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A new approach to determine vapor pressures of compounds in multicomponent systems by comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry

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ABSTRACT

A method is described to determine vapor pressures of compounds in multicomponent systems simultaneously. The method is based on temperature-gradient analysis by comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GCxGC-TOFMS). Vapor pressures are determined with the aid of known vapor pressure values of reference compounds eluting before and after the analytes. Reference compounds with the same functionalities as the analytes are preferred, but when these are not available, the alkane series can be utilized. The number of compounds whose vapor pressures can be determined is limited only by the peak capacity of the chromatographic system. Although the lowest subcooled vapor pressure determined was 0.006 Pa, for tetrahydroaraucarolone in an atmospheric aerosol sample, vapor pressures as low as 10^{-6} Pa can be measured with the described set-up. Even lower values can be measured with higher GC temperatures and longer analysis times. Since only a few picograms of compound is required, in a mixture of any complexity, the GCxGC-TOFMS method offers unique sensitivity, rapidity, and comprehensiveness.

1. Introduction

Vapor pressures, water solubilities, Henry's law constants, and distribution and partition coefficients are required in order to predict the distribution of organic compounds in the environment. Vapor pressure and water solubility are the most important of these quantities since the others can be derived from them. The most common methods for determining the vapor pressures of environmentally important, or indeed of any compounds, are effusion and gas saturation measurements and capillary gas chromatography (GC) [1–3]. In the case of effusion and gas saturation methods, great care is required for accurate results to be achieved. Errors of two orders of magnitude or more are not unusual, especially for low-volatility compounds [2–4]. With its high separation efficiency and simplicity and no need for large amounts of pure compounds, GC offers a good alternative for the determination of vapor pressures [5]. Various systems have been exploited, including isothermal [6] and temperature-programmed GC [7] and inverse gas chromatography (IGC) [8]. All of these techniques exploit the fact that the partitioning of a solute between gas and nonpolar stationary phases in the column mainly depends on vapor pressure. Retention indices obtained from chromatographic runs can be extrapolated to 298 K, where the vapor pressures can be calculated. (Vapor pressures are usually reported at 298 K). There are obvious drawbacks to the isothermal approach, including the large number of runs to be performed at different temperatures and the low separation efficiency. Methods based on temperature-programmed chromatography allow the simultaneous determination of vapor pressures of many different compounds in a mixture [9]. Even though GC methods offer advantages over effusion and gas saturation measurements, in theory they are mainly applicable to nonpolar compounds because the interactions between compounds and the stationary phase have to be chemically nonspecific. Moreover, interactions should be of the same nature for the measured and reference compounds.

In addition to the experimental methods mentioned above, theoretical calculations of vapor pressures are frequently applied, especially in the atmospheric sciences [10–12]. Even though the theoretical results, obtained, for example, by a group contribution method, are usually close to the experimental values, especially for nonpolar compounds, there remains a great need for reliable

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experimental results. Theoretical calculations cannot be applied in chamber experiments, for example, where only the reactants are known, and numerous compounds of mostly unknown structure are formed.

In previous research, we tested various GC retention index methods with flame ionization (FID) and mass spectrometric (MS) detection for the determination of vapor pressures of the oxidation products of α-pinene and β-caryophyllene. Among the factors evaluated were the effects of column polarity and phase thickness on the vapor pressure. We concluded that the most nonpolar column with a thin stationary phase should be used [13]. Because environmental sciences call for experimentally determined vapor pressures for a great number of compounds, we were prompted to continue our studies by exploiting temperature programming and the unparalleled separation power of comprehensive two-dimensional gas chromatography (GCxGC). This approach was inspired by the gas/particle-phase transition study of Williams et al. [14], who exploited thermal desorption aerosol gas chromatography (TAG) coupled to quadrupole mass spectrometry to measure the distributions of compounds in two phases (a two-phase distribution is heavily dependent on vapor pressure). Earlier, the same group evaluated the possibility of a comprehensive two-dimensional version of TAG combined with time-of-flight mass spectrometry [15,16]. In neither case, however, did they fully exploit the data obtained in the GCxGC measurements. Related to this, Hamilton et al. [17] and Welthagen et al. [18] showed that over 10000 individual organic compounds could be separated from a PM 2.5 (particulate matter with an aerodynamic diameter ≤ 2.5 μm) ambient aerosol sample.

In this work, we evaluate a system combining the excellent separation power of a comprehensive two-dimensional GC system with the structural identification ability of time-of-flight mass spectrometry (TOFMS) for the determination of vapor pressures of compounds in multicomponent mixtures. Temperature-programming was used to allow the simultaneous determination of vapor pressures in a single chromatographic run. Homologous series of *n*-alkanes, alkanols, alkanals, and alkanones were tested as reference compounds to minimize errors in the vapor pressure values arising from dissimilarities in the interactions of compounds with the column stationary phase. The possibility of measuring vapor pressures from derivatized polar compounds was also investigated. Oxidation products of terpenes were selected as model analytes, and the viability of the method was tested on an atmospheric aerosol sample.

2. Materials and methods

2.1. Chemicals and materials

β-Caryophyllene aldehyde and β-nocaryophyllene aldehyde were synthesized according to Parshintsev et al. [19] Pinonaldehyde was synthesized as reported by Glasius et al. [20]. *cis*-Pinonic and *cis*/*trans*-pinic acids were from Sigma Aldrich (St. Louis, MI, USA), and the purity of pinic acid was determined by LC-MS (mixture of *cis*- and *trans*-isomers, 75:25) according to Parshintsev et al. [21] The reference standard mixture of C_8–C_{20} *n*-alkanes was from Fluka (Steinheim, Germany), mixtures of C_6–C_{22} alkanols (except C_{17}, C_{19}, and C_{21}) and for C_3–C_{14} alkanals were from Polyscience Corp. (Niles, IL, USA), and C_5–C_{16} alkanones were purchased from AccuStandard (New Haven, CT, USA). Since the peak for decanal was no longer observed in the commercial mixture, a fresh compound from Sigma Aldrich was added. A mixture containing the model analytes and reference compounds (51 compounds) was prepared in dichloromethane (VWR, PA, USA) with concentrations of 0.5 μg mL^{-1}.

2.2. Derivatization procedure

The suitability of the method for derivatized analytes was evaluated by derivatizing a mixture of alkanols and alkanals with a mixture of *N*,*O*-bis(trimethylsilyl) trifluoroacetamide (99%, BSTFA) and trimethylchlorosilane (1%, TMCS) from Sigma Aldrich.

The mixture of alkanols and alkanals (50 μL) was mixed with 50 μL of the derivatization mixture and heated in a closed vial at 70 °C for 40 min. Then, 50 μL of alkane mixture was added. Before the analysis, dichloromethane was added to achieve the desired concentration of analytes (0.5 μg mL^{-1}).

2.3. Sampling and sample preparation

The applicability of the method for the determination of vapor pressures of compounds in complex mixtures, together with structural identification of the compounds, was tested with an atmospheric aerosol matrix. Sampling was carried out at the Station for Measuring Forest Ecosystem-Atmosphere Relations (SMEAR II) at Hyytiälä in Southern Finland (61°51'N, 24°17'E, 180 m above sea level) on March 31, 2011. The stand at the site consists mostly of Scots pine (*Pinus sylvestris* L.) together with some Norway spruce (*Picea abies* L.). For a more detailed description of the SMEAR II station, see Hari and Kulmala [22].

Total suspended particles were collected on quartz microfiber filters (i.d. 47 mm, Whatman International, Kent, UK) at a flow rate of 16 L min^{-1}. Samples were stored in a freezer until analysis. Half of the filter was used for the dynamic ultrasound assisted extraction. Extraction time was 20 min and the flow rate of the acetone (J.T. Baker, Netherlands) and methanol (Sigma, Germany) mixture (50:50 *v*/*v*) was 1 mL min^{-1}. The extraction procedure is explained elsewhere [23]. After the extraction, the sample volume was reduced to 2 mL by a gentle stream of nitrogen. For the GCxGC-TOFMS analysis, a 100 μL aliquot was taken and the sample solvent was changed to dichloromethane.

2.4. Chromatographic analysis

GCxGC-TOFMS experiments were carried out on an Agilent 7890A gas chromatograph (Santa Clara, USA) equipped with a split/splitless injector and a LECO Pegasus 4D TOFMS system (St. Joseph, USA). The GCxGC was equipped with a secondary oven and a dual-stage thermal modulator. An HP-1 column (Agilent J&W Scientific, USA; 30 m × 0.25 mm i.d., 0.1 μm film thickness), which proved to be an ideal choice in our previous study [13], was used as the first-dimension column, and an ionic liquid-based SLBTM-IL 59 (Supelco, USA; polar, 1 m × 0.1 mm i.d., 0.08 μm film thickness) was used as the second-dimension column (housed in the secondary oven).The columns were connected with a universal press-fit connector (Restek, USA). The sample (1 μL) was injected in split mode (5:1) at 250 °C, and helium was used as carrier gas at constant pressure (90 kPa). The temperature of the first-dimension column was programmed from 35 °C (2 min) to 280 °C (5 min) at a rate of 10 °C/min, and that of the second-dimension column from 40 °C (2 min) to 280 °C (5 min) at 10 °C/min. The interface between the GC × GC and TOFMS was maintained at 280 °C and the ionization source at 230 °C. Electron ionization (EI) at 70 eV was used and the spectrum storage rate was 50 Hz. Samples were analyzed three times. Data acquisition and processing were accomplished with LECO ChromaTOF™ optimized for the Pegasus 4D software (version 3.34). The National Institute of Standards and Technology (NIST) EI mass spectrum database was used for the spectral search.

For comparison, model analytes were also analyzed by GC–MS with a temperature-gradient. A gas chromatograph (Agilent 6890N, USA) equipped with a mass selective detector (Agilent

5973N, USA) was used with the same column (first-dimension column) and analysis conditions as for the two-dimensional runs.

2.5. Calculations

The subcooled liquid vapor pressure of an analyte was determined from the known vapor pressures of the reference compounds eluting immediately before and after the analyte and the retention times of the reference compounds and the analyte (Eq. (1)) [7].

$$\log P^\circ = \frac{(\log P_1^\circ - \log P_2^\circ)t_R + t_1 \log P_2^\circ - t_2 \log P_1^\circ}{t_1 - t_2} \qquad (1)$$

P° and t_R are the vapor pressure and retention time of the unknown compound, and P_1°, P_2°, t_1 and t_2 are the vapor pressures and retention times of the known reference compounds. Solid-state vapor pressure can be derived from subcooled value. However, since the later is more frequently used, it was not done in this research.

3. Results and discussion

Vapor pressures of the model analytes (oxidation products of terpenes) were first determined by conventional GC–MS with a temperature-gradient program and compared with vapor pressures determined by the retention index method [13]. A solution containing the model analytes and all reference compounds of the study was then analyzed by GCxGC-TOFMS, and the vapor pressure values obtained were compared with those obtained by our optimized GC–MS method, the retention index method (isothermal) [13], and literature values. The final steps were to test the method on an atmospheric aerosol samples and evaluate the feasibility of the method for derivatized (trimethylsilylated) compounds.

3.1. Temperature-gradient GC–MS

The method based on temperature-gradient, as proposed by Donovan [7], was tested in conventional GC–MS before the GCxGC experiments. Alkanes were used as the reference series to allow comparison of the results with those previously obtained by our group by retention index method [13]. As can be seen from Table 1, results obtained by temperature-gradient method agreed well with those obtained earlier in isothermal runs. Conventional techniques, by comparison, have numerous disadvantages for vapor pressure measurements and may produce errors of an order of magnitude or even more relative to the true values [24]. Thus, the differences shown here can be considered insignificant. Interestingly, vapor pressure values obtained by the gradient elution method were higher for acids and lower for alkanals than values obtained in isothermal runs suggesting the need for more specific reference compounds than alkanes. The analysis time was decreased markedly relative to the isothermal method where numerous runs (five repeated runs at seven temperatures) were needed. Assured that the GC–MS method worked nicely, we proceeded to a study exploiting the unique separation power of comprehensive 2D gas chromatography.

3.2. GCxGC-TOFMS

The mixture of analytes and reference compounds was analyzed three times by GCxGC-TOFMS with a temperature-gradient program. The first- and second-dimension retention times were derived manually since retention times assigned with the complicated 2D software tend to be unreliable. Vapor pressures of the model analytes were determined using equation provided above and applying the different homolog series (alkanes, alkanols, alkanals, and alkanones). In this way, interactions associated with the different functional (polar) groups were more or less taken into account. The data are given in Supporting information Tables S1–S5. The 2D plot of the analyzed mixture is presented in Fig. 1, and the vapor pressure values determined for the model analytes are given in Table 1. For comparison, values obtained by GC–MS method and theoretical values calculated by group contribution method are included [13].

As can be seen, vapor pressure values determined by the different experimental techniques deviate by less than one order of magnitude. This is understandable since the same principle underlies all. One would nevertheless expect greater deviations for the reference series representing different functionalities, which were used for the correction of specific interactions. In this study, the only notable differences in the values were for pinonaldehyde (almost one order of magnitude smaller with alkanols as reference compounds). Although the alkanal series clearly should be used for pinonaldehyde, the difference in values for pinonaldehyde obtained with the alkanals and alkanes as reference series is surprisingly small (11.41 vs 10.86 Pa). Although data for the

Table 1
Experimental vapor pressure (Pa) and $-\log P$ values obtained for model analytes by GCxGC-TOFMS using references series with different functional groups. Values obtained by GC–MS in isothermal and gradient runs and theoretical values are included for comparison. *n.a.*-Poor reference vapor pressures in the literature did not allow calculations; n.a.-Pinic acid standard was not available to us as a pure compound.

Compound	β-Caryophyllene aldehyde		β-Nocaryophyllene aldehyde		Pinonaldehyde		*cis*-Pinonic acid		*cis*-Pinic acid	
	$-\log P$	P	$-\log P$	P	$-\log P$	P	$-\log P$	P	$-\log P$	P
Reference series in GCxGC-TOFMS										
Alkanes	1.07	0.09	1.23	0.06	−1.04	10.86	−0.41	3.16	n.a.	n.a.
Alkanols	*n.a.*	*n.a.*	*n.a.*	*n.a.*	−0.26	1.81	0.26	0.54	n.a.	n.a.
Alkanals	*n.a.*	*n.a.*	*n.a.*	*n.a.*	−1.06	11.41	−0.47	2.92	n.a.	n.a.
Alkanones	0.97	0.11	1.07	0.08	−0.76	5.73	−0.08	1.19	n.a.	n.a.
Comparative method										
GC–MS (alkanes, isothermal)[a]	0.74	0.18	0.74	0.18	−1.22	16.68	−0.06	1.15	0.74	0.18
GC–MS (alkanes, gradient)	0.95	0.11	1.06	0.09	−1.14	13.71	−0.22	1.65	0.20	0.63
theory (group contribution)[a]	−0.19	1.55	0.69	0.20	−1.03	10.70	0.27	0.53	1.22	0.06

[a] From Hartonen et al. [13].

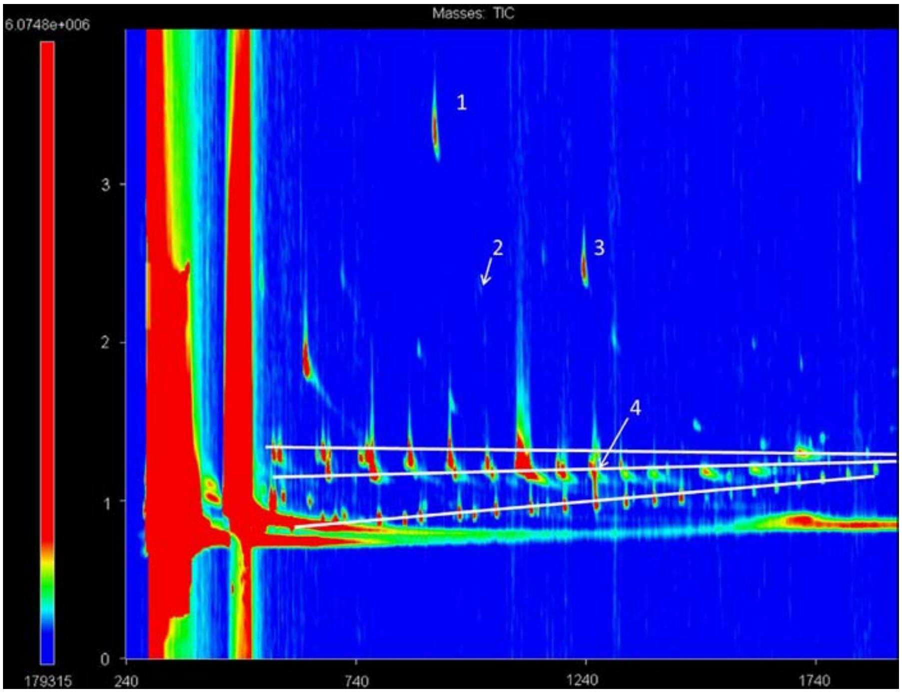

Fig. 1. GCxGC-TOFMS chromatogram (2D) of mixture containing the model analytes and all reference compounds. White lines represent the homolog series: lower line alkanes, middle line alkanals, upper line alkanols together with ketones. 1 Pinonaldehyde, 2 *cis*-pinonic acid, 3 β-caryophyllene aldehyde, 4 β-nocaryophyllene aldehyde.

alkanals of β-caryophyllene were insufficient, the data obtained with the alkane and alkanone series suggest that alkanes can be used for the calculations just as well as compounds with similar functionality (i.e., alkanals).

cis-Pinonic acid exhibited exceptional behavior: the value obtained with the alkanol series was closest to the theoretical value, and the value obtained with the alkanes was almost six times higher. Assuming that the theoretical values (obtained by the group contribution method) are the “true” values, we can conclude that a polar reference series should be used for compounds more polar than alkanals. Literature values for *cis*-pinonic acid are few, but Booth et al. [25], for example, determined its vapor pressure (by Knudsen effusion mass spectrometry) to be 1.29×10^{-4} Pa (solid) and 7.78×10^{-4} Pa (subcooled liquid) with uncertainty estimates of 40% and 75%, respectively. Our considerably higher vapor pressure for *cis*-pinonic acid is reasonable since it elutes between tridecane and tetradecane (or 1-decanol and 1-undecanol). The similarity between our experimental value and the value calculated by group contribution theory (0.53 Pa) suggests that other methods underestimate the volatility.

3.3. *Unknown compounds in aerosol sample*

Samples of atmospheric aerosols are highly complex and their chemical composition varies according to the time and place of sampling. Numerous studies have nevertheless shown that they always contain alkanes, alkanols, alkanals, and alkanones [26]. Since no addition of references standards is therefore required, an aerosol sample, as a multicomponent system, is an ideal choice for evaluating the present method. With no addition of references the authenticity of the samples is guaranteed, and quantitative analysis is possible if desired. With the present study we also wished to demonstrate the applicability of comprehensive 2D GC with MS detection for the determination of basic physicochemical properties of compounds, and atmospheric aerosol samples provide an excellent platform for this.

After extraction (Section 2.3), the sample was analyzed under the same conditions as the mixture of model analytes and reference compounds. A 2D plot of the aerosol sample is shown in Fig. 2. (The 3D-plot is reproduced in the Supporting information, Fig. S1.) As can be seen, the familiar hydrocarbon pattern appears close to one second in the second dimension through the whole chromatogram. Functionalized hydrocarbons give smaller peaks and are not clearly seen at this magnification. Eight compounds with atmospherically relevant structure were selected from the chromatogram according to NIST database search and their vapor pressures were determined (Table 2). Only first-dimension retention times were used, leaving the second dimension for the structural elucidation. Two compounds with the same retention time in the first dimension but well separated in the second dimension were selected for more detailed study. It is clear that these compounds have the same values of vapor pressure, but only GCxGC could separate them.

Reference compounds were chosen according to the proposed structures of the compounds, while only hydrocarbons were used for the late eluting compounds since no suitable polar compounds with known vapor pressures were found in the literature. Alkanol and alkanone series were used as reference compounds for the menthol derivative and, as can be seen from Table 2, the alkanone series gave the more reasonable value. This illustrates one disadvantage of the proposed method: namely, it may be difficult to find a suitable reference series for compounds with several different functionalities. The difference in values in the present case was nevertheless relatively small.

As is clear from Table 2, GCxGC-TOFMS offers the atmospheric chemist a unique tool for the determination of vapor pressures. In chamber experiments, the products produced in gas-phase reactions can be identified with the help of the high separation power of GCxGC and spectral information of TOFMS, and their vapor pressures can be calculated simultaneously. The researcher thus has the opportunity to evaluate the relevance of compounds for aerosol formation and growth and at the same time obtain other relevant information.

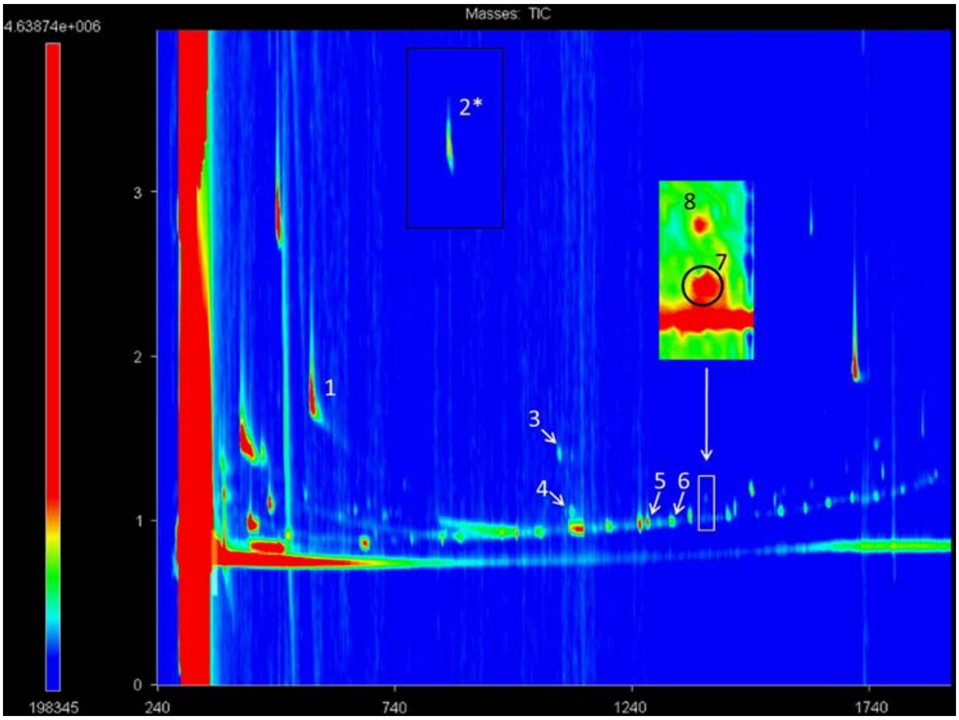

Fig. 2. GCxGC-TOFMS chromatogram (2D) of the aerosol sample. Numbering of the compounds follows that of Table 2. 2* indicates the extracted ion chromatogram of m/z 83 (pinonaldehyde), the remaining compounds are shown in total ion chromatogram mode.

Table 2
Vapor pressures of selected compounds in an atmospheric aerosol sample at 298 K. RT_1 and RT_2 are the retention times in the first and second dimensions.

N	Compound name (NIST)	Reference compound series	RT_1	RT_2	Vapor pressure, (Pa)
1	2-Butoxy-ethanol	Alkanes	564	1.779	1083.93
2	Pinonaldehyde	Aldehydes	908	3.38	12.05
3	1'-(Butyn-3-one-1-yl)-,(1S,2S,5R)-menthol	Alkanols and ketones	1088	1.408	0.140 and 0.640
4	2,6-bis(1,1-Dimethylethyl)-4-methylphenol	Alkanes	1116	1.055	0.57
5	2,4-Diisopropyl-1,1-dimethyl-cyclohexane	Alkanes	1272	0.998	0.03
6	10-Heneicosene	Alkanes	1324	1.002	0.012
7	Dodecanoic acid, methyl ester	Alkanes	1396	1.145	0.006
8	Tetrahydroaraucarolone	Alkanes	1396	1.366	0.006

3.4. *Effect of derivatization*

Trimethylsilylation is the most widely used derivatization technique, mainly but not exclusively for hydroxylic groups. Neutral and acidic (phenol and carboxyl) hydroxyl groups are likely to cause problems in GC can be derivatized by silylation. In general, derivatives are less polar, more volatile, and more thermally stable than the original compounds. The characteristic ion, $(CH_3)_3Si^+$ (m/z 73), produced by silylated compounds in MS can be helpful in the analysis. In this study, we evaluated the effect of silylation on the determination of vapor pressures of alkanols and alkanals. Silylated mixtures were analyzed, and plots of $-\log P$ of the corresponding nonderivatized compounds versus retention times of the derivatized compounds were constructed (Fig. S2 and S3). Vapor pressures of nonderivatized alkanols and alkanals were utilized because values for the silylated compounds were not available. (Vapor pressures of the silylated alkanols and alkanals could have been obtained by using alkanes as references, but as the same technique would then have been applied for the reference and studied compounds, this was not done.) Evidently, both plots were linear, like those obtained for the corresponding nonderivatized compounds. Evidently silylation does not adversely affect the determination of vapor pressures by the proposed method. On the contrary, derivatization allows it to be applied to less volatile compounds. The sole limitation pertains to multifunctional compounds with multiple derivatization sites.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.02.051.

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