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Note

Removal of gas chromatographable organic compounds from water by a spray vaporization technique

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Gas chromatographic (GC) methods for determining organic contaminants in water generally include some pre-concentration procedures¹⁻³. It is desirable to test proposed pre-concentration procedures with model compounds added to "real" water. Inorganic compounds and non-volatile organic substances, such as humic acid, can affect the efficiency of pre-concentration procedures. However, "real" water samples contain a diverse assortment of organic contaminants⁴, and these can interfere with the GC determination of added model compounds. One method of avoiding this paradoxical situation is to remove selectively volatile and semi-volatile organic compounds from water used in sample preparation.

Distillation, oxidative distillation, and reverse osmosis are undesirable techniques for removing gas chromatographable impurities from water because these procedures also produce a drastic change in the concentration of other water constituents. Sorbents such as activated carbon and macroreticular resins are effective and somewhat selective. They remove most of the gas chromatographable organic material from water, do not retain significant amounts of inorganic matter, nor do they remove humic acid and humic-associated matter which comprise the bulk of the non-volatile organic constituents in most water samples. The major drawback to the use of these sorbents is that an involved pre-cleaning procedure must be used to remove manufacturing impurities from the sorbents. In addition, the sorbents must be re-cleaned or replaced periodically. Inert gas stripping provides a convenient and simple means of removing many organic compounds from water. However, stripping is a batch process and as such it is inconvenient to process significant volumes of water. In addition, heating and prolonged stripping times are required to remove many less volatile compounds even from small volumes of water.

A variation of inert gas stripping called spray vaporization has been developed which is simple, produces 600 ml of water per hour, and leads to a significant reduction in the concentration of most gas chromatographable organic compounds. The technique consists basically of atomizing water into a high-velocity gas stream using a nebulizer of the type used on perfume bottles and throat sprayers. The very fine water mist which is produced is directed to impact on a glass surface; there it condenses and coalesces on impact and drains into a reservoir. Gas chromatographable organic impurities in the water are carried from the system in the gas stream.

EXPERIMENTAL

Apparatus

The spray vaporization device used is shown in Fig. 1. The spray head was cannibalized from a Devilbiss Model 15 throat sprayer (available in drugstores for about US\$ 4). A stopper to support the sprayer inside the device was machined from PTFE. The rest of the device was constructed from standard laboratory equipment.

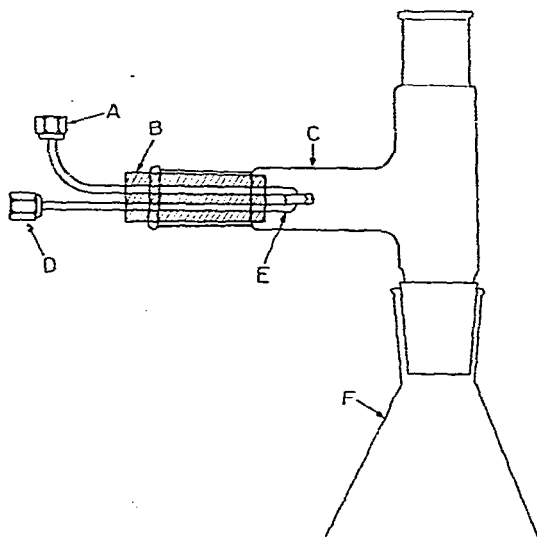


Fig. 1. Spray vaporization device. (A) Water inlet; (B) PTFE stopper; (C) $\frac{1}{8}$ 24/40 connecting tube; (D) air inlet; (E) spray head from Devilbiss Model 15 throat sprayer; (F) reservoir.

A Hewlett-Packard Model 5711A gas chromatograph equipped with dual flame ionization detectors and a Tracor Model 550 gas chromatograph equipped with a ^{63}Ni electron capture detector were used in evaluating the effectiveness of spray vaporization.

Evaluation procedures

The effectiveness of spray vaporization as a method for removing organic compounds was evaluated on solutions of forty compounds previously identified in drinking water (Table I). Samples containing acetone, methanol, or ethanol were spray vaporized and any of the added compounds remaining in the condensed water were determined directly by GC. All other model compounds were added to water as acetone solutions. After spray vaporization model compounds remaining were concentrated by solvent extraction and determined in the extraction solvent by GC. In all cases removal efficiency was based on comparison of chromatograms obtained for the nebulized samples of spiked water treated in an identical manner except that the spray vaporization step was omitted. Chloroform was extracted from drinking water by sorption on XAD-2 resin (Rohm & Haas, Philadelphia, Pa., U.S.A.) followed by elution with methanol. Chloroform was determined in the eluent by GC using a

Tenax GC column and an electron capture detector. In this instance, again, identical samples were analyzed with the only difference between them being that one was spray vaporized and the other was not. A profile of organic contaminants in Iowa State University tap water was obtained by passing 50 l of water at a flow-rate of 10 ml/min through a 5 in. \times $\frac{1}{2}$ in. I.D. XAD-2 sorption column. After 3 $\frac{1}{2}$ days the organic compounds sorbed were eluted with 50 ml of diethyl ether, the diethyl ether was dried and evaporated to 1 ml, and a profile of the organic compounds removed from the water was determined by GC. A manifold was constructed so that an identical stream of water was simultaneously introduced into the spray vaporization device. The condensed water was passed through an XAD-2 sorption column as indicated above and a profile of organic contaminants remaining was determined using identical procedures. The results are given in Fig. 2.

Headspace determination of the distribution coefficient of acetone

The distribution coefficient of acetone between water and air was determined by adding known amounts of acetone to 6.25 ml of water in a 12.50-ml septum vial. After the acetone had equilibrated between the water and the air, an aliquot of the air was withdrawn and the acetone in it was determined by GC. Since the concentration of acetone originally in the water, the concentration in the air at equilibrium, and the relative volumes of air and water were known, a distribution coefficient could be calculated.

RESULTS AND DISCUSSION

Removal of model organic compounds from water

The spray vaporization technique was applied to forty compounds typical of those previously identified in drinking water⁴. The concentration of nearly half of the compounds tested was reduced to an undetectable level and the average concentration of all compounds was reduced by *ca.* 91% (Table I). The technique was less effective when applied to some polynuclear aromatic compounds and to low-molecular-weight alcohols and ketones than when it was applied to other types of compounds. It is believed that the distribution coefficients of these types of compounds between air and water are extremely unfavorable. This was to be expected considering the high water solubility of the low-molecular-weight alcohols and ketones and the high boiling points of polynuclear aromatic compounds.

Application of spray vaporization to the removal of organic compounds from real water samples

Chloroform was determined in two identical samples of drinking water from Slater, Iowa. One sample was spray vaporized and the other was not. Spray vaporization resulted in a reduction of the chloroform concentration from 22–2.6 ppb*. A second test was performed on two identical samples of tap water from Iowa State University. The organic contaminants in one 50-l sample were concentrated using the resin sorption method³. The other sample was spray vaporized and then treated

* Throughout this article, the American billion (10⁹) is meant.

TABLE I
REMOVAL OF MODEL ORGANIC COMPOUNDS FROM WATER

Compound (b.p., °C)	Removal (%)	Compound (b.p., °C)	Removal (%)
Chloroform (62)	100	Methyl hexadecanoate (418)**	100
Chlorodibromomethane (120)	100	Methyl octadecanoate (443)**	100
Bromodichloromethane (90)	100	Acetone (56)***	75
Bromoform (150)	100	2-Pentanone (102)	94
1,1,2,2-Tetrachloroethane (131)	100	Benzaldehyde (178)	92
Hexachloroethane (187)	100	Acetophenone (202)	84
1,2,3-Trichloropropane (157)	100	β-Naphthol (285)	96
Hexachlorobutadiene (215)	95	Cumene (152)	97
Bis(2-chloroethyl) ether (178)	92	Dimethylnaphthalene (268)**	100
<i>o</i> -Dichlorobenzene (181)	100	Acenaphthalene (279)**	80
<i>m</i> -Dichlorobenzene (173)	100	Anthracene (340)**	74
<i>p</i> -Dichlorobenzene (174)	100	Fluoranthene (ca. 375)**	68
1,2,3-Trichlorobenzene (208)	100	Pyrene (393)**	60
Polychlorinated biphenyls (>275)*	94	Methanol (65)***	40
Dodecane (216)	100	Ethanol (79)***	73
Tetradecane (254)	91	Heptanol (176)	89
Hexadecane (287)	95	Dimethyl phthalate (284)	96
Octadecane (316)	94	Di(<i>n</i> -butyl) phthalate (340)	87
Eicosane (343)	91	Biphenyl (256)	82
Methyl deconate (224)**	100	Di(2-ethylhexyl) phthalate (200 at 1 mm)	80
Methyl dodeconate (262)**	100	Average % removal	90.9
		S.D.	13.2

* Arachlor 1254.

** 500 ml of water containing 100 ppb of added organic compound spray vaporized.

*** 100 ml of water containing 500 ppm of added organic compound spray vaporized, all other samples had volumes of 100 ml and contained 1 ppm of added organic compound.

in an identical manner. As shown in Fig. 2, spray vaporization resulted in a dramatic reduction in the concentration of gas chromatographable impurities in the water.

It was assumed that spray vaporization would not affect inorganic and non-volatile organic constituents of water. This assumption was proven valid in the cases of iron, residual chlorine, and humic substances in water from Slater, Iowa.

Effect of experimental variables on the efficiency of spray vaporization

Most evaluations of the effectiveness of spray vaporization were performed at an air flow-rate of 20 l/min and a water flow-rate of 10 ml/min. In tests with acetone it was found that removal was facilitated by lower water flow-rates (Table II). However, since this technique is intended as a means of producing purified water in usable quantities, a significant reduction in water flow-rate would thwart that purpose.

Basis for the removal of organic compounds from water by spray vaporization

Organic compounds equilibrate between water and gas phases and upon entering the gas phase are swept from the system. With spray vaporization, equilibrium is driven towards removal of organic compounds by the high gas-to-water ratio. Gas flow-rates of 20 l/min and water flow-rates of 10 ml/min provide the high ratio. In

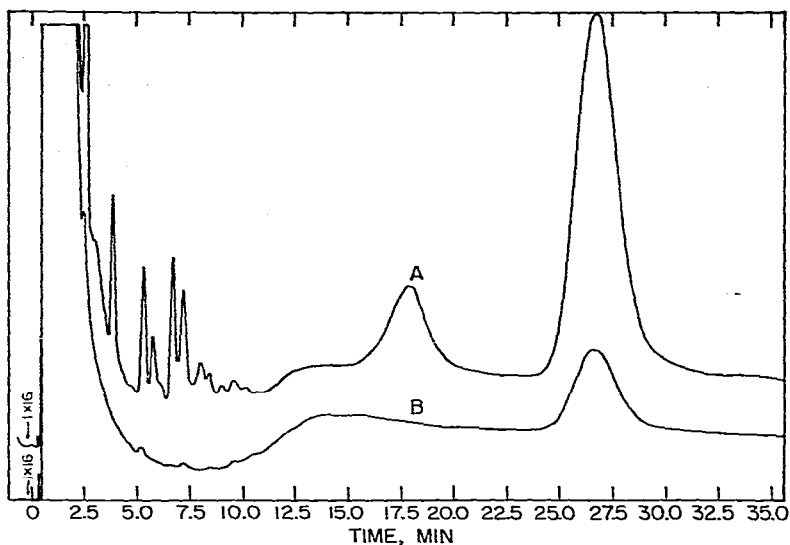


Fig. 2. Chromatograms of resin-extracts of 50 l of Iowa State University tap water. (A) Untreated water extract; (B) spray vaporized water extract.

addition, the efficient removal of organic compounds from water requires an efficient mass transfer into the gas phase which in turn requires a large contact area between the phases. The mist produced by atomization provides that large contact area. It has been shown with inert gas stripping that the overall removal efficiency is reduced due to the condensation of volatilized organic compounds on the walls of the device followed by their draining into the water⁵. This effect is less pronounced with spray vaporization because the most likely place for coalescing of the droplets occurs where the mist impacts on the glass surface. Organic compounds condensing there would tend to be re-volatilized by the high-velocity gas stream.

In the case of acetone, it has been demonstrated that removal efficiency is almost entirely determined by its distribution coefficient between air and water. The distribution coefficient, as determined by a headspace technique, was found to be $1.27 \cdot 10^{-3}$. Based on this value and the ratio of air to water introduced into the device (2000:1) a theoretical removal efficiency of 72% was calculated. It was found

TABLE II

REMOVAL OF ACETONE FROM WATER BY SPRAY VAPORIZATION AS A FUNCTION OF THE RATIO OF THE VOLUME OF WATER TO THE VOLUME OF AIR

Volume of water/volume of air	Experimental removal (%)	Calculated removal (%) ^a
2.5 ml/20 l	89	91
5.0 ml/20 l	85	84
10.0 ml/20 l	75	72
20.0 ml/20 l	54	56
50.0 ml/20 l	11	34

^a Calculated percentage removal = $100(1 + V_w/V_A K_D)$; V_w = volume of water; V_A = volume of air; K_D = distribution coefficient for acetone between air and water = $1.27 \cdot 10^{-3}$.

that experimental removal efficiencies were reasonably close to this value over a wide range of acetone concentrations. In tests at acetone concentrations ranging from 8.2–10,000 ppm an average removal efficiency of 75.3% was obtained with a standard deviation of 4.5%. In addition, the ratio of air to water was varied and again there was a reasonable agreement between the theoretical removal percentage and the experimental values (Table II). The agreement was poor only when water flow was so high that a mist was no longer produced and it is believed mass transfer became inefficient.

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