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Evaluation of tetraglyme for the enrichment and analysis of volatile organic compounds in air

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Abstract

A recently developed method for the sampling and analysis of volatile organic compounds in air has been evaluated. The system is based on the enrichment of analytes in tetraethylene glycol dimethyl ether or tetraglyme, a water-soluble organic liquid. The subsequent analysis consists of dispersion of a sample aliquot in water followed by purge-and-trap and gas chromatographic separation. Physico-chemical data were investigated for 10 volatile organic compounds, providing information on the possibilities and limitations of the tetraglyme method. The target analytes included chlorinated alkanes and alkenes, and monocyclic aromatic hydrocarbons. Air/tetraglyme partition coefficients K_{at} were determined over an environmental relevant temperature range of 2–25°C to evaluate sorption efficiencies and estimate breakthrough volumes at the sampling stage. At 2°C breakthrough volumes (allowing 5% of breakthrough) ranged from 5.8 (1,1-dichloroethane) to 312 l (1,1,2-trichloroethane) for 20 ml of tetraglyme. With regard to the desorption stage, the effect of tetraglyme on the air/water partition of organic compounds was investigated through the measurement of air/tetraglyme–water partition coefficients $K_{\mathrm{at-w}}$ for 2–31% (v/v) tetraglyme in water. Finally a clean-up procedure for tetraglyme was evaluated. Analysis of a blank tetraglyme–water (17:83, v:v) mixture by gas chromatography–flame ionization detection/mass spectrometry showed minor background signals. None of the target compounds were detected.

Keywords: Air analysis; Partition coefficients; Breakthrough volumes; Air/tetraglyme(–water) partition coefficients; Purge-and-trap methods; Headspace analysis; Sample handling; Tetraglyme; Volatile organic compounds; Tetraethylene glycol dimethyl ether; Alkanes; Alkenes; Hydrocarbons, aromatic

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1. Introduction

Interest and demand for analytical methods allowing accurate measurements of volatile organic compounds (VOCs) in ambient air has increased tremendously over the past decades. Airborne VOCs are known to play a major role in atmospheric photochemical processes. VOC oxidation ultimately results in the disturbance of the natural tropospheric ozone level, and leads to the formation of other harmful oxidants such as peroxyacetyl nitrate (PAN) [1–2].

In most applications, a preconcentration step prior to gas chromatographic separation and subsequent

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detection is necessary. Adsorbent trapping, cryogenic trapping, solid-phase microextraction (SPME), and canister sampling combined with cryogenic or sorbent enrichment are widely used for this purpose. The relative merits and disadvantages of each technique have been extensively discussed in the literature [3–5].

Recently, Troost [6] described a new sample enrichment method for VOC determinations in ambient air based on the water-soluble organic liquid tetraethylene glycol dimethyl ether or tetraglyme. The analytes of interest are first collected in impingers filled with tetraglyme. The liquid phase is then dispersed in water and further analysis is performed by means of purge-and-trap followed by gas chromatography–mass spectrometry (GC–MS). This approach enables analytical laboratories involved in the routine measurement of VOCs in water to rapidly extend their activities towards air analysis studies. Unlike most of the ‘‘conventional’’ sample enrichment techniques described above, this method does not require any special expertise or equipment in air sampling if know-how on analysis of VOCs is available. Furthermore, besides low cost and simplicity the use of tetraglyme eliminates some of the problems encountered with existing air sampling techniques. The sampling procedure is free from water vapour interference, chilled samples can be stored for long periods of time without measurable loss of analytes and, in contrast to, e.g., adsorbent sampling, the use of tetraglyme is not restricted to ‘‘one-shot’’ analyses.

Similar analytical methods have been described for the determination of various VOCs in soil [7] and solid waste samples [8]. The protocols involved solvent extraction of the solid matrix with tetraglyme and transfer of an aliquot in water for either static [7] or dynamic [8] headspace analysis.

Although the applicability of tetraglyme as a sample enrichment tool in air analysis has been shown [6], a limited amount of work has been done so far to explore the boundaries of this new technique. Whereas Troost [6] focused primarily on the practical use through empirical observations, this work aimed to acquire insight into the physicochemical aspects to provide additional information on the possibilities and limitations of the tetraglyme method. Ten volatile organic compounds of environmental interest, chlorinated alkanes and alkenes, and monocyclic aromatic hydrocarbons, were investigated. In order to allow comparisons with some of the results obtained previously [6], the same analytes were targeted in this study.

2. Experimental

2.1. Materials

The VOCs trichloroethene, 1,1,2-trichloroethane, chlorobenzene, *o*-xylene, (Aldrich, Milwaukee, WI, USA), benzene, tetrachloroethene (Merck, Darmstadt, Germany), chloroform, 1,1-dichloroethane, toluene and *m*-xylene (Fluka, Milwaukee, WI, USA) were used in the experiments. In all but one case (1,1-dichloroethane, purity ≥96%), quoted purities exceeded 99%. Tetraglyme (99%) was purchased from Aldrich. Artificial sea water (35 ppt) was prepared with deionized water and commercial sea salt (Wiegandt, Krefeld, Germany). The major ions of the sea salt were chloride (54.93%), sodium (30.53%), sulphate (7.67%), magnesium (3.68%), cadmium (1.18%) and potassium (1.11%).

2.2. Determination of air/tetraglyme partition coefficients

2.2.1. Static headspace experiments

The air/tetraglyme partition coefficient K_{at} was determined by means of static headspace analysis. Into three vials of 118 ml each, 0.5 ml of tetraglyme was pipetted. In each vial 100 μl of a stock solution was injected under the liquid surface. In order to avoid GC-separation problems, two stock solutions in 10 ml of tetraglyme were prepared. Mixture A contained 1,1-dichloroethane (100 μl), benzene (25 μl), 1,1,2-trichloroethane (300 μl), chlorobenzene (80 μl) and *o*-xylene (40 μl) and mixture B contained chloroform (250 μl), trichloroethene (40 μl), tetrachloroethene (30 μl), toluene (60 μl) and *m*-xylene (10 μl). The vials were closed with Mininert valves (Alltech, Deerfield, IL, USA) and incubated upside down in a thermostatic water bath overnight. With a Hamilton gas syringe (Alltech) 100 μl of headspace was injected into a Varian 3700 gas chromatograph (Varian, Palo Alto, CA, USA) equipped with a flame ionization detection (FID) system. Separation was done on a 30 m×0.53 mm I.D. DB-1 polydimethylsiloxane fused-silica column (J&W Scientific, Folsom, CA, USA) with a 5.0 μm film thickness. The temperature of the GC oven was kept at 30°C for 10 min, then followed by heating at a rate of 5°C min^{-1}. Data acquisition was done with a HP3388A integrator (Hewlett-Packard, Palo Alto, CA, USA). Helium was used as carrier gas at a flow-rate of 3.6 ml min^{-1}. Injector temperature was set at 220°C and detector temperature was equal to 250°C. The flame ionization detector was fed with air at 293 ml min^{-1} and H_2 at 33.8 ml min^{-1}.

If the air/tetraglyme partition coefficient is defined as $K_{\text{at}} = C_g/C_t$ at equilibrium, then K_{at} (mol m^{-3} air over mol m^{-3} tetraglyme) can be derived from:

$$K_{\text{at}} = \frac{C_g V_t}{M - C_g V_g} \qquad (1)$$

with M the mass of analyte brought in the two-phase system (mol), C_g and C_t the headspace and tetraglyme concentration of the analyte respectively (mol m^{-3}), and V_g and V_t the volume of headspace and tetraglyme respectively (m^3). The gas phase concentrations were calculated from the peak areas in the chromatograms. Calibration curves were constructed from gaseous standards prepared in closed two-phase systems [9]. Five vials of 118 ml each were filled with 0.5, 5, 20, 50 and 90 ml of deionized water. In each vial 5 μl of a stock solution in methanol, containing all analytes, was injected under the liquid surface. Bottles were closed with Mininert valves (Alltech) and placed in a thermostatic water bath at 25.0±0.1°C overnight. With a Hamilton gas syringe (Alltech) 100 μl of headspace was injected into a GC-injector. Each vial was analysed in triplicate.

2.2.2. Dynamic headspace experiments

Two purge vessels (3.0 cm I.D., height 14 cm), each provided with a glass frit, were connected in series with 1/16 inch (1 inch=2.54 cm) stainless steel tubing, and placed in a thermostatic water bath set at 25.0±0.1°C. A magnetic stirrer was placed under the bath. A volume of 20 ml stock solution containing 200 μl of 1,1-dichloroethane and 100 μl of benzene in 25 ml of tetraglyme was pipetted into the first purge vessel. The second purge vessel was filled with 20 ml of pure tetraglyme. A magnetic stirring bar (volume 0.55 ml) was placed in both vessels. Ultra-pure He gas (Alphagas 2, Air Liquide, Liège, Belgium) was passed through both purge vessels at a flow-rate of 50 ml min^{-1}. Nine bottles of 118 ml volume each were filled with 20 ml of deionized water. After a predetermined time of purging, 5 μl of tetraglyme contained in the first purge vessel was injected into three vials. Into another set of three vials 5 μl of tetraglyme present in the second purge vessel was injected under the water surface. Finally 5 μl of the remaining stock solution was injected into the last three vials. All bottles were incubated overnight in a thermostatic water bath at 25.0±0.1°C and analysed according to the procedure described above.

2.3. Determination of air/tetraglyme–water partition coefficients

Air/tetraglyme–water partition coefficients $K_{\text{at-w}}$ were measured by means of the EPICS (equilibrium partition in closed systems) technique in combination with SPME [10]. As for the determination of air/tetraglyme partition coefficients, two stock solutions were prepared in 10 ml of tetraglyme. The stock solutions contained the same analytes as described previously. The volumes injected in 10 ml of tetraglyme ranged from 5 to 350 μl, hereby assuming that the amount of analyte added to the closed two-phase system should result in a water concentration equal or lower than one tenth of the analyte maximum aqueous solubility.

A set of six vials, each with a total volume of 118 ml, was used in the experiments. Into three vials, 0.5 ml of an aqueous solution was pipetted. A volume of 90 ml of the same solution was brought into the other set of three vials. In a first experiment, 1% (v/v) tetraglyme in deionized water was used. In experiments 2, 3 and 4, the tetraglyme concentration was increased to 10, 20 and 30% (v/v), respectively. Experiments 5 through 8 were similar to the first four experiments, but this time the solutions were made in artificial sea water (35 ppt) instead of deionized water. Within one experiment, 5 μl of a stock solution in tetraglyme was injected under the water surface in all six vials. In order to balance the tetraglyme/water ratio, 0.9 ml of tetraglyme was pipetted into the vials with a high liquid content so that both types of bottles had final concentrations of 2, 11, 21 or 31% (v/v) tetraglyme in water, respectively. The bottles were then closed with Mininert valves (Alltech) and incubated overnight in a thermostatic water bath without mixing.

The headspace was sampled with a 100 μm polydimethylsiloxane SPME fiber (Supelco, Bellefonte, PA, USA) for 30 min. Before sampling, the fiber had been conditioned in a GC injector (220°C) for 5 min. The chromatographic analysis was similar to the procedure described above.

The EPICS method provides nine estimates of $K_{\mathrm{at-w}}$ (mol m^{-3} air over mol m^{-3} liquid) by combining the results of the headspace analysis of three vials with a low liquid content with that of three vials with a high liquid content:

$$K_{\mathrm{at-w}} = \frac{rV_{\mathrm{w1}} - V_{\mathrm{w2}}}{V_{\mathrm{g2}} - rV_{\mathrm{g1}}} \tag{2}$$

where $r = C_{\mathrm{g1}}/C_{\mathrm{g2}}$ with C_{g1} and C_{g2} the headspace concentrations of a vial with a low liquid and a high liquid content, respectively (mol m^{-3}), and V_{g1} and V_{g2} the gas volumes and V_{w1} and V_{w2} the liquid volumes of the vials considered (m^3). The theoretical considerations leading to Eq. (2) have been described elsewhere [11].

The same experimental set-up was used to determine air/water partition coefficients at 25°C for aqueous solutions containing 1% (v/v) of a stock solution in methanol.

2.4. Evaluation of the blank profile

A tetraglyme aliquot of 10 ml was pipetted into a purge vessel (3.4 cm I.D., height 20 cm) kept in a water bath set at 45.0±0.1°C. The vessel was equipped with a glass frit at the bottom and an injection septum, and contained 50 ml of artificial sea water (35 ppt) previously purged to blank at a flow-rate of 80 ml He min^{-1} for 45 min. The aqueous mixture was then purged for 45 min at a flow-rate of 80 ml min^{-1}. The analytes were trapped onto a multibed sorbent trap containing 350 mg of Carbosieve SIII (carbon molecular sieve, 820 m^2 g^{-1}, 60–80 mesh, Supelco) and 170 mg of Carbopack B (graphitized carbon black, 100 m^2 g^{-1}, 60–80 mesh, Supelco). The sorbent materials were hold separately with glass wool plugs in open glass tubes (O.D. 1/4 inch, height 16 cm). The traps had been conditioned at 300°C under a helium flow of 30 ml min^{-1} during 5 h before use. A wet trap consisting of two U-shaped glass tubes (1/8 inch I.D., length 2×42 cm) submerged in a temperature-controlled ethylene glycol bath set at −15°C was placed between the purge vessel and the multibed sorbent trap to avoid water vapour from entering the chromatographic system.

Thermal desorption and gas chromatographic separation were performed in a Varian 2700 gas chromatograph (Varian). Analytes were measured with flame ionization detection and identified with a Finnigan MAT 112S mass spectrometer (Finnigan MAT, Bremen, Germany) [12].

3. Results and discussion

3.1. The air/tetraglyme partition coefficient

In order to assess the sorption efficiency of tetraglyme during sampling, air/tetraglyme partition coefficients K_{at} were experimentally determined for 10 VOCs at five different temperatures between 2 and 25°C. Three experimental determinations were performed for each VOC at each temperature. The mean values for K_{at} ($n=3$) and the relative standard deviations RSDs (in %) are given in Table 1.

As literature data on K_{at} are inexistent, dynamic breakthrough experiments were performed as a check. 1,1-Dichloroethane and benzene were stripped from a tetraglyme solution in a purge-vessel, and trapped into a second vessel filled with the same volume of pure absorbens. Both analytes were chosen as model compounds since they displayed the lowest K_{at} values, hence limiting the time necessary to observe breakthrough.

Time/concentration profiles were estimated for purge-vessel 1 and 2 from the following mass balances:

$$\frac{\mathrm{d}M_1}{\mathrm{d}t} = G(C_{\mathrm{gi1}} - C_{\mathrm{go1}}) \tag{3}$$

$$\frac{\mathrm{d}M_2}{\mathrm{d}t} = G(C_{\mathrm{gi2}} - C_{\mathrm{go2}}) \tag{4}$$

Table 1
Experimental results of the air/tetraglyme partition coefficient K_{at} (mol m^{-3} air over mol m^{-3} tetraglyme) as a function of temperature T, with RSD ($n=3$)

Compound	T (°C)	K_{at}	RSD (%)	Compound	T (°C)	K_{at}	RSD (%)
Chloroform	2.9	$9.22\cdot10^{-5}$	4.2	Benzene	2.2	$24.10\cdot10^{-5}$	5.6
	8.3	$14.10\cdot10^{-5}$	8.9		7.9	$33.20\cdot10^{-5}$	2.9
	13.9	$19.60\cdot10^{-5}$	4.7		14.2	$47.20\cdot10^{-5}$	2.1
	18.9	$23.80\cdot10^{-5}$	3.9		19.2	$63.80\cdot10^{-5}$	3.6
	24.9	$33.30\cdot10^{-5}$	4.1		24.9	$79.50\cdot10^{-5}$	2.0
1,1-Dichloroethane	2.2	$35.60\cdot10^{-5}$	5.9	Toluene	2.9	$8.83\cdot10^{-5}$	5.7
	7.9	$51.20\cdot10^{-5}$	3.0		8.3	$13.50\cdot10^{-5}$	9.0
	14.2	$73.10\cdot10^{-5}$	6.7		13.9	$17.40\cdot10^{-5}$	3.3
	19.0	$93.80\cdot10^{-5}$	3.6		18.9	$22.00\cdot10^{-5}$	4.1
	24.9	$120.00\cdot10^{-5}$	2.0		24.9	$34.40\cdot10^{-5}$	5.4
1,1,2-Trichloroethane	2.2	$0.66\cdot10^{-5}$	5.7	Chlorobenzene	2.2	$1.44\cdot10^{-5}$	7.4
	7.9	$1.23\cdot10^{-5}$	3.2		7.9	$2.16\cdot10^{-5}$	9.2
	14.2	$1.94\cdot10^{-5}$	11.0		14.2	$3.53\cdot10^{-5}$	8.5
	19.0	$3.12\cdot10^{-5}$	8.6		19.0	$5.25\cdot10^{-5}$	9.6
	24.9	$4.98\cdot10^{-5}$	6.6		24.9	$7.77\cdot10^{-5}$	5.7
Trichloroethene	2.9	$11.50\cdot10^{-5}$	10.0	*m*-Xylene	2.9	$3.30\cdot10^{-5}$	5.3
	8.3	$19.50\cdot10^{-5}$	4.9		8.3	$4.69\cdot10^{-5}$	9.5
	13.9	$26.10\cdot10^{-5}$	3.9		13.9	$6.17\cdot10^{-5}$	3.4
	18.9	$31.60\cdot10^{-5}$	6.9		18.9	$8.36\cdot10^{-5}$	8.2
	24.9	$46.80\cdot10^{-5}$	4.8		24.9	$10.10\cdot10^{-5}$	2.9
Tetrachloroethene	2.9	$12.10\cdot10^{-5}$	3.7	*o*-Xylene	2.2	$2.14\cdot10^{-5}$	6.6
	8.3	$16.10\cdot10^{-5}$	5.7		7.9	$2.60\cdot10^{-5}$	1.0
	13.9	$25.10\cdot10^{-5}$	7.0		14.2	$4.05\cdot10^{-5}$	9.1
	18.9	$32.20\cdot10^{-5}$	9.2		19.0	$6.44\cdot10^{-5}$	7.9
	24.9	$39.10\cdot10^{-5}$	5.0		24.9	$10.90\cdot10^{-5}$	4.4

where G represents the gas flow-rate (m^3 min^{-1}), C_{gi} and C_{go} the concentrations of analyte in the incoming and outgoing gas stream, respectively (mol m^{-3}), and t the purge time (min).

Since the gas stream entering purge vessel 1 is free of analytes, $C_{gi1}=0$. The following assumptions were made to simplify Eqs. (3) and (4). First, one can assume that no loss of analytes occurs between both purge vessels, therefore $C_{go1}=C_{gi2}$. Next, the liquid content in both vessels is well-mixed so that $M=VC_t$ with V the volume of tetraglyme in the impinger (m^3) and C_t the concentration of the organic compound in tetraglyme at time t (mol m^{-3}). Finally, if the outgoing gas stream concentration C_{go} is in equilibrium with the concentration in the liquid phase with $K_{at}=C_{go}/C_t$, then Eqs. (3) and (4) can be written as:

$$V\frac{\mathrm{d}C_{t1}}{\mathrm{d}t} = -GK_{at}C_{t1} \tag{5}$$

$$V\frac{\mathrm{d}C_{t2}}{\mathrm{d}t} = GK_{at}(C_{t1}-C_{t2}) \tag{6}$$

Calculating the time derivative of Eq. (6) yields:

$$V\frac{\mathrm{d}^2C_{t2}}{\mathrm{d}t^2} = GK_{at}\left(\frac{\mathrm{d}C_{t1}}{\mathrm{d}t}-\frac{\mathrm{d}C_{t2}}{\mathrm{d}t}\right) \tag{7}$$

Substitution of Eqs. (5) and (6) in Eq. (7) gives:

$$V\frac{\mathrm{d}^2C_{t2}}{\mathrm{d}t^2} = GK_{at}\left[-\frac{GK_{at}}{V}\left(\frac{V}{GK_{at}}\frac{\mathrm{d}C_{t2}}{\mathrm{d}t}+C_{t2}\right)-\frac{\mathrm{d}C_{t2}}{\mathrm{d}t}\right] \tag{8}$$

After rearrangement Eq. (8) becomes:

$$\frac{d^2C_{t2}}{dt^2} + \frac{2GK_{at}}{V}\frac{dC_{t2}}{dt} + \frac{G^2K_{at}^2}{V^2}C_{t2} = 0 \tag{9}$$

Integration of Eq. (9) for $C_{t2}=0$ at $t=0$ yields:

$$C_{t2} = C_{t1}^0 \frac{GK_{at}t}{V} e^{-\frac{GK_{at}t}{V}} \tag{10}$$

with C_{t1}^0 the concentration of analyte in tetraglyme in purge-vessel 1 at time $t=0$ (mol m^{-3}).

Integration of Eq. (5) for $C_{t1}=C_{t1}^0$ at $t=0$ results in:

$$C_{t1} = C_{t1}^0 e^{-\frac{GK_{at}t}{V}} \tag{11}$$

Using the air/tetraglyme partition coefficients determined in the static headspace experiments, the change of C_{t1}/C_{t1}^0 and C_{t2}/C_{t1}^0 as a function of time was estimated from Eqs. (10) and (11) (Fig. 1). The actual recovery of 1,1-dichloroethane and benzene in both vessels, with respect to the amount initially present in purge-vessel 1, was determined after 60, 180 and 360 min of purging from gas chromatographic data. From these values the least square method generated an estimate of K_{at} for both analytes at 25°C. A dimensionless air/tetraglyme partition coefficient of $K_{at}=104\cdot10^{-5}$ for 1,1-dichloroethane and $K_{at}=69.7\cdot10^{-5}$ for benzene was found. A difference of 13.2% and 10.2% for 1,1-dichloroethane and benzene, respectively, was noted with the values listed in Table 1. These differences are probably due to the limited mass transfer from tetraglyme to the gas phase. Since the equilibrium constants of 1,1-dichloroethane and benzene appear to be in good agreement with the values observed in the dynamic breakthrough experiments, the data presented in Table 1 constitute a good estimate of the air/tetraglyme partition behaviour of the VOCs investigated.

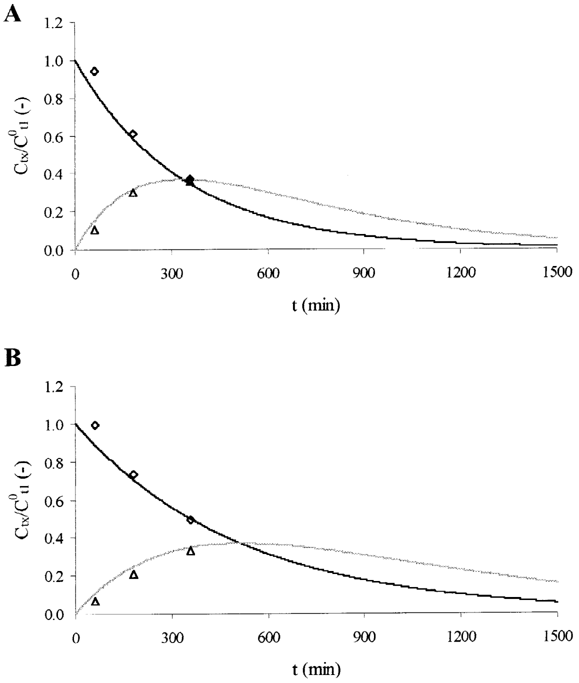

Fig. 1. Estimated and measured change of C_{t1}/C_{t1}^0 and C_{t2}/C_{t1}^0 during purging as a function of time t for 1,1-dichloroethane (A) and benzene (B). ——$=(C_{t1}/C_{t1}^0)_{calculated}$; ······$=(C_{t2}/C_{t1}^0)_{calculated}$; $\Diamond=(C_{t1}/C_{t1}^0)_{measured}$; $\triangle=(C_{t2}/C_{t1}^0)_{measured}$.

3.2. Temperature dependency of K_{at}

According to the Van't Hoff equation the temperature dependency of K_{at} is expected to be:

$$\ln K_{at} = a\frac{1}{T} + b \tag{12}$$

The regression parameters a and b are related to the molar change of enthalpy and entropy for the air/tetraglyme equilibrium process, respectively. If a small temperature range is considered, both parameters can be regarded as constants. Results of the linear regression are presented in Table 2. The plots of ln K_{at} versus T^{-1} exhibit linearity ($0.966<r^2<$

Table 2
Linear regression of $\ln K_{at} = aT^{-1} + b$ ($n=5$; $275<T<298$ K)

Compound	A	B	r^2
Chloroform	−4663±266	7.656±0.927	0.990
1,1-Dichloroethane	−4420±137	8.136±0.478	0.997
1,1,2-Trichloroethane	−7229±221	14.350±0.771	0.997
Trichloroethene	−4965±411	8.998±1.432	0.980
Tetrachloroethene	−4562±348	7.527±1.213	0.983
Benzene	−4417±153	7.715±0.534	0.996
Toluene	−4840±304	8.221±1.062	0.988
Chlorobenzene	−6173±123	11.251±0.431	0.999
m-Xylene	−4231±237	5.040±0.827	0.991
o-Xylene	−6014±655	10.946±2.288	0.966

0.999) with values of K_{at} increasing by 69–87% over a temperature range of 2 to 25°C ($n=5$). Temperature is expected to greatly affect breakthrough volumes at the sampling stage.

3.3. Calculation of breakthrough volumes

The breakthrough volume V_b of a given compound is usually defined as the volume of air that can be passed through a sampler before the concentration ratio of the effluent gas C_{go} to incoming gas C_{gi} reaches a predefined value (from 1 to 50% according to different definitions) [13]. If 5% of breakthrough is allowed, air is sampled until $C_{go}/C_{gi}=0.05$. Besides this ‘‘point’’ definition, breakthrough volumes can be calculated based on an ‘‘integrated’’ approach. In this perspective, V_b is defined as the volume of air which can be passed through the impinger before 5% of the analyte sampled between $t=0$ and $t=t_{5\%}$ is allowed to escape. In this case, air is sampled until $\int_{t=0}^{t=t_{5\%}} C_{go}Q\ \mathrm{d}t / \int_{t=0}^{t=t_{5\%}} C_{gi}Q\ \mathrm{d}t = 0.05$. The latter definition was preferred in this study since the amount and concentration of the analyte retained in the liquid is directly proportional to the incoming concentration corrected with the % of breakthrough.

Based on this approach breakthrough volumes were calculated from the air/tetraglyme partition coefficients listed in Table 1.

The amount of analyte M (mol) accumulating in tetraglyme during sample enrichment is given by:

$$\frac{\mathrm{d}M}{\mathrm{d}t} = G(C_{gi} - C_{go}) \tag{13}$$

with t the sampling time (min).

If the outgoing gas stream concentration C_{go} is in equilibrium with the concentration in tetraglyme so that $K_{at}=C_{go}/C_t$, and if the liquid phase is homogeneous with $M=VC_t$, Eq. (13) can be written as:

$$V\frac{\mathrm{d}C_t}{\mathrm{d}t} = G(C_{gi} - K_{at}C_t) \tag{14}$$

Integrating Eq. (14) results in:

$$C_t = \frac{C_{gi}}{K_{at}}\left(1 - \mathrm{e}^{-\frac{GK_{at}t}{V}}\right) \tag{15}$$

If 5% of breakthrough is allowed, the amount of analyte sorbed in tetraglyme ($=VC_t$) can be substituted by $0.95GC_{gi}t$ in Eq. (15), and the corresponding breakthrough volume $V_b=Gt$ can be calculated from:

$$0.95V_b = \frac{V}{K_{at}}\left(1 - \mathrm{e}^{-\frac{V_bK_{at}}{V}}\right) \tag{16}$$

Table 3 summarizes breakthrough volumes for all analytes at five different temperatures (2–25°C).

One should bear in mind that the calculation method leading to Eq. (16) relies on the assumption of equilibrium between air and tetraglyme. Therefore, the practicality of any data calculated with Eq. (16) depends on the accomplishment of equilibrium conditions during sampling. In order to fulfil this requirement a proper sample flow-rate and impinger configuration must be selected to ensure a sufficient exchange-time within phases.

As only a fraction of the original sample is dispersed into water for analysis by purge-and-trap/gas chromatography, large volumes of air should be sampled to ensure measurements above method detection limits. At 25°C breakthrough volumes ranged from 0.08 l ml^{-1} in the case of 1,1-dichloroethane to 2.1 l ml^{-1} for 1,1,2-trichloroethane. Hence, the simultaneous measurement of all analytes investigated in this study is restrained to a sample volume of 1.7 l for 20 ml of tetraglyme at 25°C. Depending on the desired detection limits and detector sensitivity this may be too low to collect measurable quantities of VOCs in ambient air. As breakthrough volumes increase exponentially with decreasing temperatures, larger amounts of air can be passed through the impinger cooled at sub-zero temperatures without loss of analytes. However, this requires the use of special cooling devices, hence complicating field sampling. Furthermore, since the flow should remain low to ensure equilibrium (50–100 ml min^{-1}) [6], large sample volumes stand for long sampling times. With the exception of 1,1-dichloroethane, about 9 l of air can be drawn through 20 ml of tetraglyme at temperatures close to 0°C without any breakthrough of the compounds considered. Ice can easily be taken along at the sampling site to chill the impinger. If 1,1-dichloroethane is considered, the breakthrough volume is reduced to 6 l and detectability could be hampered.

Table 3
Breakthrough volumes V_b (allowing 5% of breakthrough) for 10 VOCs over a temperature range of 2–25°C

Compound	T (°C)	V_b ($\mathrm{l\ ml}^{-1}$)	Compound	T (°C)	V_b ($\mathrm{l\ ml}^{-1}$)
Chloroform	2.0	1.13	Benzene	2.0	0.43
	5.0	0.94		5.0	0.36
	10.0	0.70		10.0	0.28
	15.0	0.52		15.0	0.21
	20.0	0.40		20.0	0.16
	25.0	0.30		25.0	0.13
1,1-Dichloroethane	2.0	0.29	Toluene	2.0	1.26
	5.0	0.24		5.0	1.04
	10.0	0.18		10.0	0.76
	15.0	0.14		15.0	0.56
	20.0	0.11		20.0	0.42
	25.0	0.08		25.0	0.31
1,1,2-Trichloroethane	2.0	15.60	Chlorobenzene	2.0	7.49
	5.0	11.70		5.0	5.88
	10.0	7.43		10.0	3.97
	15.0	4.77		15.0	2.72
	20.0	3.11		20.0	1.89
	25.0	2.06		25.0	1.33
Trichloroethene	2.0	0.82	*m*-Xylene	2.0	3.19
	5.0	0.68		5.0	2.71
	10.0	0.50		10.0	2.07
	15.0	0.37		15.0	1.60
	20.0	0.28		20.0	1.24
	25.0	0.21		25.0	0.98
Tetrachloroethene	2.0	0.88	*o*-Xylene	2.0	7.20
	5.0	0.74		5.0	5.44
	10.0	0.55		10.0	3.46
	15.0	0.42		15.0	2.23
	20.0	0.32		20.0	1.46
	25.0	0.25		25.0	0.97

3.4. Effect of tetraglyme on the air/water partition of organic compounds

The most obvious way to further improve the limits of detection is to disperse a larger portion of sample into water. Concentrations of 2% (v/v) tetraglyme in water were used by Troost [6] while up to 4% (v/v) tetraglyme in water was purged by Gurka et al. [8]. If the tetraglyme/water ratio is hereby increased, the air/water partition of organic compounds will be affected. As the cavity surrounding the analytes is lined with both water and co-solvent molecules, the compound water solubility will increase [14]. Gossett [15] observed a significant drop of air/water partition coefficients K_{aw} for trichloroethene in water containing 5% (v/v) methanol. In order to investigate the impact of various tetraglyme concentrations on the purge-process, air/tetraglyme–water partition coefficients K_{at-w} were determined for 10 VOCs at different temperatures, salinities and tetraglyme concentrations in water C_{tw}. The results are given in Table 4. A t-test ($\alpha=0.05$; $n=13$) indicated no significant difference for any analyte investigated between air/tetraglyme–water partition coefficients for 2% (v/v) tetraglyme in water and K_{aw} determined in pure water. However, as shown in Fig. 2 for chlorobenzene, K_{at-w} decreased exponentially as higher amounts of tetra-

Table 4
Experimental results of air/tetraglyme–water partition coefficients K_{at-w} (mol m^{-3} air over mol m^{-3} liquid) vs. tetraglyme concentrations in water C_{tw}, temperatures T and salt concentrations S, with RSD ($n=9$)

Compound	C_{tw} (v/v %)	T (°C)	S (ppt)	K_{at-w}	RSD (%)	Compound	C_{tw} (v/v %)	T (°C)	S (ppt)	K_{at-w}	RSD (%)
Chloroform	0	24.9	0	0.165	4.0	Benzene	0	24.9	0	0.221	1.4
	2	24.9	0	0.169	2.6		2	24.9	0	0.201	5.2
			35	0.178	2.5				35	0.259	0.8
		44.8	0	0.320	7.6			44.8	0	0.375	4.9
			35	0.388	5.1				35	0.540	7.8
	11	24.9	0	0.132	9.6		11	24.9	0	0.160	2.9
			35	0.146	2.0				35	0.191	6.1
		44.8	0	0.269	5.2			44.8	0	0.311	4.2
			35	0.298	9.3				35	0.351	3.5
	21	24.9	0	0.093	8.4		21	24.9	0	0.113	2.0
			35	0.107	3.3				35	0.148	7.7
		44.8	0	0.163	3.1			44.8	0	0.239	6.9
			35	0.199	8.6				35	0.241	7.0
	31	24.9	0	0.074	10.9		31	24.9	0	0.072	8.4
			35	0.072	3.8				35	0.101	3.9
		44.8	0	0.109	6.3			44.8	0	0.173	9.4
			35	0.103	4.0				35	0.188	7.6
1,1-Dichloroethane	0	24.9	0	0.220	2.8	Toluene	0	24.9	0	0.257	2.7
	2	24.9	0	0.231	6.1		2	24.9	0	0.237	4.0
			35	0.270	0.7				35	0.293	1.1
		44.8	0	0.401	7.0			44.8	0	0.485	5.1
			35	0.556	10.1				35	0.627	3.7
	11	24.9	0	0.189	4.4		11	24.9	0	0.175	3.4
			35	0.223	6.1				35	0.197	4.6
		44.8	0	0.381	4.7			44.8	0	0.308	3.8
			35	0.391	0.4				35	0.424	7.9
	21	24.9	0	0.150	2.4		21	24.9	0	0.102	5.6
			35	0.197	4.8				35	0.122	2.5
		44.8	0	0.276	4.8			44.8	0	0.190	6.3
			35	0.302	7.6				35	0.226	7.0
	31	24.9	0	0.115	2.7		31	24.9	0	0.071	4.7
			35	0.131	3.4				35	0.072	3.1
		44.8	0	0.154	4.5			44.8	0	0.115	8.7
			35	0.174	7.3				35	0.135	9.3
1,1,2-Trichloroethane	0	24.9	0	0.033	2.8	Chlorobenzene	0	24.9	0	0.133	3.8
	2	24.9	0	0.031	3.5		2	24.9	0	0.126	4.2
			35	0.038	1.1				35	0.152	2.1
		44.8	0	0.070	3.8			44.8	0	0.257	5.3
			35	0.090	3.2				35	0.362	4.8
	11	24.9	0	0.027	5.3		11	24.9	0	0.084	3.5
			35	0.029	8.9				35	0.095	9.1
		44.8	0	0.056	5.6			44.8	0	0.174	5.9
			35	0.064	1.9				35	0.190	7.5
	21	24.9	0	0.018	2.7		21	24.9	0	0.048	3.0
			35	0.022	4.3				35	0.056	3.8
		44.8	0	0.040	3.1			44.8	0	0.101	2.0
			35	0.044	5.7				35	0.102	2.9
	31	24.9	0	0.013	12.6		31	24.9	0	0.027	7.0
			35	0.012	1.6				35	0.027	3.8
		44.8	0	0.020	8.4			44.8	0	0.042	6.0
			35	0.021	9.3				35	0.041	4.9

Table 4. Continued

Compound	C_{tw} (v/v %)	T (°C)	S (ppt)	K_{at-w}	RSD (%)	Compound	C_{tw} (v/v %)	T (°C)	S (ppt)	K_{at-w}	RSD (%)
Trichloroethene	0	24.9	0	0.393	5.1	*m*-Xylene	0	24.9	0	0.292	2.9
	2	24.9	0	0.395	3.8		2	24.9	0	0.282	5.5
			35	0.446	8.2				35	0.298	2.1
		44.8	0	0.818	7.7			44.8	0	0.558	8.8
			35	1.014	4.6				35	0.747	4.7
	11	24.9	0	0.300	8.5		11	24.9	0	0.156	5.7
			35	0.339	7.4				35	0.195	3.2
		44.8	0	0.543	2.9			44.8	0	0.378	22.9
			35	0.784	3.6				35	0.426	6.1
	21	24.9	0	0.172	4.5		21	24.9	0	0.096	5.2
			35	0.241	7.0				35	0.117	9.9
		44.8	0	0.414	5.7			44.8	0	0.179	4.4
			35	0.453	11.8				35	0.228	5.3
	31	24.9	0	0.164	4.9		31	24.9	0	0.059	1.1
			35	0.222	3.2				35	0.060	2.6
		44.8	0	0.326	5.1			44.8	0	0.094	6.2
			35	0.396	5.8				35	0.089	3.6
Tetrachloroethene	0	24.9	0	0.762	4.4	*o*-Xylene	0	24.9	0	0.176	4.5
	2	24.9	0	0.719	6.1		2	24.9	0	0.170	2.7
			35	0.654	4.5				35	0.203	1.4
		44.8	0	1.342	15.2			44.8	0	0.357	5.1
			35	1.778	14.7				35	0.538	7.9
	11	24.9	0	0.453	4.1		11	24.9	0	0.114	9.0
			35	0.567	4.3				35	0.132	9.1
		44.8	0	1.030	5.0			44.8	0	0.250	5.7
			35	1.066	8.6				35	0.278	5.5
	21	24.9	0	0.334	6.0		21	24.9	0	0.095	5.5
			35	0.369	13.6				35	0.086	2.7
		44.8	0	0.517	4.2			44.8	0	0.140	2.4
			35	0.674	7.6				35	0.152	4.1
	31	24.9	0	0.207	3.9		31	24.9	0	0.044	10.0
			35	0.215	6.2				35	0.050	1.4
		44.8	0	0.267	7.6			44.8	0	0.079	6.2
			35	0.265	6.3				35	0.074	3.2

glyme were added to the aqueous phase. At 25°C and in the absence of sea salt, K_{at-w} dropped by 13–50% in the case of 11% (v/v) tetraglyme in water depending on the analyte, while for 21% (v/v) and 31% (v/v) tetraglyme in water K_{at-w} was reduced by 42–66% and 50–79%, respectively.

In an attempt to counteract the effect caused by the presence of tetraglyme, the influence of temperature and/or ionic strength on air/tetraglyme–water partition coefficients were evaluated. Aqueous mixtures containing 0 and 35 ppt of artificial sea salt were investigated at a temperature of 25 and 45°C. Regardless of tetraglyme and salt concentrations, air/tetraglyme–water partition coefficients increased by a factor 1.3 to 2.5 when the water temperature was raised from 25 to 45°C. The exponential decrease of K_{at-w} versus C_{tw} was more explicit at higher temperatures. In contrast with temperature, the salting-out effect on K_{at-w} was much less pronounced.

A decrease of air/tetraglyme–water partition coefficients results in a longer purge-time and thus longer analysis time. If 60 ml of a tetraglyme–water (2:98, v/v) mixture is considered, about 25 min is required to purge all analytes targeted in this study with a removal efficiency of at least 95% in the

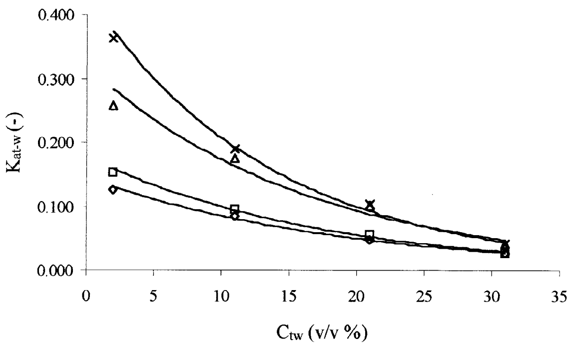

Fig. 2. Air/tetraglyme–water partition coefficients K_{at-w} of chlorobenzene at various tetraglyme concentrations in water C_{tw}, temperatures T (°C) and salinities S (ppt). ◇=25°C and 0 ppt; □=25°C and 35 ppt; △=45°C and 0 ppt; × =45°C and 35 ppt.

presence of 35 ppt of sea salt at 45°C and a flow-rate of 80 ml min^{-1}. The purge-time increases by a factor 1.4 to strip all analytes in the case of 11% (v/v) tetraglyme in water under the same experimental conditions. For 21% (v/v) and 31% (v/v) tetraglyme in water, purge-times 2.0 and 4.2 times as long, respectively, are required.

3.5. Evaluation of the blank profile

Solute enrichment by sorptive extraction requires that background signals remain minimal. Since tetraglyme can generate peroxides [8], which in turn can easily produce artefacts, it must be cleaned before use and stabilized to prevent further peroxide formation. The following procedure by Gurka et al. [8] was evaluated to purify tetraglyme. Peroxides were removed by passing tetraglyme through a column of activated alumina (Janssen Chimica, Beerse, Belgium). Contaminants were evaporated under high vacuum [0.8–1 mmHg (1 mmHg=133.32 Pa); 5 h] at 50°C. Finally, in order to avoid peroxide formation during storage, ±0.1 mg ml^{-1} 2,6-di-*tert.*-butyl-4-methylphenol (Janssen Chimica) was added. Prior to analysis, tetraglyme was kept in a contaminant-free area. Fig. 3 shows a blank run of a tetraglyme–water (17:83, v/v) mixture (10 ml of tetraglyme in 50 ml

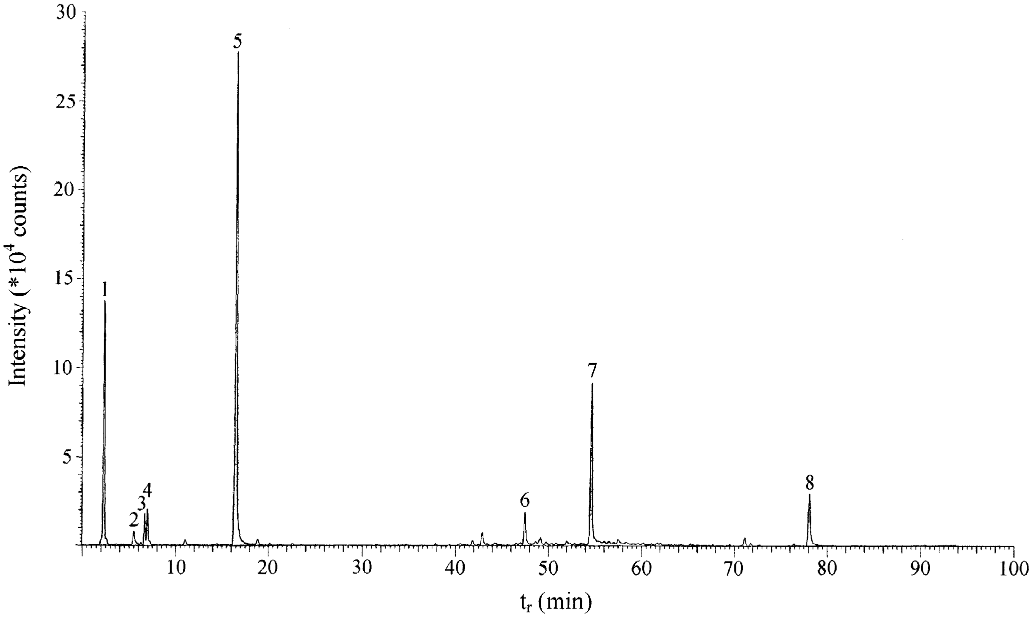

Fig. 3. Blank chromatogram of a tetraglyme–water (17:83, v/v) mixture after 45 min of purging at 45°C and a gas flow-rate of 80 ml min^{-1}. Numbers indicate peaks tentatively identified: 1, carbon dioxide; 2, acetone; 3, bromoethane; 4, dichloromethane; 5, dibromomethane; 6, 2-methyl-4-octanone; 7, 1-methoxy-2,2-dimethylpropane; 8, 2,6-di-*tert.*-butyl-4-methylphenol.

of artificial sea water) purged for 45 min at 45°C and a flow-rate of 80 ml min^{-1}. None of the target VOCs were found with FID/MS detection. Only a minor number of interfering compounds were found and tentatively identified. It is plausible to assume that all contaminants, with the exception of acetone and CO_2, originate from tetraglyme since only acetone and CO_2 were present in a blank run of pure water.

4. Conclusion

Physico-chemical data have been measured to provide additional information on the possibilities of air sampling and analysis through tetraglyme enrichment, hereby focussing on the simultaneous determination of 10 VOCs of environmental interest.

Air/tetraglyme partition coefficients, measured over an environmental relevant temperature range of 2–25°C, allowed the calculation of breakthrough volumes. Up to 6 l of air can be sampled through 20 ml of chilled tetraglyme without any breakthrough of the targeted solutes.

In the original paper [6] only 2% (v/v) tetraglyme was injected into water for purge-and-trap/gas chromatography, hence restricting the applicability of the technique towards low concentration levels. This report however showed that large portions of tetraglyme can be transferred into the purge vessel to minimise the loss of concentrating power. Aqueous solutions with a high tetraglyme content can still be purged within acceptable time-limits, resulting into lower limits of detection. Furthermore a minor number of interfering signals were found in a blank run of a tetraglyme–water (17:83, v/v) mixture by GC–FID/MS analysis.

From the data presented in this report it is clear that the tetraglyme method can hardly cope with existing sampling tools, e.g., adsorbent trapping, for VOC measurements in remote or ambient air masses. However at concentration levels typically encountered near, e.g., emission sources and working place environments, an analytical method based on tetraglyme enrichment may provide satisfactory results. The advantages offered by the tetraglyme method, e.g., low cost, simplicity, possibility to run several analyses from one sample and freedom from water vapour interference, may then favour its use over conventional air sampling techniques.

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