

Selective removal of water in purge and cold-trap capillary gas chromatographic analysis of volatile organic traces in aqueous samples

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Selective Removal of Water in Purge and Cold-Trap Capillary Gas Chromatographic Analysis of Volatile Organic Traces in

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Summary

The design and features of an on-line purge and cold-trap pre-concentration device for rapid analysis of volatile organic compounds in aqueous samples are discussed. Excessive water is removed from the purge gas by a condenser or a water permeable membrane in order to avoid blocking of the capillary cold-trap. Synthetic mixtures covering concentrations ranging from tenths to tens of ppb's and different chemical classes are used to study the effect of various process factors on the efficiency and selectivity of water removal as well as on the purging recovery. The importance of the concentration of the solutes, the flow rate in conjunction with the volume of the purge gas, and the temperature of the condenser, the cold-trap and the sample is emphasized. Theoretical models describing the purge process and the blocking of the cold-trap agree fairly well with the highly reproducible experimental results ($\sigma = 2-4\%$). Both the condenser and the Nafion membrane successfully remove water, although some compounds, dependent on volatility and polarity, are partly or completely lost. It is shown that non-polar volatile organic compounds are efficiently enriched so that recoveries between 80-100% and a detection limit of 1 ppt can be obtained. The applicability of the system is illustrated on some examples.

1 Introduction

The need for determination of trace amounts of volatile organics in complex aqueous samples at concentration levels down to ppb's ($1:10^9$) and ppt's ($1:10^{12}$) is rapidly growing. Because of the complexity of most of these samples, capillary gas chromatography is the method of choice. Consideration of the limited sample size, isolation and preconcentration techniques are required prior to gas chromatographic analysis for such low concentrations. Dynamic headspace and gas stripping in combination with adsorption and/or cryogenic trapping are highly efficient

and suitable methods for preconcentration of volatile compounds present in aqueous samples. Dynamic headspace in combination with cryogenic sorbent trapping has been described firstly by Swinnerton and Linnenbom [1-3], for the analysis of ppt concentrations of C_1-C_4 hydrocarbons. Dynamic headspace and sorbent trapping in closed circuits (closed-loop stripping; CLS) was introduced by Novák [4] and Grob [5]. An extensive fundamental and systematic study on the effect of various parameters on CLS recoveries has been reported by Curvers *et al.* [6]. Cryogenic concentration [7,8] and refocusing [9-13] of the analytes have been successfully applied in dynamic headspace analysis.

Blocking of the cryotrap by ice formation should be avoided. Recently, Badings *et al.* [14,15] reported an automatic system for trace analysis of volatile organic compounds by an on-line combination of gas-stripping, cryogenic trapping, and refocusing, on a capillary pre-column. Essential in their design was the positioning of a condenser in between the sample flask and the capillary cold-trap in order to avoid blocking with ice.

A theoretical model describing ice formation and growth in the capillary trap is evaluated in this paper. The effect of various process factors on the efficiency and selectivity of the removal of water vapor prior to cryogenic capillary trapping is studied as well as the efficiency of the purge process. The efficiency and selectivity of an alternative way of selective water removal by means of a Nafion* membrane [16] is studied in a similar way and compared to the former method. The applicability of the system is demonstrated for both techniques.

2 Experimental

2.1 Purge-and-Cold-Trap Injection System

The purge-and-cold-trap (PCT) injection device (Chrom-pack, Middelburg, The Netherlands) used in this work is commercially available and is described elsewhere [15,17].

In order to improve the purging efficiency the original design of the sample flask was modified (**Figure 1**).

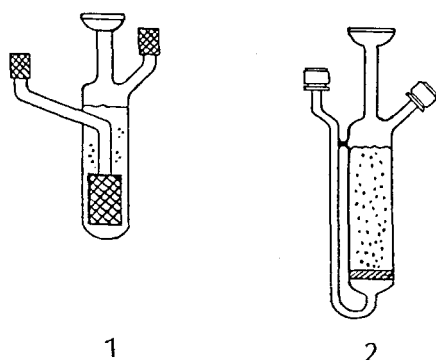


Figure 1
Schematic design of the original (1) and the modified (2) sample flask.

The cold-trap consists of 30 cm length of a fused silica capillary column, 0.32 mm i.d., coated with CP SIL 5 CB, film thickness 1.2 μm , surrounded by an electrical resistance heating capillary. In the trapping mode approximately 10 cm of the capillary is cooled by nitrogen gas. The purging of the sample is started after a preset period of time needed to cool down the cold-trap (-120°C). The purge gas flow rate is adjusted by a needle valve to a commonly used value of 10-80 ml/min. Most of the entrained water vapor is frozen out in the condenser, thus avoiding the blockage of the capillary cold-trap. After passage through the condenser the organic compounds are cryofocused in the cold-trap. At the end of the purge period the nitrogen cooling gas is stopped and within a few seconds the cold-trap temperature is increased to 200°C by electrical heating, providing a narrow injection band width.

2.2 Nafion Drying Tube

In order to compare the selectivity and efficiency of the water removal, the condenser was replaced by a Nafion tube ($L = 120$ cm, i.d. = 0.5 mm, wall thickness 0.25 mm). The Nafion permeation tube is preassembled inside a second tube (i.d. 2.5 mm) which is flushed by a stream of dry nitrogen gas (100 ml/min, dried over Molecular Sieve 5A).

2.3 Synthetic Aqueous Samples

Synthetic samples were prepared by spiking 8 ml of doubly distilled water with 1 μl of one of the following stock solutions (all 1 or 100 ppm (w/v) in methanol):

- (1) "Multimix", a mixture containing solutes with different functional groups (e.g. hydrocarbons, alcohols, ketones and aromatics, boiling point 111 to 233°C).
- (2) "Hydrocarbon mix", a mixture of *n*-hydrocarbons (*n*-heptane to *n*-hexacosane, boiling point 98 to 412°C).
- (3) "Volatiles mix" containing relatively volatile compounds with boiling points from 56 to 111°C .

2.4 Gas Chromatography

The PCT-unit was mounted on top of a Packard Becker gas chromatograph, type 427 (Packard Becker, Delft, The Netherlands), equipped with a flame ionization detector. The GC analyses were performed on a CP-Sil 5 CB fused silica column ($L = 24$ m, i.d. = 0.32 mm, $d_f = 1.1$ μm ; Chrom-pack, Middelburg, The Netherlands). A Spectra Physics SP 4000 system (Spectra Physics, Santa Clara, CA, USA) was used for data handling.

3 Theory

3.1 Purge Process

In a previous paper on Closed-Loop Stripping we presented a theoretical model describing the purge process [6]. A relationship was derived expressing the recovery (defined as the mass ratio of the trapped amount of a solute and the amount initially present in the sample) as a function of process and component parameters. Because the PCT system incorporates a relatively long glass tube between the sample flask and the cold-trap, the recovery equation had to be slightly modified. It now reads:

$$R = 1 - \exp \frac{-F(t - t_d)}{KV_1 + V_g} \quad (1)$$

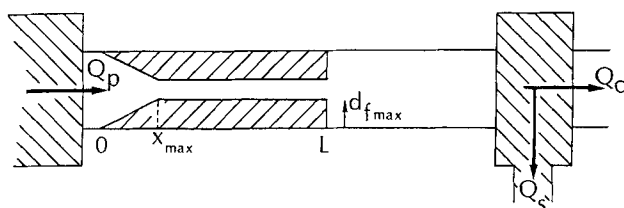
where

- R = recovery
- F = purge gas flow rate
- t = purge time
- t_d = gas hold-up time in the glass tube.
- K = mass based gas-liquid distribution constant
- V_1 = sample volume
- V_g = gas volume over the liquid sample in the sample flask

This expression only holds in the case of thermodynamic equilibrium, homogeneity of V_1 and V_g , and constant sample temperature and purge flow rate. Furthermore, breakthrough of the cold-trap is supposed not to happen. As shown by *Badings et al.* no loss of 1,2-dichloroethylene (b.p. = 60.3°C) occurs, when 200 ml of purge gas is passed at a cold-trap temperature of -100°C [15].

3.2 Blocking of the Cold-Trap

Figure 2 shows a possible situation during the purge process, when water is frozen out in the cold-trap.


Figure 2

Schematic representation of ice formation inside the capillary cold-trap.

/// = deposited ice; Q_p = purge gas flow; Q_c = column flow; Q_s = split flow; $d_{f,max}$ = ice layer film thickness; L = ice layer length.

An extensive treatment of the increasing flow resistance of the cold-trap during the purge process has been published elsewhere [17] and is available upon request. Here only the theoretical resulting decrease of the purge gas flow rate is given (Fig. 3).

4 Results and Discussion

4.1 Efficiency of the Condenser

In practice ice formation is only observed in the initial 0.5-1 cm of the condenser tube. This indicates that the condenser removes the water efficiently. Therefore, the dew point of the gas leaving the condenser is expected to equal the condenser temperature. The results presented in **Table 1**, where the water concentrations calculated according to this statement are shown to be in excellent agreement with experimental data, tend to confirm this. Actual water concentrations were determined by reaction with calcium carbide [18] and monitoring by FID detection of the concentrations of ethyne formed.

Table 1

Comparison of experimental and calculated water concentrations at the condenser outlet for different condenser temperatures.

T_{cond} (°C)	mg H ₂ O/l calc.	mg H ₂ O/l exp.
-20	0.42	0.40
-15	0.68	0.70
-10	1.07	1.08
- 5	1.65	1.78
0	2.50	2.55

Moreover, it was found that an increased water concentration in the purge gas at a higher sample temperature does not affect the water concentration at the condenser outlet.

4.2 Efficiency of the Nafion Tube

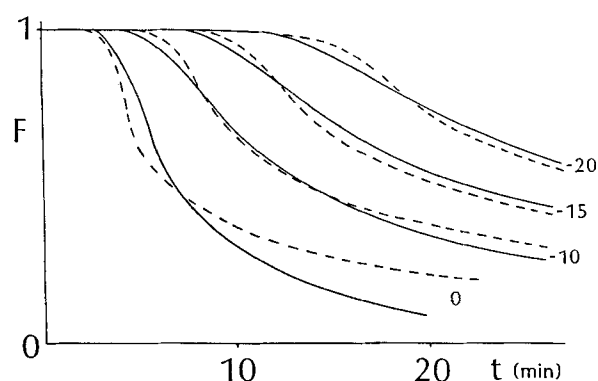
Replacement of the condenser by a Nafion tube (see Experimental) results in a water concentration of 0.36 mg/l

at the outlet of the condenser, independent of the purge gas flow rate and/or the sample temperature. This concentration corresponds to a water content at a condenser temperature of -22°C .

4.3 Blocking of the Cold-Trap

An increased resistance of the cold-trap due to ice deposition can easily be monitored by a continuous measurement of the split-flow rate. In this way the influence of several process parameters on obstruction of the cold-trap was determined.

(1) *Influence of the condenser temperature:* As indicated before, the water concentration in the purge gas entering the cold-trap is determined by the condenser temperature. Consequently it will have a significant effect on the blocking rate of the cold-trap. This is illustrated in **Figure 3**. Obviously the trap does not block completely, but a narrow open capillary path remains, which is in agreement with the assumption of axial growth of the ice layer (cf. Fig. 2).


Figure 3

Effect of the condenser temperature ($^{\circ}\text{C}$) on the decrease of the purge gas flow rate. Initial flow: 16.5 ml/min at atmospheric pressure. — experimental; - - - theoretical.

Theoretical and experimental curves agree quite well except for that at 0°C . Most probably, this deviation is caused by the relatively large water concentration of the purge gas resulting in a different shape of the ice layer.

(2) *Influence of the cold-trap temperature:* In accordance with the theory [17], a decrease of the purge gas flow rate was observed experimentally, by decreasing the cold-trap temperature from -60 to -100°C . An unexpected deviation from this trend, however, is seen at -120°C , which is believed to be caused by a different crystal structure of the deposited ice.

(3) *Influence of the purge gas flow rate:* In order to observe the effect of flow rate variations, as such, one has to ensure that the mass flow of water entering the cold-trap is

constant. Listed in **Table 2** are the discrete mass flows of water vapor with the attendant condenser temperatures and the purge gas flow rates.

Table 2

Combinations of condenser temperatures and initial flow rates for a constant water mass flow to the cold-trap.

	Low flow		High flow		Mass flow (H ₂ O) μg/s
	°C	ml/min	°C	ml/min	
1.	-15	10.5	-20	16.5	0.11
2.	-10	16.5	-15	26.0	0.30
3.	0	16.5	-15	62.0	0.72

It was found that the blocking of the cold-trap tends to be somewhat faster at higher flow rates. The suggested theoretical model does not provide a direct relationship between the initial flow rate and its decrease.

4.4 Overall Recovery and Selectivity of Water Removal

The use of a condenser or a Nafion tube introduces the risk of an undesired loss of compounds. This may occur by condensation or adsorption on the ice surface or on the tube wall.

In order to judge the selectivity of water removal, the recoveries obtained by purging using a condenser or a Nafion tube are compared to those obtained by trapping of the organics on a Tenax adsorption tube, which is placed in the oven compartment of the PCT system. After purging,

the Tenax is flushed with a stream of dry helium in order to dispose of the remaining water, prior to thermal desorption and cold-trapping of the compounds. The experimental overall recoveries of the PCT-GC system are compared to recoveries obtained with the Tenax adsorption thermal-desorption (ATD) mode, closed loop stripping (CLS) [6] and theoretically calculated values according to eq. (1).

The results for the three test mixtures are shown in **Table 3**. The sample (25°C) was purged for 10 minutes at a flow rate of 16.5 ml/min. The memory effects of the condenser and the Nafion tube were determined by restarting the purge process after replacement of the sample flask by a dry one, while the condenser temperature was simultaneously raised from -15°C to 15°C.

For the non-polar volatile compounds, good agreement exists between the recoveries obtained with the condenser and the Nafion tube and those of the ATD and CLS measurements. Non-volatile compounds represented by *n*-C12 to *n*-C16 remain trapped in the cold condenser and to much lesser extent in the Nafion tube.

Slightly polar compounds that can only partly be recovered by the stripping process (e.g. 3-heptanone, 2-nonanone, 1-nonanol, acetone, and ethyl acetate) are completely removed by the Nafion tube and considerable amounts of them are also lost in the condenser. This is clearly demonstrated by the behavior of 2-nonanone, where the memory-effect of the condenser (25%) and the ATD and CLS recoveries (28% resp. 20%) are in fairly good agreement.

Table 3

Overall recoveries of different purge techniques.

	ATD		PCT				CLS
	Recovery	Memory	Nafion tube		Theory		
			Recovery	Memory			
Multimix							
Toluene	95	93	1.4	87	5	95	90
3-Heptanone	15	11	6.6	0	1	-	8
1,2,4-Trimethylbenzene	87	89	5.5	84	3	92	85
<i>o</i> -Dichlorobenzene	64	58	10	49	3	59	51
2-Nonanone	28	0	25	0	0	-	20
1-Nonanol	9	0	0	0	0	-	3
Hydrocarbon mix							
<i>n</i> -C8	100	100	-	100	-	100	101
<i>n</i> -C10	100	99	-	100	-	100	116
<i>n</i> -C12	95	0	-	86	-	100	100
<i>n</i> -C14	87	0	-	13	-	100	86
<i>n</i> -C16	21	0	-	0	-	100	71
Volatiles mix							
Acetone	19	9	-	0	-	-	-
Ethyl acetate	12	5	-	0	-	8	-
1,2-Dichloroethane	51	49	-	49	-	45	-

4.5 Reproducibility

In this work the reproducibility was determined, not only by replicates using the same sample flask, but also by consecutive purging using four different sample flasks of the same design.

Table 4 shows only minor differences for the average recovery values and the relative standard deviations in both cases. When the recovery exceeds 30% the standard deviation is small.

Table 4

Comparison of the reproducibility within one sample flask and between four sample flasks (purge time: 5 minutes).

	"within"		"between"	
	R (%)	RSD (%)	R (%)	RSD (%)
Toluene	74	3.7	71	3.3
3-Heptanone	4	26	4	20
1,2,4-Trimethylbenzene	57	1.3	55	3.5
o-Dichlorobenzene	31	15	29	24

4.6 Effect of the Purge Gas Volume

The theoretical model predicts a large dependence of the recovery on the purge gas volume. The recovery can be calculated by substitution of the proper values of the process parameters in equation (1). As only few published data exist in the literature, the vapor pressures were calculated using the Clausius-Clapeyron equation and the activity coefficients of some compounds could be calculated from their solubility in water. These are presented in **Table 5**.

Table 5

Approximate values of the activity coefficients and saturated vapor pressures of some compounds at 25°C.

	γ_i	p_i^0 (bar)
Toluene	9.9×10^3	3.7×10^{-3}
o-Dichlorobenzene	5.5×10^4	2.0×10^{-2}
1,2-Dichloroethane	6.8×10^2	0.10

Experimentally, synthetic samples containing 15 ppb per compound were purged at 25°C during different periods of time with an initial purge flow rate of 16.5 ml/min and a condenser temperature of -15°C. The total volume is corrected for the decrease of the flow rate.

Figure 4 shows the excellent agreement between experimental and theoretical recoveries for three components as a function of the purge gas volume. Similar experimental relationships were found for the other compounds as well.

Using the new design of sample flask the observed recoveries were not affected by an increase of the purge flow rate up to 80 ml/min in combination with a proportionally reduced process time. This indicates that at high flow rates the thermodynamic equilibrium is maintained, offering the possibility of a fast and efficient process.

4.7 Effect of the Concentration

Assuming a 100% recovery and a minimum detectable amount of 10 pg/s for a FID detector, a minimum concentration of 1 ppt can be detected for a peak width of 1 s and a sample size of 10 ml. No significant effects on overall recovery could be observed within a concentration range of 15 ppb-150 ppt.

4.8 Effect of Sample Temperature

According to the theoretical model, purging at elevated temperatures will drastically improve the recovery, because the solute's saturated vapor pressure is increased.

In our experiments the sample flask was wrapped with heating tape and the temperature was measured by a thermocouple stuck on the outer glass wall. The recoveries observed in this way are tabulated in **Table 6**.

Table 6

Recoveries at different sample temperatures. Experimental conditions as in Table 3.

	25°C	45°C	65°C	95°C
3-Heptanone	11	30	64	101
1,2,4-Trimethylbenzene	89	91	99	102
o-Dichlorobenzene	58	79	95	103
2-Nonanone	0	0	1.6	10

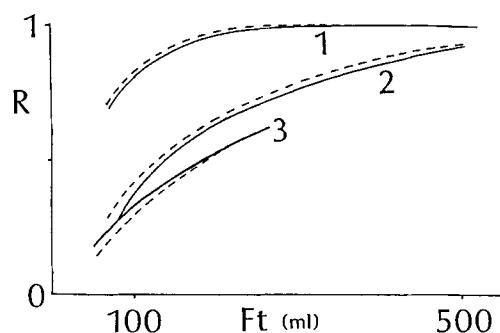


Figure 4

Comparison of calculated (---) and experimental (—) recoveries as a function of purge gas volume. 1 = toluene; 2 = o-dichlorobenzene; 3 = 1,2-dichloroethane.

The effect of an increased sample temperature is most obvious for 3-heptanone, whose recovery is complete at 95°C, whereas it is only 11% at 25°C. At 95°C no problems occurred concerning excessive deposition of ice inside the condenser because most of the evaporated water condenses before entering the condenser.

4.9 Effect of Condenser Temperature

The influence of the condenser temperature on losses occurring in this part of the equipment is shown in **Table 7**. Obviously the effect is limited to non-polar compounds of moderate volatility: for *n*-C12 a sudden increase is observed, when the condenser temperature is changed from -15°C to 0°C. For larger *n*-hydrocarbons 0°C is still too cold for them to pass. A lower condenser temperature greatly increases the efficiency of water removal, while it hardly influences the selectivity.

Table 7

Recoveries at different condenser temperatures. Experimental conditions as in Table 2.

T _{cond}	-20°C	-15°C	-10°C	-5°C	0°C
3-Heptanone	9.1	8.8	11	9.7	7.1
<i>o</i> -Dichlorobenzene	59	58	57	56	50
2-Nonanone	0	0	0	0	0
<i>n</i> -C10	-	99	-	-	100
<i>n</i> -C11	-	86	-	-	96
<i>n</i> -C12	-	0	-	-	80
<i>n</i> -C13	-	0	-	-	1

4.10 Chromatograms

Some representative chromatograms of reference solutions prepared from a "multimix" stock solution and wine and beer samples are presented in **Figure 5**.

5 Conclusions

With the on-line purge and cold-trap system described in this paper the water concentration in the purge gas entering the cold-trap can be reduced sufficiently to avoid blocking of the capillary trap. Either a condenser or a Nafion water permeable membrane can be used successfully for selective removal of water for non-polar compounds. Polar and high boiling non-polar solutes are partly or completely lost with both methods.

The required process time can be reduced drastically by purging at elevated sample temperatures and/or large purge gas flow rates. Highly reproducible and reliable experimental results are obtained at concentrations down to 1 ppt, which agree fairly well with the theoretically predicted values.

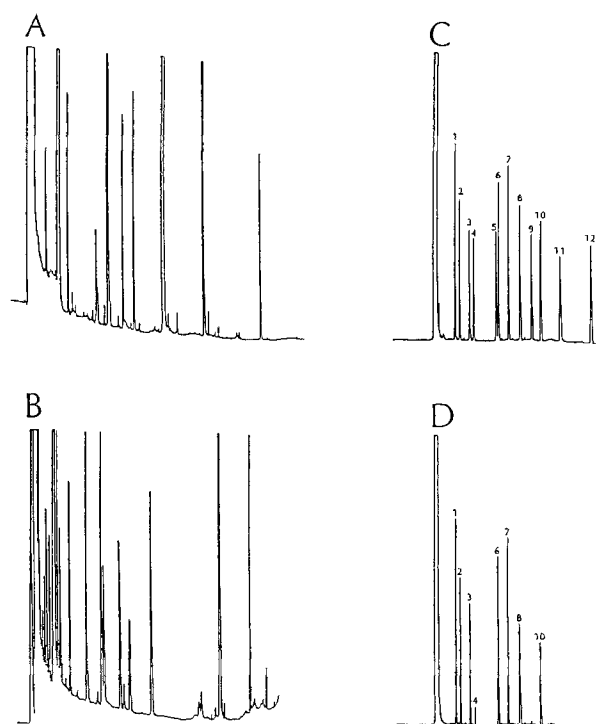


Figure 5

A) Chromatogram of 8 ml beer, 10 min purged at 16.5 ml/min, condenser at -15°C, GC-oven temperature program: 3 minutes isothermal at 40°C, programmed at 10°/min up to 170°C.

B) Chromatogram of 8 ml wine, conditions as in (A).

C) Chromatogram of 100 ppm multimix stock solution, split injection (1:100). GC-oven temperature: 120°C isothermal.

D) Chromatogram of a purged multimix sample in water, 15 ppb, 10 min purged at 16.5 ml/min, condenser at -15°C, GC-oven temperature 120°C isothermal.

1 = toluene; 2 = *n*-octane; 3 = *n*-hexyl chloride; 4 = 3-heptanone; 5 = 1-heptanol; 6 = *p*-chlorotoluene; 7 = 1,2,4-trimethylbenzene; 8 = *o*-dichlorobenzene; 9 = 2-nonanone; 10 = *n*-undecane; 11 = 1-nonanol; 12 = benzyl acetone.

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