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DETERMINATION OF THE SATURATED VAPOUR PRESSURE OF FRAGRANCES USING GAS CHROMATOGRAPHY

T. A. RUDOLFI[*], M. M. SHCHEDRINA, L. O. MINDLIN and K. K. PRILEPSKAJA

All-Union Research Institute of Natural and Synthetic Odour Substances, Profsojusnaja 66, Moscow (U.S.S.R.)

SUMMARY

A simple method of determination of saturated vapour pressure has been developed using gas chromatographic and temperature programming. The concentration of the saturated vapour over 150 fragrances has been measured in the carrier gas flow ($P^{20} = 7.47 \cdot 10^{-4}$–140 Pa), using a comparative method involving a standard hydrocarbon. The saturated vapour pressures at 20°C for the substances studied were found by means of extrapolation.

INTRODUCTION

Data on the saturated vapour pressure (SVP) of fragrances are of great interest in perfumery because this basic physical parameter gives an indication of the rate of evaporation.

Using gas chromatography (GC) we have developed some different methods of SVP determination which yielded very similar results[1,2]. The most convenient method is the use of flame ionization detection (FID) under temperature-programmed conditions[3].

The concentration of saturated vapour in the carrier gas flow is measured, the saturation having been attained by cooling the capillary tube containing the vapour–gas mixture obtained in the injector. A comparative measurement is performed for a standard hydrocarbon having a SVP close that of substance being examined. The standard and the examined substance are injected simultaneously into two injection ports of the same chromatograph in order to ensure identical conditions of measurement. The signals corresponding to the SVP of the substance and of the standard from two independent flame ionization detectors at the same temperature are recorded by a dual-pen recorder on the same chart. So, we obtained a number of SVP values in one (temperature-programmed) experiment at different temperatures. The range of determination was mainly 50–150°C with SVP values of 13.3–1333 Pa. The SVP values for the examined substances at 20°C were found by linear extrapolation. The validity of the data obtained at low temperatures was confirmed by comparison with data obtained earlier by the effusion technique[4].

The accuracy of these measurements was about 15–20%.

EXPERIMENTAL

A sample of the substance to be examined and of the standard (6 μl of each) were injected simultaneously into two injection ports of the Model LCM-8MD gas chromatograph in which two stainless-steel capillary columns (0.5 m × 1 mm I.D.) had been installed. The sensitivities of the two detectors were made equal by correction of the hydrogen flow-rate of each flame, using the responses from the same substance. The temperature programme runs from 50 to 150°C at 2°C/min.

The SVP was calculated from

$$P = \frac{h}{h_{st}} \cdot \frac{n_{st}}{n} \cdot P_{st}$$

where P and P_{st} are the SVP values of the substance being studied and of the standard, respectively; h and h_{st} are the responses of the detectors to the substance and the standard, respectively measured over intervals of 5°C; and n and n_{st} are the effective numbers of carbon atoms in the substance and the standard, respectively, as calculated from increments.

After each experiment the apparatus was operated at 230°C until a constant baseline was obtained.

DISCUSSION

The SVP values of more than 150 different fragrances having 9–17 carbon atoms have been measured using the method described. The range of values was $7.5 \cdot 10^{-4}$–140 Pa at 20°C.

According to their volatilities, the examined compounds can be separated into five groups for which the vapour pressure differs by an order of magnitude (Table I). The first group includes compounds with SVP values of 18.9–140 Pa. The molecules of these compounds mostly contain nine carbon atoms. The second group has SVP values in the range of 1.62–9.1 Pa and includes the compounds with 10–13 carbon atoms. The third and largest comprises compouns with SVP values in the range $1.35 \cdot 10^{-1}$–$12.8 \cdot 10^{-1}$ Pa. These compounds have 10–15 carbon atoms. The fourth group includes compounds with low SVP values of $1.44 \cdot 10^{-2}$–$10.9 \cdot 10^{-2}$ Pa and 15–17 carbon atoms. The fifth group had the lowest SVP values in the order of 10^{-3}–10^{-4} Pa and 11–17 carbon atoms.

TABLE I

VOLATILITY CLASSIFICATION OF FRAGRANCES

Group	P (Pa) at 20°C	No. of carbon atoms in the molecule
I	18.9–140	9
II	1.62–9.1	10–13
III	$1.35 \cdot 10^{-1}$–$12.8 \cdot 10^{-1}$	10–15
IV	$1.44 \cdot 10^{-2}$–$10.9 \cdot 10^{-2}$	15–17
V	$7.5 \cdot 10^{-4}$–$11.1 \cdot 10^{-3}$	11–17

TABLE II

SATURATED VAPOUR PRESSURES OF FRAGRANCES AT 20°C (SUMMARY)

Class of substance	Mol.wt.	P (Pa)	Ref.
Unsaturated aldehydes and aliphatic alcohols	140–210	$1.35 \cdot 10^{-1}$–84	5
Cyclic acetals of aliphatic aldehydes	158–214	$9.7 \cdot 10^{-1}$–29	6, 8
Phenylsubstituted aldehydes (analogues of cinnamic aldehydes)	134–160	$4.8 \cdot 10^{-1}$–4.3	6
Phenylsubstituted alcohols	164	$2.4 \cdot 10^{-1}$–$4.7 \cdot 10^{1}$	6
Macrocyclic lactones	212–268	$1.87 \cdot 10^{-2}$–$3.1 \cdot 10^{-1}$	1
Esters of methylisohexyl-cyclohexanols	240–268	$3.6 \cdot 10^{-2}$–$8.3 \cdot 10^{-1}$	7
Tetrahydropyran derivatives	172–242	$7.9 \cdot 10^{-2}$–$1.87 \cdot 10^{-1}$	8
Macrocyclic oxalactones and macrocyclic diesters	228–284	$7.5 \cdot 10^{-4}$–$1.76 \cdot 10^{-1}$	1, 9

This classification is of great practical interest (Table II). Unsaturated aldehydes and aliphatic alcohols having molecular weights from 140 to 210 are the most volatile compounds. Cyclic acetals of aliphatic aldehydes are of similar volatility. Phenyl-substituted aldehydes (analogues of cinnamic aldehydes) and phenyl-substituted alcohols of medium volatility (mol.wt. = 134–164). Macrocyclic lactones and esters of methylisohexylcyclohexanols have low volatility (mol.wt. = 212–268). Tetrahydropyran derivatives, macrocyclic oxalactones and macrocyclic diesters of the compounds studied are the least volatile fragrances (mol.wt. = 172–284).

Certain SVP values can be used in assessing the fragrances in perfumery as well as in classifying substances according to their flammability and explosiveness.

REFERENCES

1 S. A. Voitkevich, M. M. Shchedrina, N. P. Solovjeva and T. A. Rudolfi, *Maslo-jirovaja promichlennost*, N11 (1971) 27.
2 M. M. Shchedrina, T. A. Rudolfi, L. O. Mindlin and K. K. Prilepskaja, *Maslo-jirovaja promichlennost*, N10 (1981) 33.
3 T. A. Rudolfi, M. M. Shchedrina, L. O. Mindlin and K. K. prilepskaja, *Maslo-jirovaja Promichlennost*, N9 (1984) 23.
4 S. A. Voitkevich and N. J. Lubochiz. *Masloboinojirovaja promichlennost*, N4 (1957) 20.
5 S. A. Voitkevich, M. M. Shchedrina, K. K. Prilepskaja and T. A. Rudolfi, *Maslo-jirivaja promichlennost*, N9 (1974) 29.
6 S. A. Voitkevich, M. M. Shchedrina, K. K. Prilepskaja, N. P. Solevjeva, E. D. Laskina and T. A. Rudolfi, *Maslo-jirovaja promichlennost*, N1 (1977) 35.
7 S. A. Voitkevich, M. M. Shchedrina, A. S. Podberezina, T. A. Rudolfi and K. K. Prilepskaja, *Maslo-jirovaja promichlennost*, N1 (1979) 27.
8 S. A. Voitkevich, M. M. Shchedrina, K. K. Prilepskaja, N. P. Solovjeva, T. M. Cirkel and T. A. Ruldofi, *Maslo-jirovaja promichlennost*, N12 (1977) 23.
9 S. A. Voitkevich, M. M. Shchedrina, S. G. Poljakova, L. A. Chutikova, T. A. Rudolfi and K. K. Prilepskaja, *Maslo-jirovaja promichlennost*, N2 (1980) 25.