

Breakthrough characteristics of volatile organic compounds in the -10 to $+170$ °C temperature range on Tenax TA determined by microtrap technology

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Abstract

In this work the breakthrough volumes (BTVs) of volatile organic compounds (VOCs) on Tenax TA were determined in the -10 to 170 °C temperature range by using microtrap (MT) technology. The MT technology allowed experimental investigation of the temperature dependence of BTVs. Along with the BTV data, we also discuss the thermodynamics of the temperature dependence of the BTV through a two-parameter equation $\ln(\text{BTV}) = A_1/T + C_1$ where T is temperature (K), $A_1 = -\Delta H/R$ where ΔH is enthalpy of sorption and C_1 is constant. This equation fitted well the experimental results with R^2 values between 0.9737 (acetone) and 0.9995 (dimethyl disulfide), with n between 6 and 11. However, for n -pentane, n -hexane and 1-hexene it proved that a three parameter equation $\ln(\text{BTV}) = A_2/T + BT_B + C_2$ fitted better to the experimental results, with $A_2 = -\Delta H_{T_0}/R$, $B = \Delta C_p/R$, $T_B = \ln(T/T_0) + (T_0 - T)/T$, C_2 a constant, ΔH_{T_0} the adsorption enthalpy at reference temperature T_0 and ΔC_p the difference in the molar heat capacity of compound under investigation between the sorbed and the free gas phase state. The statistical analysis showed for example for n -pentane now $R^2 = 0.9969$ instead of $R^2 = 0.9746$, and Fisher statistics $F = 487$ instead of $F = 153$, with a significance level $P = 0.018$ for the third parameter. The results show that microtrap technology well serves as a technology to get information on temperature dependence of BTVs in an extended range. Simultaneously, it turns out that MT technology, extending the operational temperature range, is well served by a careful investigation of the temperature dependence models of BTVs.

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1. Introduction

Several sampling methods are in use for the analysis of volatile organic compounds in (VOCs) ambient air. Samples can be taken in sample loops, by adsorption on solid matrices, by condensation in cold traps or whole air samples are taken in canisters or bags. For sorbent sampling, commercially available sorbents like activated charcoal, Carbotrap, Carbosieve, XAD-2, Tenax GC, Tenax TA etc are available [1]. Also combinations of these sorbents in so-called multi-stage traps are common practice [2].

With a typical surface area of $35 \text{ m}^2 \text{ g}^{-1}$ and a pore volume $2.4 \text{ cm}^3 \text{ g}^{-1}$, Tenax TA (poly-2,6-diphenyl-*p*-phenylene oxide) might be the most common sorbent due to its excellent properties [3]. It is a hydrophobic polymer with high temperature stability (maximum temperature limit typically 350 °C [4]), allowing the sampling of compounds in a relatively wide range of volatility [5].

The combination of good adsorption characteristics at ambient temperature with appropriate desorption at moderate temperatures makes that Tenax TA is widely used. The flexibility of Tenax TA is basically due to the strong dependence on temperature of the breakthrough volume (BTV). However, systematic investigation of sorption characteristics of Tenax TA (like breakthrough volumes, number of theoretical plates, sorption capacity etc.) in larger temperature ranges

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can be hardly found in literature. Available experimental results are usually obtained specifically at high temperature (because of the use of high amount of sorbent) or in limited temperature ranges or with limited number of measurements and compounds [6–8].

Besides physico-chemical properties, breakthrough volumes are the most important information for practical application of adsorbents. In the literature, many different definitions of BTV are available. BTV is expressed by collection efficiency, the retention volume for the adsorbate versus adsorbent combination, and the number of theoretical plates of the adsorbent [3,9–11]. In this work the elution model for determination of BTV is used and BTV is defined as net retention volume of adsorbate on 1 g of adsorbent at given temperature. From this definition BTV depends on the amount of adsorbent and temperature. Other factors also affect BTVs. Dependence of BTV on concentration of injected compounds is discussed in several works [12–15], although at lower concentrations BTVs can be independent of concentration [16]. With respect to temperature, typically Van't Hoff equations are proposed [7,16]. Another widely discussed parameter is the flow rate dependence of BTV [17]. Too high velocity of patterned air through the adsorption bed leads to expansion of the part where adsorption occurs, decreasing the BTV. Finally also the number of theoretical plates determines the BTV, a point which is often overlooked in experimental studies [11].

The breakthrough characteristics and especially the breakthrough volumes give practical information for field sampling, e.g. in order to calculate safe sampling volumes. The safe sampling volume denotes the maximum volume of air per mass of adsorbent that is possible to sample without a substantial loss of the target compound at the sampling temperature. Safe sampling volumes are usually expressed as a fraction of BTV at the same temperature for the same compound (e.g. 2/3 BTV) [18]. However, safe sampling volumes do not only depend on BTV, but also on the sampling flow rate and the targeted collection efficiency [11]. Collection efficiencies are a function of the fraction of analyte that is allowed to pass through the sampler without collection, typically between 0.001 and 0.2 [11].

During the last decade microtraps (MTs) have been developed with typical masses of 20–40 mg of sorbent material [14]. These reduced masses are combined with subambient temperatures (typically from 0 to -15°C) to maintain appropriate BTV characteristics at the sampling stage, and to allow immediate injection into GC equipment without cryofocussing [19]. MTs are made by packing narrow metal or glass tubes with small amounts of one or more sorbents [19,20]. Inner MT diameters are typically between 0.25–2.00 mm and lengths 10–20 cm [21]. Low thermal mass allows rapid electrical heating (e.g. 60°C/s) and cooling to subambient temperatures [22]. MTs are not only in use as preconcentrators for the analysis of air samples from bags, canisters, sampling tubes [23], but they can be used for direct air sampling as well.

The purpose of this work was to investigate the BTVs of VOCs on Tenax TA in an extended temperature range. This investigation is based on the involvement of MT technology, enabling the use of small masses of sorbent material and accurate temperature control. The results should bring information about BTV characteristics of sorbent material where limited information is available so far, especially at lower temperatures. Additionally, the results will be compared to thermodynamic equations, governing the sorption characteristics. To do so, fifteen compounds *n*-pentane, *n*-hexane, 1-hexene, benzene, toluene, *m*-xylene, acetone, 2-pentanone, dimethyl sulfide, dimethyl disulfide, chloroform, trichloroethene, tetrachloroethene, methyl acetate and ethyl acetate were selected, based on differences in chemical structure and physico-chemical properties.

2. Theory

Breakthrough characteristics of VOCs on adsorbents are usually expressed by BTV. In this work specific breakthrough volume V_{g}^T ($\text{cm}^3 \text{g}^{-1}$) is used, i.e. the retention volume per gram of adsorbent which is calculated from [24,25]:

$$V_{\text{g}}^T = \frac{F_{\text{A}} t'_{\text{R}} T_{\text{M}}}{M j T_{\text{A}}} \quad (1)$$

where F_{A} is the flow rate of carrier gas ($\text{cm}^3 \text{min}^{-1}$) measured at temperature T_{A} (K), t'_{R} the net retention time (min), M the mass of adsorbent (g), T_{M} the temperature of the adsorbent (K) and j the pressure correction factor (dimensionless); j is expressed by [26]:

$$j = \frac{3(p_{\text{i}}/p_{\text{o}})^2 - 1}{2(p_{\text{i}}/p_{\text{o}})^3 - 1} \quad (2)$$

where p_{i} and p_{o} are the inlet and outlet pressure, respectively. The ratio T_{M} over T_{A} expresses a temperature correction for the flow rate F_{A} measured at T_{A} in order to calculate the actual flow rate in the tube [27]. V_{g}^T is related to the temperature by the Van't Hoff type relationship:

$$\frac{d(\ln V_{\text{g}}^T)}{dT} = \frac{\Delta H_T}{RT^2} \quad (3)$$

where ΔH_T is the adsorption enthalpy (J mol^{-1}) at temperature T (K) and R is the gas constant.

ΔH_T can be calculated at any temperature according to the Kirchhoff law:

$$\Delta H_T = \Delta H_{T_0} + \int_{T_0}^T \Delta C_{\text{P}} d\tau \quad (4)$$

where ΔH_{T_0} is the adsorption enthalpy at reference temperature T_0 ; σ represents integration from the reference temperature T_0 to the actual temperature T . ΔC_{P} is the difference in the molar heat capacity of compound i between final and initial state ($\text{J K}^{-1} \text{mol}^{-1}$). In this case ΔC_{P} is equal to:

$$\Delta C_{\text{P}} = C_{\text{Psorb}} - C_{\text{Pg}} \quad (5)$$

where $C_{\text{P}_{\text{sorb}}}$ is the molar heat capacity of the organic compound i sorbed on the sorbent material and $C_{\text{P}_{\text{g}}}$ the molar heat capacity in the free gas phase ($\text{J K}^{-1} \text{mol}^{-1}$). ΔH_T and ΔH_{T_0} are the changes of enthalpy during the sorption of 1 mol of compound i from the gas phase to the sorbed state at T and T_0 , respectively.

$C_{\text{P}_{\text{g}}}$ can be easily calculated at different temperatures from:

$$C_{\text{P}_{\text{g}}} = a + bT + cT^2 + dT^3 \quad (6)$$

where a , b , c and d are constants [28].

However, in most sorption studies where a limited temperature range is investigated, the enthalpy of sorption is considered to be independent of the temperature:

$$\Delta H_T = \Delta H_{T_0} = \Delta H \quad (7)$$

Considering ΔH constant, integration of Eq. (3) leads to:

$$\ln V_{\text{g}}^T = \frac{-\Delta H}{RT} + C_1 \quad (8)$$

or simply to:

$$\ln V_{\text{g}}^T = \frac{A_1}{T} + C_1 \quad (9)$$

where C_1 and $A_1 = -\Delta H/R$ are constants. Eq. (9) expresses linear dependence of $\ln V_{\text{g}}^T$ on $1/T$ in the studied temperature range. This model is used in many works for linear extrapolation of BTV data from high temperatures of measurements to the ambient temperature and for calculation of the safe sampling volume [3,23,29].

If ΔH_T is not constant and if ΔC_{P} is assumed to be constant, then substitution of Eq. (4) into Eq. (3) leads to:

$$\ln V_{\text{g}}^T = \frac{-\Delta H_{T_0}}{RT} + \frac{\Delta C_{\text{P}}}{R} \left(\ln \frac{T}{T_0} + \frac{T_0 - T}{T} \right) + C_2 \quad (10)$$

or simply to:

$$\ln V_{\text{g}}^T = \frac{A_2}{T} + BT_{\text{B}} + C_2 \quad (11)$$

where C_2 is a constant and $A_2 = -\Delta H_{T_0}/R$, $B = \Delta C_{\text{P}}/R$ and $T_{\text{B}} = \ln(T/T_0) + (T_0 - T)/T$. This relation expresses nonlinear dependence of $\ln V_{\text{g}}^T$ on $1/T$ in the studied temperature range. Similar three-parameter relations have been investigated for the temperature dependence of retention in capillary gas chromatography [30] and air–water partitioning [31]. To our knowledge, the three-parameter model has not yet been used in the study of the temperature dependence of BTVs of VOCs on sorbent materials.

3. Experimental

3.1. Materials and methods

3.1.1. Chemicals

1-Hexene (purity 97%), methyl acetate (99%), acetone (99.9%), dimethyl sulfide (99%), dimethyl disulfide

(99%), ethyl acetate (99.99%) (Acros Organics, NJ, USA), *n*-pentane (99%), *m*-xylene (99%) (Fluka, Buchs, Switzerland), chloroform (99%), benzene (99%), 2-pentanone (99%), tetrachloroethene (99%) (Janssen Chimica, Geel, Belgium), toluene (99.8%), trichloroethene (99.5%) (Aldrich, Milwaukee, WI, USA), *n*-hexane (98%) (VEL, Leuven, Belgium) and methanol (99.8%) (J.T. Baker, Phillipsburg, USA) as solvent, were used in this work without purification.

The compounds were split into two groups with respect to their expected breakthrough volumes. Two basic solutions were prepared in methanol and used for preparation of gaseous samples.

3.1.2. Preparation of gaseous samples

The closed two-phase system (CTS) [32] was used for the preparation of gas phase mixtures with VOCs concentration between 4 and 6 g m^{-3} . CTS is based on equilibrium partitioning between water and gas of compounds in a closed system. From the mass m of the compounds introduced to the system in a methanolic solution ($300 \mu\text{l}$), the volume of water V_{w} (30 cm^3), the headspace V_{g} (88 cm^3) and Henry's law constant H (obtained from Ref. [33]) of all compounds at the incubation temperature ($25.0 \pm 0.1 \text{ }^\circ\text{C}$), concentrations of the compounds in the gas phase C_{g} (g m^{-3}) are calculated:

$$C_{\text{g}} = \frac{m}{V_{\text{g}} + V_{\text{w}}/H} \quad (12)$$

From the CTS, $100\text{--}250 \text{ mm}^3$ of gaseous samples were taken by Hamilton 1750 gas-tight syringes (Hamilton, Bonaduz, Switzerland) through Mininert valves (Alltech Associates, Lokeren, Belgium) and injected subsequently into the carrier gas flow.

3.1.3. Apparatus

A Unity thermal desorber and air server (Markes International, Pontyclun, UK) was used for controlling MT temperatures and flow rates. The MT was made of a quartz tube (length 120 mm, i.d. 2 mm, o.d. 2.9 mm, Markes International). It was packed in the laboratory with 29.4 or 3.3 mg Tenax TA (60–80 mesh, Supelco, Bellefonte, PA, USA) and held by quartz wool plugs (Interscience, Louvain-la-Neuve, Belgium). For injection of prepared gaseous samples, a 1/8 in. T-piece (Swagelok, Solon, USA; 1 in. = 2.54 cm) was installed into the carrier gas supply line. The T-piece was closed by a septum (Alltech Associates), installed into a 1/8 in. open nut.

Through a heated transfer line, the Unity was coupled with a GC Trace 2000 gas chromatograph (ThermoFinnigan, Milan, Italy), equipped with a Chrompack CP-SIL 5 capillary column ($60 \text{ m} \times 0.32 \text{ mm}$, $0.25 \mu\text{m}$ film thickness) and a MS Trace DSQ WE-250 mass spectrometer (ThermoFinnigan, Austin, TX, USA). The whole system was controlled by a personal computer Compaq PC-EVO-310 with Unity 1.2.0 (Markes International) and Xcalibur 1.3 (ThermoFinnigan, Austin, TX, USA) software.

3.1.4. Pressure drop measurements

Pressure drop measurements over the MTs were done to obtain data for calculation of the pressure correction factor. To do so, a Chrompack BFU103 flow rate regulator and pressure meter, a GC oven for thermal stabilization and a soap film flow meter were used. Helium (Helium 2, Alphagaz, Liege, Belgium) was used as carrier gas in all these experiments.

3.2. Determination of BTVs

Gaseous samples were injected into the MT–GC–MS system (see Fig. 1). The overall retention of a VOC (t_{VOC}) consists of three parts: the net retention on the MT (t'_{R}), the net retention on the GC column (t'_{GC}) and the dead time (t_{N_2}), the latter being equal to the overall retention of nitrogen, injected simultaneously with the VOC from the CTS:

$$t_{\text{VOC}} = t'_{\text{R}} + t'_{\text{GC}} + t_{\text{N}_2} \quad (13)$$

In the experiments, Δt , being equal to $t_{\text{VOC}} - t_{\text{N}_2}$, was determined from characteristic mass fragments in the total ion chromatogram. In a separate experiment, t'_{GC} was determined by setting the MT at 280 °C (negligible retention of VOCs on Tenax TA). The temperature of the GC column was set at 200 °C in all measurements. This allowed to calculate the net retention of the microtrap t'_{R} from:

$$t'_{\text{R}} = \Delta t - t'_{\text{GC}} \quad (14)$$

The experiments were done at MT temperatures between –10 and 170 °C. Flow rates through the MT were between 15 and 55 cm³ min^{–1} and split ratios ranged from 27 to 96 in order to keep flow rates towards the GC column constant at 0.58 cm³ min^{–1}. All experiments were repeated five times.

3.2.1. Statistics

The data processing was performed using software programs MS Office XP and statistical program SPSS (SPSS Inc., Chicago, USA).

4. Results and discussion

Results of the net retention times were used for the calculation of BTV data by using Eq. (1) on two conditions. First, the compounds needed to be detectable, i.e. the retention needed to be moderate so that longitudinal diffusion did not hamper peak detection. Secondly, detected peaks had to be symmetric. This was quantified by determining the peak asymmetry factor (A_s) [34]. In case of limited retention, peaks became asymmetric at higher flow rates ($A_s \geq 5.1$). Experimental BTV results are shown in Table 1 for all investigated VOCs. A typical chromatogram is given in Fig. 2.

The results show a strong temperature dependence of BTVs. For example, BTVs decrease by a factor of 190 (chloroform) to 458 (methyl acetate) if temperature increases from 0 to 100 °C. Even within smaller temperature ranges, e.g. those typically observed during sampling (0–30 °C), as a rule of thumb BTVs change one decade (e.g. dimethyl sulfide: 9.3; methyl acetate: 14).

To our knowledge, immediate systematic comparison to experimental BTV volumes for the investigated compounds at the extended temperature range is not possible, especially because of the lower temperatures. One resource with experimental and calculated data that is well suitable is from Scientific Instrument Services, (SIS) [35,36], except for sulfur containing VOCs. In the reported studies, BTVs were determined in a GC oven, with 250–1000 mg sorbent material at gas flow rates of 5–500 cm³ min^{–1}. Retention times were between 0.1 and 3.0 min. The authors report that they were able to set up linear BTV temperature dependence curves by extrapolating 7 experimental data to predict BTVs for temperatures not determined experimentally. The authors end up with the presentation of BTVs typically for the 0–300 °C range. From a simple calculation, given that flow rates in the reported study were maximally 500 cm³ min^{–1}, mass of sorbents minimally 250 mg and retention times maximally 3.0 min, it is clear that experimentally determined BTVs in the reported study were maximally 6000 cm³ g^{–1}. This suggests that the reported BTV data at (sub)ambient temperature were extrapolated data, being out of the experimental temperature range. Indeed, for

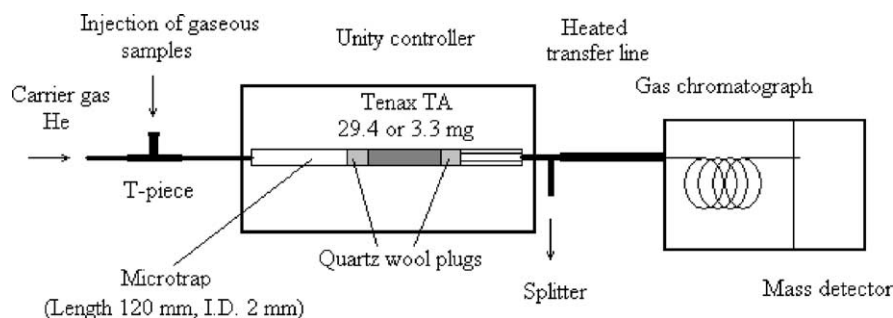


Fig. 1. Schematic diagram of MT–GC–MS system for breakthrough measurement.

Table 1
Experimental data of breakthrough volumes V_g^T ($\text{cm}^3 \text{g}^{-1}$) of compounds on Tenax TA and relative standard deviations R.S.D. (%) ($n = 5$)

Compound	V_g^T (T , °C)															
	-10	0	10	20	30	35	40	50	60	80	100	120	140	160	170	
<i>n</i> -Pentane						1.26×10^3	1.00×10^3	8.12×10^2	6.00×10^2	2.26×10^2	9.28×10^1					
R.S.D. (%)						5.2	7.9	3.2	2.5	5.7	8.1					
<i>n</i> -Hexane					7.16×10^3		4.97×10^3	3.38×10^3	2.27×10^3	7.79×10^2	3.05×10^2					
R.S.D. (%)					8.1		5.9	2.2	3.9	1.9	4.15					
1-Hexene					1.09×10^4	8.06×10^3	6.33×10^3	3.86×10^3	2.30×10^3	8.17×10^2	2.98×10^2	1.18×10^2				
R.S.D. (%)					2.4	4.3	4.4	5.1	2.4	1.8	5.1	7.7				
Benzene							1.28×10^4	6.79×10^3	3.81×10^3	1.39×10^3	6.62×10^2	2.85×10^2	1.24×10^2			
R.S.D. (%)							2.7	1.5	1.6	2.1	2	5.9	9.3			
Toluene					8.42×10^4			3.09×10^4	1.58×10^4	4.84×10^3	1.95×10^3	7.58×10^2	3.14×10^2			
R.S.D. (%)					6.7			3.9	1.5	1.1	0.7	2	5.1			
<i>m</i> -Xylene											6.15×10^3	2.00×10^3	7.73×10^2	3.21×10^2	1.80×10^2	
R.S.D. (%)											0.8	0.9	2	3.1	7.3	
Acetone	1.70×10^5				2.88×10^3	2.14×10^3	1.56×10^3	9.70×10^2	6.95×10^2	2.83×10^2						
R.S.D. (%)	4.0				2.6	1.4	1.6	2.8	1.8	2.7						
2-Pentanone					1.25×10^5		3.56×10^4	1.73×10^4	8.75×10^3	2.67×10^3	1.09×10^3	4.31×10^2				
R.S.D. (%)					3.8		2.6	2.8	0.9	0.6	1	3.7				
Dimethyl sulfide		2.57×10^4	1.38×10^4	8.13×10^3	2.75×10^3	2.03×10^3	1.52×10^3	9.31×10^2	6.27×10^2	2.45×10^2	9.37×10^1					
R.S.D. (%)		5.6	3.8	2.3	1.4	2	1.1	2.5	1.4	4	6.8					
Dimethyl disulfide				$2.67E \times 10^5$				2.14×10^4	1.18×10^4	3.38×10^3	1.14×10^3	4.47×10^2	1.71×10^2	7.25×10^1		
R.S.D. (%)				2.3				0.9	1	0.4	1.1	1.5	7.4	4		
Chloroform		6.31×10^4	3.95×10^4	2.68×10^4	1.08×10^4	7.89×10^3	5.77×10^3	3.44×10^3	2.16×10^3	7.86×10^2	3.31×10^2	1.32×10^2				
R.S.D. (%)		5.9	3.9	3.7	1.9	1.4	2.0	1.7	0.6	1.0	1.4	5.3				
Trichloroethene					2.98×10^4		1.65×10^4	8.46×10^3	4.50×10^3	1.54×10^3	7.01×10^2	2.85×10^2				
R.S.D. (%)					2.5		1.8	1.7	1.6	1.6	2.0	3.7				
Tetrachloroethene					8.58×10^4			3.06×10^4	1.54×10^4	4.83×10^3	2.01×10^3	7.65×10^2	3.21×10^2			
R.S.D. (%)					5.5			4.2	1.8	1.5	0.8	2.4	2.6			
Methyl acetate		7.61×10^4	3.92×10^4	2.41×10^4	5.45×10^3	3.93×10^3	2.92×10^3	1.79×10^3	1.13×10^3	4.21×10^2	1.66×10^2					
R.S.D. (%)		4.9	3.7	4.3	1.6	1.3	1.5	1.9	1.2	2.0	4.4					
Ethyl acetate				6.92×10^4	3.71×10^4		1.26×10^4	5.89×10^3	3.10×10^3	1.01×10^3	4.76×10^2	1.74×10^2				
R.S.D. (%)				8.2	4.4		1.8	4.0	2.4	2.2	2.1	8.8				

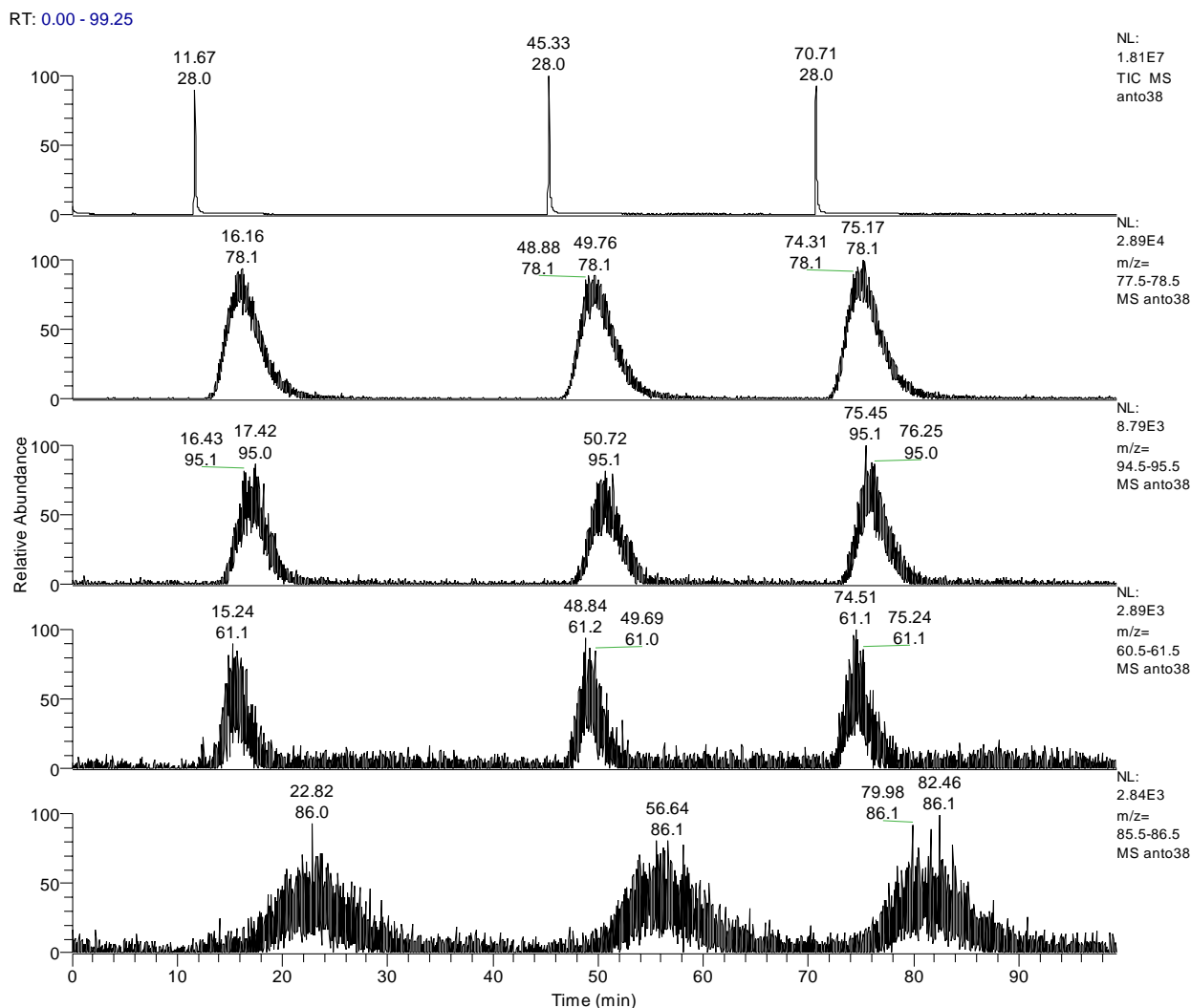


Fig. 2. Illustration of three consecutive breakthrough chromatograms for a 29.4 mg trap at 50°C with a gas flow of 45.58 cm³ min⁻¹. The upper Total Ion Current chromatogram shows nitrogen elutions (mass 28) at 11.67, 45.33 and 70.71 min (t_{N₂}). The lower selected ion current chromatograms show breakthroughs of benzene (mass 77.5–78.5), trichloroethylene (mass 94.5–95.5), ethyl acetate (60.5–61.5) and 2-pentanone (mass 85.5–86.5) (t_{VOC}).

typical volatile compounds like alkanes (*n*-hexane), alkenes (1-hexene), ketones (2-pentanone), monocyclic aromatic hydrocarbons (toluene) or chlorinated compounds (chloroform, tetrachloroethylene), BTVs lower than 6000 cm³ g⁻¹ are only observed at supra-ambient temperatures (>30°C).

The difference in experimental setup but mainly the fact that the SIS data at (sub)ambient temperatures are presumably largely based on extrapolation, may explain the different level and temperature dependence of the BTVs between both studies. For example, if one compares the results of the BTVs of chloroform at 0, 20, 40 and 60°C, the current study shows BTVs being a factor 1.6, 0.71, 0.78 and 0.57 different from the reported SIS data.

In a next step, the experimental results of this study were fitted into the two-parameter model in order to investigate the temperature dependence within the studied temperature range (Eq. (9)). From the statistical results presented in Table 2 it can be seen that the theoretical model explains

well the experimental observations, with R^2 values ranging from 0.9737 (acetone, $n = 7$) to 0.9995 (dimethyl disulfide, $n = 8$). From the slope of the regression line, molar enthalpies of adsorption are calculated, being in the range of -38.0 ± 3.1 kJ mol⁻¹ (*n*-pentane) to -68.0 ± 1.7 kJ mol⁻¹ (*m*-xylene). The more negative the ΔH , the larger the interaction between the adsorbate and sorbent (Tenax TA). The ΔH results are comparable with similar data in [20,37–39] where different sorbents were used. For example, in the work of Bilgiç and Aşkin [30], adsorption enthalpies for *n*-hexane on alumina and 3A and 5A molecular sieves were -41.0 , -27.5 and -34.7 kJ mol⁻¹, respectively, based on experimental determinations above 200°C. Grajek et al. [31] report adsorption enthalpy data for three types of activated carbons (WS-4, NP-5 and R) for several compounds in the 250–320°C temperature range and their results for *n*-hexane on said adsorbents were -75.9 , -100.2 and -88.3 kJ mol⁻¹, respectively.

Table 2
Estimation of parameters A, B and C by two and three-parameter models; included are statistics on ground of n measurements

Compound	Number of parameters	Parameters			$-\Delta H$ or $-\Delta H_{298}$	Statistics				
		A_1 or A_2	C_1 or C_2	B		R^2	F	R^2_{adj}	P	n
<i>n</i> -Pentane	2	4567 ± 368	-7.55 ± 1.11		38.0 ± 3.1	0.9746	153	0.9683		6
	3	1466 ± 680	2.39 ± 2.18	-77.24 ± 16.54	12.2 ± 5.7	0.9969	487	0.9949	0.018	6
<i>n</i> -Hexane	2	5168 ± 321	-7.99 ± 0.97		43.0 ± 2.7	0.9848	259	0.9810		6
	3	2868 ± 389	-0.57 ± 1.25	-60.76 ± 9.92	23.8 ± 3.2	0.9989	1332	0.9981	0.009	6
1-Hexene	2	5955 ± 136	-10.25 ± 0.41		49.5 ± 1.1	0.9969	1908	0.9963		8
	3	4705 ± 111	-6.23 ± 0.36	-27.83 ± 2.39	39.1 ± 0.9	0.9999	22346	0.9998	0.0001	8
Benzene	2	5869 ± 92	-9.32 ± 0.26		48.8 ± 0.8	0.9988	4040	0.9985		7
Toluene	2	6455 ± 150	-9.78 ± 0.43		53.7 ± 1.2	0.9973	1845	0.9968		7
<i>m</i> -Xylene	2	8180 ± 201	-13.19 ± 0.49		68.0 ± 1.7	0.9982	1650	0.9976		5
Acetone	2	6650 ± 489	-13.62 ± 1.58		55.3 ± 4.1	0.9737	185	0.9684		7
2-Pentanone	2	7212 ± 319	-12.41 ± 0.94		60.0 ± 2.7	0.9903	511	0.9884		7
Dimethyl sulfide	2	5769 ± 165	-10.95 ± 0.53		48.0 ± 1.4	0.9935	1225	0.9927		10
Dimethyl disulfide	2	7349 ± 69	-12.66 ± 0.20		61.1 ± 0.6	0.9995	11254	0.9994		8
Chloroform	2	5631 ± 127	-9.30 ± 0.40		46.8 ± 1.1	0.9954	1952	0.9949		11
Trichloroethene	2	6166 ± 90	-10.04 ± 0.27		51.3 ± 0.7	0.9989	4701	0.9987		7
Tetrachloroethene	2	6430 ± 138	-9.71 ± 0.39		53.5 ± 1.1	0.9977	2178	0.9973		7
Methyl acetate	2	6399 ± 285	-12.20 ± 0.91		53.2 ± 2.4	0.9844	504	0.9824		10
Ethyl acetate	2	6908 ± 230	-12.51 ± 0.70		57.4 ± 1.9	0.9934	900	0.9923		8

ΔH and ΔH_{298} are in kJ mol^{-1} , R^2 is the square of the correlation coefficient; F the Fischer criterion and P the significance level of added parameter B .

For three weakly adsorbed compounds, i.e. *n*-pentane, *n*-hexane and 1-hexene, it was noticed that the two-parameter thermodynamic model resulted in systematic error. This is well illustrated by plotting the residuals (experimental value – value predicted by the model) in Fig. 3. It demonstrates systematically concave curves. In conclusion, the two-parameter equation cannot adequately describe the temperature dependence of V_g^T for *n*-pentane, *n*-hexane and 1-hexene in the extended temperature range. This can be explained by the fact that the assumption that the enthalpy

of adsorption is constant is no longer valid in extended temperature ranges. Similar observations are reported in studies of air–water partitioning and retention in capillary GC [30,31]. Therefore, the three-parameter Eq. (11) was tested.

The results of the three-parameter model are depicted in Table 2. It is statistically shown that this equation better explains the experimental results. This is clear from the plot of the residuals with now lower residuals being more randomly distributed (Fig. 4), from the F values and from the improved R^2 values. Moreover, the new term in the equa-

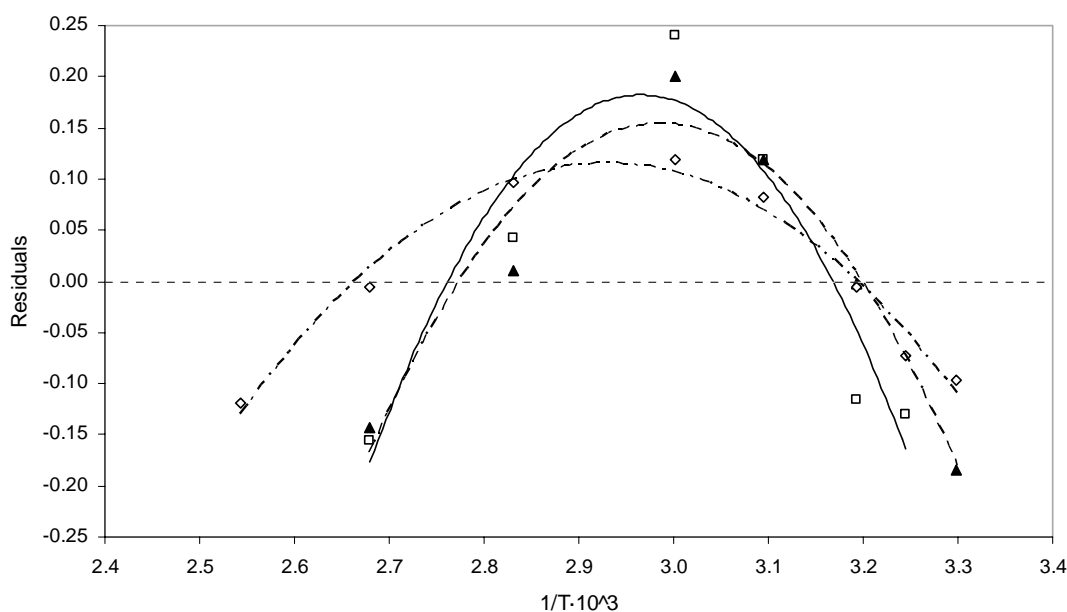


Fig. 3. Plot of residuals (experimental value – value predicted by the model) against temperature using the two-parameter model: (□) *n*-pentane, (▲) *n*-hexane, (◇) 1-hexene.

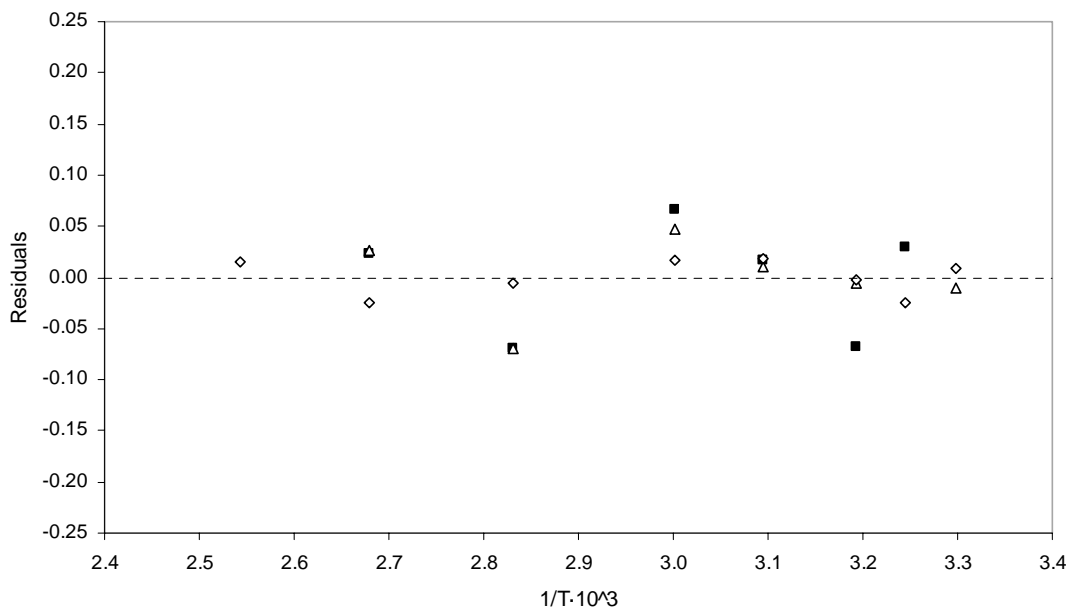


Fig. 4. Plot of residuals (experimental value – value predicted by the model) against temperature using the three-parameter model: (□) *n*-pentane, (▲) *n*-hexane, (◇) 1-hexene.

tion proved to be significant at $P = 0.05$. From the results it can be calculated that simple linear extrapolation of BTVs typically obtained at higher temperatures over 160°C [3] can result in inaccurate BTV estimations at ambient and subambient temperatures. For example, application of the two-parameter model, i.e. linear extrapolation of BTV data, results in overestimation up to 43.1% (acetone) or underestimation up to 37.1% (ethyl acetate) at ambient temperature. This study shows that implementation of a three parameter model contributes to a more accurate extrapolation: under/overestimations for *n*-hexane, *n*-pentane and 1-hexene are reduced to 0.9, 3.1 and 1.2% in the three-parameter model, whereas 13.6, 20.2 and 9.7% overestimation were noticed in the two-parameter model.

5. Conclusions

The BTV results for fifteen compounds on Tenax TA in an extended temperature range were determined. Total temperature range was between -10 and 170°C . Owing to the new MT technology, BTVs have been determined experimentally at subambient, ambient and supra-ambient temperatures. The results show the prominent temperature dependence of BTVs of VOCs on Tenax. This fact confirms the sorption/desorption capabilities of the Tenax sampling technique. However, the study also shows that the sorbent sampling stage, carried out at ambient conditions being typically in the 0 – 30°C range, has to take into account this strong temperature dependence: as a rule of thumb BTVs change by a factor 10. The experimental results at (sub)ambient temperatures show to be significantly different from reported, presumably extrapolated, data.

From experimental data changes of the enthalpy during the sorption process were calculated by using a two-parameter equation for BTV temperature dependence. It turned out that this typical Van't Hoff equation can not explain the results systematically. For *n*-pentane, *n*-hexane and 1-hexene, this equation was compared with a three-parameter equation and it proved that the three-parameter equation is a more accurate model. It shows that simple linear extrapolation of BTV results, obtained at high temperatures within a limited temperature range, to (sub)ambient temperature conditions may contribute to incorrect safe sampling volume calculations.

In conclusion, this research has shown that microtrap technologies require and provide new scientific insights. Investigations of other adsorbents than Tenax that are in use with microtraps might be of value as well.

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