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Determination of selected chlorinated benzenes in water by purging directly to a capillary column with whole column cryotrapping and electron-capture detection

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ABSTRACT

The purge with whole column cryotrapping (P/WCC) method for the determination of volatile organic compounds (VOCs) in aqueous samples is adapted for use with an electron-capture detector. In this method, VOCs are stripped from an aqueous sample with an inert purge gas and transferred directly to the head of a capillary column for subsequent GC analysis. To prevent the column from plugging with ice during the purge step, and to reduce the chromatographic interference caused by the reaction of small amounts of water with thermal electrons in the detector, a glass-bead water trap is placed in-line between the purge vessel and the gas chromatograph. The water trap is constructed of a short length of 0.32 cm O.D. stainless-steel tubing filled with 0.5 mm diameter glass beads. By maintaining the trap at −10°C during the purge, most of the water can be removed from the purge gas. Transmission of the analytes to the column is then achieved with a subsequent, short purge of the trap at 25°C. The method was tested with the chlorinated benzenes. Despite their high molecular masses, the more chlorinated members of this group have large enough Henry's law constants that they *can* be determined with a purge technique. Experimental purging efficiencies were determined and compared to theoretical values. This method allows the simplicity and the high reliability of the P/WCC method to be combined with the exceptionally high sensitivity of an electron-capture detector.

INTRODUCTION

The EPA purge and trap (P&T) method [1,2] is the standard technique for the determination of volatile organic compounds (VOCs) in aqueous samples. In the P&T method, VOCs are stripped from the aqueous phase with an inert gas and transferred to a sorbent bed. Analytes trapped on the bed are then thermally desorbed to the column of a gas chromatograph for analysis. Recently, Pankow [3] and Pankow and Rosen [4] introduced the purge with whole column cryotrapping (P/WCC) method, in which analytes purged from the aqueous phase are transferred immediately to the head of a capillary GC column, eliminating the need for an intermediate sorbent trap. Due to its inherent simplicity, the P/WCC method offers a variety of advantages over conventional P&T [3,4], including improved detection of very volatile compounds, lower background contamination, shorter analysis times, and lower capital costs.

Due to the finite vapor pressure of water, a small amount of water is transferred to the GC column during the purge step of the P/WCC method. Applying the ideal gas law, 0.023 μl of water is expected to be removed from solution per ml of purge gas at 25°C. The presence of water in the purge

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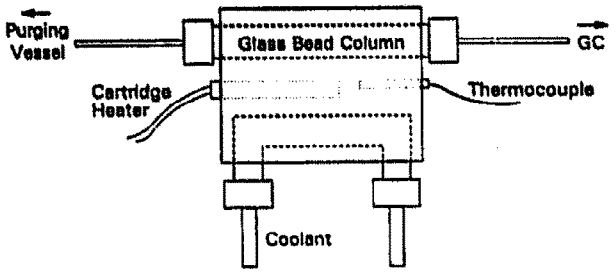

Fig. 1. The glass-bead water trap.

gas is a potential problem. Purging for long periods of time can transfer enough water that a small-bore capillary column held at cryotrapping temperature can become plugged with ice. Too much water on the column can cause chromatographic problems such as peak-splitting [4]. In addition, water can interfere with the response of some types of detectors. The electron-capture detector is particularly sensitive to trace amounts of water. Indeed, a few microliters of water passing through an electron-capture detector can produce a very large, asymmetrical peak that can completely obscure a portion of the chromatogram. In order to combine the simplicity and reliability of the P/WCC method with the selectivity and extreme sensitivity of the electron-capture detector, most of the water in the purge gas must be removed before it is allowed to reach the gas chromatograph.

Purge gas desiccation is commonly effected by forcing the gas to pass through a short length of polar tubing such as Nafion [5,6]. Transmission of analytes through Nafion tubing, however, has been found to be less than quantitative for some compounds, causing unacceptable memory effects [6,7]. Alternatively, a simple cold-zone, glass-bead water trap has been developed by Rosen [7] and Pankow [8]. A schematic of the glass-bead water trap is illustrated in Fig. 1. The water trap consists of a 6.5 cm length of 0.32 cm stainless-steel tubing packed with 0.5 mm diameter glass beads to provide a large, inert surface area. The trap is encased in an aluminum block whose temperature can be regulated with coolant or with a cartridge heater and thermocouple. In the first part of the purge (phase I), the water trap is held at a subambient temperature such as −10 C with a liquid coolant. Because the vapor pressure of ice at −10 C (260.4 Pa) is substantially lower than that of water at 25°C (3171.5 Pa), most of the water purged from solution will be retained in the cold trap. By rapidly raising the temperature of the trap to 25°C during the last minute or so of the purge (phase II), any analytes retained in the trap during phase I are quickly and efficiently removed and focussed on the GC column [8]. By minimizing the phase II purge time, the amount of water transferred to the column is minimized. The theoretical desiccation efficiency of the water trap has been discussed in detail by Pankow [8].

In this study, the P/WCC method is adapted for use with an electron-capture detector and tested with a set of chlorinated benzenes. Purge gas desiccation is effected with the glass-bead water trap. Theoretical purging efficiencies are calculated and compared to experimentally determined values.

THEORY

When a clean, inert gas is bubbled at a flow-rate F (ml/min) through a volume of water V_{w1} (ml) for a period of time t_1 (min), the removal of a volatile analyte from aqueous solution is given by [9]

$$\frac{c_1}{c_{1,0}} = \exp\left[-\left(\frac{H}{RT_1}\right)\frac{F}{V_{w1}}t_1\right] \quad (1)$$

where c_1 is the aqueous concentration of the analyte at time t_1, $c_{1,0}$ is the initial aqueous concentration, H (Pa · m^3/mol) is the Henry's law constant of the analyte at temperature T_1 (K), and R is the gas constant (8.314 Pa · m^3/mol · K). The derivation of eqn. 1 involves a number of assumptions. The temperature and aqueous volume are assumed to be constant during the purge. The liquid phase is considered to be well mixed, and the gas phase is assumed to behave ideally. The partial pressure of the analyte must be small compared to the total pressure, and Henry's law must apply over the concentration range of interest. In addition, the distribution of analyte between the gas and liquid phases is assumed to reach equilibrium by the time the bubbles leave the liquid phase.

Because the bubbles are in contact with the solution for a limited amount of time, full gas/liquid equilibrium will probably not be achieved before the bubbles exit the liquid phase [10]. Eqn. 1, therefore, may slightly overpredict the removal of analyte from

the aqueous phase. Despite this possibility, Pankow and Rosen [4] obtained excellent agreement with eqn. 1 for all of the purgeable priority pollutants. With $c_1/c_{1,0}$ given by eqn. 1, the maximum possible efficiency (fractional removal) of the purging process e_{p1} is defined as

$$e_{p1} = 1 - c_1/c_{1,0} \quad (2)$$

For a given compound, purging efficiency increases with t_1 and is largely a function of V_{g1}/V_{s1} ($= F \cdot t_1/V_{s1}$), where V_{g1} is the total volume of purge gas bubbled through the solution at time t_1.

The transfer efficiency of analytes through the water trap during phase II of the purge can also be modeled as a purging process. Some portion of each analyte will probably be transmitted to the GC column when the trap is cold (temperature T_2). In the worst case, the analytes purged from solution during phase I are fully retained in the water trap. The concentration of analyte in the water trap at the beginning of phase II, then, is given by

$$c_{2,0} = \frac{c_{1,0}V_{s1}}{V_{s2}}\left\{1 - \exp\left[-\left(\frac{H}{RT_1}\right)\frac{F}{V_{s1}}t_c\right]\right\} \quad (3)$$

where t_c is the time during which the trap is cold (phase I purge time, minutes), and V_{s2} is the volume of water retained in the trap during phase I. The magnitude of V_{s2} is easily calculated by considering the vapor pressures of ice and water at T_2 and T_1, respectively [8].

Taking into account the fact that the purge gas entering the water trap is not necessarily free of analyte, the concentration in the trap during phase II is given by

$$c_2 = \frac{c_{1,0}V_{s1}}{V_{s2}}\left[\lambda_{2,2} - \frac{\lambda_{1,c}}{V_{s1}-V_{s2}}(V_{s1}\lambda_{2,2} - V_{s2}\lambda_{1,2})\right] \quad (4)$$

$$\lambda_{i,j} = \exp\left[-\left(\frac{H}{RT_1}\right)\frac{F}{V_{si}}t_j\right] \quad (5)$$

where t_2 is the phase II purge time ($t_2 = t_1 - t_c$, min). Following Pankow [8], the purging efficiencies for the water trap e_{p2} and for the overall purge $E_{overall}$ are defined as

$$e_{p2} = 1 - c_2/c_{2,0} \quad (6)$$

$$E_{overall} = e_{p1}e_{p2} \cdot 100\% \quad (7)$$

Given sufficient time to strip analytes from the water trap, e_{p2} will approach 100% and e_{p1} will approximate $E_{overall}$. The correspondence between e_{p1} and $E_{overall}$ is illustrated in Fig. 2 as a function of t_2, using $V_{s1} = 5$ ml, $V_{s2} = 4.23$ μl, $F = 20$ ml min, $t_c = 10$ min, $T_1 = 298$ K, and various values of H. Even for compounds with H values as low as 10 Pa · m³/mol, theory predicts that a phase II purge time of 0.5 min is sufficient to efficiently transfer analytes from the warmed water trap to the GC column. Because the experimental application of this method will require *ca.* 0.5 min to warm the trap from T_2 to T_1, a phase II purge time of 1 to 2 min should be adequate to prevent significant retention of analytes in the trap.

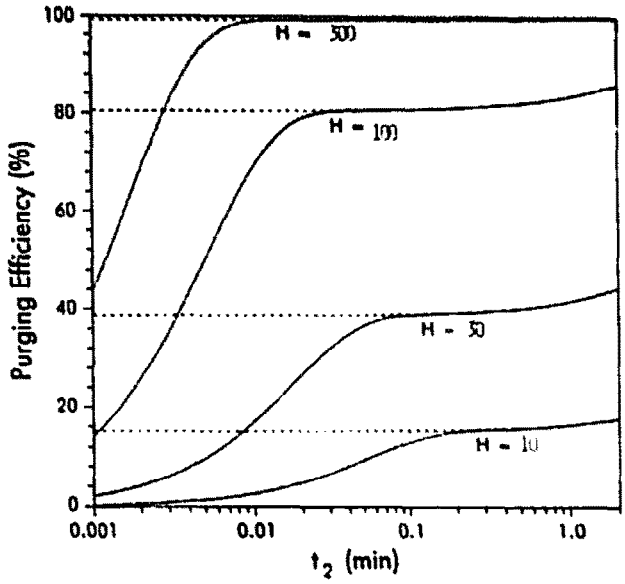

Fig. 2. Theoretical purging efficiencies as a function of t_2 for a range of H values. The dashed lines represent e_{p1}, the maximum possible purging efficiency, while the solid lines denote $E_{overall}$, the overall purging efficiency when all analytes are assumed to be retained completely in the water trap during phase I of the purge. Conditions: $V_{s1} = 5$ ml, $V_{s2} = 4.23$ μl, $F = 20$ ml min, $t_c = 10$ min, $T_1 = 298$ K, $T_2 = 263$ K.

EXPERIMENTAL

A schematic of the P/WCC apparatus with incorporation of the water trap is illustrated in Fig. 3. Notable modifications to the setup discussed by Pankow [8] are the use of a 6-port Carle valve (Hach, Loveland, CO, USA) to control carrier gas pressure

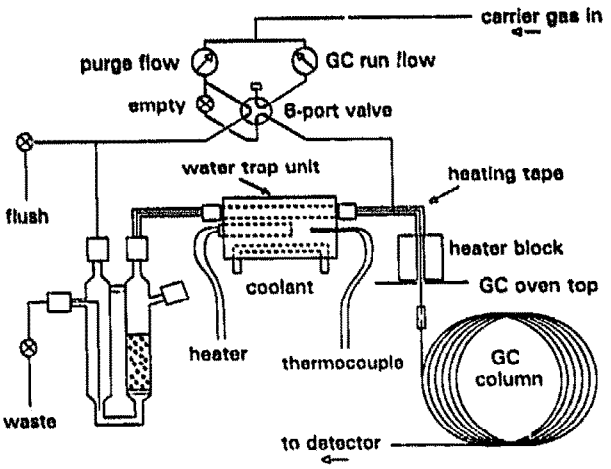

Fig. 3. Schematic of the P/WCC apparatus with the glass-bead water trap. Snap valves are denoted by cross-hatched circles.

and flow direction, and the use of heating tape on the transfer line between the purge vessel and the gas chromatograph. The Carle valve provides a simple method to start and stop the purge, while the heated transfer line eliminates cold spots near the water trap and increases the transmission efficiency of the less volatile analytes to the GC. The basic operating procedures of both the P/WCC method and the water trap have been described elsewhere [3,4,8].

The P/WCC apparatus was interfaced to a Varian 3400 gas chromatograph equipped with an electron-capture detector. The electron-capture detector temperature was set at 350°C, and the most sensitive range was used. Ultra-high-purity nitrogen was used as detector make-up gas at a flow-rate of 28.5 ml/min. The GC column was a 27 m × 0.32 mm I.D. DB-624 fused-silica capillary column with a 1.8 μm film thickness manufactured by J&W Scientific (Folsom, CA, USA). To further reduce the ability of ice to plug the column, a 0.5 m × 0.53 mm I.D. DB-624 column with a 3.0 μm film thickness was installed in front of the main column. The two columns were joined with a universal press-fit connector (Restek, Bellefonte, PA, USA). The head of the column was connected to the transfer line in a "non-ice-trap" configuration [4]; the column was extended through the transfer line union and into the heated zone above the GC oven. The temperatures of the transfer line and the GC interface heater block were both 220 C.

Ultra-high-purity helium was used as the purge and carrier gas. A purge gas flow-rate of 20 ml/min was maintained with a purge pressure of 269 kPa. The carrier gas pressure for the GC run was 90 kPa. To prevent overpurging and erratic flow-rates at both the start and end of the purge, precautions were taken to equalize the gas pressure across the purge vessel at those times. Such equalization was achieved before the start of the purge by selecting the purge position on the 6-port valve and opening the "empty" snap valve. The purge was then started by closing the "empty" valve. At the end of the purge, the 6-port valve was turned to the GC run position, and the excess pressure upstream of the purge vessel was vented by temporarily opening the "flush" snap valve.

The total purge time (t_1) for all analyses was 12 min. All were performed at ambient laboratory temperature ($T_1 \approx 298$ K). During phase I of the purge, the water trap was held at −10 C ($T_2 = 263$ K) with a liquid coolant composed of ethylene glycol–water (50:50, v/v). The phase I purge time (t_c) was 10 min. Phase II of the purge was 2 min (t_2) and was performed at 298 K. Whole column cryotrapping was performed at −30 C. The GC temperature program was ballistic from −30 C to 50 C, then at 5 C/min to 250 C. After the GC run was completed, the water trap was backflushed at 100 C to remove the trapped water, and the sample was drained from the purge vessel through the waste line. The three characteristic modes of the water trap are summarized in Table I.

RESULTS AND DISCUSSION

The glass-bead water trap effectively reduced the

TABLE I

CHARACTERISTICS OF THE THREE WATER TRAP MODES

	Phase I purge	Phase II purge	Backflush
Coolant	On	Off	Off
Heater	Off	On	On
Temperature	−10 C	25 C	100 C
Flow	to GC	to GC	to PV[a]
Duration	10 min	2 min	4 min

[a] PV = Purge vessel.

amount of water transmitted to the GC column. When the water trap was in use, the column never plugged with ice. Purge times of up to 17 min were tested (t_2 = 2 min, V_{g1} = 340 ml). Not only did the column never plug with ice under these conditions, but no measurable decrease in the purge flow-rate was observed. Without the water trap, purge volumes of approximately 100 ml were sufficient to plug the column, even when the column was installed in the "ice-trap" [4] configuration. Moreover, the water trap reduced the chromatographic interference of water to a manageable level. Unlike flame ionization detectors, electron-capture detectors are extremely sensitive to relatively small amounts of water. In the absence of a water trap, enough water was transmitted to the column to create a very large, asymmetric peak that obscured several minutes of the chromatogram. The use of the water trap, therefore, was key to the successful coupling of an electron-capture detector to P/WCC.

This method was tested with a standard containing several chlorinated benzenes. Electron-capture detector response is quite sensitive to the degree of chlorination; in general, the detection limit for a given compound class will decrease as the number of chlorines increases. Consequently, the chlorobenzenes in the aqueous standard were present at different concentrations: chlorobenzene (3.7 ng/ml), each dichlorobenzene (0.11 ng/ml), each trichlorobenzene (0.028 ng/ml), each tetrachlorobenzene (0.019 ng/ml), pentachlorobenzene (0.011 ng/ml), and hexachlorobenzene (0.011 ng/ml). Fig. 4a shows the chromatogram that results from purging 5.0 ml of the standard, while Fig. 4b is the result of repurging the same standard. Both chromatograms are plotted on identical scales. The electron-capture detector was not very sensitive to chlorobenzene, and hexachlorobenzene behaved erratically; neither is shown in Fig. 4. Good resolution was obtained for all but two of the remaining compounds. Fig. 5 illustrates the overlap of the 1,2,3,5- and 1,2,4,5-tetrachlorobenzene peaks. For a 5.0-ml sample, representative method detection limits are 0.01 ng/ml for 1,2-dichlorobenzene, 0.003 ng/ml for 1,2,4-trichlorobenzene, and 0.0006 ng/ml for 1,2,4,5-tetrachlorobenzene.

Experimentally purging efficiencies were calculated by [4]

$$E_{obs} = \frac{A_i - A_r}{A_i} \cdot 100\% \quad (8)$$

where A_i is the peak area resulting from the initial purge and A_r is the corresponding peak area from the repurge. Values of E_{obs} were obtained for both

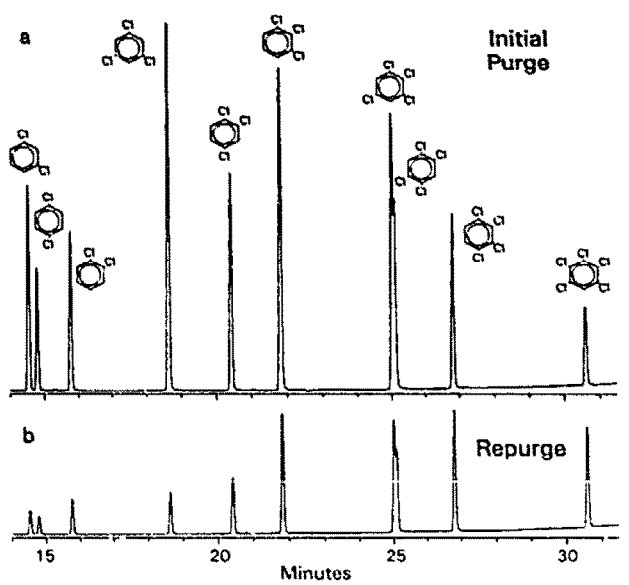

Fig. 4. Portions of (a) the initial and (b) repurge chromatograms of a 5-ml water sample containing each of the chlorinated benzenes. Temperature program: 50 to 250 C at 5 C min.

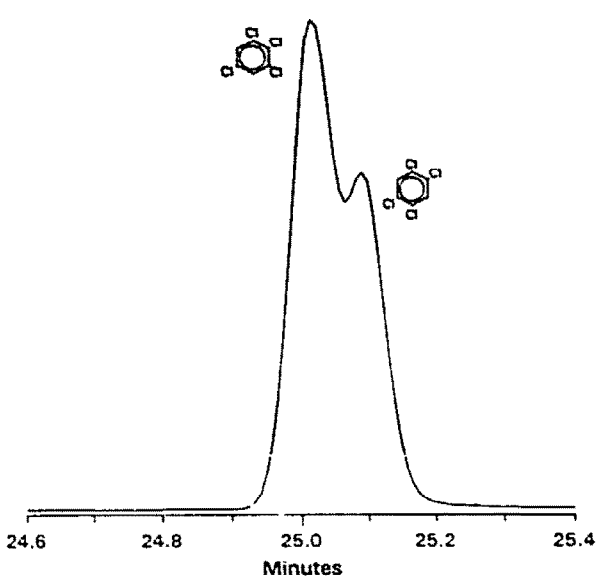

Fig. 5. Representative section of a chromatogram showing the overlap of peaks for 1,2,3,5- and 1,2,4,5-tetrachlorobenzene.

TABLE II

HENRY'S LAW CONSTANTS (H), PREDICTED PURGING EFFICIENCIES ($E_{overall}$), AND OBSERVED PURGING EFFICIENCIES (E_{obs}) FOR THE CHLORINATED BENZENES

Compound	H[a] (Pa · m³/mol)	5-ml sample		1-ml sample	
		$E_{overall}$[b] (%)	E_{obs}[c] (%)	$E_{overall}$[b] (%)	E_{obs}[c] (%)
Chlorobenzene	364	99.9	ND[d]	100.0	ND
1,2-Dichlorobenzene	192	97.6	77.6	100.0	92.7
1,3-Dichlorobenzene	364	99.9	88.0	100.0	94.4
1,4-Dichlorobenzene	314	99.8	85.1	100.0	94.0
1,2,3-Trichlorobenzene	131[e]	92.2	62.8	100.0	82.8
1,2,4-Trichlorobenzene	233	98.9	73.4	100.0	88.6
1,3,5-Trichlorobenzene	233[e]	98.9	88.5	100.0	94.3
1,2,3,4-Tetrachlorobenzene	263[e]	99.4	30.7	100.0	30.4
1,2,3,5-Tetrachlorobenzene	162[e]	95.7	61.3	100.0	63.9
1,2,4,5-Tetrachlorobenzene	263[e]	99.4	52.7	100.0	54.8
Pentachlorobenzene	162[f]	95.7	NA[g]	100.0	NA
Hexachlorobenzene	83[h]	90.0	NA	100.0	NA

[a] H data from Mabey *et al.* [11] except as noted (T_1 = 298 K).
[b] $E_{overall}$ was calculated from eqns. 1–7, using T_1 = 298 K, R = 8.314 Pa · m³/mol · K, F = 20 ml/min, t_c = 10 min, t_2 = 2 min, and V_{s2} = 4.23 μl.
[c] E_{obs} was calculated using eqn. 8.
[d] ND = Not detected.
[e] H data from Mackay and Shiu [12].
[f] Vapor pressure estimated from a vapor pressure *versus* boiling point regression; H estimated using that vapor pressure and solubility data from Verschueren [13].
[g] NA = Not available. Results were inconsistent.
[h] H estimated using vapor pressure and solubility data from Verschueren [13].

1.0- and 5.0-ml samples. The results are compared to theoretical values of $E_{overall}$ in Table II. $E_{overall}$ represents the maximum possible purging efficiency because e_{p2} is approximately 100% and e_{p1} is known to be a theoretical maximum. All experimental values are lower than expected on the basis of theory. The differences between theoretical and observed values increase with decreasing compound volatility. Portions of the discrepancies might be due to errors in the values of H. Inefficient transmission of compounds through the water trap at T_1 also would result in E_{obs} values less than $E_{overall}$. Retention in the trap or the transfer line would be more problematic for the heavier compounds such as tetra- and pentachlorobenzene. In addition, if gas–liquid equilibrium was not fully achieved as each gas parcel contacted the liquid phase, then negative deviations in the values of E_{obs} would be expected.

If the degree to which gas–liquid equilibrium *is* achieved is constant throughout the purge, then better predictions of $E_{overall}$ might be obtained through the use of an *effective* Henry's law constant, where the effective value of H is given by

$$H_{eff} = \gamma H \tag{9}$$

and γ is the fraction of equilibrium attained. The value of γ is expected to be smaller for a 1.0-ml sample than for a 5.0-ml sample due to the shorter contact time with the liquid phase. Using this approach, the differences between E_{obs} and $E_{overall}$ in Table II for the di- and trichlorobenzenes can be reconciled using a single value of γ for each value of V_{s1}. Those γ values, however, are not small enough to explain the low E_{obs} values of the tetrachlorobenzenes or the inefficient transmission of pentachlorobenzene to the gas chromatograph. Given the need to heat the transfer line to 220°C to increase throughput of the heavier compounds, and the fact

that E_{obs} values for the tetrachlorobenzenes were found to be independent of V_{s1}, the lower than expected purging efficiencies might be due to hold-up in the transfer line or in the water trap. A higher phase II water trap temperature or a longer phase II purge time might increase these purging efficiencies.

CONCLUSIONS

The purge with whole column cryotrapping method of Pankow and Rosen [4] was adapted for use with an electron-capture detector and tested with a set of chlorinated benzenes. Purge gas desiccation with a simple glass-bead water trap allowed the use of large purge gas volumes, prevented the GC column from plugging with ice, and reduced the interference of water in the chromatogram. Good chromatographic resolution was obtained. Despite smaller than expected purging efficiencies, this simple P/WCC method shows promise for the quick and effective determination of volatile and semi-volatile compounds such as the di-, tri- and tetrachlorobenzenes. With further study, this method might also be extended to include pentachlorobenzene and the even less volatile hexachlorobenzene.

SYMBOLS

A_i	peak area from initial purge
A_r	peak area from repurge
c_1	concentration of analyte in aqueous sample (ng/ml)
$c_{1,0}$	initial concentration of analyte in sample (ng/ml)
c_2	concentration of analyte in water trap during phase II purge (ng/ml)
$c_{2,0}$	concentration of analyte in water trap at beginning of phase II (ng/ml)
e_{p1}	maximum possible purging efficiency from the sample
e_{p2}	purging efficiency of analytes from the water trap
E_{obs}	observed purging efficiency (%)
$E_{overall}$	overall efficiency (%) for purging of analytes from a sample to the GC column
F	flow-rate of purge gas through the purge vessel (ml/min)
H	Henry's law constant (Pa · m³/mol) for the analyte at T_1
H_{eff}	effective Henry's law constant (Pa · m³/mol)
R	gas constant (8.314 Pa · m³/mol · K)
t_c	time during which the water trap is cold (min)
t_1	total purge time (min)
t_2	phase II purge time (min)
T_1	temperature in the purge vessel and in the warm trap (K)
T_2	temperature in the cold trap (K)
V_{g1}	volume of purge gas bubbled through the sample (ml)
V_{s1}	volume of sample (ml)
V_{s2}	volume of liquid water in the trap (ml)
γ	fraction of gas–liquid equilibrium attained

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