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Dynamic measurements of partition coefficients using proton-transfer-reaction mass spectrometry (PTR–MS)

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Dedicated to the memory of Werner Lindinger.

Abstract

Liquid–gas partition coefficients (HLC) of volatile organic compounds (VOCs) in water–air systems are determined using a novel dynamic approach by coupling a stripping cell directly to a proton-transfer-reaction mass spectrometer (PTR–MS). Two complementary set-ups are evaluated, one suited for determining HLCs of highly volatile compounds (<10 M/atm), the second adapted for medium to low volatile compounds ($\sim$10–1000 M/atm). We validated the method using 2-butanone, investigated the temperature dependence of various HLCs and applied the stripping technique to a series of VOCs. Compared to alternative state-of-the-art techniques the present approach has the advantage of being simple, fast and less prone to artefacts. Furthermore, it allows to quantify volatile compounds in the headspace without calibration or addition of standards. (Int J Mass Spectrom 223–224 (2003) 383–395)

Keywords: Proton-transfer-reaction mass spectrometry; Volatile organic compounds; HLC

1. Introduction

Gases dissolve in liquids to form solutions. Since the liquid–gas partitioning is an equilibrium process, an equilibrium constant, $K = c(\text{aq})/p(\text{gas})$, can be defined. This definition, known as Henry's law, was first proposed by J.W. Henry as an empirical law well before the development of our modern ideas of chemical equilibrium around 1800. Since then a variety of definitions have been proposed in the literature to express liquid–gas partitioning, two of which are particularly relevant to us. The partition coefficient in environmental sciences is typically represented as the ratio of the molar concentration c (mol/L) and the partial pressure in the headspace, p (atm). By this definition the Henry's law constant (HLC or simply H) is given in units of (M/atm). Food and flavour sciences usually focus on volatilities; it is common to express the partitioning as $K_{\text{PC}} = c(\text{gas})/c(\text{aq})$ ((mg/L)/(mg/L)). Using SI units K_{PC} can be easily converted to HLC, $\text{HLC} = 1/(10^{-2*} R^* T^* K_{\text{PC}})$. Throughout this paper, we will use the definition of $\text{HLC} = \text{H} = c(\text{aq})/p(\text{gas})$ in units of (M/atm).

Henry's law is found to be an accurate description of the behaviour of dissolved gases when concentrations and partial pressures are low. The solvent is only

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slightly modified and still reacts like the pure liquid, the solute on the other hand generally behaves entirely differently from its pure state. Solutions which are found to obey Henry's law are called ideal dilute solutions.

The partitioning of volatile organic compounds between liquids and air is a fundamental process and of significance to a large variety of phenomena. It plays an important role in atmospheric sciences and environmental chemistry, e.g., aerosol formation, cloud nucleation or ocean uptake of chemical species. Knowledge of HLCs in complex liquid matrices on the other hand is essential when investigating the distribution of metabolites in living organism or the aroma release from food products.

1.1. Human metabolism

Due to the large surface to volume ratio of the alvioles in the lung, equilibrium between the concentrations of volatile organic compounds (VOCs) in exhaled air and the blood and body liquids exists in most cases. Therefore, from measured concentrations of VOCs in the breath and known Henry's law constants as well as the mass of the body, the total amounts of these VOCs in the body can be calculated and modelled [1,2].

1.2. Decaying bio-matter

Within decaying bio-matter a big variety of VOCs are formed from Maillard reactions. By wetting bio-matter and measuring the headspace concentrations of VOCs Warneke et al. [3] demonstrated that $\sim 10^{-4}$ g acetone/g dry-matter is produced during the decay process of leaves or grass. This represents a substantial additional tropospheric source for acetone and various other oxygenated VOCs.

1.3. Aroma release from food products

Release of aromatic VOCs from food products is of great importance for the optimisation of food processing techniques and for understanding a variety of food properties such as flavour or ageing [4,5]. These properties are of fundamental significance for the design of controlled flavour release from low fat and microwave heatable products, modelling and optimisation of aroma recovery processes and the above-the-cup aroma of beverages such as coffee or tea. All these processes are linked to the partitioning of VOCs.

These examples demonstrate the importance of accurate data on HLCs. A recent survey of partition coefficients has revealed important discrepancies among data obtained by different techniques; a problem that has been mainly traced back to experimental issues [8]. Here, we introduce a novel method for the determination of partition coefficients based on a stripping experiment first described by Leroi et al. [6] and Mackay et al. [7] in the late seventies, who measured HLCs of highly volatile compounds such as alkanes, alkenes and arenes. A similar stripping cell set-up was interfaced with a proton-transfer-reaction mass spectrometer (PTR–MS), a new analytical technique used for on-line VOC monitoring [8–13]. Additionally we modified the original stripping cell set-up and extended its capability for measuring HLCs up to 1000 M/atm. The main advantage to alternative methods [6] for determining HLCs is its simplicity and the fact that continuous sampling is less prone to artefacts. Furthermore, as will be demonstrated, volatile compounds can be quantified in the headspace without calibration or addition of standards.

A short discussion of the theoretical and experimental background of the dynamic method will be followed by a detailed evaluation of the partition coefficient of 2-butanone and its temperature dependence. The obtained results will be compared with values from other studies using alternative methods. Besides the HLC of 2-butanone we were able to measure partition coefficients for seventeen additional VOCs, some of which were not reported prior to this work.

2. Experimental

Currently there are two common experimental approaches for measuring HLCs. The first, and more widespread approach, is based on gas chromatography

(GC) and relies on the static determination of headspace concentrations, thus called Headspace(HS)-technique [5,6,15,22]. Since a HS-sample has to be collected from an equilibrated system, adsorption of volatiles on walls, tubings or the syringe may affect the results [16]. Especially for compounds only sparingly soluble in water and having low vapour pressures, reported values for HLCs were found to scatter by more than a factor of 10 [6]. Furthermore, the equilibrium between the liquid and the gas phase may get perturbed when HS-samples are taken (usually using a syringe [17,18]). This may result in an overestimation of the measured HLCs.

An advanced dynamic technique for determining partition coefficients was reported by Leroi et al. [6] and Mackay et al. [7]. A flow of inert gas bubbling through a solution strips dissolved VOCs and leads to a decrease of their liquid concentration. By measuring the concomitant decrease of VOCs in the gas phase (in the flow of the stripping gas), partition coefficients can be calculated. The experimental error hereby can be reduced to <10%. Here we have adapted the dynamic stripping technique to perform on-line measurements of VOC concentrations in the stripped gas by PTR–MS. Proton-transfer-reaction mass spectrometry has been extensively described in a series of review papers [8–14] and will not be further discussed here.

For compounds of low volatility, the stripping process can easily exceed hours. Hence, the original stripping cell design is more suitable for highly volatile compounds with HLCs <10 M/atm. To overcome these limitations, which particularly gets important for unstable compounds, we introduce a modification of the stripping experiment more suited for compounds of medium to low volatility.

2.1. Single stripping cell configuration

Clean air (zero air) is introduced through a sintered glass disk into a stripping vessel, which typically contains doubly distilled water and traces of one or more volatile organic compounds (see Fig. 1). On the way through the vessel the VOC reaches an equilibrium concentration in the air bubbles according to Henry's

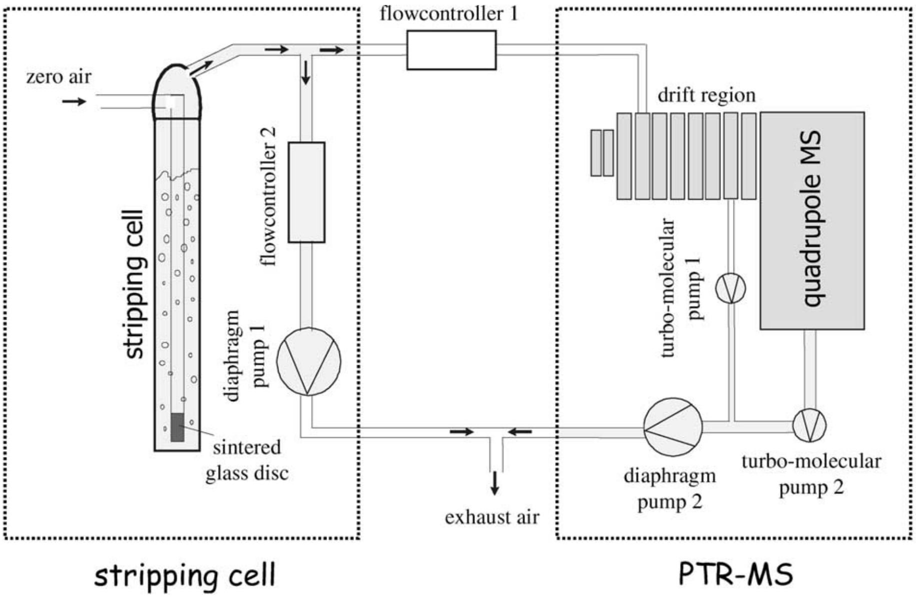

Fig. 1. Single stripping cell configuration. Humidified zero air is introduced into the stripping cell ($V = 60\,\text{mL}$, liquid height $= 20\,\text{cm}$), which subsequently bubbles through the cell removing dissolved compounds from the liquid according Henry's Law. The exponential decrease in the HS concentration is monitored on-line with PTR–MS.

law. Due to mass transport of the dissolved VOC by means of the air bubbles, its concentration in the solution, as well as in the HS, decreases as a function of time according to:

$$-V\frac{dC}{dt}=\frac{pF}{RT}=\frac{FC}{HRT}, \tag{1}$$

where V is the liquid volume, p the partial pressure of the compound, F the air flow (STP) through the vessel, T the temperature, R the molar gas constant, C the liquid concentration and t is the time.

By solving Eq. (1) we obtain two solutions. Both correspond to the set-ups shown in Figs. 1 and 3. The first solution of Eq. (1) describes the concentration C as dependent on time in the form:

$$\ln\left(\frac{C(t)}{C_0}\right)=\ln\left(\frac{Hp(t)}{Hp_0}\right)=\ln\left(\frac{p(t)}{p_0}\right)=-\frac{F}{HVRT}t, \tag{2}$$

with C_0 being the initial concentration in the liquid and p_0 the initial concentration in the headspace. It reflects the situation where clean air is bubbled through a dilute solution of VOCs. This set-up is particularly suited for highly volatile compounds. In equilibrium, the VOC concentration in the gas phase (air-bubbles), which is proportional to the vapour pressure, p, is linked to the liquid concentration C via Henry's law (see Section 1). Thus, the ratio on the left side of Eq. (2) can be directly transformed to $C/C_0=(H^*p)/(H^*p_0)=p/p_0$.

Eq. (2) contains the concentration of the VOC in the HS, indicated as $p(t)$ and p_0 at $t=0$, a quantity which is not known a priori. Yet, as outlined in [9,11], a simple relation exists between the experimentally measured PTR–MS mass spectral intensity (counts per seconds, cps) and the actual concentration in the HS, which does not require any calibration or addition of a standard.

$$[\mathrm{VOC}]=\frac{1}{k_{\mathrm{R\,rate}}t_{\mathrm{R\,time}}}\frac{\mathrm{cps}(\mathrm{VOC}\cdot\mathrm{H}^+)}{\mathrm{cps}(\mathrm{H_3O^+})}. \tag{3}$$

The headspace concentrations of VOCs, [VOC], is proportional to the ratio between measured count rates of protonated VOCs, cps($\mathrm{VOC{\cdot}H^+}$), and of protonated water, cps(H_3O^+), and inversely proportional to the reaction rate, $k_{\mathrm{R\,rate}}$ ($\sim10^{-9}\,\mathrm{cm^3/s}$), [19,20] and the reaction time, $t_{\mathrm{R\,time}}$ ($\sim$105 μs). Hence, in a ln(cps(t)/cps$_0$) vs. t plot,

$$\ln\left(\frac{\mathrm{cps}(t)}{\mathrm{cps}_0}\right)=-\frac{F}{HVRT}t, \tag{4a}$$

the HLC can be calculated from the slope, with cps(t) being the count rate of [$\mathrm{VOC{\cdot}H^+}$] at time t, and cps$_0$ being the initial count rate of [$\mathrm{VOC{\cdot}H^+}$], at time 0. Except H, all values in the slope ($F/HVRT$) are known, such that H can be calculated. Since only the ratio of the experimentally measured count rates is needed to calculate the HLC, the system does not have to be calibrated and experimental errors originating from adsorption on glass surfaces and tubings are cancelled out. Furthermore, fragmentation or switching reactions via the $H_2O{\cdot}H_3O^+$-cluster do not affect the results [9]. All measurements were performed at 22 °C with gas flow rates varying from 17 to 500 sccm/min (sccm corresponds to cm^3 under standard conditions: 22 °C, 1 atm) and at 820 mbar total pressure.

In order to determine the absolute headspace concentration in such an experiment, Eq. (4a) can be slightly transformed:

$$\ln(\mathrm{cps}(t))=-\frac{F}{HVRT}t+\ln(\mathrm{cps}_0). \tag{4b}$$

The initial concentration can be obtained from the intercept of ln(cps(t)) vs. t plot, and using Eq. (3) which transforms count rates into concentrations.

For highly volatile compounds (HLC $<$ 1 M/atm), the partition coefficient can be determine with good accuracy within about an hour (typical flow rates of 100 cm^3/min); e.g., a compound having a HLC of 1 M/atm, dissolved in 50 mL water and stripped at a flow rate of 100 cm^3/min, will show a reduction of the HS concentration by 10% within 2 h, which is needed for an accurate calculation of the HLC. For stable, medium volatile compounds (1 M/atm $<$ HLC $<$ 10 M/atm), the liquid has to be stripped for several hours, before a 10% reduction in the HS concentration is reached. Finally, for low volatile compounds (HLC $>$ 10 M/atm) the slope of a ln(cps(t)) vs. t plot can be very small. To assure a reasonable precision of the determination of HLCs, the time for analysis can easily exceed ten hours. This time can be shortened by

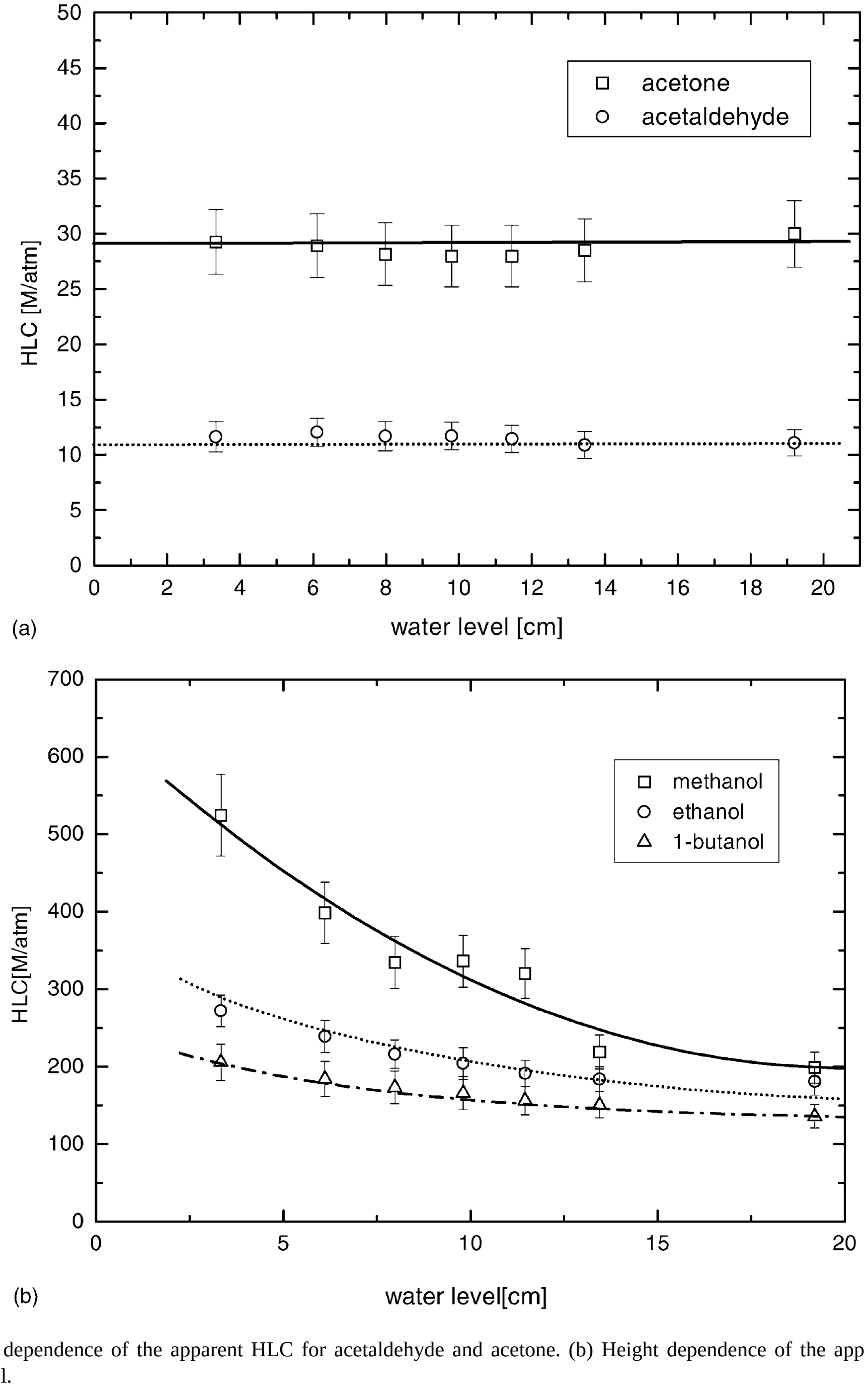

Fig. 2. (a) Height dependence of the apparent HLC for acetaldehyde and acetone. (b) Height dependence of the apparent HLC for a C1, C2 and C4 alcohol.

increasing the flow rate and hence the strip-rate. Yet, there are limits to an increase of the strip rate due to equilibrium conditions, turbulences and foaming that may occur above 600 cm^3/min [23].

The dynamic approach relies on the fact that equilibrium is reached inside the gas-bubbles during their residence time in the liquid. The residence time is given by the liquid height in the column and the vertical speed of the bubbles travelling from the disc to the surface. The bubble speed was measured to be approx. 10 cm/s. The flow rate affects the number of bubbles generated at the sintered glass disc but has no strong impact on the bubble speed. When equilibrium with the liquid is not reached an expression for the mass transfer rate can be derived under the assumption of a well mixed liquid [7]: $P = H \times C \times (1 - \exp(-K_{ol}ART/FH))$, with P (partial pressure), H (Henry's Law constant), C (liquid concentration), T (temperature), F (flow rate), R (gas constant), K_{ol} (overall liquid phase mass transfer coefficient) and A (total interfacial area of the bubbles). Thus, low HLC's and/or high mass transfer coefficients (K_{ol}) result in fast equilibrium (the exponential term approaches zero). By changing the level of the liquid in the column, checks were made in order to assure that the equilibrium concentration is reached in the air bubbles passing through the liquid. For relatively highly volatile compounds, such as acetone or acetaldehyde, equilibrium is reached within a fraction of a second, as shown in Fig. 2a. In contrast low volatile compounds, such as methanol or ethanol (Fig. 2b), exhibit a marked dependence on the level height. It can be clearly seen that compounds with lower volatility (higher solubility) require longer residence times for equilibration. A distance of 20 cm between the sintered glass disk and the surface of the solution was sufficient for reaching the equilibrium concentration for all VOCs investigated.

For compounds of low volatility, a modification of the above set-up was developed, which allows to speed up the experiment without compromising the accuracy. This corresponds to the second solution of Eq. (1).

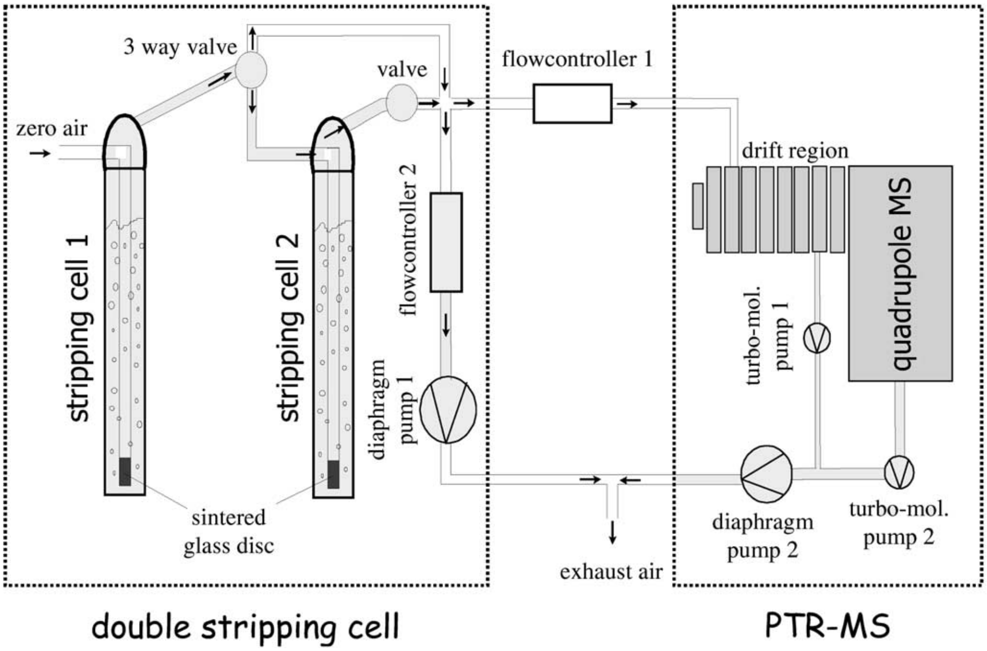

Fig. 3. Double stripping cell configuration: Zero air is introduced into the stripping cell 1 ($V = 330$ mL, liquid height $= 20$ cm) and gets enriched with a compound on the way through the cell. The air exiting cell 1 is then bubbled through stripping cell 2 ($V = 60$ mL, liquid height $= 20$ cm) containing pure water. The exponential increase of the HS concentration in cell 2 is monitored on-line with PTR–MS.

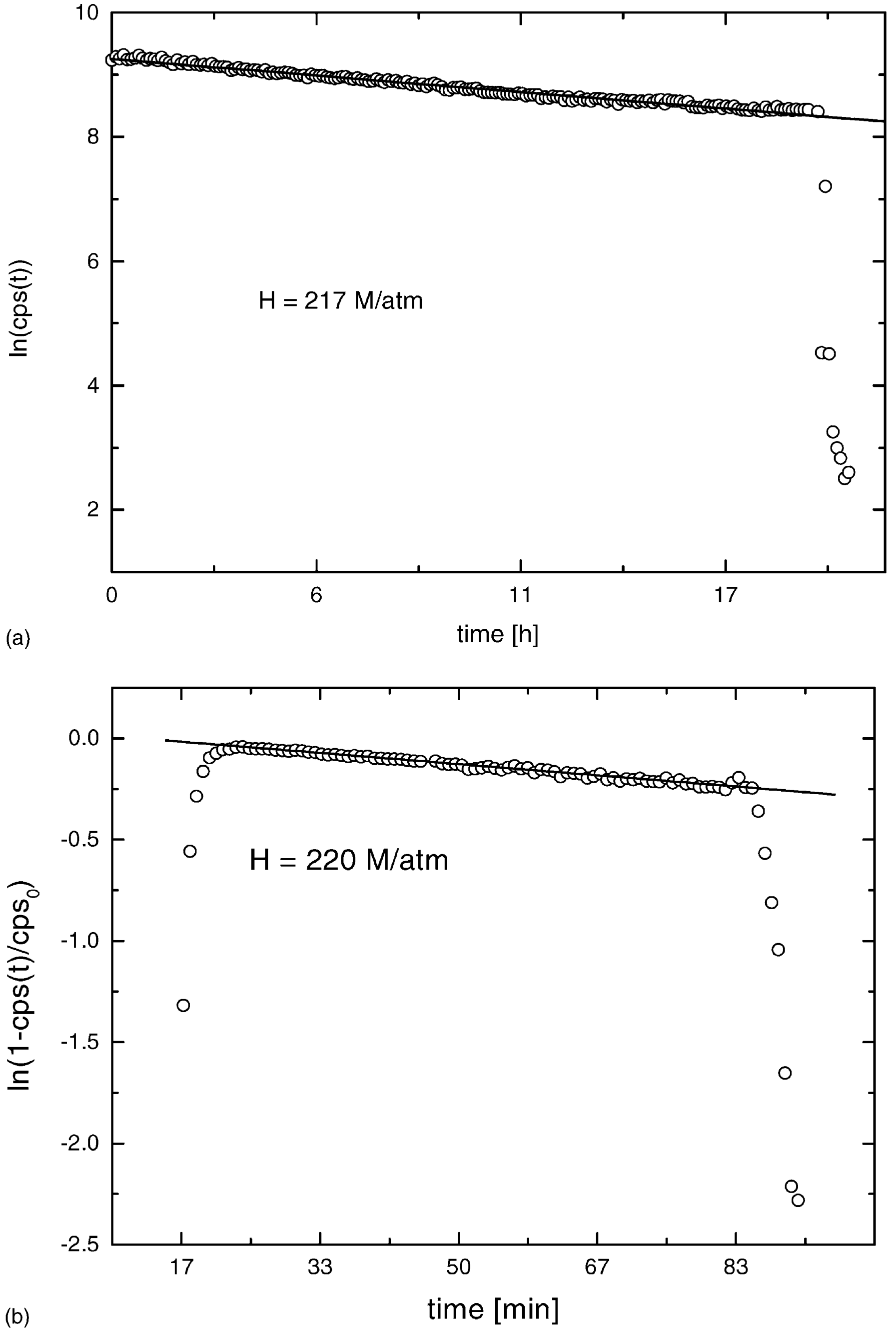

Fig. 4. (a) Methanol measured with the single stripping cell configuration. (b) Methanol measured with the double stripping cell configuration.

2.2. Double stripping cell configuration

A second solution satisfying Eq. (1) yields,

$$\ln\left(1-\frac{p(t)}{p_0}\right)=-\frac{HF}{VRT}t. \quad (5)$$

This form describes the case where air with a given concentration, p_0, of a VOC is bubbled through the stripping cell 2 (Fig. 3) filled with doubly distilled water. The solvent in cell 2 will gradually be enriched with the solute according to Henry's law. The concentration of the VOC in the air leaving cell 2, $p(t)$, will asymptotically increase from essentially zero (background signal is on average below 1 ppb) to the concentration p_0 that enters cell 2. In our case we used a second cell, shown as stripping cell 1 in Fig. 3, which contained a prepared solution of the VOC whose HLC was to be determined. Referring to Eq. (3), the ratio of HS concentration, $p(t)/p_0$, can be expressed by the ratio of measured count rates, $\mathrm{cps}(t)/\mathrm{cps}_0$. By plotting the natural logarithm of $(1-\mathrm{cps}(t)/\mathrm{cps}_0)$ against time one can determine the HLC from the slope. Since this configuration is used for low volatile VOCs, the HS concentration in cell 1 will not decrease noticeably during the experiment (less than 1 h), and the assumption of a constant concentration of VOCs entering cell 2 is valid. Alternatively one could also use a humidified gas standard.

Referring to the example given for the single stripping cell configuration, a VOC with a HLC of 1 M/atm, dissolved in 50 mL water and stripped at a flow rate of 100 cm^3/min, will show an increase of the HS concentration to about 50% of its final concentration (considering an average background intensity of 1 ppb) within only 6 min.

Note that only relative intensities are required and the absolute liquid concentration in cell 1 does not need to be known. For all compounds of low volatility the decrease of concentration in cell 1 is negligible during the measurement period.

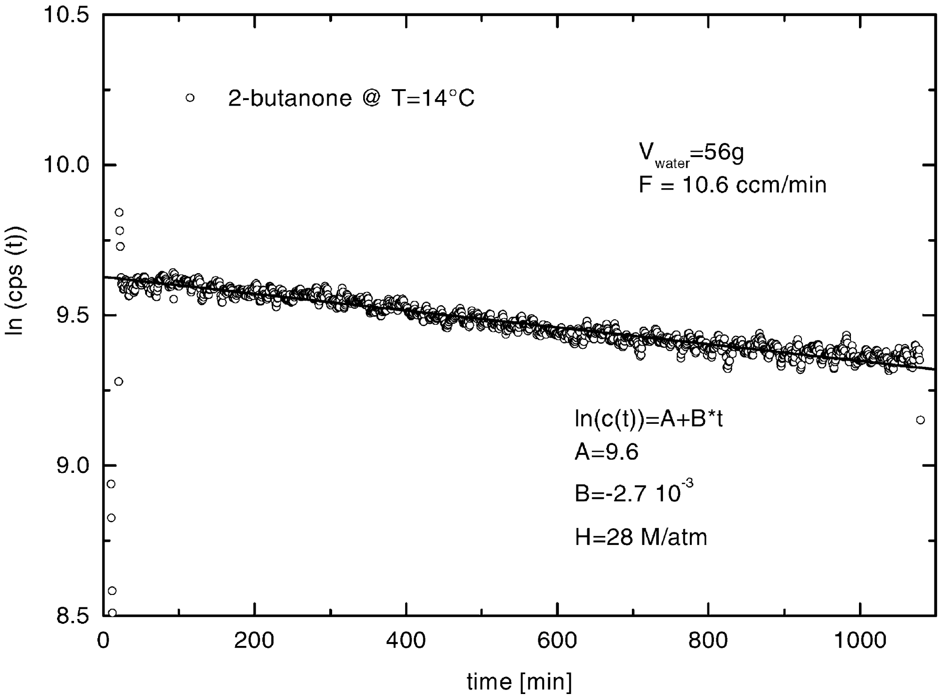

Fig. 5. ln(C) for 2-butanone as dependent on time, yielding a HLC of 20 M/atm. This particular experiment was performed at 14 °C. Measurement at other temperatures are included in Fig. 6. The vertical axis ln(cps) corresponds to counts per seconds, normalised such that the value corresponds to the actual ln(concentration) in the gas flow.

Table 1
Summary of HLC values and partition coefficients K_{PC} for 2-butanone

HLC (M/atm) at $T = 25\,^{\circ}C$	K_{PC} at $T = 25\,^{\circ}C$	Authors (references)[a]
21	1.9e−3	Buttery et al. [21] (HS)[b]
18	2.2e−3	Snider and Dawson [25] (HS)
7.7	5.2e−3	Ashworth et al. [24]
20	2.0e−3	Zhou and Mopper [26] (HS)
7.7 to 4.1	5.2e−3 to 9.8e−3	Betterton [27]
19 to 14 ($T = 30\,^{\circ}C$) 10.35	2.1e−3 to 2.9e−3 ($T = 30\,^{\circ}C$) 3.9e−3	Chaintreau et al. [8] (HS)
14.8	2.73e−3	Morillon et al. [28]
11.2	4.5e−3	This work

[a] Values can also be found in the "*Compilation of HLCs for Inorganic and Organic Species of Potential Importance in Environmental Chemistry*" [29].

[b] (HS): Headspace technique.

Molecular diffusion in the gas-phase is much greater than in the liquid-phase, which on the one hand would relax equilibrium conditions for the double stripping cell setup; on the other hand the liquid phase is well mixed and the general diffusion equation is mainly governed by convection. Equilibrium conditions therefore should be similar for both stripping cell configurations; however it is noted that equilibrium has to be considered more carefully the higher the HLC gets.

In order to compare both stripping configurations quantitatively, the HLC of methanol was measured with the single as well as the double stripping cell

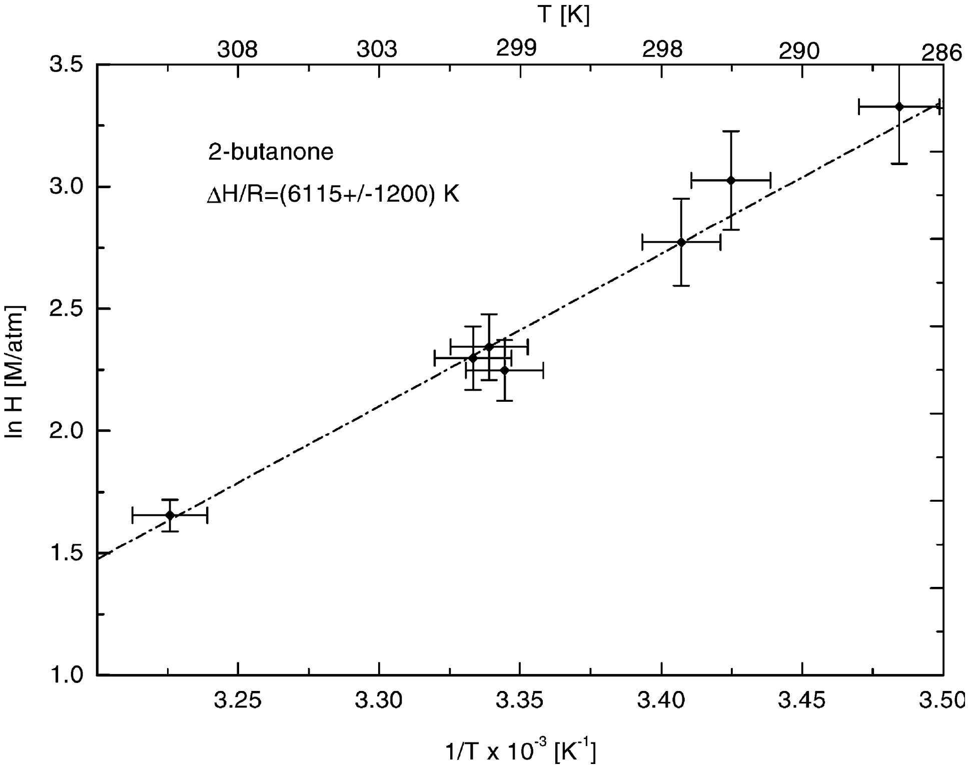

Fig. 6. Temperature dependence of the HLC for 2-butanone over the range from 14 to 40 °C.

configuration, as shown in Fig. 4. Methanol has a HLC of approx. 220 M/atm [25]. Twenty hours are needed to achieve a decrease of the HS concentration by about 10% with the single stripping cell configuration (Fig. 4a). From the slope, we calculate the HLC to be (217 ± 15) M/atm. Using the double stripping cell configuration for the same compound, a comparable result (220±15) M/atm is obtained within less than 1 h.

3. Results and discussions

3.1. HLC of 2-butanone: intercomparison of various methods

One of the most thoroughly studied oxygenated compound in terms of liquid to gas phase partitioning is 2-butanone. The results obtained in this work can be compared with those of other established techniques. Fig. 5 shows a typical ln(cps(t)) vs. t plot for 2-butanone at 14 °C from which we calculated a HLC of 28 M/atm.

Table 1 summarises the HLC of 2-butanone as obtained in this work and reported in the literature. A significant scatter can be observed among some experimental values. Especially some head space techniques appear to show systematically higher values which can be explained by experimental problems encountered by some of these methods [8]. Based on this work we propose 11.2 M/atm as the HLC of 2-butanone at 25 °C.

Additionally we investigated the temperature dependence of the HLC according to,

$$\ln\left(\frac{H}{H_0}\right) = -\frac{\Delta H_E}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right), \qquad (6)$$

where H_0 represents the HLC at T_0, R is the molar gas constant and ΔH_E is the enthalpy of solution. The data obtained between 14 and 40 °C for 2-butanone are shown in Fig. 6. Based on Eq. (6), the enthalpy of

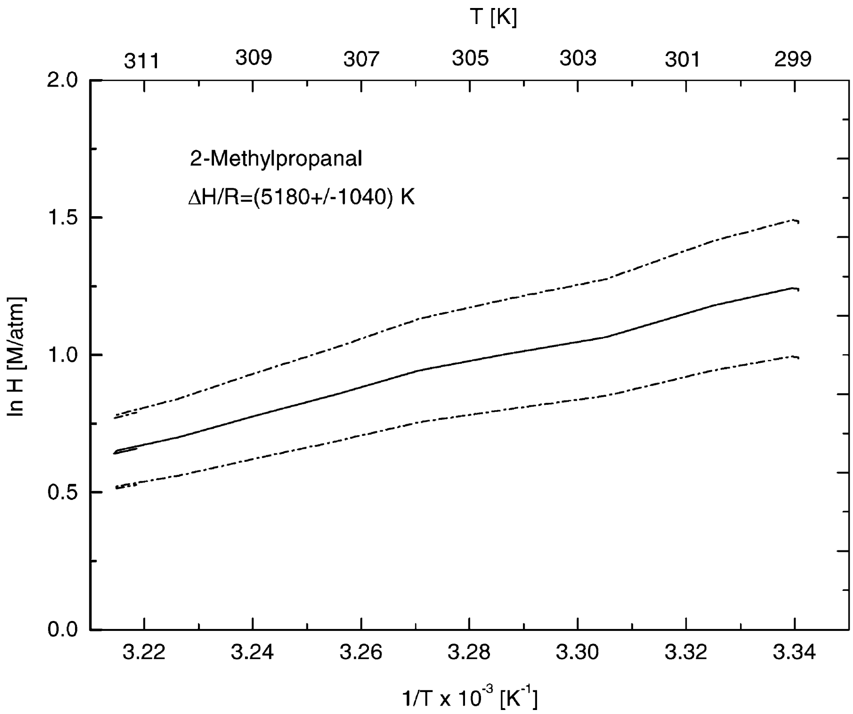

Fig. 7. Continuous trace of the temperature dependence of the HLC for 2-methylpropanal during a heating cycle from 29 to 39 °C. Dotted lines represent estimated errors.

solution, $\Delta H_E/R$, was calculated from the slope and determined to be $\Delta H_E/R = 6115 \pm 1200$ K. Using the real time monitoring capabilities of PTR–MS we tested a second simple and continuous approach for measuring the temperature dependence of HLCs. By reducing the flow-rate through the stripping cell or simply by choosing a big liquid reservoir, continuous heating of the sample will cause an increase in the headspace concentration, p, due to the decreased solubility of a VOC at higher temperatures. This increase of the headspace concentration is directly proportional to the temperature dependence of the HLC, through $p_{t1}/p_{t2} = H_{t2}/H_{t1}$. In these experiments a larger stripping cell (60 cm length, i.d. 6 cm) was wrapped with heating tape and purged with air at a flow-rate of 10 sccm. A sensor (pt100) in the centre of the cell logged the temperature continuously during the heating and cooling procedure. For a temperature increase from 22 to 39 °C the heating cycle typically lasted 12 min and the cooling cycle (39–22 °C) 30 min. In case of a homogenous temperature increase of the liquid no hysteresis of VOC headspace concentrations between heating and cooling cycles were observed. At too high heating rates (>5 °C/min) equilibrium was not reached during the heating cycle; the cooling cycle was typically used as the reference curve and gave a more accurate value for $\Delta H_E/R$ in these cases. Fig. 7 shows a continuous profile of the temperature dependence of the HLC for 2-methylpropanal, yielding $\Delta H_E/R = 5180 \pm 1040$ K.

3.2. HLC of volatile organic compounds

We have validated the dynamic stripping method interfaced with a proton-transfer-reaction mass spectrometer and compared obtained results for 2-butanone with alternative approaches. The described experimental set-up was further used to measure HLCs for a series of alcohols, aldehydes and ketones as listed in Table 2. For some compounds experimentally determined HLCs have been reported in the literature and are listed together with our results. The values for eight

Table 2
HLCs in units of (M/atm) and partition coefficients (PCs) obtained from the present work as well as the literature

Number	Compound	T (°C)	HLC this work (M/atm)	HLC error (%)[a]	HLC literature (M/atm)[b]	K_{PC} (c_{air}/c_{liq})	$-\Delta H_E/R$ (K)[c]
1	Benzene	22	0.18	20	0.179	2.24e−01	3772 ± 10%
2	Toluene	22	0.14	6	0.147	2.88e−01	–
3	Propylbenzene	22	0.15	16	0.14	2.69e−01	–
4	1,3,5-Trimethylbenzene	22	0.20	19	0.17	2.02e−01	–
5	*m*-Xylene	22	0.136	4	0.139	2.97e−01	–
6	α-Pinene	22	0.059	24	–	6.84e−01	–
7	β-Pinene	22	0.050	20	–	8.08e−01	–
8	α-Terpinene	22	0.046	9	–	8.78e−01	–
9	Isoprene	18	0.029	11	0.013	1.39e+00	–
10	(*E*)-2-Hexenal	25	14.5	12	20	2.78e−03	–
11	Hexanal	22	3.2	13	3.3	1.26e−02	7572 ± 23%
12	(*E*)-3-Hexenylacetate	25	3.3	12	–	1.22e−02	8160 ± 26%
13	(*Z*)-3-Hexenylacetate	25	3.1	12	–	1.30e−02	–
14	Hexylacetate	25	1.5	12	–	2.69e−02	6960 ± 30%
15	2-Methylpropanal	25	3.3	10	–	1.20e−02	5180 ± 20%
16	2-Butanone	25	11.2	10	5–20	3.61e−03	6115 ± 20%
17	3-Ethylphenol	25	500	10	–	8.08e−05	3440 ± 10%
18	2-Isobutyl-3-methoxypyrazine	22	17	20	20	2.38e−03	7021 ± 11%

[a] Standard deviation of 5 or more values measured.

[b] From "*Compilation of HLCs for Inorganic and Organic Species of Potential Importance in Environmental Chemistry*" [29].

[c] The temperature dependence of the HLC was investigated for some compounds and is included in the last column as enthalpy of solution, $\Delta H_E/R$. Most experiments were performed at either 22 or 25 °C except for isoprene which was measured at 18 °C. Also listed is the dimensionless partition coefficient (PC) commonly used in the flavour literature.

compounds investigated in this study have not been reported previously to our knowledge. The measured HLCs were all standardised to 1013 mbar, i.e., 1 atm.

Comparison with HLCs reported in the literature shows that most values agree within the combined experimental error limits.

4. Conclusions

This work presents a novel, simple and fast dynamic method for measuring HLCs. We briefly outlined the theoretical background and discussed the experimental approach. Based on our results we propose the combination of one (or alternatively two) dynamic stripping cell(s) interfaced with the PTR–MS instrument and use this setup for obtaining HLCs of various low to medium soluble VOCs. Depending on the volatility two different experimental configurations were applied. The *single stripping cell configuration* is particularly suited for compounds of high volatility, while the *double stripping cell configuration* can be used when determining HLCs for medium to low volatile compounds. This allows to extend the stripping method to compounds having higher solubilities.

A comparison of HLC values for 2-butanone reported in the literature showed that previously measured HLCs scattered from 5 to 20 M/atm. Our results suggest a HLC of (11.2 ± 1.1) M/atm at 25 °C. Additionally, we were able to determine HLCs for a series of compounds. Where literature values are available, they are usually in good agreement with our results. For several compounds—α-pinene, β-pinene, α-terpinene, (*E*)-3-hexenylacetate, (*Z*)-3-hexenylacetate, hexylacetate and 3-ethylphenol—no experimentally determined HLCs prior to our work were found.

From our results we infer that the dynamic technique together with PTR–MS as described here can provide HLCs for compounds over a wide range of volatility. Comparison with alternative state-of-the-art techniques shows that the PTR–MS technique has the advantage of being simple, fast and less prone to artefacts. Furthermore, it allows to quantify volatile compounds in the headspace without calibration or addition of standards and enables to measure HLCs for many compounds simultaneously.

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