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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 tetrahydroararucalone 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.

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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 $\leq 2.5 \mu\text{m}$) 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 $0.5 \mu\text{g mL}^{-1}$.

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 ($0.5 \mu\text{g mL}^{-1}$).

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 \times 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 \times 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 \times 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

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