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Short communication

Packed capillary column solvating gas chromatography of aldehydes

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Abstract

The rapid separation of aldehydes of environmental interest was investigated using packed capillary column solvating gas chromatography (SGC). Fused-silica capillary columns (250 μm I.D.) were packed with poly(dicyanoallylsiloxane)-encapsulated 10 μm spherical porous (80 Å) silica particles. Excellent resolution and good peak shapes were achieved for underivatized aldehydes using carbon dioxide as mobile phase. The effects of temperature and pressure on column efficiency and selectivity were studied. Packed capillary SGC gave better resolution of ten standard aldehydes than open tubular gas chromatography using poly(biscyanopropylsiloxane) as stationary phase, and near-baseline resolution of these aldehydes was obtained in approximately 60 s.

Keywords: Solvating gas chromatography; Aldehydes

1. Introduction

Recently, a new separation method, particularly useful for fast separations, called solvating gas chromatography (SGC) was introduced which utilizes compressible, solvating mobile phases [1–6]. The utilization of a solvating mobile phase in packed column gas chromatography (GC) can greatly improve chromatographic performance, including column efficiency and separation speed [1,2]. The applicability of SGC for the analysis of different compound classes has only begun to be examined [6].

Separation of underivatized aldehydes necessitates the use of polar stationary phases in order to achieve the required selectivity. Low-molecular-mass aldehydes can differ structurally by only a double bond, thus the stationary phase must provide a high degree of selectivity in order to successfully resolve these aldehydes. In this study, we separated low-molecular-mass aldehydes without derivatization using polymer-encapsulated porous silica in packed capillary SGC. We also compared the SGC results to open tubular column GC analysis of the same aldehydes.

2. Experimental

2.1. Materials and instrumentation

All aldehyde standards were purchased from Aldrich (Milwaukee, WI, USA). Spherical porous (80 Å) 10 μm silica particles were purchased from Phenomenex (Torrance, CA, USA). The silica par-

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ticle deactivation polymer, 25% cyanopropyl-substituted polymethylhydrosiloxane, was synthesized in the laboratory. The SGC stationary phase, poly(dicyanoallylsiloxane) (OV-275), and the open tubular GC column, poly(biscyanopropylsiloxane) (SP-2340), were purchased from Supelco (Bellefonte, PA, USA). Fused-silica capillary tubing was purchased from Polymicro Technologies (Phoenix, AZ, USA). Column packing and SGC experiments were performed using the same instrument as described in Ref. [1] with the exception that the chart recorder was replaced with a data acquisition system (EZ Chrome version 6.6, Scientific Software, San Ramon, CA, USA) using an SS420 analog-to-digital converter (Scientific Software) which sampled the flame ionization detection (FID) signal at 60 Hz with an IBM-compatible Pentium 166 personal computer running Windows 95.

2.2. Preparation of OV-275-encapsulated particles for SGC

Porous silica (0.20 g of 10 μm, 80 Å) was coated with 0.040 g of 25% cyanopropyl-substituted polymethylhydrosiloxane following a previously described method [6]. The particles were then transferred into a reaction vessel [7] with 0.030 g of OV-275 stationary phase dissolved in 20 ml of dichloromethane. Argon gas was then bubbled through the mixture at room temperature (~25°C) until the solvent evaporated. Fused-silica capillary columns (250 μm I.D.) were then packed using a CO_2 slurry method previously described [8].

2.3. GC experiments

GC experiments were carried out using manual injection on a Hewlett-Packard 5890 Series II gas chromatograph with FID. Helium mobile phase was used at a split ratio of 100:1. Data were acquired using the data acquisition system mentioned above.

3. Results and discussion

3.1. SGC of aldehydes

In this study, both saturated and unsaturated low-molecular-mass (C_1–C_7) aldehydes were used as test solutes. Because of the structural similarities of these aldehydes, inert and selective stationary phases are needed to provide sufficient resolution. Polymer-encapsulated particles are more inert than conventional bonded phases [9] and cyano groups have been shown to provide selective interaction with double bonds [10–13]. For this study, silica particles were first deactivated with 25% cyanopropyl-substituted polymethylhydrosiloxane and then coated with OV-275. The deactivation step eliminates many of the strong polar silanol groups on the silica surface, and the OV-275 coating provides a highly polar stationary phase. Fig. 1 shows an SGC separation of various aldehydes using both OV-275-encapsulated and ODS-bonded particles. The OV-275-encapsulated particles provided excellent resolution of the aldehydes with good peak shapes and minimal tailing, while the commercial ODS-bonded particles gave tailing peaks and poor selectivity. This suggests that the OV-275-encapsulated particles are more inert than the ODS-bonded particles and simultaneously provide the desired selectivity.

3.2. Column efficiency and selectivity

One advantage of SGC is its ability to utilize the solvating power of the mobile phase to enhance analysis speed. As the inlet pressure is increased, the solvating power of the mobile phase increases, resulting in lower solute retention and thus an increase in theoretical plates s^{-1} (N_t). Increasing the column inlet pressure from 150 to 250 atm at constant temperature led to a decrease in overall column efficiency from 60 000 to 43 000 theoretical plates, but a significant increase in N_t from 181 to 290 plates s^{-1} (1 atm=101 325 Pa). Efficiency calculations for both constant temperature and constant pressure conditions are listed in Table 1.

Selectivity in SGC can be greatly affected by changing either the temperature or pressure. This is shown in Table 2. Increasing the temperature from 70 to 170°C (at constant inlet pressure) resulted in a decrease in the selectivity for caproic aldehyde and heptaldehyde by 0.2. Constant temperature conditions revealed similar results. Even among similar aldehydes, changing the mobile phase properties appears to significantly affect their separation. Using

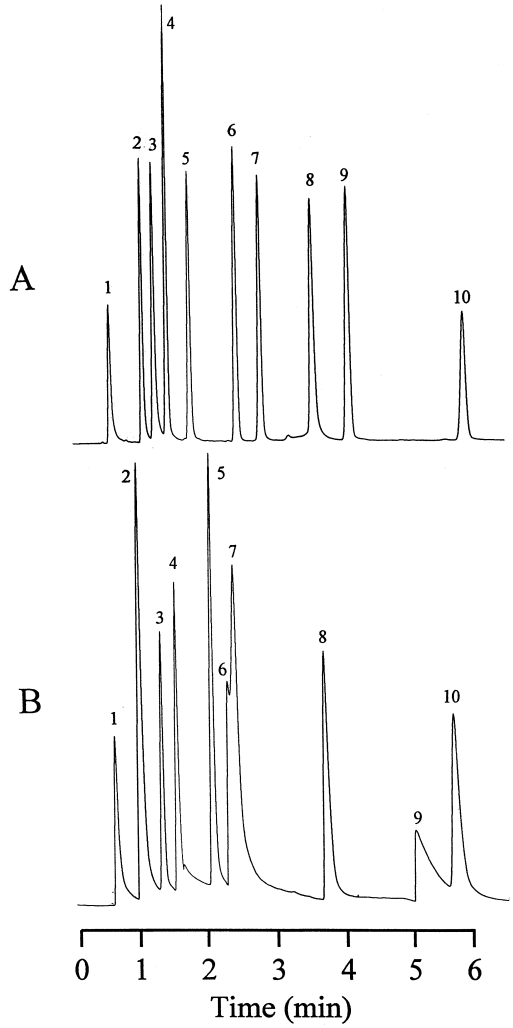

Fig. 1. Separation of underivatized aldehydes using packed capillaries with (A) OV-275-encapsulated silica and (B) ODS-bonded silica. Conditions: (A) 1.57 m×250 μm I.D. capillary column packed with OV-275-encapsulated particles (10 μm, 80 Å), CO_2, 190 atm, 150°C, FID. (B) 30 m×250 μm I.D. capillary column coated with SE-54 (0.25 d_f), He, 40°C, FID. Peaks: (1) Acetaldehyde, (2) propionaldehyde, (3) acrolein, (4) isobutyraldehyde, (5) butyraldehyde, (6) isovaleraldehyde, (7) valeraldehyde, (8) crotonaldehyde, (9) caproicaldehyde, (10) 2-furaldehyde.

a combination of pressure and temperature, the selectivity can be optimized for the separation of closely related compounds.

The observance of only a slight increase in mobile phase linear velocity with increasing pressure initially seemed unusual. When the temperature was increased from 90 to 170°C at 170 atm column inlet pressure, only a 4% increase in linear velocity occurred. However, this was also observed when using carbon dioxide in supercritical fluid chromatography [14,15]; similar results would be expected under SGC conditions.

Table 1
SGC column efficiencies at constant temperature or constant pressure[a]

P_i (atm)[b]	T (°C)	u^c_{ave} (cm s^{-1})	N	N_t (plates s^{-1})	k
150	150	1.79	60 000	181	2.7
190	150	2.13	52 000	232	2.1
250	150	2.59	43 000	290	1.5
170	90	2.01	29 000	86	3.3
170	130	2.05	46 000	169	2.5
170	170	2.00	55 000	241	1.9

[a] Conditions: 0.70 m×250 μm I.D. fused-silica capillary packed with 10 μm porous (80 Å) OV-275-encapsulated silica, CO_2 mobile phase, FID.
[b] P_i=Pressure at column inlet.
[c] u_{ave}=Average mobile phase linear velocity measured using methane as an unretained marker.

3.3. GC versus SGC

Stationary phases such as SE-54 (94% dimethyl, 5% phenyl, 1% vinyl polysiloxane) are routinely used in GC for a wide range of separations, however, stationary phases with higher polarity and selectivity are required to adequately separate all of the low-molecular-mass aldehydes. Even when a test mixture was injected at relatively low temperature (40°C), the SE-54 stationary phase was not able to separate isobutyraldehyde and butyraldehyde, as shown in Fig. 2. The SE-54 stationary phase likewise does not possess enough selectivity to resolve isovaleral-

Table 2
SGC selectivities at constant temperature or constant pressure[a]

P_i (atm)	T (°C)	$\alpha_{1/2}$	$\alpha_{2/3}$	$\alpha_{5/6}$	$\alpha_{8/9}$	$\alpha_{9/10}$	$\alpha_{10/11}$
150	150	1.1		1.2		1.2	
210	150	1.1		1.1		1.1	
250	150	1.2		1.1		1.0	
170	70		1.4		1.3		1.5
170	110		1.4		1.3		1.4
170	170		1.4		1.2		1.3

[a] Conditions as in Table 1.

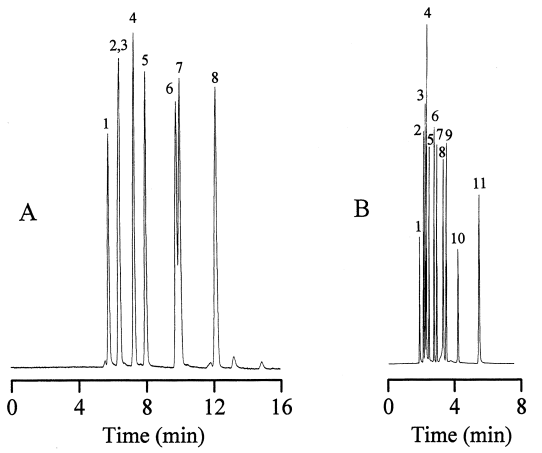

Fig. 2. Separation of underivatized aldehydes using (A) SE-54-coated open tubular capillary column and (B) OV-275-encapsulated silica packed capillary column. Conditions: (A) 30 m×250 μm I.D. capillary column coated with SE-54 (0.25 d_f), He, 40°C, FID. (B) 1.57 m×250 μm I.D. capillary column packed with OV-275-encapsulated particles (10 μm, 80 Å), CO_2, 190 atm, 150°C, FID. Peaks: (1) Acetaldehyde, (2) propionaldehyde, (3) acrolein, (4) isobutyraldehyde, (5) butyraldehyde, (6) isovaleraldehyde, (7) valeraldehyde, (8) crotonaldehyde, (9) caproicaldehyde, (10) heptaldehyde, (11) 2-furaldehyde.

dehyde and valeraldehyde completely within a reasonable amount of time. Although open tubular columns containing moderately polar stationary phases are available, columns coated with strongly polar stationary phases such as OV-275 are not commercially available due to problems associated with their immobilization. One of the highest polarity general purpose stationary phases available for GC is poly(biscyanopropylsiloxane). Although not currently available as a bonded phase, it has been used for an extended period for the analysis of fatty acid methyl esters, dioxins and aromatic compounds [16]. Other polar stationary phases which are not common in GC may find applicability in packed column SGC due to the added wettability of the porous particles.

Fig. 3 shows chromatograms of standard aldehydes under conditions giving similar retention times. Temperature programming was used with the Supelco SP-2340 poly(biscyanopropylsiloxane) open tubular column, and isothermal SGC was used with the OV-275-encapsulated particles. SGC was able to perform better separations under isothermal conditions than was GC using temperature programming.

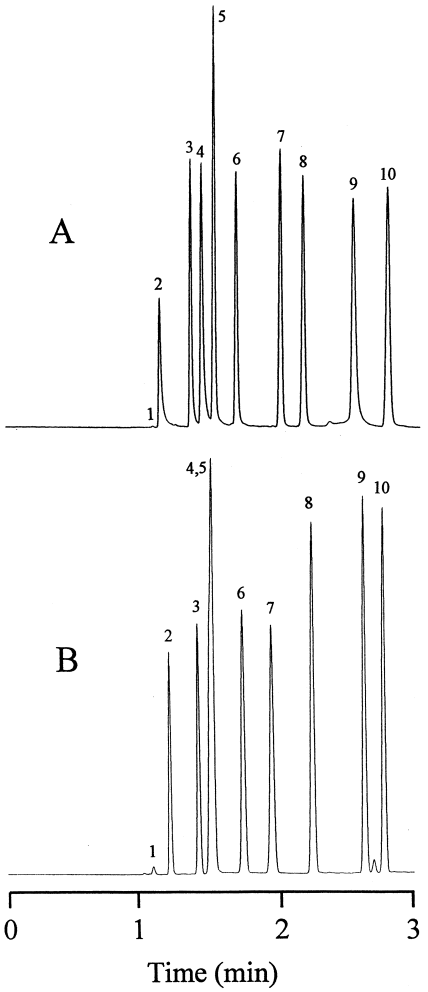

Fig. 3. Separation of underivatized aldehydes using (A) OV-275-encapsulated silica packed capillary column and (B) SP-2340 open tubular capillary column. Conditions: (A) 0.70 m×250 μm I.D. capillary column packed with OV-275-encapsulated particles (10 μm, 80 Å), CO_2, 170 atm, 150°C, FID. (B) 15 m×250 μm I.D. capillary column coated with poly(biscyanopropylsilxoane), 0.25 d_f, He, 40°C for 1.5 min, 40–225°C at 30°C min^{-1}, FID. Peaks: (1) Formaldehyde, (2) acetaldehyde, (3) propionaldehyde, (4) acrolein, (5) isobutyraldehyde, (6) butyraldehyde, (7) isovaleraldehyde, (8) valeraldehyde, (9) crotonaldehyde, (10) caproicaldehyde.

Since there is no cool-down step required for subsequent runs, SGC can provide substantial time savings with equal or better performance than conventional GC for the separation of aldehydes. GC was not able to resolve isobutyraldehyde and butyraldehyde, while SGC was able to produce near-

baseline separation under constant temperature and pressure conditions. Using OV-275-encapsulated particles, all of the aldehydes were resolved with relatively good peak shapes. Some tailing was observed for fast eluting peaks and is likely due to some dead volume in the SGC injector. For faster separations, the column was shortened by 20 cm, and the resulting chromatogram in Fig. 4 shows a similar separation in approximately 60 s.

A number of advantages arise from using CO_2 as the mobile phase compared with lighter gases in GC. The solvating power of CO_2 allows for a significant increase in column efficiency per unit time and better retention using similar polar stationary phases. In GC, mobile phases such as helium and hydrogen offer little, if any, solvating power. Although the use of packed columns often results in large solute retention, the solvating power of CO_2 can offset this effect and produce high efficiency and fast separations. By using packed capillary columns with carefully chosen bonded stationary phases, selective separation of underivatized aldehydes can be achieved under SGC conditions. While bonded and crosslinked stationary phases are clearly most desirable, the experiments reported here illustrate the advantages of using a high cyanopropyl content phases for the separation of aldehydes in SGC. Since SGC can provide equal or better separation under isothermal conditions, significant time savings may be realized due to the elimination of a ''cool-down'' step normally required for temperature-programmed GC analyses.

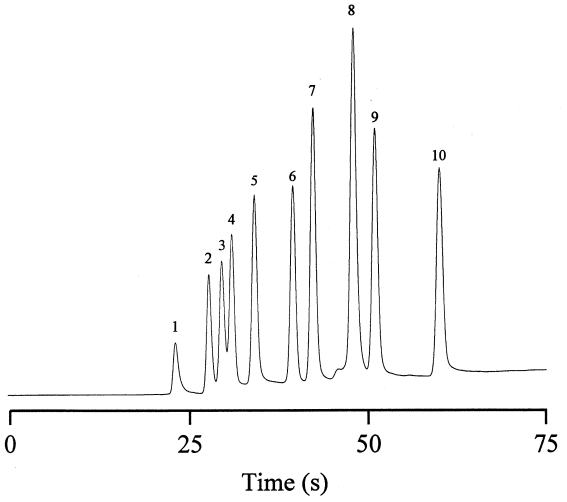

Fig. 4. Fast separation of underivatized aldehydes using SGC. Conditions: 0.50 m×250 μm I.D. capillary column packed with OV-275-encapsulated particles (10 μm, 80 Å), CO_2, temperature program, 150°C for 45 s, 150–180°C at 40°C min^{-1}, pressure program, 100 atm for 30 s, 100–180 atm at 40 atm min^{-1}, FID. Peaks: (1) Acetaldehyde, (2) propionaldehyde, (3) acrolein, (4) isobutyraldehyde, (5) butyraldehyde, (6) isovaleraldehyde, (7) valeraldehyde, (8) crotonaldehyde, (9) caproicaldehyde, (10) heptaldehyde.

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