Preparation of packed capillary columns using supercritical carbon dioxide on cyclone-type slurry reservoir

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Abstract

Fused silica packed capillary columns has been prepared using a new type of reservoir designed and engineered in house. We named it "cyclone" in analogy to an industrial equipment having similar shape. The performance of these columns was evaluated using solvating gas chromatography (SGC), a particular case of the transition phase chromatography (TPC); experiments showed that high efficient columns with a reduced plate height of ca. 2.0 were obtained even using 10 microns ODS particles. The advantageous features, obtained by using the cyclone device, make the newly developed columns suitable for separations of very complex samples and trace analysis. All steps involved in the preparation of the columns are addressed and discussed.
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1. Introduction

The column plays a critical role in transition phase chromatography (TPC), since it is responsible not only for the separation of the analytes but also for the pressure variation that occurs along the column, besides several favorable features presented by the technique [1]. In TPC different mobile phase conditions exist inside the column. This phase conditions transformation within the column, results in huge differences in density ($\rho_{inlet} \cong 330 \, kg \, m^{-3}$ to $\rho_{outlet} \cong 0.2 \, kg \, m^{-3}$; $P_{inlet} = 150 \, atm$, $P_{outlet} = 1 \, atm$, $T = 380 \, K$) [2], solvating power (e.g., $\delta_{inlet} = 4.7 \, Mpa^{1/2}$ to $\delta_{outlet} \cong 0.0$ at 380 K, where δ = Hildebrand parameter)[3], viscosity (e.g., $\eta_{inlet} = 27.05$ to $\eta_{inlet} = 18.79 \, \mu Pa \, s$ at 380 K) [4] and diffusivity [3] and, as a consequence, in the chromatographic properties of the mobile phase.

Various methods have been considered for the preparation of highly efficient fused silica packed capillary columns, mainly based on slurry packing [5–10] or dry packing technologies [11–14]. Fermier and Colón [15] introduced the use of centripetal forces to pack capillary columns. The method uses centripetal forces to drive the packing material into the column. A few years ago supercritical carbon dioxide was introduced as a packing medium [16,17]. This technique combines the advantages of the slurry packing technique, which uses a suspension of the material in a proper solvent and dry-packing techniques that employ a compressed gas as packing carrier.

The most obvious advantage of using carbon dioxide compared with other techniques is that it allows longer columns be packed, due to the low viscosity of carbon dioxide. The columns prepared with this technique have good stability [16]. In addition, carbon dioxide is not toxic to work with as are most solvents used in slurry packing techniques.

Tong et al. [18] studied factors that affected the preparation of packed capillary columns, including the influence of the physical conditions of CO_2, effect of packing pressure on packing density and sonication effect. According to Knox, it is important that the particles hit the accumulating bed at a high impact velocity [19]. However, if the velocity is too high the particles might not be expected to have time to settle uniformly.

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Koivisto et al. [20] determined that the geometry of the packing reservoir plays an important role to attain efficient columns. The carbon dioxide flow rate trough the column might thus be important.

In recent work, Planeta et al. [21] described a modified procedure for the preparation of packed capillary columns by use of supercritical or liquid carbon dioxide slurries. High efficiency were achieved, with a typical minimum reduced plate height (h) in the order of 2.2.

In the present study, packed capillary columns, prepared with a new type of reservoir named Cyclone, are described and evaluated.

2. Experimental

2.1. Instruments

The apparatus used for column preparation (Fig. 1) comprised of a Varian 8500 syringe pump (Walnut Creek, CA, USA); a CO_2 cylinder, which supplied carbon dioxide via a needle valve; a ultrasonic bath from Unique (São Paulo, Brazil); a home-made stainless steel cyclone reservoir and a cylindrical reservoir, fitted with a stainless steel frit (pore size $< 0.2\,\mu m$), a two stage vacuum pump from Edwards (Sussex – England).

Chromatographic columns prepared using the developed systems were evaluated using a GC oven, GC-2010 series gas chromatograph (Shimadzu, Kyoto, Japan), modified in-house for supercritical fluid chromatography [22]. A 4 ports Valco
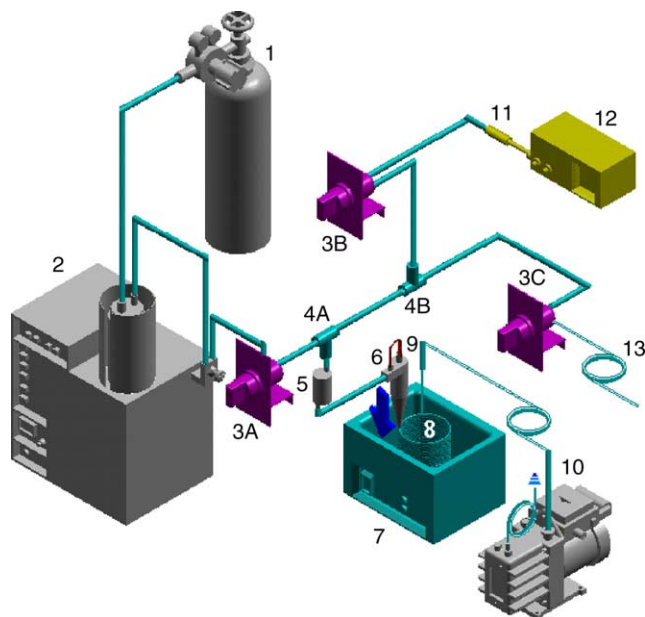

Fig. 1. Three dimensional diagram of the column packing system: (1) SFC grade CO_2 cylinder and valve; (2) high pressure pump; (3) valves; (4) tee connectors; (5) primary reservoir; (6) cyclone reservoir; (7) ultrasonic bath; (8) silica capillary; (9) valco zero dead volume connector; (10) vacuum pump; (11) pressure transducer; (12) pressure display; (13) capillary flow restrictor.

Cheminert Valve (Houston, TX, USA) with a 50 nL internal loop (cat no. C4-0004-.05) was used for sample introduction.

A Shimadzu 17A series gas chromatograph (Shimadzu, Kyoto, Japan) was used for open tubular GC experiments.

2.2. Columns and packing materials

Spherical porous (300 Å) octadecyl bonded silica (ODS) particles (Nucleosil) having nominal average diameter of $10\,\mu m$ were purchased from Alltech (Avondale, PA, USA). Fused silica capillaries ($250\,\mu m$, I.D.; $360\,\mu m$, O.D.) were purchased from Polymicro Technology (Phoenix, AZ, USA).

2.3. Reagents and chemicals

Hydrocarbons mixture 21C containing n-dodecane, n-tridecane n-tetradecane and n-hexadecane, was obtained from PolyScience (Niles, IL, USA); n-octane was obtained from E. Merck (Darmstadt, Germany). Methane and CO_2 chromatographic grade were obtained from AGA (São Paulo, Brazil). Other chemicals used were purchased from E.M. Merck (Darmstadt, Germany).

2.4. Built in-house cyclone-type reservoir

In this work, the cyclone reservoir dimensions were based on the work developed by Zhu and Lee [23]. These authors found that when both the pressure drop and the particle collection efficiency are considered, a cyclone with h/Dc equal to 2.0, where h is the cylinder height; Dc is the cyclone body diameter, and S/Dc equal to 1.0, where S is the exit tube length, or more accurately $(h - S)$/Dc equal to 1.0, would provide an optimum design of cyclone type device.

The cyclone-type reservoir was made of stainless steel (99 mm × 25 mm, O.D.). In the cyclone reservoir, the phase-laden gas enters into a cylindrical chamber tangentially at one point and leaves trough a central opening (Fig. 2). The solid particles, due to their inertia, will tend to move toward the outside cyclone wall from which they are led into a column.

At the employed operating conditions (20.27 MPa = 200 atm, 50 °C), the centrifugal separating force or acceleration in the cyclone can reach up to 2500 times the gravity, due the very small diameter of the "cyclone packing device".

Fig. 3 displays a photograph showing a detail of the containing the primary reservoir (1) and the cyclone reservoir (2). To sustain a cyclone behavior inside the reservoir the CO_2 flow rate through the capillary was maintained high by means of the vacuum pump. In addition, an outlet top of the cyclone device was included which uses the Venturi effect, thus providing a good exaustion tax for gases on the top of the cyclone, once operating at reduced CO_2 flows (Fig. 4, item 3).

2.5. Column preparation

The packing material and the "cyclone packing device" were dried at 110 °C for 12 h, after which the materials were
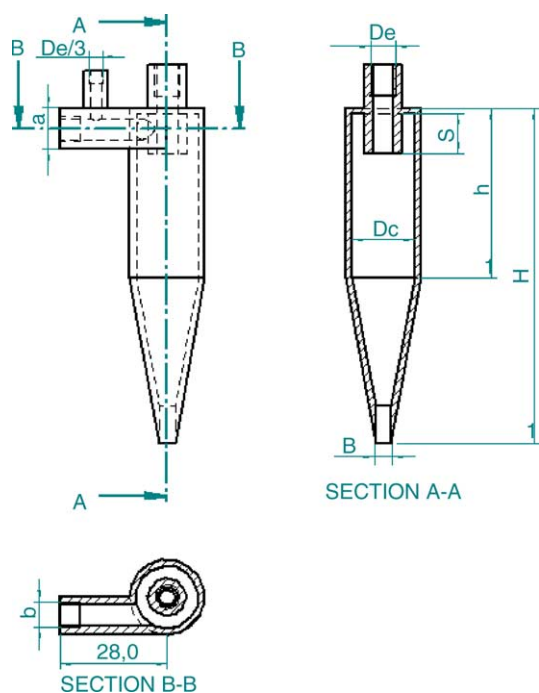
Fig. 4. Photograph of the primary reservoir (1), and cyclone reservoir (2) and recycling loop (3).

Fig. 2. Cross-section of the cyclone reservoir (internal shape) showing its dimensions, where $De = 7$ mm; $Dc = 16$ mm; $S = 15$ mm; $h = 30$ mm; $H = 98$ mm; $a = 12$ mm; $b = 6$ mm; $B = 3$ mm.

put in desiccator to cool down. According to the volume of the column being packed, an appropriate amount of the packing material was put into the packing device, was assumed a packing density of 0.800 g/cm^3.

One end of the capillary tubing (Fig. 1, item 8) to be packed was connected to the cyclone reservoir (Fig. 1, item 6), while the other end of the tubing was connected to a vacuum pump by means of a Valco union (Fig. 1, item 9) fitted with a metal frit (2-μm pores). The column tubing, the Valco union and the cyclone reservoir were them placed underwater in the ultrasonic bath (Fig. 1, item 7). To start the packing procedure, liquid carbon dioxide (Fig. 1, item 1) was introduced to the primary reservoir (Fig. 1, item 5); the column was then sonicated during the whole packing process at the temperature of
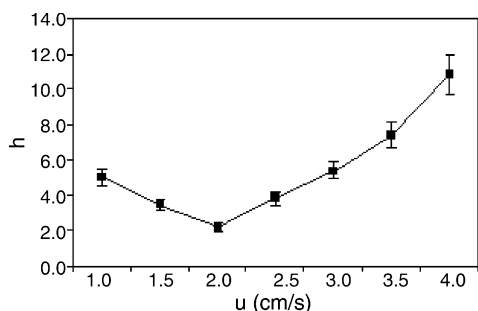

Fig. 3. Plots of reduced plate height versus linear velocity in TPC. Conditions: 70 cm × 250 μm, I.D. fused silica capillary columns packed with 10 μm porous silica (300 Å) ODS bonded particles. Carbon dioxide was used as mobile phase, methane as test solute, detector FID. Conditions: 120 °C and $P_{inlet} = 12.16$–18.23 Mpa (120–180 atm).

the ultrasonic bath maintained at 50 °C. The carbon dioxide was kept in the liquid state (room temperature, 20 °C) in the primary reservoir and under supercritical conditions in the section beneath the warm water (50 °C). During the packing process, valves 3A and B were open, while valve 3C was closed.

The packing material was carried to the "cyclone packing device" employing the double vortex movement of the carrier gas and particles. Once supercritical carbon dioxide flowing through a water thermostat section has a lower viscosity, therefore it flows faster and accelerates the packing process and improves formation of a homogeneous packing bed. This procedure in conjunction with the suction effect generated by the vacuum pump (Fig. 1, item 10) sustain the cyclone behavior inside the reservoir, as far as the CO_2 flow rate trough the packed capillary (250 μm, I.D.; 360 μm O.D.) is maintained high enough (15–20 mL/min). The carbon dioxide packing pressure was maintained at 20.27 MPa (200 atm). Once the packing bed in the column was formed the packing pressure was held for additional 30 min before stopping the sonication and proceeding to the reduction of packing pressure; valve 3 A was closed and the vacuum pump (Fig. 1, item 10) was stopped.

The column was left at the bath temperature (50 °C) for two additional hours. The initial pressure then decreased to about 5.06 MPa (50 atm). A pressure transducer (Fig. 1, item 11) monitored the residual pressure of system. Valve 3C was carefully opening to allow an additional slow release of the pressure through restrictor (200 mm, 10 μm I.D., Fig. 1, item 13) connected to a Valco union with a metal screen (2-μm pores).

The vacuum pump connected to the end of the column (Fig. 1, item 10) was then removed in order to allow a spontaneous depressurization of the column. When the pressure had decreased to zero the column was disconnected from the cyclone reservoir and a frit [24] was created at the open end, a fused silica piece of 200 mm × 50 μm, I.D. was connected

to the other extremity by means of a Valco union with a metal screen (2-μm pores).

2.6. Column evaluation

The prepared columns were evaluated using a gas chromatograph modified in house to work with supercritical fluids [22]. Column tests were carried out by measuring plate number (N), average linear velocity ($\bar{u}$), reduced plate height (h) and retention factor (k).

Split injection was employed by means of a fused silica capillary piece (100 mm × 2 5 μm, I.D.) and a stainless steel "T" piece [22].

3. Results and discussion

The design of the packing reservoir represents an important factor in obtaining efficient columns (Table 1) due to the carbon dioxide path in the cyclone reservoir, which involves a double vortex with the CO_2 spinning downward at the outside and upward at the inside.

When carbon dioxide enters the cyclone reservoir, its velocity undergoes a redistribution so that the tangential component of velocity increases with decreasing radius as expressed by $V_{ct} \sim r^{-n}$, where V_{ct} is the tangential component of the velocity; r, the radius of cyclone and n, an empirical constant. Theoretical considerations indicate that n should be equal to 1.0 in the absence of wall frictions and 0.5–0.7 in presence of wall frictions [25].

The spiral velocity into the reservoir may reach a value several times the average inlet CO_2 velocity, thus allowing the particles to form more homogeneous suspensions, consequently resulting in higher packing densities. In addition, this method allows the particles to achieve a higher uniformity and more stable arrangement in the packed structure through a pre-selection of the particle size in the cyclone-packing device.

It has been observed, for a set of experiments, that a dispersion of the particles started occurs in the inlet cyclone
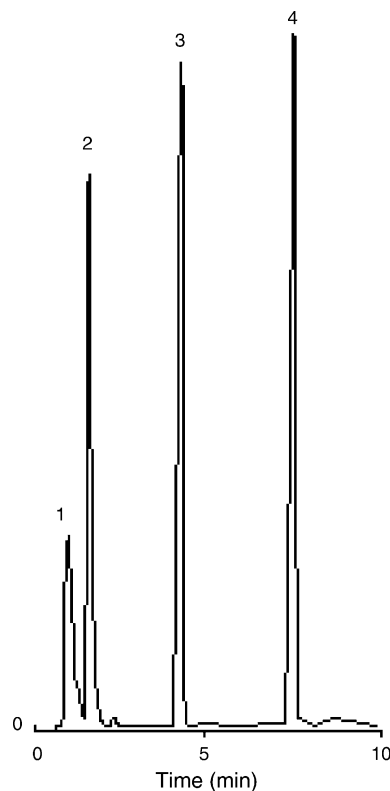

Fig. 5. Packed capillary TPC (SFC to GC transition) of selected hydrocarbons. Conditions: 120 °C and 15.20 MPa (150 atm) inlet pressure. Column: 60 cm × 250 μm, I.D. fused silica capillary column packed with 10 μm spherical porous (300 Å) ODS particles. Peak identifications: (1) *n*-dodecane, (2) *n*-tridecane, (3) *n*-tetradecane, (4) *n*-hexadecane.

reservoir being higher in the tubing between the reservoir and the packed bed. This observation was made by replacement, early of packing process, the stainless steel tubing with fused silica capillary tubing between the primary reservoir and the cyclone reservoir.

Table 1 too shows the average number of the plates by centimeter and standard deviation obtained using the cyclone-type reservoir. From the data displayed in Table 1 it can be seen, as expected, that there is a linear relationship between

Table 1

Measured column efficiencies for the capillary columns packed with 10 μm ODS particles in the cyclone reservoir[a]

Column	L (cm)[b]	d_p (μm)[c]	P (atm)[d]	$\bar{u}$ (cm s^{-1})[e]	N[f]	k[g]	h[h]	N/L (plate/cm)
1	40	10	85	2.8	16,980	1.5	2.35	424
2	70	10	100	2.0	31,260	1.8	2.24	446
3	100	10	120	1.8	46,016	2.1	2.17	460
4	180	10	170	1.5	73,824	2.4	2.44	410

[a] Conditions: 220 μm I.D. columns, 120 °C operating temperature, CO_2 mobile phase, FID. *n*-octane was used as test solute, methane used as unretained peak marker.

[b] Column length.

[c] Particle diameter.

[d] Inlet pressure.

[e] Average linear velocity.

[f] Total plate number.

[g] Retention factor.

[h] Reduced plate height.

plates number and column length: $N = 435$ (L/cm), $s = 22.3$, where L is length column; N, the number of plates and s, the standard deviation. All columns were packed with 10 μm particles and evaluated for use in solvating gas chromatography (SGC), a particular case of the transition phase chromatography (TPC). Columns up to 2.0 m long were successfully prepared using the proposed technology.

Fig. 3 shows a Van Deemter plot of a typical TPC column prepared with the cyclone system. As it can be seen, even using 10 μm particles, reduced plate numbers (h) close to 2.0 are obtained at the optimum average linear velocity, showing the excellent columns efficiency.

Fig. 5 illustrates a separation of a hydrocarbon mixture demonstrating the excellent resolution provided by the packed TPC column, by using 10 μm particles.

The device reported here allowed us also to prepare highly efficient columns, suitable for separations involving more complex mixtures. A practical example is presented in Fig. 6A, which illustrates a highly efficient separation of a

diesel oil sample on a 1.80 m long column, prepared using the cyclone-packing device described here. Similar profile was obtained for the same sample using capillary gas chromatography (Fig. 6B) in a 30 m length capillary column.

In all these experiments, it was found that, when increasing the inlet pressure, the analysis time decreases. The separation of lighter components in the samples was better in packed that in open tubular column as shown in Fig. 6A; this results from the higher retention on packed capillary column, the higher column efficiency when carbon dioxide is used as mobile phase and the higher sample capacity. A bimodal profile may be observed in Fig. 6A, related to the SGC characteristics (SFC to GC transition). It is evident from Table 1 that the reproducibility of the cyclone packing method is excellent; a coefficient of variation value $R^2 = 0.9918$ was obtained when packing four columns of different lengths. Further work to prepare longer columns with smaller particles using the cyclone packing system is in progress.
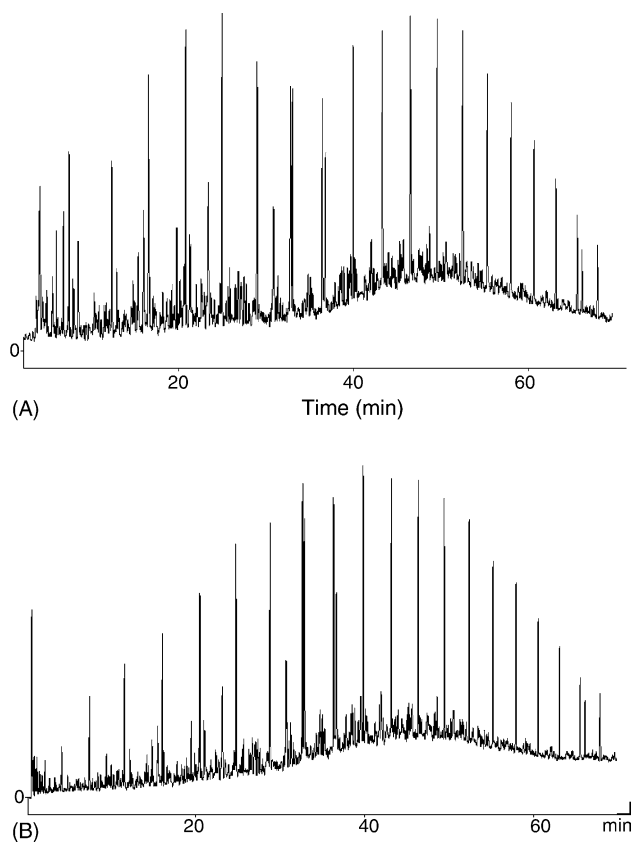
Acknowledgments

Fig. 6. Chromatograms of a diesel fuel sample. (A) Packed capillary TPC (supercritical fluid to gas transition, SGC); (B) open tubular column GC. (A) Conditions SGC: column inlet pressure program: 15.0 MPa/10 min–0.2 MPa min^{-1}–18.0 MPa. Temperature program: 90 °C/10 min–3 °C min^{-1}–240 °C. Column: 180 cm × 250 mm I.D., CO$_2$ carrier gas. Detector: FID. (B) Conditions GC: temperature program: 80 °C/2 min–3 °C min^{-1}–260 °C/5 min. Post temperature: 280 °C, post time: 10 min. Column: 30 m × 250 mm I.D., fused silica capillary column coated with 0.30 mm CROMA-5 poly(5% diphenyl/95% dimethylsiloxane), H$_2$ carrier gas. Detector: FID.

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