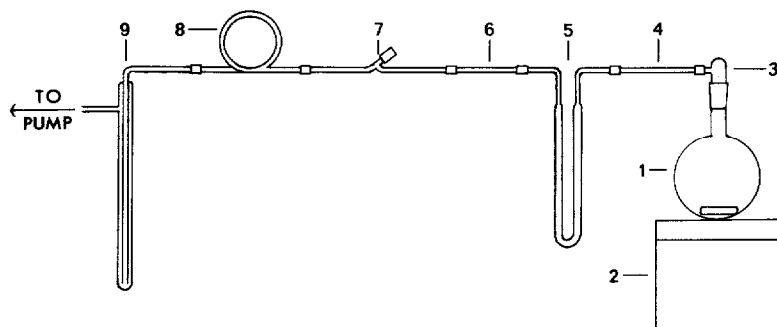
Fig. 1. Vacuum purging system. 1 = Purging flask and magnetic stirring bar; 2 = magnetic stirrer; 3 = adaptor; 4 = glass tube; 5 = U-tube trap containing glass beads; 6 = capillary tubing (optional); 7 = polytetrafluoroethylene stopcock; 8 = polyethylene tubing; 9 = vacuum trap.

U-tube in Fig. 1 to avoid overlap in the diagram). This provided a compact system and greater convenience in connecting the U-tube trap to the purge-and-trap sampler. The trap was filled with 5 g of 3 -mm glass beads. The air in the system was evacuated through a 5-cm length of 0.49 mm I.D. capillary tubing (6) (cut from a 10-$\mu l$ micro-syringe) connected to the trap. A Rotaflo polytetrafluoroethylene stopcock, Corning No. 7500-3 (Corning Glass Works, Corning, NY, U.S.A.) (7) isolated the capillary tube from the high vacuum portion of the system. A 10-cm diameter loop of poly-ethylene tubing (8) shaped by heating in a steam bath connected the stopcock to the liquid nitrogen vacuum trap (9) and provided flexibility to the system. The vacuum source for the system was a two stage mechanical vacuum pump.

*Connection to purge-and-trap sampler*

After concentrating the volatiles, the U-tube trap was connected to a Hew-lett-Packard 7675A purge-and-trap sampler with 1/4 to 1/16 in. stainless-steel Swage-lok reducing unions. The U-tube was joined to the reducing unions with 1/4 in. I.D. polyethylene tubing. The connections to the purge tube and purge return tube of the purge-and-trap sampler were of 15-gauge polytetrafluoroethylene tubing obtained from Penntube Plastics (Clifton Heights, PA, U.S.A.).

*Purging technique*

Before evacuating the system the U-tube trap was immersed in liquid nitrogen to a depth of 1 cm above the glass beads for a minimum of 2 min. The Dewar flask was filled with liquid nitrogen to within 6 cm of the top. The stopcock was slowly opened until gurgling from the vaccum pump was heard, at which time stirring at full speed was begun. With the stopcock open to the air, the flow-rate corresponded to about 350 ml/min. After 1 min the stopcock was slowly opened further. The Dewar flask was raised for 1 to 2 s each minute to the top of the U-tube. This helped to initiate a continuous distillation of water into the U-tube. If condensate was already moving down the lower portion of the tube the raising of the Dewar flask was delayed until the condensate reached the level of the liquid nitrogen. Once continuous distil-lation of the water began, the level of the liquid nitrogen was kept about 1 cm above the frozen section of the tube by raising the Dewar flask. The distillation was stopped

when the frozen condensate reached a mark 13 cm from the bottom of the tube. The average amount of water collected in the experiments was 4.41 $\pm$ 0.24 g S.D. ($n$ = 15).

The U-tube is best removed from the system by cutting the polyethylene connections lengthwise with a razor blade so that the cuts form a shallow "V". The liquid nitrogen vacuum trap should be kept under vacuum when cooled to prevent possible hazardous liquid air accumulation.

Since the purge-and-trap sampler inlet and outlet were vented to the atmosphere when in the prepurge mode, the U-tube was connected to the sampler immediately, without concern for pressure build-up as the tube warmed. After bringing the tube to 25°C by placing it upright in a beaker of water, the concentrate was purged for 10 min with a helium flow-rate of 20 ml/min.

*Gas chromatography*

The purge-and-trap sampler was coupled to a Hewlett-Packard 5840A gas chromatograph equipped with a flame ionization detector. An 8 ft. × 1/8 in. O.D. stainless-steel column packed with 1% SP-1000 on 60–80 mesh Carbopack B (Supelco, Bellefonte, PA, U.S.A.) was used for the analyses. The helium flow-rate was 30 ml/min. The temperature programming was started at 45°C with a 3-min hold followed by an 8°C/min heating rate to 200°C. Purge and column flow-rates were regulated with a mass flow controller.

*Measurement of recoveries*

To obtain the GC response factors of the volatiles selected for the determination of recovery efficiencies, a 5-$\mu$l portion of the volatiles dissolved in methanol was transferred to a 10-ml purge-and-trap sampler tube. Heating was found to be unnecessary for the transfer of the compounds used in the recovery tests. Less volatile compounds can be transferred by placing aluminium foil behind the tube to act as a heat shield and heating the tube with a heat gun. Care must be taken to begin the purge before heating or a portion of the compounds may escape out the purge vents. Standards were analyzed after each vacuum distillation to compensate for time-dependent variations when calculating the recoveries.

While slowly momentarily stirring, the 1-l water samples were spiked directly in the flask with a 5-$\mu$l injection of a methanolic solution of the volatiles.

RESULTS AND DISCUSSION

Not all stirring bars or magnetic stirrers were found to be able to achieve the high stirring speed used in this technique. Flat-ended stirring bars appeared to have much less rotational stability then those with rounded ends. This may be due to the flat-ended stirring bars slightly higher positioning in the flask and the resulting weaker interaction with the stirring plate magnet. Differences in stirring bar stability were also noted among the brands of magnetic stirrers. Some makes were unable to keep the stirring bar centered at high speed or their highest speed was insufficient to form a vortex 2.4 cm wide at the bottom of the flask. The speed of the stirrer under the stirring load used was 1280 rpm, which is significantly greater than the nominal speed listed by the manufacturer. A preliminary experiment with a lower-speed stirrer,

TABLE I

RECOVERIES AND PURGE RATIOS OF SELECTED COMPOUNDS

| Compound | Recovery (%) ± S.D. (n = 4) | | Purge ratio |
|---|---|---|---|
| | With capillary | Without capillary | |
| Hexane | 83 ± 3 | 87 ± 7 | 0.12 |
| Carbon tetrachloride | 85 ± 1 | 85 ± 3 | 0.14 |
| Chloroform | 82 ± 2 | 83 ± 2 | 0.32 |
| Dichloromethane | 81 ± 3 | 82 ± 3 | 0.42 |
| Benzene | 81 ± 2 | 81 ± 3 | 0.25 |
| 1,2-Dichloroethane | 68 ± 1 | 67 ± 2 | 0.66 |
| Diethyl ether | 63 ± 3 | 62 ± 3 | 0.68 |
| Methyl isobutyl ketone | 12.3 ± 0.3 | 12.2 ± 0.6 | 0.96 |
| Methyl acetate | 11.8 ± 0.6 | 11.2 ± 0.6 | 0.94 |
| Tetrahydrofuran | 3.7 ± 0.2 | 3.6 ± 0.1 | 0.97 |

which formed a vortex reaching to within 3.5 cm from the bottom, gave an 11% lower average recovery of the volatiles than when the faster stirrer was used.

Differences in the weight and volume of flasks of even the same brand were found to have an effect on the stirring. The rotational stability of the stirring bars was greater in the lighter flasks. On the assumption that this greater stability was due to better interaction between the stirring bar and stirrer magnet because of thinner glass, the height of the stirrer magnet was increased by adjusting the set screw positioning the magnet. This resulted in a considerable increase in the rotational stability of stir bars used in the heavier flasks.

The volume of the flask used in the experiments was such that when it was filled to 1 l, the diameter of the surface of the water was 8.4 cm. The diameter of the water surface should be as wide as possible, since this will make a strong vortex easier to form. If necessary a smaller volume of water may have to be used in order to obtain a strong vortex.

A phenomenon is observed during the vacuum distillation that can mistakenly lead one to believe a leak is present in the system. After the initial condensation of water in the U-tube there is a period when no material appears to be distilling over. Normal distillation is eventually resumed when water begins to condense on the inside surface of the tube and then falls into the liquid nitrogen zone. This effect is believed to be the result of dissolved gases escaping from the water in the flask after the initial transfer of water seals off the flask from the vacuum pump. These residual gases which impede the transfer of water vapor finally become trapped in condensing moisture and normal distillation resumes.

Hexane, carbon tetrachloride, chloroform, dichlormethane, benzene, 1,2-dichloroethane, diethyl ether, methyl isobutyl ketone, methyl acetate and tetrahydrofuran were used to determine the recovery efficiencies achieved by vacuum distillation (Table I). The recovery tests were conducted at 25°C with the volatiles at a concentration of 40 ppb* by weight. Tests with and without the capillary tube were performed in quadruplicate. The purpose of the capillary tube in the system was to

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* Throughout the article the American billion ($10^9$) is meant.

decrease the initial flow of gases through the U-tube and thus increase the trapping efficiency of the more volatile components. The results in Table I show that there are insufficient differences in the data sets to indicate a statistically significant difference in recoveries between the two techniques.

To determine if the recovery efficiencies of volatiles could be estimated, purge ratios[7] were used. Purge ratios were calculated from GC data obtained by repeated purges of a water sample using a Hewlett-Packard purge-and-trap sampler. A 10-ml water sample was spiked with 5 $\mu$l of the methanolic standard. The sample was purged for 5 min at 25°C with a stream of helium at a flow-rate of 20 ml/min. The purge ratios, which are a measure of the ease of purging a volatile component, were calculated by dividing the GC response of a purge by the response of the preceding purge. Since a low purge ratio indicates that a compound is easily purged from water, it should indicate a high recovery rate.

The data in Table I show that readily purged compounds with a purge ratio between 0.12 and 0.42 had a narrow recovery range of 81 to 87%. The less readily purged 1,2-dichloroethane and diethyl ether had purge ratios of 0.66 and 0.68, respectively, and were recovered in the 62-67% range. The difficult to purge compounds with purge ratios between 0.94 and 0.97 had recoveries from 4 to 12%.

Overall this vacuum distillation technique has been found to be an effective method of concentrating purgeable water contaminants for analysis.

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