Fast Headspace Analysis with Short Microcapillary Columns

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Key Words
Gas chromatography
Headspace analysis
Microcapillary columns
Short columns
Volatile compounds

Summary
A new method of analysis using headspace gas chromatography with microcapillary columns is proposed. Small diameter (50 μm I.D.) fused-silica capillary columns with non-extractable SE-54 and PS-255 poly-siloxane stationary phases were used for the analysis of low boiling organic compounds. The small diameter columns possess the usual very high efficiency so that the method can be employed for the headspace analysis of complex mixtures. The use of short microcolumns reduces the analysis times in comparison to conventional capillary columns. Good performances were obtained in the analysis of volatile compounds in some lemon essential oil, perfumes, and water samples.

Experimental
Reagents
N-pentane, n-hexane, n-heptane, benzene, toluene, methycyclohexane, p-xylene, m-xylene, o-xylene, isopropylbenzene (cumene), n-octanol, methyl alcohol, dichloromethane, trichloromethane, 1,1,1-trichloroethylene, tetrachloromethane, trichloroethene and tetrachloroethene were all from Carlo Erba (Milan, Italy). Sabine, α-thujene, α-pynene, camphene, β-pynene, myrcene, p-cymene, limonene, γ-terpinene, terpinolene, linalool, citronnell, nerol, 4-terpinolene, α-terpineol, neral, linalylacetate, geranylacetate, bornylacetate, citronellylacetate, gerianol, nerylacetate, β-carophyllene, bergamotene and humulene were all from Carl Roth (Germany). The reagents were of analytical-reagent grade with purity ≥ 99%.

The lemon essential oils of Petit-Grain were supplied by the Experimental Station of Essential Oils of Reggio Calabria (Italy). The perfume samples analyzed were commercial products. Distilled water was prepared in our laboratory.

Apparatus
Analysis were performed using a DANI 86.10 HT gas chromatograph (Monza, Italy), equipped with a programmed temperature vaporizer (PTV) injector, a flame-ionization detector (FID) and an electron capture detector (ECD) connected to a Shimadzu recorder-integrator model CR3A.

Headspace vials (20 mL) were sealed with aluminum caps with tear-out center disks and teflon-faced septa. Headspace gas chromatography (HSGC) was carried out on two fused-silica microcapillary columns. The 3 m and 3.60 m long columns (I.D. = 50 μm) were prepared and evaluated according to the procedure described elsewhere [15–19].

Fused-silica microcapillary columns were obtained from SGE (Melbourne, Australia). They were washed with dichloromethane and then leached overnight with 20% hydrochloric acid at 175°C. The microcapillaries were
washed with 1% hydrochloric acid, water and acetone and finally dried under pure nitrogen at 300 °C for 3 hours.

The columns were silanized with a 1:4 mixture of divinyltetramethyldisilazane (DVTMDS) and hexamethyldisilazane (HMDS (Fluka, Buchs, Switzerland), at 400 °C overnight. Appropriate amounts of stationary phases (SE-54 or PS-255, Fluka) and dicumyl peroxide (Fluka) were dissolved in n-pentane to give the desired film thicknesses. The columns were coated statically at room temperature, both ends of the columns were closed by melting, and curing was performed by temperature programming from 50 °C to 160 °C at 3 °C min⁻¹ and holding the final temperature for 30 minutes. After conditioning at 350 °C under hydrogen, the columns were washed with methyl alcohol, dichloromethane and n-pentane.

The microcapillary columns were evaluated by gas chromatography at 90 °C with n-dodecane (C₁₂) using hydrogen as carrier gas.

The first microcolumn (3.00 m) with stationary phase hydrogen as carrier gas. The columns were evaluated by gas chromatography at 90 °C with n-dodecane (C₁₂) using hydrogen as carrier gas.

Essential Oil and Perfume Samples

5 mL of pure lemon essential oil or 10 mL of perfume were put into the vial. It was then closed with a cap containing a polytetrafluoroethylene (PTFE)-coated rubber septum and kept at room temperature for 1 hour. Gas chromatographic analysis was carried out by manually injecting 20 μL of the vial headspace from each sample by means of a 100 μL Hamilton gas tight syringe using the operating conditions described above.

To identify the compounds in the lemon essential oil and perfume samples the following reference solutions were prepared: α-thujene (1 mg mL⁻¹), α-pinene (1 mg mL⁻¹), myrcene (1 mg mL⁻¹), camphene (1 mg mL⁻¹), β-pinene (1 mg mL⁻¹), sabinene (1 mg mL⁻¹), p-cymene (1 mg mL⁻¹) in toluene and limonene (1 mg mL⁻¹), γ-terpinene (1 mg mL⁻¹), terpinolene (1 mg mL⁻¹), linalool (1 mg mL⁻¹), citronellol (1 mg mL⁻¹), 4-terpinolene (1 mg mL⁻¹), α-terpineol (1 mg mL⁻¹), nerol (1 mg mL⁻¹), linalylacetate (1 mg mL⁻¹), geraniol (1 mg mL⁻¹), geranylacetate (1 mg mL⁻¹), bornylacetate (1 mg mL⁻¹), citronellylacetate (1 mg mL⁻¹), nerylacetate (1 mg mL⁻¹), β-cariophyllene (1 mg mL⁻¹), bergamotene (1 mg mL⁻¹) and humulene (1 mg mL⁻¹) in n-pentane. As stated above, these solutions were used only for qualitative analysis.

Water Samples

A concentrated reference solution of n-pentane (12.5 mg mL⁻¹), n-hexane (13.0 mg mL⁻¹), n-heptane (13.6 mg mL⁻¹), benzene (17.5 mg mL⁻¹), toluene (17.2 mg mL⁻¹), methycyclohexane (16.5 mg mL⁻¹), p-xylene (17.3 mg mL⁻¹), m-xylene (17.1 mg mL⁻¹), o-xylene (17.7 mg mL⁻¹), isopropylbenzene (17.3 mg mL⁻¹) and n-octanol (13.9 mg mL⁻¹) was prepared by transferring by means of microsyringe a known volume of each compound into a volumetric flask containing 50 mL of methyl alcohol. A dilute reference solution of the hydrocarbons was prepared by introducing into a 20 mL vial, 10 mL of distilled water to which 1 μL of the concentrated reference solution was added by microsyringe. The vial, which was closed with a cap containing a PTFE-coated rubber septum, was kept at room temperature. The concentration in the liquid phase of each hydrocarbon was as follows: n-pentane (1.25 μg mL⁻¹), n-hexane (1.30 μg mL⁻¹), n-heptane (1.36 μg mL⁻¹), benzene (1.75 μg mL⁻¹), toluene (1.72 μg mL⁻¹), methycyclohexane (1.65 μg mL⁻¹), n-octanol (1.39 μg mL⁻¹), p-xylene (1.73 μg mL⁻¹), m-xylene (1.71 μg mL⁻¹), isopropylbenzene (1.73 μg mL⁻¹).

A dilute reference solution of dichloromethane, trichloromethane, tetrachloromethane, 1,1,1-trichloroethane, trichloroethene and tetrachloroethene was prepared by the same process.

Gas Chromatographic Analysis

Gas chromatographic analysis was carried out by manually injecting 10 μL, for the lemon essential oil and the perfume samples, and 100 μL, for the water samples, of the vial headspace of each sample, under the following conditions:

- PTV total injector analysis, temperature from 50 °C to 260 °C for 2 minutes;
- Splitter valve, always closed;
- Hydrogen as carrier gas, linear velocity as in Figures;
- Column temperature, operating conditions as in Figures;
- Detector temperature, 260 °C for the flame-ionization detector (FID); 240 °C for the electron capture detector (ECD), using nitrogen as auxiliary gas; operative mode with modulated frequency.

Results and Discussion

The chromatograms obtained from the headspace analysis of a sample of lemon essential oil of Petit-Grain are shown in Figures 1 (A and B). The first chromatogram (Figure 1A) was obtained using an SE-54 column (7 m length, 100 μm I.D. with N/m-8600), the second