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Adsorption/thermal desorption for the determination of volatile organic compounds in water

MICHAEL E. ROSEN and JAMES F. PANKOW*
Department of Environmental Science and Engineering, Oregon Graduate Institute, 19600 NW Von Neumann Drive, Beaverton, OR 97006 (U.S.A.)
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ABSTRACT

An adsorption/thermal desorption (ATD) method for volatile organic compounds is developed using small bed volume (0.68 cm^3) cartridges of the sorbent Tenax-TA. The method allows an ATD cartridge to be desorbed and analyzed with *ca.* 30 μl of residual water still on the cartridge. The method employs a water trap between the ATD thermal desorber and the capillary column. Results obtained indicate that (1) column plugging by ice can be avoided completely, (2) the water trap has a high transmission efficiency, (3) excellent chromatography can be obtained and (4) good comparability of results is obtainable between purge and trap and ATD for many volatile organic compounds at concentrations ranging for fractions of μg/l to hundreds of μg/l.

INTRODUCTION

Adsorption/thermal desorption (ATD) is a method that can be used for the determination of organic compounds in both air and water [1,2]. During the adsorption (sampling) step, the sample is passed at a controlled flow-rate through a cartridge containing the sorbent Tenax. If the sorption takes place efficiently, the cartridge effluent will be essentially free of analytes. Following aqueous sampling, most of the water in the sorbent bed is removed, the cartridge is thermally desorbed, and the analytes are focussed on a capillary gas chromatography (GC) column using whole column cryotrapping (WCC).

The advantages of ATD are its sensitivity and wide range of compound applicability. With aqueous samples containing 1,1,1-trichloroethane (1,1,1-TCA), ATD can be used with sample volumes of the order of 50 ml; for polycyclic aromatic hydrocarbons (PAHs), sample volumes of many liters can be used. Detection limits are in the low μg/l range for 1,1,1-TCA, and in the low ng/l range for PAHs. Prior work in our laboratory with aqueous ATD has emphasized compounds of volatility equal to or less than that of 1,1,1-TCA. Therefore, up to now, many important volatile organic compounds (VOCs) have not been considered in the context of ATD.

As a class, VOCs in water can be determined by purge and trap (P&T), or by the very simple method of purge with whole column cryotrapping [3,4] (P/WCC). However, since dissolved VOCs can be lost during sampling, the availability of an

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ATD-based method applicable to the full range of VOCs will be advantageous. For example, ATD allows direct *in situ* sampling in groundwater wells and in surface waters in a manner that avoids volatilization losses [5]. Following sampling, the small ATD cartridge can be returned to the laboratory for analysis.

In order to develop ATD for VOCs, a technique was needed that would separate the residual water on a sample cartridge from the VOCs without also losing large portions of the analytes. Indeed, μl quantities of water can plug a capillary GC column under WCC conditions. The repeated injection of 2 μl of water can also cause a loss in reproducibility when detection is by mass spectrometry [4]. The centrifugation/vacuum desiccation procedure for ATD cartridges developed by Pankow and Isabelle [6] for semi-volatile compounds cannot be used for VOCs due to unacceptable losses during the vacuum step [2][a]. Losses will also occur with the desiccation methods of Bertsch *et al.* [7] and Versino *et al.* [8]. However, the water trap technique described by Pankow [4] can remove large amounts of water from a gas stream while still allowing volatile analytes to pass quantitatively onto a GC column.

Use of the Pankow [4] water trap to desiccate a hot, moist gas stream provides for the condensation of water in a short trap packed with glass beads. Condensation will occur whenever the temperature of the trap is below the dewpoint of the original gas stream; if the trap is cooled to a low, subambient temperature, a high desiccation efficiency can be obtained. (Even when some cooling is used, very volatile analytes will pass directly onto the column. Less volatile analytes may be partially condensed in a cold water trap; once the transfer of analytes is nearly ended, the trap can be returned to ambient temperature for a short period to transfer condensed analytes to the column.) In general, the overall transfer efficiency of the water trap will be very high for VOCs since the volume of condensed water will be small.

The water trap is ideally suited for use in an ATD-based method for VOCs. Such a trap can be placed between an ATD desorber and the column. A cartridge from which only the bulk of the water has been removed by centrifugation can then be desorbed. This paper describes the development of that application; cooling of the water trap was not employed.

EXPERIMENTAL

Basic methodologies

Cartridges were prepared according to methods described by Pankow and co-workers [2,5]. Briefly, each sorbent cartridge was constructed of Pyrex glass. Each 0.68 cm^3 bed volume was packed with *ca.* 0.13 g of 60/80 mesh Tenax-TA (Alltech Assoc., Deerfield, IL, U.S.A.). Small plugs of silanized glass wool held the Tenax in place. Cartridges were cleaned by a combined solvent extraction/thermal desorption procedure. Prior to introduction of sample water to a cartridge, a mild vacuum was pulled on the cartridge to maximize wetting when the water flow was initiated. After sampling, each cartridge was centrifuged at 3500 rpm for 10 min, leaving *ca.* 30 μl of water on the cartridge. The thermal desorption apparatus used has been described by

[a] A 20-min vacuum desiccation of a cartridge from which the bulk of the water has been removed by centrifugation causes unacceptable losses for compounds with Henry's gas law constants of $2 \cdot 10^{-3}$ atm m^3/mol, or greater [9].

Pankow *et al.* [2]. The Hewlett-Packard 5790 GC used was interfaced to a Finnigan 4000 mass spectrometer/data system (MS/DS) as described by Pankow and Isabelle [10].

Water trap

Fig. 1 is a schematic diagram illustrating the water trap and its position between the desorber and the GC. An 8 cm long piece of 0.32 cm O.D. × 0.22 cm I.D. stainless-steel (SS) tubing filled with 0.5 mm diameter glass beads served as the water trap. The beads were held in place using small plugs of glass wool. A small aluminum block which could be heated with a 150-W cartridge heater surrounded the trap. The temperature in the block was measured using a thermocouple.

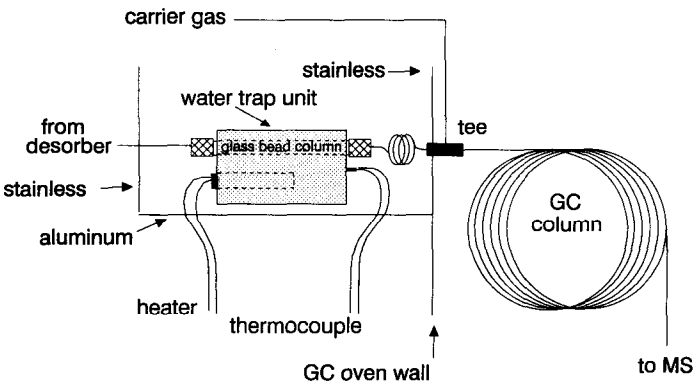

Fig. 1. Schematic diagram showing location of water trap unit between ATD desorber and GC column. Gas line connected to tee inside of GC oven supplied carrier gas for backflushing the water trap and for the GC run.

The water trap system was housed in an open aluminium box measuring 6.4 × 6.4 × 15.2 cm. One end of the box was mounted on the front of the GC. The other end served as a mounting plate for the desorber. Six 0.64 cm diameter holes were drilled in the floor of the box to permit air circulation through the box. The ends of the box were of SS to help insulate the box from the GC and from the desorber.

The water trap was connected to the desorber and the column using 1/16 in. O.D. SS tubing and Swagelok reducing unions. The 8-cm long piece of tubing for the trap/column connection was coiled and was connected to a SS union tee mounted on the endplate of the box. This coil provided additional thermal isolation from the GC oven. The fused-silica capillary GC column used was 30 m long with a "megabore" I.D. of 0.53 mm. The phase was DB-624 with a 3.0 μm film thickness (J&W Scientific, Folsom, CA, U.S.A.). The column was inserted into the GC end of the tee, and to the midpoint of the tee. The connection was made with a Vespel/graphite ferrule. The middle arm of the tee was connected to an auxiliary source of carrier gas that was used after the desorption and during the actual GC run. A 0.64 cm O.D. SS tube connected to a small carbon vane air pump was inserted through one of the holes in the floor of the box and served to keep the water trap system at ambient temperature during the

desorption. Of special interest in this regard was avoiding the formation of any cold zones in the line leading from the trap into the GC.

Desorption procedure

Each cartridge was desorbed for 5 min at 250°C (column head pressure, 10 p.s.i.; column flow-rate, 9 ml/min). The WCC temperature used during the desorption was −30°C. The use of a megabore column helped prevent the column from plugging with ice during the desorption. The trap remained at ambient temperature during the desorption. After the desorption, a valve was switched and flow was diverted from the desorber to the lower carrier line (LCL) leading to the SS tee. At the same time, the GC oven temperature was first raised ballistically to 10°C, then upwards at 5°C/min. For the GC run, the LCL provided carrier gas at 10 p.s.i. and 9 ml/min with the "sweep" line of the desorber in the open position. After beginning the GC run, the cartridge heater in the aluminum block was activated for 5 min. This heated the water trap to 150°C to backflush water and any residual analytes out of the trap and then out of the sweep line of the desorber. In preparation for the next run, the temperature of the desorber was then brought back to ambient temperature with coolant water, and the water trap was brought back to ambient with the compressed air.

"Dry" vs. wet standards comparison

A series of analyses were performed to compare the response of the system when desorbing cartridges containing just 2 μl of a methanol standard solution, *vs.* cartridges containing the same amount of standard plus 30 μl of water. The methanol standard contained *ca.* 50 ng/μl of a series of VOCs and internal standard compounds. The raw MS area for the main quantitation ion of each compound was determined for each analysis. The mean areas were compared for the two different types of analyses.

Analysis of actual groundwater samples

Groundwater samples were collected on 6/20/86 from a well located in Repauno, NJ, U.S.A. Using procedures described by Rosen [9], eight replicate samples were collected at the surface for analysis by ATD, and eight were collected for analysis by capillary P&T using WCC as described by Pankow and Rosen [11].

RESULTS AND DISCUSSION

Prevention of column plugging

The water trap was found to remove enough water from the cartridge desorption analysis stream to consistently prevent the column from plugging with ice during the WCC trapping step. In fact, during the analysis of over 60 samples (see also Rosen [9]), the column never plugged. Tests showed that even 70 μl of water could be desorbed from a cartridge without plugging the column. Indeed, the amount of water transferred to the column will be independent of the amount of water desorbed from the cartridge to the trap. The factors affecting the efficiency of the trap are discussed in detail by Pankow [4].

"Dry" vs. wet standards comparison

Table I presents average responses for the analyses of the wet and "dry"

TABLE I

AVERAGE GC–MS AREA COUNTS ±S.D. FOR 100 ng EACH OF SELECTED COMPOUNDS DESORBED FROM DRY AND WET ATD CARTRIDGES (THREE REPLICATES EACH)

30 μl of water on each wet cartridge

Compound	Dry cartridge	Wet cartridge
1,1-Dichloroethane	73 300 ± 692	60 900 ± 9320
Bromochloromethane	35 300 ± 607	31 800 ± 479
Trichloromethane	55 000 ± 894	52 900 ± 269
Benzene	162 000 ± 3160	148 000 ± 1200
Trichloroethene	38 000 ± 809	30 100 ± 255
1-Chloro-2-bromopropane	41 600 ± 137	39 300 ± 548
Tetrachloroethene	21 200 ± 184	19 100 ± 275
1,4-Dichlorobutane	192 000 ± 1910	213 000 ± 6340
1,1,2,2-Tetrachloroethane	68 200 ± 2440	87 300 ± 2830

standards for VOCs with a range of volatilities. The reproducibilities for both sets of standards were very good. In some cases, the responses for compounds desorbed from wet cartridges were slightly higher than the responses obtained from dry cartridges, and *vice versa*. Though relatively small, in some cases, the differences were statistically significant at the 95% confidence level. As discussed below, incomplete transmission through the trap due to analyte retention in the 30 μl of condensed water could not have been responsible for significant losses. The differences were most likely due to the fact that water transferred to the column during the cartridge desorption affected: (1) the column flow-rate and therefore the analyte concentrations in the MS source; and (2) the MS source ionization characteristics. Though not used here, Pankow [4] has recommended using the water trap at a subambient temperature so as to minimize such effects by condensing as much water as possible in the trap. In any event, the amount of water placed on the standard cartridges should always be similar to the amount on the sample cartridges.

Transmission efficiency of the water trap

A lower limit for the transmission efficiency of the water trap for a given analyte will be given by [4]

$$E \approx \{1 - \exp[-(H/RT)(V_g/V_s)]\} \cdot 100\% \quad (1)$$

where H is the Henry's gas law constant of the analyte (atm m^3/mol), R is the gas constant (8.2 · 10^{-5} m^3 atm/mol K), T is temperature (K), V_g is the volume of gas that flows past the water condensed in the trap, and V_s is the volume of condensed water. The value of E will decrease as H decreases. Most VOCs have H values significantly greater than 1 · 10^{-4} atm m^3/mol. For a desorption carrier gas flow-rate of 9 ml/min, a transfer time of 5 min will give V_g = 45 ml. Thus, under the conditions of this work, for V_s = 0.030 ml, at T = 293 K, we obtain $E \approx 100\%$ for all VOCs. This theoretical result was verified experimentally by: (1) analyzing a wet standard cartridge without back-flushing the trap; then (2) re-analyzing it. The re-analysis allowed analytes

a second chance to move onto the column: just trace amounts of a few less volatile compounds were found in the resulting chromatogram.

Chromatography

Fig. 2 presents a typical total ion chromatogram for the analysis of a wet standard cartridge. The analyte peaks were very sharp, and most were baseline resolved. All analytes in the chromatogram exhibited peak widths of no more than 10 s, *i.e.*, peaks widths as sharp as can be obtained on a column of this bore. Background contamination obscured the first peak. However, the extracted mass chromatogram for the primary quantitation ion for that compound was clean and sharp.

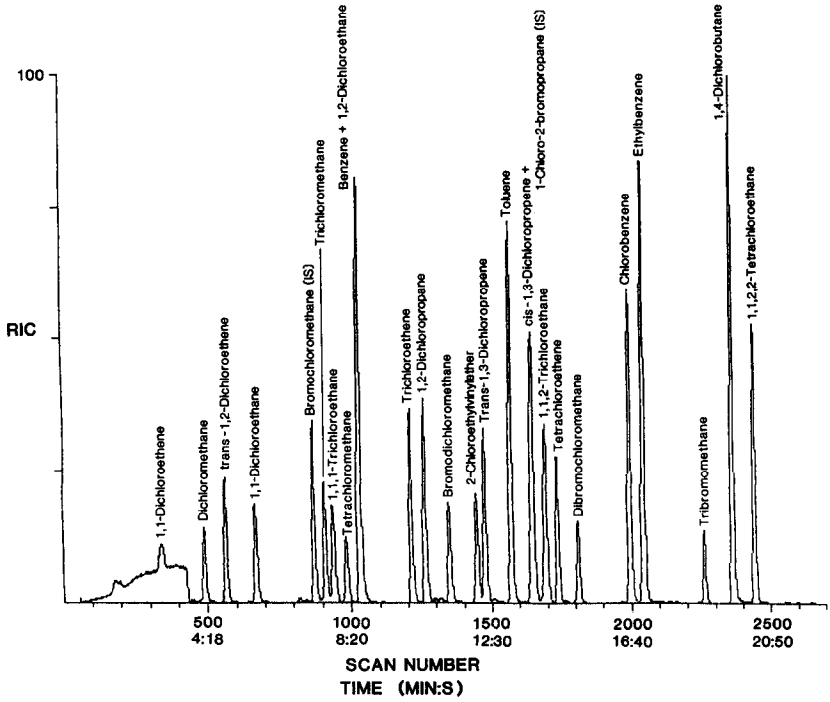

Fig. 2. Chromatogram obtained analyzing a wet cartridge for a range of VOCs. Each peak represents 100 ng.

Comparison of ATD with results obtained by P&T

The results of the analyses of the groundwater samples collected at a well in Repauno, NJ, U.S.A. are presented in Table II. The ATD and P&T results are quite comparable for a wide range of compounds and concentrations.

TABLE II

COMPARISON OF ATD AND P&T/WCC RESULTS FOR SAMPLES FROM REPAUNO, NJ, U.S.A. [9]

Compound	Method	Mean conc.[a] (μg/l)	S.D. (μg/l)	C.V.[b] (%)
Dichloromethane	ATD	0.24	0.037	15.0
	P&T/WCC	ND[c]	–	–
cis-1,2-Dichloroethene	ATD	1.9	0.035	1.8
	P&T/WCC	2.7	0.37	14.0
Trichloromethane	ATD	29.0	0.53	1.8
	P&T/WCC	32.0	0.64	2.0
1,2-Dichloroethane	ATD	1.4	0.083	5.9
	P&T/WCC	1.1	0.095	8.6
Tetrachloromethane	ATD	1.8	0.12	6.7
	P&T/WCC	1.4	0.035	2.5
Benzene	ATD	18.0	0.53	2.9
	P&T/WCC	20.0	0.83	4.2
Trichloroethane	ATD	35.0	0.52	1.5
	P&T/WCC	35.0	1.3	3.7
Toluene	ATD	0.15	0.010	6.7
	P&T/WCC	NQ[d]	–	–
Tetrachloroethene	ATD	340.0	20.0	5.9
	P&T/WCC	370.0	17.0	4.6
Chlorobenzene	ATD	36.0	2.6	7.2
	P&T/WCC	48.0	1.8	3.8
o-Xylene	ATD	0.34	0.012	3.5
	P&T/WCC	NQ	–	–
Nitrobenzene	ATD	210.0	15.0	7.1
	P&T/WCC	250.0	14.0	5.6

[a] Mean of eight replicates.
[b] C.V. = (S.D./mean conc.) · 100%.
[c] ND = not detected.
[d] NQ = detected, but too low to be quantitated.

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