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Headspace gas chromatography with open-tubular columns for determining the evaporation rate of essential oils, perfumery compositions and perfumes

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ABSTRACT

A simple method was developed for determining the evaporation rate of multi-component mixtures using headspace gas chromatography with open-tubular columns. The method allows information to be obtained about changes in the vapour-phase composition during the evaporation of the mixture and is useful for comparing evaporation rates of essential oils, perfumery compositions and perfumes.

INTRODUCTION

The odour stability (the time of characteristic fragrance preservation) of perfumery goods such as perfumes, eau de cologne and soap fragrances depends on the evaporation rate of their constituents.

Well known weighing procedure [1–4] or the use of gas chromatography [5] for the determination of evaporation rate give information only about the total amount of components evaporated up to a predetermined time. The method described here makes it possible not only establish the volatility of sample but also to follow all changes in vapour-phase composition during the evaporation process. This information may be very useful in investigations of essential oils, perfumery compositions and perfumes.

EXPERIMENTAL

The components were evaporated in a glass vessel (Fig. 1) at 30°C from a strip of paper (2.5 × 1.5 cm) moistured with 4 µl of essential oil or perfumery composition or 8 µl of perfume or eau de toilette. Viscous substances were diluted with ethanol. The evaporated substances were transferred by a nitrogen flow (30 ml/min) to a trapping tube (50 × 3 mm I.D.) containing Tenax GC (60–80 mesh). After completion of adsorption (10 min) the tube was inserted into the heated (200°C) injection port of a Biochrom-I gas chromatograph as described previously [6]. The desorbed products were analysed using a glass open-tubular column (50 m × 0.25 mm I.D.) containing OV-101. The flame ionization detector and injection port were kept at 200°C. The column temperature was programmed from 50 to 190°C at 2°C/min. The carrier gas

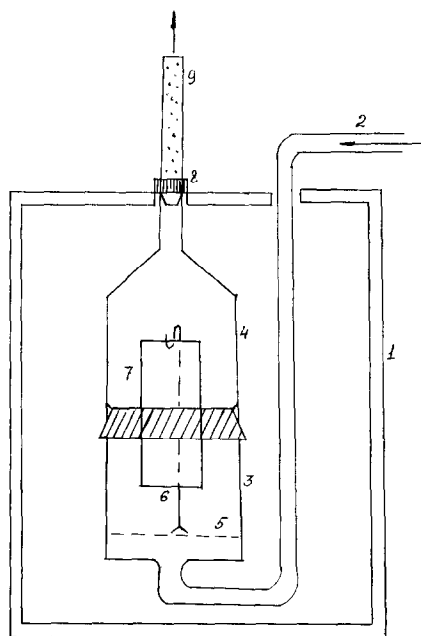


Fig. 1. Glass vessel for liquid sample evaporation: 1 = thermostat; 2 = inlet gas flow tube; 3 = glass vessel for evaporation; 4 = the vessel cap; 5 = porous glass bottom; 6 = support for paper strip; 7 = paper strip moistened with sample; 8 = septum; 9 = trapping tube.

(helium) flow-rate through the capillary column was 1,5 ml/min with an inlet splitting ratio of 1 : 100 for the essential oils and perfumery compositions and 1 : 25 for perfumes and eau de toilette. A Model 1-02 integrator was used to measure the peak areas. Such sampling was repeated every 20–30 min during 5–6 h of evaporation without interruption of the gas flow through the experimental vessel.

The evaporation rate was characterized by means of evaporation curves of plots of the amount of compounds evaporated or the complete area of all chromatographic peaks calculated by the integrator as a function of evaporation time.

RESULTS AND DISCUSSION

According to the theory of evaporation [2], the main part of the evaporation curve (excluding its initial and final parts) may be approximated by an exponential function that gives the quantitative characteristics of the intensity (the amount of substances evaporated) and velocity of the evaporation:

$$S = a \exp(-bt)$$

where S is the total area of all chromatographic peaks, *i.e.*, the total area of the chromatogram, t is the evaporation time and a and b are constants. The constant b characterizes the velocity of the evaporation; a higher value means that the sample evaporates more rapidly. The constant a is equal to $\ln S_0$ at the initial time t_0 , but the

evaporation curve in the initial period cannot be approximated by the exponential function. The values of a and b for various products were determined and are given in Table I.

In a separate experiment with alcoholic solutions containing three odour substances, limonene, linalool, linalyl acetate it was found that the technique described makes it possible to detect less than 10^{-7} g of substance. For headspace analysis the relative standard deviation was less than 0.2% (for clary sage oil, $n = 5$).

The comparative evaporation rates of some essential oils studied previously [5] were determined to confirm the correctness of the method. Lemon oil had the highest evaporation rate (Fig. 2). It evaporates almost completely in less than in 2 h. The absolute value of the constant b for this oil was the highest (Table I).

Initially the clary sage oil evaporates slowly (the evaporation curve has a maximum only after 20 min). The evaporation process for this oil was not finished even after 5 h. The absolute value of b was the smallest. Lavender oil has an intermediate value of b . Fig. 3. shows the vapour-phase chromatograms of this oil after 10 and 50 min of evaporation. For comparison the chromatogram of the liquid phase is shown. Large differences in the relative contents of the components can be seen in the three chromatograms presented.

Under the experimental conditions used, the content of odour substances in the vapour phase for sandalwood and patchouli oils was low (and smaller for the former). During the evaporation it slowly increases in the initial period then very slowly decreases (Fig. 2). Hence the comparative evaporation rates of essential oils studied by headspace gas chromatography were in good agreement with literature data [5], indicating the correctness of the procedure described.

TABLE I

CONSTANTS OF THE EVAPORATION EQUATIONS FOR ESSENTIAL OILS, PERFUMERY COMPOSITIONS, PERFUMES AND EAU DE TOILETTE (CALCULATED ON 5-7 EXPERIMENTS)

Product	Name	Constant	
		$a \times 10^4$	$b \times 10^2$
Essential oils	Clary sage	46.4	1.4
	Lavender	24.0	2.0
	Lemon	50.7	5.4
Perfumery compositions	Shalita	5.1	1.0
	Aethery	23.5	1.1
	Iora	11.7	1.2
	Kontenell	15.5	1.5
	Bergamot oil No. 7	83.6	3.0
Perfumes	Renome (U.S.S.R.)	9.2	0.5
	Legend-I (U.S.S.R.)	12.1	0.6
	Pompon (U.S.S.R.)	8.8	1.0
	Cléa (France)	22.6	0.8
Eau de toilette	Climat (France)	1.2	0.44
	Poison (France)	2.6	0.74
	Lumière (France)	3.7	1.1

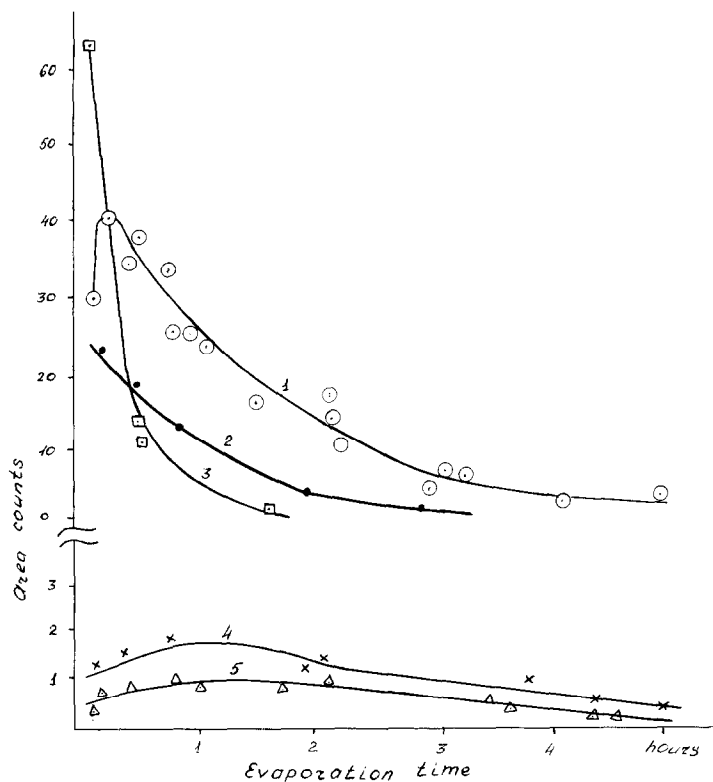


Fig. 2. Evaporation curves for essential oils: 1 = clary sage oil; 2 = lavender oil; 3 = lemon oil; 4 = patchouli oil; 5 = sandalwood oil.

The method was also used to characterize the evaporation rates of some industrial perfumery compositions (Table I). The sensitivity of the method was sufficient for the analysis both perfumes containing 5–50% of perfumery composition and eau de toilette containing 1–15%. The adsorption of ethanol on the adsorbent used (Tenax GC) was poor and did not prevent the gas chromatographic determination of composition.

The evaporation curves for some perfumes of the best quality (the “extra” group) produced in the U.S.S.R. and in France had a similar character (Fig. 4a). The eau de toilette produced in France having a smaller content of perfumery composition had a lower evaporation rate than perfumes (Fig. 4). The evaporation rates for perfumes and eau de toilette were smaller than for essential oils and perfumery compositions. The constant b for these products was 0.0049–0.0100.

Organoleptic examinations by perfumers led to conclusion that all samples of perfumes had sufficient odour stability but was the best for the brand Legend-I (U.S.S.R.) and worst for Pompon (U.S.S.R.). This conclusion was in good agreement with the headspace analysis results. Comparison of the vapour-phase chromatograms showed that during evaporation the odour substances content changed more for

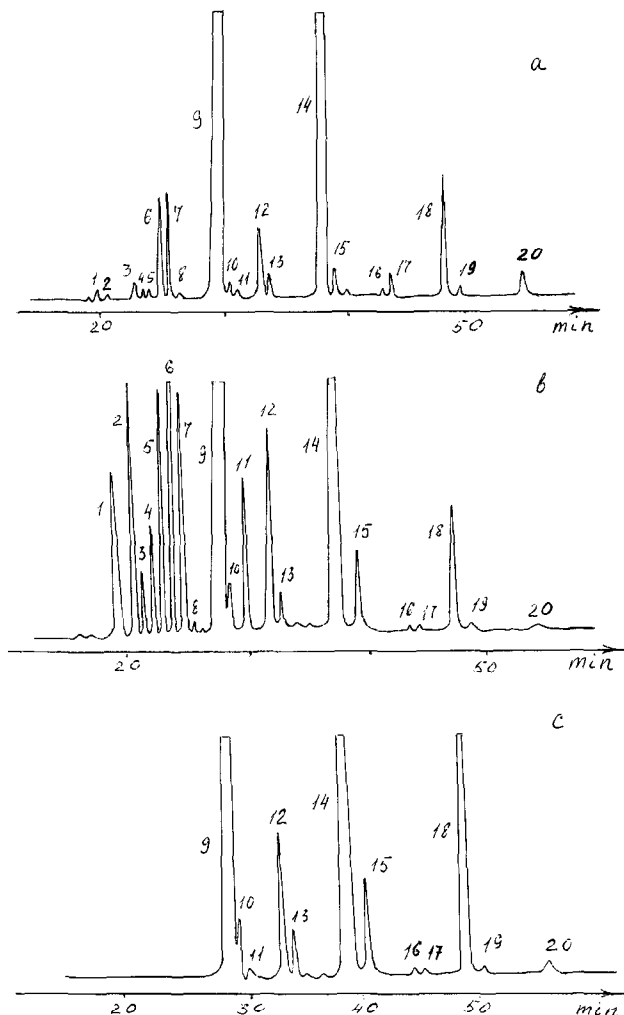


Fig. 3. Chromatograms of lavender oil: (a) liquid sample; vapour phase after (b) 10 min and (c) 50 min of evaporation. Peaks: 1,4,7,8,10,19,20 = unidentified components; 2 = β -pinene; 3 = myrcene; 5 = limonene; 6 = 1,8-cineole; 9 = linalool; 11 = camphor; 12 = terpin-1-en-4-ol; 13 = terpineol; 14 = linalyl acetate; 15 = lavandulyl acetate; 16 = neryl acetate; 17 = geranyl acetate; 18 = caryophyllene.

Pompon than for Legend-I. The constant b for these two perfumes was 0.0110 and 0.0061, respectively.

Both organoleptic and gas chromatographic data showed that the stability of the perfume Cléa (France) is intermediate. For the perfume Renome (U.S.S.R.) direct correspondence between odour stability and evaporation rate was not observed.

Because the content of odour compounds in the vapour phase is the important factor determining the intensity of odour perception, headspace gas chromatography is extremely useful for quality estimation of perfumery products. It gives information about the quantitative and qualitative contents of fragrances in the vapour phase and about changes in composition during evaporation.

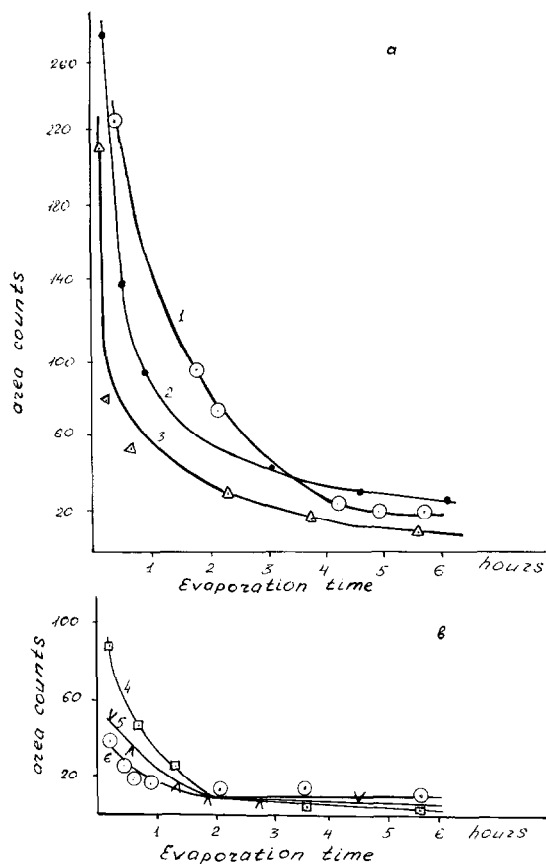


Fig. 4. Evaporation curves for (a) perfumes and (b) eau de toilette. 1 = Cléa; 2 = Legend-I; 3 = Pompon; 4 = Poison; 5 = Lumière; 6 = Climat.

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