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Vapor pressure determinations of 8-2 fluorortelomer alcohol and 1-H perfluorooctane by capillary gas chromatography Relative retention time versus headspace methods

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Abstract

Two distinctly different capillary gas chromatographic methods were used to determine the vapor pressure of 8-2 fluorotelomer alcohol (8-2 FTOH) and 1-H perfluoroheptane at several temperatures. For measurements employing the relative retention-time method, a short polymethylsiloxane column was used from 25 to 65 °C. For the 8-2 FTOH, hydrocarbon alcohols and perfluoroalcohols were used as reference standards. For 1-H perfluoroheptane, hydrocarbons were used as reference standards. Vapor pressure estimates could differ by as much as an order of magnitude compared to published results determined by other (nonchromatographic) methods. This variance may be a function of solvent-solute interactions within the gas chromatographic column and the infinite dilution assumption, both used in the relative retention method. For comparison, data were also gathered using headspace gas chromatography (GC) with atomic emission detection (AED). The results from this novel GC/AED method were consistent with prior nonchromatographic results. A discussion of why headspace is the preferred technique for the determination of vapor pressure for fluorinated compounds is presented.

Keywords: Vapor pressure; Gas chromatography; AED; 1-H perfluoroheptane; Fluorotelomer alcohol; Headspace

1. Introduction

Aqueous solubility and vapor pressure are two important physicochemical parameters used to estimate the potential for transport of chemical substances in the atmosphere. For fluorotelomer alcohols and fluorinated hydrocarbons that are sparingly soluble in water, vapor pressure is probably the more significant factor. Vapor pressure is an essential physical property widely used to quantify the "volatility" of a chemical and is a key input parameter used to predict and understand environmental partitioning behavior [1].

Gas chromatography has provided a tool used by environmental scientists for quickly estimating the vapor pressure of volatile organic compounds. If compounds of known vapor pressure (by another non-gas chromatographic method of measurement) and of similar chemical structure are used as reference compounds, vapor pressure can be estimated quite accurately and precisely, even for extremely impure substances which can be separated on the chromatographic column. The gas chromatographic method is based on the principle that retention time is inversely related to vapor pressure. A wide variety of alcohol vapor-pressure estimates have been performed by GC [2–6]. The key assumptions for this technique are that the molecule behaves inside the column just as it does in the bulk, and that the reference and analytical materials interact with the stationary phase identically (and preferably in a nonspecific manner). Column selectivity is not desired.

Recently fluorotelomer alcohol vapor pressure measurements were reported by Lei et al. [7]. The method was based on the methods of Bidleman [8] and Wania et al. [9] using isothermal gas chromatographic retention time measurements.

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These data on fluorotelomer vapor pressure agreed with other work published by the same group (Stock et al. [10]), but differed significantly from other recently published measurements [11,12] determined by nonchromatographic methods. The expected trend for the vapor pressure of the homologous series reported by both Lei [7] and Stock et al. [10] were not consistent with the trend derived from data from homologous series of perfluorinated alkanes [13,14]. The expected trend did apply to the data [11,12] obtained from nonchromatographic measurements.

For comparison, we also present vapor pressure data gathered via headspace GC/AED from 45 to 60 °C. Headspace GC has a distinct advantage compared to the relative retention time method for semi-volatile compounds, as the two major assumptions present in the relative retention time method are not applicable when determining vapor pressure via headspace GC. However, in the headspace method the compound of interest must be reasonably pure (>98%).

1-H perfluoroheptane has been reported as a degradation product in the thermolysis of ammonium perfluorooctanoate [15], a fluoropolymer processing aid [16], and perfluorooctanoic acid [17]. Since vapor pressure data are needed to understand its fate in the environment, it is necessary to determine this information accurately.

2. Experimental

2.1. Chemicals

The 8-2 FTOH (CAS #678-39-7); CAS name 1-decanol,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro) was obtained from Clariant (Germany) and was shown to be 99.2% pure via gas chromatography. The major impurity was identified as an unsaturated 8-2 fluorotelomer alcohol (CAS No. 256384-09-5, $C_7F_{15}CF{=}CHCH_2OH$).

1-H perfluoroheptane (CAS No. 27213-61-2, $CHF_2(CF_2)_5CF_3$) was obtained from Matrix Scientific (Columbia, SC, USA) and was shown to be 98.7% pure via both electron impact (EI) and chemical ionization (CI) mass spectrometry (MS). The two most prominent impurities are identified as 1-H perfluorohexane (∼0.1%) and 7-chloroperfluorohept-1-ene (0.5%).

Vapor pressure standards were purchased from various vendors and used as received (Table 3).

2.2. Equipment

Agilent (Wilmington, DE, USA) model 6890N series gas chromatographs equipped with a split/splitless injection port and either a flame ionization detection (FID) system, a mass-selective detection (MS) system (5973N), or an atomic emission detection (AED) system (G2350A) were employed in these studies. For the 8-2 FTOH using AED, the carbon 193 nm emission line was monitored; for the 1-H perfluoroheptane, the carbon 496 nm line was monitored since the signal was strong and this is a less sensitive emission line.

2.3. Procedure

2.3.1. Relative retention time method

Chromatographic conditions varied depending on the temperature. For the 25 °C study, a 0.75 m Restek RTX-1 column (100% dimethylpolysiloxane) (0.32 mm, 3 μm film thickness) was used. For the higher temperature experiments, a 4 m column was used. Carrier gas linear velocity was typically 100 cm/s. Injections were split but, importantly, the gas saver was not used in order to minimize disruptions in the pressure at the head of the column. Temperatures were controlled by the gas chromatograph but monitored with a US National Institute of Standards and Technology (NIST)-traceable digital thermometer. The variation between the set point and measured temperatures was typically 0.1 °C. This variation was ignored in subsequent calculations. The transit time through the column for a non-retained peak was estimated by injecting methane using the same syringe and injection system as for the rest of the study.

Vapor pressure was determined using the relative retention time measurement method [8]. Reference standards of known vapor pressure were diluted in 1-octanol (∼500 ppm). The split ratio was set to 50:1. Data treatment followed that of Bidleman [8]. For the 8-2 FTOH measurement, sets of normal hydrocarbon alcohols and fluoroalcohol standards were used. Vapor pressure data for the vapor pressure standards were obtained from the CRC Handbook [18] and from the literature [19].

2.3.2. Headspace GC/AED method

For the 8-2 FTOH, the AED response was calibrated with decane; for the 1-H perfluoroheptane, octane was used. The vapor pressure of the standard at the temperatures of interest was calculated by fitting literature values of the vapor pressure to the Antoine equation and interpolating. A temperature program starting at 50 °C for 1 min followed by a 10 °C/min ramp to 140 °C on a Phenomenex (cross-linked arylene) ZB5MS column (30 m × 0.25 mm, 1.0 μm film thickness) was used. One injection from each of six vials (three reference standards and three sample) (20 mL headspace vials, Agilent, Little Falls, DE, USA) was made after equilibrating for a total of 16 h. The vapor pressure was calculated by the following equation:

$$P_i = P_{ref} RF \left(\frac{A_i}{A_{ref}}\right)\left(\frac{M_{ref}}{M_I}\right)$$

where P is the vapor pressure, RF the relative response factor for the two compounds (1.02 for the present case at both wavelengths), A the detector area response, and M is the molar mass.

3. Results and discussion

The determined vapor pressures via all methods for the 8-2 FTOH are presented in Table 1. Note that the results for the headspace method and the nonchromatographic methods (NMR and boiler) agree quite well. The vapor pressure results for 1-H perfluoroheptane appear in Table 2. The retention time method vapor pressure results are two orders of magnitude higher than that of the headspace method for both substances. The adjusted retention times of the analyte and standards were not very great

Table 1
Vapor pressures for 8-2 fluorotelomer alcohol

Temperature (°C)	Retention time method (Pa)	Headspace GC/AED method (Pa)	Krusic (ref. [11]) (Pa)	
			NMR[b]	Boiler[c]
25[a]	31	–	4	7
35	81	–	11	18
45	205	29	30	45
50	–	40	47	69
55	418	47	73	103
60	–	80	110	151
65	912	–	163	218

[a] 3 Pa @ 21 °C (ref. [10]); 45.90 Pa (ref. [6]).
[b] Via gas-phase nuclear magnetic resonance spectroscopy.
[c] Via Scott method.

Table 2
Calculated vapor pressures for 1-H perfluoroheptane

Temperature (°C)	Retention time method (kPa) (vs. pentane reference)	Retention time method (kPa) (vs. heptane reference)	Headspace GC/AED (kPa)
45	226	171	3.9
55	319	239	5.8
65	445	316	8.2
75	605	423	11.5
85	808	558	15.4

since neither the hydrocarbon standards nor 1-H perfluorheptane are very well retained under these conditions.

The vapor pressure standards are listed in Table 3. The vapor pressures of the standards at different temperatures were derived by fitting literature values to the Antoine equation. The fits were typically quite good with a correlation coefficient, R^2 greater than 0.999. Vapor pressures interpolated from these Antoine fits were used for the calibration standards.

The relative retention time method for determining vapor pressures can be quite accurate when two conditions have been met. The first condition is that the calibration standards and the analytes must exhibit similar behavior in both the bulk and inside the column. In other words, the standards and the analytes must be as chemically and structurally similar as possible. Bidleman [8], for example, recommended the relative retention time method for nonpolar molecules where there would not be any appreciable hydrogen bonding. He found that *n*-alkanes were preferable for this work and that one reference, di-*n*-butyl

Table 3
Calibration standards for relative retention time method

1-Propanol (100%, J.T. Baker, Phillipsburg, NJ)
1-Butanol (99.5%, Aldrich, Milwaukee, WI)
1-Pentanol (>99.5%, Aldrich, Milwaukee, WI)
1-Hexanol (98%, Eastman Kodak, Rochester, NY)
1-Octanol (>99%, TCI America, Portland, OR)
n-Pentane (>99%, Aldrich, Milwuakee, WI)
n-Heptane (99.9%, EMD Scientific, Darmstadt, Germany)
2,2,3,3,3-Pentafluoropropan-1-ol (97%, Aldrich, Milwaukee, WI)
2,2,3,3,4,4,4-Heptafluorobutan-1-ol (98%, Oakwood, West Columbia, SC)

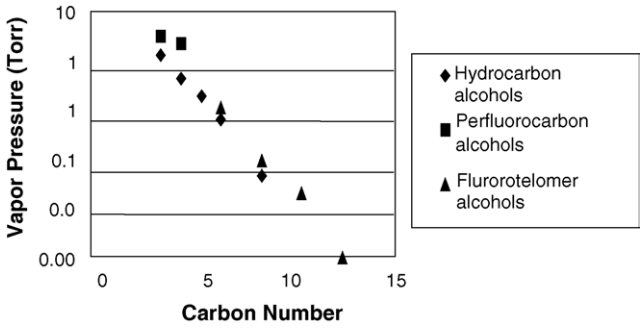

Fig. 1. Plot of log vapor pressure vs. carbon number for several alcohols.

phthalate showed evidence of specific interaction with some gas chromatographic phases. Thus, alcohols can only be calibrated with other alcohols. The reason is straightforward. Hydrogen bonding causes alcohols to have a significantly reduced vapor pressure relative to non-hydrogen bonded molecules of identical molecular weight. Within a gas chromatographic column, the molecules are ideally isolated from all others. This is the so-called "infinite dilution" condition. Alcohols under this condition cannot hydrogen bond and behave as if they were alkanes. For instance, at 40 °C decane and octanol have almost identical retention times, even though their vapor pressures differ by greater than an order of magnitude (555 and 40 Pa, respectively). Inadvertently calibrating with alkanes will cause a systematic over-estimation of the vapor pressure of telomer alcohols. Based on the example above, this error can easily be an order of magnitude or greater.

The second condition that must be met in order to generate accurate vapor pressure determinations via the relative retention time method is related to the stationary phase of the column. These measurements are often performed on a 100% poly(dimethylsiloxane) (PDMS) column- the so-called "boiling point" column since there are predominantly nonspecifically interactive methyl groups on the surface. The applicable assumption is that all molecules will dissolve into and diffuse out of the PDMS coating similarly and that the vapor pressure alone will determine the relative amount of time that the molecule remains in the mobile phase. For most compounds, this is a good assumption. For fluorinated materials including fluoroalcohols, this condition is not met; a plot of log vapor pressure versus carbon number for several alcohols yields essentially parallel lines for the fluorotelomer and hydrocarbon alcohols. [*Note*: retention for the two perfluoroalcohols on this column was short, so it is not possible to make a similar comparison (Fig. 1).] The oleophobic nature of the perfluorinated tails may account for their lack of retention on the boiling point column [20]. Hydrocarbon moieties, on the other hand, are oleophilic and will probably partition into the stationary phase readily. The oleophilicity of the hydrocarbon references may account for their longer retention on this column relative to perfluorocarbons of the same carbon chain length.

The headspace method can only be used with relatively pure substances, so it is not as flexible as the relative retention time method. However, these results demonstrate that the headspace method is a more direct way of measuring vapor pressure of

organic substances and also avoids the problems inherent in interaction between the stationary phase and the analytes. The fact that the headspace data agree with two different nonchromatographic measurements indicates that the headspace data are most likely accurate.

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