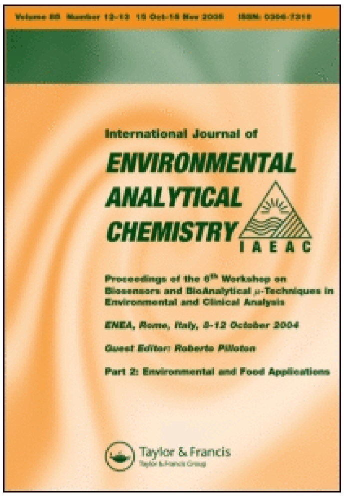

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ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN WATER BY PURGE-AND-TRAP AND GAS CHROMATOGRAPHY TECHNIQUES

Operational Parameters Optimization of the Purge Step

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In order to analyse volatile organic compounds (VOCs) in water by the dynamic headspace method, an adapted purge and trap set up was used along with on-column trapping (packing = Tenax GC) and flame ionisation detection.

Optimization of the purge step working conditions is discussed with respect to extraction efficiency for 14 representative VOCs used to spike a 25 ml water sample. With that aim in mind, the effect of the following parameters were studied: purge gas volume (Vg/Vl = 20 and 40), sparger vessel temperature (25, 30, 35 and 40°C) and ionic strength (dissolution of 10 and 20% of NaCl in the studied sample). A fair increase of the purge gas volume enhances the recovery of most of the VOCs examined. However, the extraction is still unsatisfactory for the less volatile compounds. Nevertheless, a better purge efficiency for all the VOCs studied is observed when the temperature is increased, at the expenses of an increase of the RSD of the results (= 14%). Moreover, for all the less volatile and less soluble purgeable compounds, the increase of the extraction efficiency is significant when NaCl is dissolved in the water examined. The selected purge operational conditions are as follows: dissolution of 20% NaCl in a 25 ml sample, purge at 35°C with helium during 10 minutes and a flow rate of 50 ml min^{-1}. When applied to a tap water spiked with 30 VOCs, including the purgeable priority pollutants listed by U.S. EPA, these conditions lead to a better than 90% recovery for most of these compounds (RSD < 10% for triplicate sample analysis).

KEY WORDS: Purge and trap GC, water analysis, organic volatile pollutants.

INTRODUCTION

The number of chemical pollutants liable to contaminate sources and springs is steadily growing and it reaches now to many thousands of compounds which are mainly organic and whose toxicities pose potential hazards to man and fauna[1]. Volatile organic compounds (VOCs) are an important chemical class of water pollutants. They are already found in polluted surface waters as well as in bad protected ground water tables. Their concentration, especially for the trihalomethanes (THM), may greatly increase after chlorination, particularly if natural precursors such as humic and fulvic acids or seaweed metabolic breakdown products are present[2–4].

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Trace water VOCs determination is often carried out by GC using two different analytical techniques, namely, headspace analysis (HSA) and chromatographic analysis after a preconcentration step.

In the first case, the determination is focused on the titration of a VOCs particular class, hence the use of a selective chromatographic detection system, e.g. ECD for volatile halocarbons titration has been proposed[5–7].

However, the second technique is more used. The preconcentration step allows the reduction of the investigated sample volume; moreover, it extends the studied VOCs range. In this last instance, the detection is either nonspecific (e.g. FID)[8] or universal, such as mass spectrometry (MS)[9].

The various techniques used for performing the preconcentration call on the liquid–liquid extraction[10–14] or more often on the dynamic headspace analysis (DHSA)[15,16]. This latter method was first introduced by Grob[17] as a closed circuit purge and by Bellar and Lichtenberg[18] as an open system (or the so called purge and trap technique "P&T").

The purge and trap technique is the most used, especially for the VOCs determination of the purgeable priority pollutants listed by U.S. E.P.A.[19–28]. Here, an inert gas bubbles in the studied water sample, the volatile compounds are then either swept by the flowing gas and trapped in a cold trap (Cryotrapping)[29] or adsorbed on a suitable support[30]. The next step is the thermal desorption of the trapped solutes and their subsequent transfer on an analytical column.

The literature shows that some investigators have avoided the desorption step by trapping the purged compounds directly on a suitable packing, e.g., Tenax or Chromosorb 101[20,31], in a chromatographic column at about ambient temperature; temperature programming was subsequently used to elute the trapped compounds for detection.

Whatever version of the P&T technique used, the water VOCs extraction is in fact a thermodynamic equilibrium shifting of the vapor phase from the water sample.

Table 1 Bibliography data of the purge step operational conditions for VOCs analysis in water

V_l (ml)	V_g (ml)	$V_l V_l$	Tp (°C)	FI	Reference
200	25 × 20	2.5	30	30% Na2SO4	(9)
100	50 × 30	15	35	0	(19)
40	40 × 30	30	40	10% Na2SO4	(20)
50	40 × 15	12	(a)	0	(21)
10	20 × 11	22	(a)	0	(22)
0	25 × 10	50	(a)	0	(23)
5	40 × 11	88	(a)	0	(24) (25)
5	18 × 6	21.6	25	0	(26)

V_1: Sample volume; V_g: Purge gas volume (= flow rate (ml/min^{-1}) × time (min)); T: Temperature in the purge vessel environment; IS: ionic strength (salt concentration). (a) ambient temperature.

Thus, the parameters which control the equilibrium shifting rule also the purging efficiency. These are: the purge gas volume (V_g), the temperature (T) and the ionic strength (IS) of the examined solution.

Usually not all these variables are taken into account by the various authors whose purge working conditions vary (Table 1). The purge is mainly controlled by these workers by means of the purged gas volume.

In this study, the P&T technique with on-column trapping is applied to water VOCs determination. The various working parameters ruling the purge efficiency are discussed. The selected working conditions were tested on a tap water spiked by 30 purgeable organic compounds, 21 of which are on the U.S. E.P.A. priority pollutant list.

EXPERIMENTAL SECTION

Reagents

The VOCs studied standards came from various suppliers (Aldrich, Merck, Fluka and Prolabo) and their purity is, in every case, better than 98%. Our methanol standard solution have 2000 and 200 μg ml^{-1} concentration and are checked against Supelco reference standard solutions: Mix 4 (Cat. No. 4-8786), Mix 6 (Cat. No. 4-8799), Purgeable A (Cat. No. 4-8851) and Purgeable B (Cat. No. 4-8852).

The pure water used for the aqueous standard solution is obtained as a 500 ml batch following this procedure. A bidistillated water is purged at 90°C for 2 hours by an helium flow at a 100 ml min^{-1} rate; it is afterwards cooled to the room temperature while the gas stream is maintained.

Every purified water batch is checked against an analytical blank. Aqueous standard stocks were made up by addition of 5 μl of the methanolic standard to 100 ml of water. Subsequent secondary aqueous standards are prepared by dilution to the desired concentration.

Apparatus

The analyses were carried out with the experimental setup sketched in Figure 1. The gas chromatograph used is a Delsi GC 121 DFL (France). It is equipped with a flame ionisation detector (FID) and is connected to an integrator recorder ICR-1B Intersmat (France). The stainless steel chromatographic column is 1.8 m length (2.2 mm ID) and is packed with Tenax GC 60/80 mesh (Alltech, Europe). The injector port temperature was maintained at 220°C and gas flow of 30 ml min^{-1} and 300 ml min^{-1}, respectively, for hydrogen and air were used for FID which was set at 250°C. The 25 ml purge vessel (Supelco SA, Cat. No. 2-2426) is placed in a thermostated bath and is modified in order to fit 1/4–1/8 in. reductors on its three ports in order to be connected to the experimental setup. The pressure regulators R_1 and R_2 (Supelco SA, Cat. 2-3748) serve to set the helium (Quality U), the purge and vector gas flows. The 3 way valves (TV_1, TV_2 and TV_3) and the snap valves (SV_1, SV_2 and SV_3) purchased from Chrompack (Cat. No. 12693 and 12698) allow gas

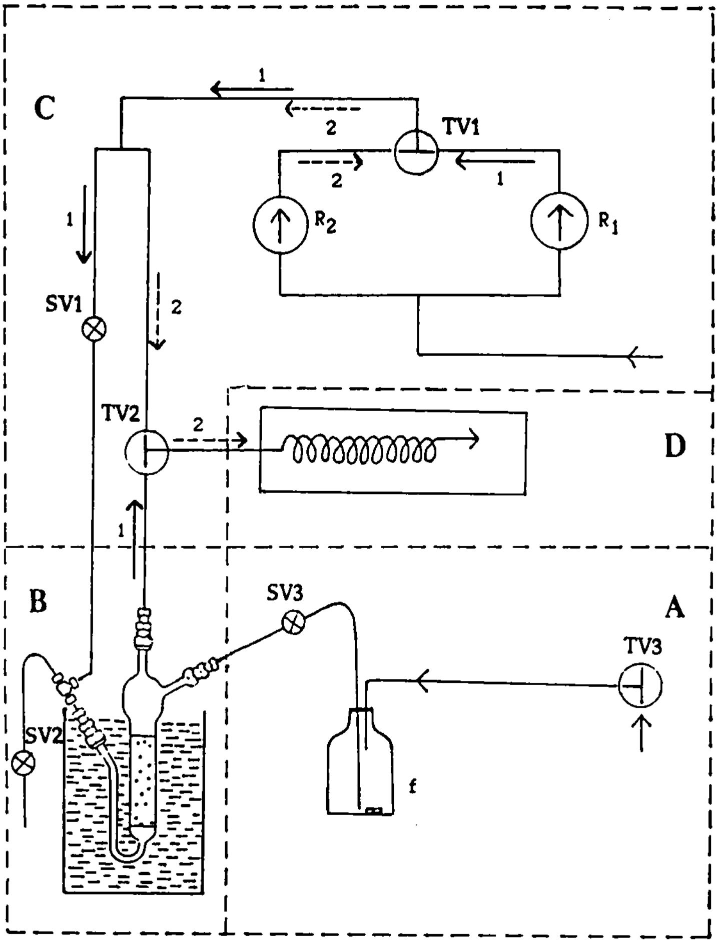

Figure 1 Experimental apparatus assembly: (A) pressurized sample delivery system; (B) purge vessel; (C) flow rate control system; (D) G.C system; TV1, TV2 and TV3 = 3 way valves; SV1, SV2 and SV3 = snap valves; R1 and R2 = pressure regulators, f = 100 ml flask.

direction selection during the purge vessel loading step, the purge and the chromatographic analysis steps, respectively. All tubings are in stainless steel (1/8 in.) (Delsi, France).

Working conditions

The analytical experiment comprises three steps: purge vessel loading, P&T, and desorption-chromatographic analysis.

Purge vessel loading When the SV_1, SV_2 and SV_3 valves are closed, 25 ml of water and then a suitable quantity of NaCl are introduced in the flask "f" (Figure 1).

Afterwards, the flask "f" is shut by a PTFE plug and the water sample is kept under helium pressure by valve TV_3. When the NaCl is dissolved by magnetic stirring the obtained solution is flushed through the purge vessel by valve SV_3 opening.

P&T The purge starts 5 min after the purge loading, in order to reach the thermal equilibrium between the aqueous sample and the thermostated bath. The purge begins when the valve VA_1 is open and by adjusting the valves VT_1 and VT_2 so the purge gas runs along the path 1. The gas flow measured at the chromatographic column exit is adjusted by the regulator R_1 to the value of 50 ml min^{-1}. The flushed solutes during that stage are trapped at the head of the analytical column which is maintained at 30°C.

Desorption-Chromatographic analysis At the purge end, the valve SV_1 is closed and the valves TV_1 and TV_2 are set so that the helium, gas vector runs along the path 2. The gas rate is adjusted by means of the regulator R_2 to 35 ml min^{-1}. At the beginning, the column temperature is programmed between 30° and 120°C at a rate of 20°C min^{-1}, then, between 120°–200°C at 5°C min^{-1}. The blowing off of the purge vessel is made during the chromatographic analysis by opening the valve SV_2.

In order to clean the purge and its loading circuit, 50 to 100 ml of bidistillated water are flushed in the flask "f" and one proceeds as for the loading but now the valve SV_2 is kept open. The purge vessel is then loaded for the next analysis.

Purge efficiency determination

There are two means to evaluate the purge efficiency:

a) The predicted purge efficiency (PPE), drawn from theoretical considerations.

b) The observed purge efficiency (OPE), obtained from experimental data.

When dealing with an aqueous standard solution or a spiked tap water sample, the OPE is calculated thanks to Simmond's method[23] from two successive purge data obtained onto the same sample. The applied relation is as follows:

$$E\ (\%) = [A/(A + B)] \times 100$$

where A and B are the peak areas obtained after the first and the second purge, respectively.

The PPE calculation is drawn from the theoretical expression giving the partition equilibrium shifting of a solute in solution, between the gaseous and the liquid phases. This equilibrium is given for a diluted solution by Henry's law:

$$P_i = H_i c_i \qquad (1)$$

where P_i is the solute partial pressure i (atm); c_i is the liquid phase concentration (mol l^{-1}) and H_i is the Henry's constant (atm. m^3 mol^{-1}).

When a gaseous volume V_g passes through the liquid phase, a decrease of the solute mole number i in the liquid phase (n_{il}) occurs and by the same token, the mole number of the same solute in the gaseous phase (n_{ig}) increases. The equilibrium shifting at constant pressure and temperature is given by the following differential equation;

$$(dn_{ig})_{P,T} = -(dn_{il})_{P,T} \tag{2}$$

In the liquid phase, the solute mole number i variation may be written with respect to the concentration c_i and the volume V_l as follows:

$$(dn_{il})_{P,T} = V_1 dc_i \tag{3}$$

In the gaseous phase, considered as a perfect gas, the mole number i variation is drawn from the following equation;

$$(dn_{ig})_{P,T} = (P_i/RT)dV_g \tag{4}$$

R is the perfect gas constant ($= 8{,}210^{-5}$ m^3 atm mol^{-1} K^{-1}).

The substitution of Equation (2) terms by this expression drawn from the relations (1), (2) and (4) leads to the new differential Equation (5);

$$V_1 dc_i = (Hc_i/RT)dV_g \tag{5}$$

The integration of Equation (5) gives:

$$c/c_0 = \exp - [(HV_g)/(RTV_1)] \tag{6}$$

where c and c_0 are the concentration of the analyte of interest before and after the liquid phase flushing by a gaseous volume V_g. Then the purge maximum efficiency (E) is given by

$$E\,(\%) = (1 - c/c_0) \times 100 \tag{7}$$

Thus, Eqs. (6) and (7) express the extraction efficiency variation for each solution in function of the parameters ruling the purge and allow the PPE calculation.

Results and discussion

Purge gaseous volume effect (V_g) The literature indicates that the purge gaseous volume varies from one laboratory to another. In the same volume range, we determined for the same quantity of studied water ($V_l = 25$ ml) the purge efficiency for 14 representative VOCs, using two V_g values: $V_g/V_l = 20$ and 40. The PPE and OPE values show variations in the two directions. Except for bromoform and 1.2-dichloroethane, the OPE of the studied VOCs is lower than the PPE. This result may come from the following factors:

a) The equilibrium state, during the purge, between the gas bubbles and the liquid phase is not reached.

b) The H value accuracy obtained experimentally is often poor.

c) The purge temperature is less than the specific temperature of the H value used.

The cases for which the OPE is greater than the PPE can be explained only by the difference between the purge temperature and H specific temperature. However, the said reasons are not enough to deal with margins greater than 25% between the corresponding PPE and OPE, as observed for 1,1-dichloroethylene and *m*-dichlorobenzene. The low OPE of the former compound, comes from its bad retention on Tenax among others. It is for that reason that the purge study of the somehow very volatile other compounds such as CH_3Cl, C_2H_5Cl and vinyl chloride was not possible.

In the case of *m*-dichlorobenzene, the great discrepancy between OPE and PPE stem from the integration errors produced by the chromatographic peak tailing.

Despite, the observed differences, between OPE and PPE, the Equations (6), (7) as well as the values at hand are anyway useful for the optimum gaseous purge volume determination.

In other respects, the recovery of most of the tested compounds during a 20 minute purge ($V_g/V_l = 40$) is greatly enhanced compared with a 10 minute purge ($V_g/V_l = 20$). However, the extraction is still poor for the volatile compounds such as the dichlorobenzenes as well as in the case of relatively water soluble chemicals, such as bromoform. For these compounds too, the purge stays incomplete even with greater purge gaseous volumes[23].

The OPE fluctuations of most of the studied VOCs are good enough with a RSD lower than 5%. However, the accuracy for bromoform, chlorobenzene and dichlorobenzenes is less satisfactory. The low extraction efficiency of the more water soluble and less volatile VOCs may be responsible for their lower analytical precision.

Temperature effect The extraction efficiency of representative VOCs was also determined at other temperatures, namely 30, 35 and 40°C for a 10 min purge duration ($V_g/V_l = 20$) (Table 3). The expected improvement of purge efficiency of all the VOCs tested by temperature increase of the treated water lays essentially in the Henry's constant increase. In fact, this parameter (H) variation as a function of the temperature T obeys to an exponential law[32]: $H = \exp(A - B/T)$; where A and B are correlation factors. The purge results at 25°C for 20 min and at 40°C during 10 min are comparable and reflect the gain in terms of purge efficiency and analysis duration obtained by purge temperature raising. In return, a relatively important fluctuation of purge efficiency expressed by the RSD of the results was observed for most of the VOCs studied. This fact was reported by many workers[19,23,26]. Moreover, the purge performed at a somehow high temperature carries a significant water quantitiy into the analytical system which may harm the column or some detection systems e.g. mass spectrometry. It is for that reason that purge temperatures greater than 40°C are not suitable.

Ionic strength effect Table 3 summarizes the ionic strength (IS) variation results for the investigated solution when sodium chloride dissolution is checked against the examined VOCs purge efficiency. The OPE increase for all the VOCs studied is significant for all the less soluble and less volatile solutes such as xylenes and dichlorobenzenes. Conversely, the bromoform relatively important solubility may be the reason for its low purge efficiency. The VOCs purge improvement by means of

Table 2 Henry's Law constants (H) for selected volatile organic compounds at 20–25°C and boiling points (Bp) and solubilities in water and predicted (PPE) and observed purging efficiencies (OPE) for $V_g/V_l = 20$ and $V_g/V_l = 40$ at 25°C (low ionic strength)

Compound	H^a *atm.m³/mol⁻¹*	Bp^b (°C)	*Solubility*^{c} g/l^{-1}	$(V_g/V_l) = 20^d$			$(V_g/V_l) = 40^d$		
				PPE, %	*OPE, %*	*(% RSD)*	*PPE, %*	*OPE, %*	*(% RSD)*
methylene chloride	0.00219*	40	20*	83.34	88.27	(1.8)	97.22	91.42	(2.4)
chloroform	0.00367*	61	2.52**	95.04	78.06	(1.7)	99.75	91.81	(0.98)
bromoform	0.00059**	149.5	3.93**	36.77	55.69	(5.68)	60.01	62.29	(4.8)
1,2-dichloroethane	0.00091**	83.5	3.50**	52.51	60.55	(1.01)	77.45	88.10	(2.2)
1,1-dichloroethylene	0.0261*	31.7	2.23**	99.99	64.92	(1.3)	100	75.77	(1.3)
trichloroethylene	0.00958*	87	0.74**	99.96	92.88	(0.88)	99.99	99.11	(0.38)
tetrachloroethylene	0.0177*	121	i*	99.99	98.03	(1.4)	100	99.10	(0.78)
benzene	0.0055**	80	0.82*	98.89	83.99	(1.78)	99.98	93.10	(3.20)
toluene	0.0067**	111	0.47*	99.58	85.73	(0.84)	99.99	93.12	(3.20)
chlorobenzene	0.0036**	132	0.49*	94.75	74.94	(5.47)	99,72	83.95	(7.27)
o-dichlorobenzene	0.0019**	181	1.45*	78.88	59.86	(5.1)	95.54	66.82	(6.23)
m-dichlorobenzene	0.0036**	173	1.23*	94.74	60.61	(11.6)	99.72	76.61	(10.4)
o-xylene	0.0050**	144.4	i*	98.33	81.86	(3.9)	99.97	84.28	(4.7)
m-xylene	0.0070**	139.1	i*	94.67	89.36	(2.6)	99.99	96.11	(2.6)

(a): H* data are from ref. [32]; H** data are from ref. [33].
(b): Bp data are from ref. [34].
(c): * data at 30°C are from ref. [35]; ** data are from ref. [34].
(d): Average (OPE, %) and % RSD for triplicate determinations.

Table 3 Purging efficiencies (%) of selected organic compounds from aqueous standard solutions with respect to temperature and solution ionic strength.

Compound	*Mean percent efficiency (% RSD)**				
	Temperature			*Ionic strength at 35°C*	
	30°C	*35°C*	*40°*	*10% NaCl*	*20% NaCl*
methylene chloride	90.03 (2.1)	91.25 (1.2)	94.15 (1.1)	93.54 (1.2)	94.66 (0.42)
chloroform	82.01 (0.39)	83.63 (1.87)	87.63 (2.9)	93.98 (1.8)	98.52 (1.5)
bromoform	58.11 (5.42)	60.34 (5.8)	66.04 (6.8)	60.36 (5.4)	66.88 (4.6)
1,2-dichloroethane	62.48 (0.67)	63.2 (2.5)	64.75 (3.8)	67.97 (2.1)	76.17 (1.5)
1,1-dichloroethylene	69.66 (2.65)	70.23 (4.25)	75.77 (4.75)	74.4 (3.5)	78.2 (4.3)
trichloroethylene	95.91 (1.04)	97.01 (0.92)	100	99.2 (1.3)	100
tetrachloroethylene	97.94 (1.7)	100	100	100	100
benzene	86.43 (1.42)	90.12 (1.35)	92.81 (3.05)	97.22 (2.1)	99.50 (2.5)
toluene	88.63 (1.32)	92.66 (1.83)	94.05 (1.73)	98.1 (0.92)	99.42 (1.1)
chlorobenzene	75.76 (5.45)	81.48 (6.42)	85.97 (6.9)	92.52 (2.5)	98.43 (2.9)
o-dichlorobenzene	60.94 (7.7)	63.88 (8.23)	65.41 (9.97)	79.18 (4.9)	88.76 (3.6)
m-dichlorobenzene	65.93 (11.6)	72.45 (10.7)	73.48 (14.4)	81.59 (3.7)	91.5 (3.9)
o-xylene	84.99 (3.2)	86.43 (4.37)	89.66 (5.1)	96.72 (2.3)	98.91 (1.5)
m-xylene	91.32 (2.5)	93.83 (3.2)	95.41 (2.7)	93.56 (2.5)	98.9 (2.1)

* Percent relative standard deviation from triplicate determinations.

a salt dissolution in the solution to analyse is the result of the activity coefficient variation of the solutes subjected to the purge (salting out effect)[32]. Hence, the treated solution can no longer be considered as an ideal system. The solute *i* Henry's constant (H_i^*) is then expressed by the relation: $H_i^* = \gamma H_i$; H_i being the solute *i* Henry's constant in an ideal system. Thus, in such a case, the E raising comes from *H* increase.

Application The above results were checked for the various purge conditions for a real tap water. In this case, the detected VOCs confirmation—which is out of the scope of this paper—was made according to the working protocole worked out by the U.S. E.P.A. (Method 502.1), that use GC analysis on a packed column with 60/80 Carbopack B/1% SP.1000. Figure 2 shows, as an example, the detected VOCs purge efficiency variations as a function of various experimental parameters ruling the purge

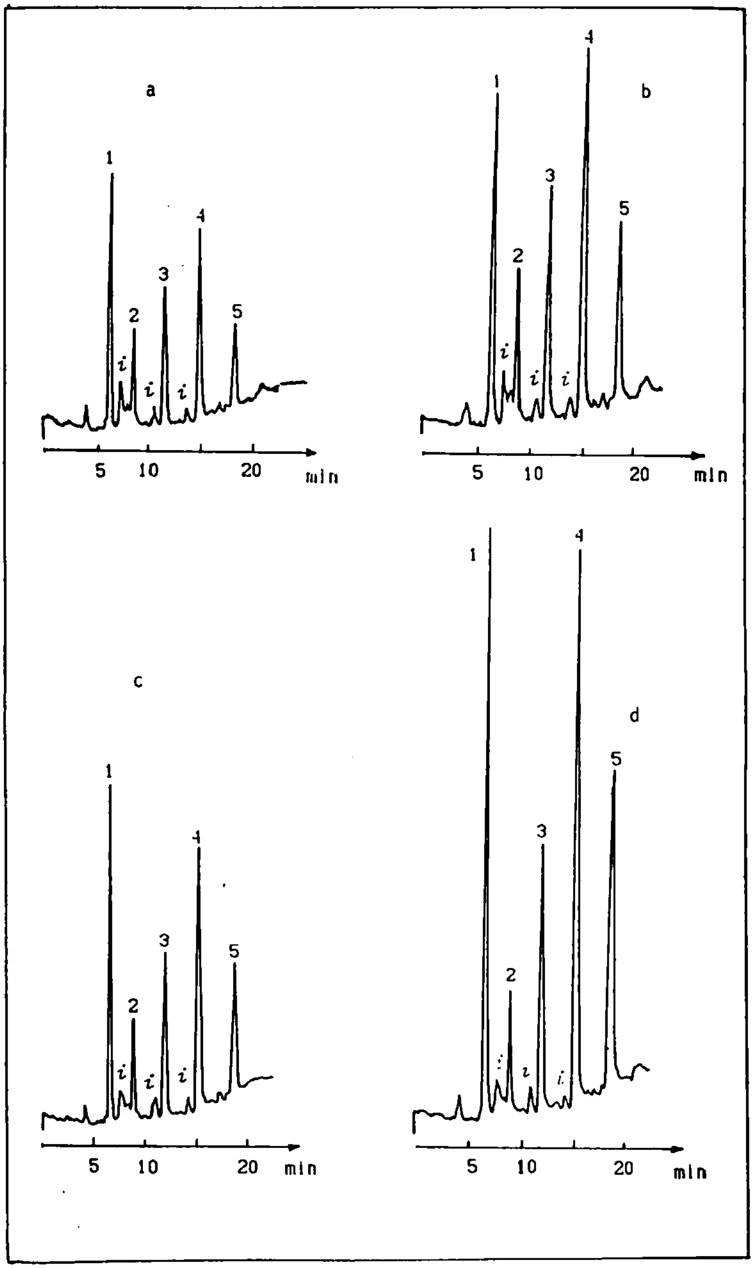

Figure 2 FID chromatograms of volatile pollutants present in tap water. 180 × 0.22 cm ID Tenax GC packed column. Conditions: helium carrier gas 30 ml min^{-1}, initial temperature 30°C then at 20°C min^{-1} to 120°C and then at 5°C min^{-1} top 200°C. Peak identification: 1 = 1,1-dichloroethylene; 2 = chloroform; 3 = dichlorobromomethane; 4 = dibromochloromethane; 5 = bromoform; *i* = unidentified peak. Purge step operational conditions: (a) $V_g/V_l = 20$, T = 25°C and IS = 0; (b) $V_g/V_l = 40$, T = 25°C and IS = 0; (c) $V_g/V_l = 20$, T = 35°C and IS = 0; (d) $V_g/V_l = 20$, T = 35°C and IS = 20%NaCl.

Table 4 Recovery of volatile organic compounds (VOCs) from tap water[a]

Compound	[b]		*Compound*	[b]	
	%	*RSD*		%	*RSD*
methylene chloride	91.98	1.4	*cis*-1,3-dichloropropene	90.21	1.71
chloroform	94.1	3.8	*trans*-1,3-dichloropropene	87.89	7.63
bromodichloromethane	91.4	3.9	pentane	84.72	1.32
dibromochloromethane	79.33	2.75	hexane	97.2	1.25
bromoform	62.33	7.4	heptane	96.29	1.89
carbon tetrachloride	ND		benzene	99.25	1.35
1,1-dichloroethane	92.78	4.59	toluene	99.11	0.77
1,2-dichloroethane	77.5	5.5	ethylbenzene	97.21	1.73
1,1,1-trichloroethane	ND		bromobenzene	93.63	2.9
1,1,2-trichloroethane	72.3	6.48	chlorobenzene	97.4	0.88
1,1-dichloroethylene	76.63	1.6	*o*-dichlorobenzene	77.7	8.5
trans 1,2-dichloroethylene	84.03	6.22	*m*-dichlorobenzene	77.5	5.7
trichloroethylene	98.4	1.08	*o*-xylene	98.38	1.46
tetrachloroethylene	98.8	1.3	*m*-xylene	98.5	1.5
1,2-dichloropropane	93.6	2.86	*p*-xylene	98.3	1.7

(a) Sample (25 ml) was spiked with 4 $\mu g l^{-1}$ of the appropriate standard mixture in methanol and purged at 35°C with helium at a flow rate of 50 ml min^{-1} for 10 min.

(b) Average (%) and % RSD for triplicate determinations.

ND: Could not be determined: broad chromatographic peak.

in the THM case. The applied working conditions which led to Figure 2 chromatogram were selected for the VOCs current analysis in tap water. These conditions allow a faster analysis when compared to the literature data (Table 1). As far as the extraction efficiency is concerned, which was determined for 30 VOCs (Table 4), it is better than 90% for most of the compounds tested. In this case, the analysis accuracy expressed in terms of RSD is fairly acceptable (RSD < 8.5%). Moreover, the adopted compact experimental setup handles all the analysis steps (purge, trap, thermal desorption and chromatographic analysis) and facilitates the VOCs current titrations, in tap water, especially for THM.

CONCLUSION

The P&T method is an efficient technique and it is widely used for water VOCs determination. The optimization of the various experimental parameters allows, in particular, the extraction yield improvement for less volatile purgeable solutes or relatively soluble in water. These parameters control the extraction steps. These parameters are the purge gaseous volume, the purge vessel temperature and the ionic strength. By an adequate selection of them, it is then possible to widen the investigated volatile pollutants range.

The purge working conditions proposed in this paper provide for 30 VOCs a purge efficiency better than 90%, a fairly sound determination accuracy (RSD < 10%) and an acceptable analysis duration.

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