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Research Article

Feasibility of ultra high performance supercritical neat carbon dioxide chromatography at conventional pressures

The implementation of columns packed with sub-2 μm particles in supercritical fluid chromatography (SFC) is described using neat carbon dioxide as the mobile phase. A conventional supercritical fluid chromatograph was slightly modified to reduce extra column band broadening. Performances of a column packed with 1.8 μm C18-bonded silica particles in SFC using neat carbon dioxide as the mobile phase were compared with results obtained in ultra high performance liquid chromatography (UHPLC) using a dedicated chromatograph. As expected and usual in SFC, higher linear velocities than in UHPLC must be applied in order to reach optimal efficiency owing to higher diffusion coefficient of solutes in the mobile phase; similar numbers of theoretical plates were obtained with both techniques. Very fast separations of hydrocarbons are presented using two different alkyl-bonded silica columns.

Keywords: Sub-2 μm particles / Supercritical fluid chromatography / Ultra high performance liquid chromatography
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1 Introduction

The use of ultra high performance liquid chromatography (UHPLC) holds advantages in terms of speed for most analyses performed in liquid chromatography (LC) [1]. Thus, the implementation of UHPLC is growing very fast despite a dedicated hardware is required. Nowadays, most of the manufacturers of column packings and LC systems propose columns packed with sub-2 μm particles and LC systems adapted to high pressure. The reason for this fast development can be found in the fact that the principles and the benefits associated with the use of small particles in LC are well defined by the theory of packed column chromatography, i.e. several relationships between efficiency, linear velocity, column length and particle diameter [1]. Unfortunately, the consequence on column pressure drop can also be easily predicted: the UHPLC system must be operated at higher pressures than a regular LC system and short

columns must be used. Generally speaking, if one is willing to handle long columns packed with particles smaller than 2 μm , much higher pressures are required [2–4] whatever the column diameter; otherwise, the flow rate of the mobile phase must be reduced in order to keep the pressure within the operating range of the chromatograph [1]; in that case, the column might not be operated at its optimum performances.

To reduce the column pressure drop, columns packed with larger particles than the initial 1.7 μm particles (1.9, 2.2, 2.4 μm , etc.), partially non-porous supports and monoliths are also proposed; however, bonding chemistry is limited to only a few commercial stationary phases. Moreover, when 4.6-mm internal diameter columns are used, solvent consumption is high. Another approach to decrease the pressure drop is high-temperature liquid chromatography (HTLC) [5–7]. Increasing the temperature induces a significant reduction in the mobile phase viscosity and, consequently, a limitation of pressure drop; the diffusion coefficient of the solutes in the mobile phase increases with temperature; better kinetics and peak shape improvement of basic compounds are the main advantages of HTLC. Unfortunately, the stability of both the compounds and stationary phases is of major concern; as opposed to UHPLC, the transposition of separations from conventional to high-temperature conditions is not straightforward [8].

Another way to reduce column pressure drop in packed columns is supercritical fluid chromatography (SFC). As the mobile phase consists of carbon dioxide, modified or not by organic solvents and ‘buffers’, it has a low-to-medium viscosity when compared with liquids. For the same reasons as

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Abbreviations: **FID**, flame ionisation detector; **HTLC**, high-temperature liquid chromatography; **UHPLC**, ultra high performance liquid chromatography; **UHPSFC**, ultra high performance SFC; **SFC**, supercritical fluid chromatography

in HTLC, SFC enables better kinetics and shorter analysis times (3–10 times shorter) than LC, whereas the pressure drop is several times lower than in LC. Since its commercial development in the 1990s, SFC has demonstrated that separations could be performed as fast as in UHPLC using neat carbon dioxide for the separation of hydrocarbons or medium polarity species [9, 10] or modified carbon dioxide for a wide range of applications, including fast chiral separations in analytical or preparative scale [11]. Indeed, very high speed separations using sub-2 μm particles were demonstrated recently by Berger in SFC with CO_2 – polar modifier mobile phase [12]. SFC is also a ‘green’ method because expensive and hazardous organic solvents are partly replaced by CO_2 ; CO_2 can be easily recycled when used in preparative scale chromatography.

Using neat CO_2 as the mobile phase, flame ionisation detector (FID) can be hyphenated to SFC [9]. This is another reason why SFC has niche applications in the petroleum industry. ASTM method has been issued for group-type analysis of hydrocarbons [13], and SFC is a complementary technique to gas chromatography (GC) for simulated distillation [9]. The main drawback of SFC using neat carbon dioxide as the mobile phase lies in its lack of solubility for polar compounds despite the fact that well-protected stationary phases showing very low silanol activity can allow elution of medium polarity compounds without polar modifiers [10].

Whatever the mobile phase, SFC requires a dedicated apparatus equipped with a backpressure regulator for proper pressure control of the mobile phase; for efficient fluid delivery cooling of the CO_2 pump head is mandatory except if the pump is fed with dense CO_2 ; last but not least, SFC uses a non-aqueous-based mobile phase.

This paper reports one of the first implementations of conventional SFC system with sub-2 μm packed columns; supercritical neat carbon dioxide is used as the mobile phase. The aim was to conjugate SFC advantages to those of sub-2 μm packed columns for the separation of non-polar compounds and its subsequent application to oil industry, polymers and pollutants with minor modifications of a standard SFC chromatograph equipped with flame ionisation detection. Using the same column, the SFC behaviour is compared with UHPLC results obtained on a dedicated apparatus. Very fast separations of aromatic hydrocarbons and alkanes demonstrate potential applications for simulated distillation and separation of oil-related compounds.

2 Materials and methods

2.1 Chemicals

Acetonitrile (HPLC ultra gradient grade) was purchased from VWR (Fontenay-sous-bois, France). Water was produced by a Millipore Direct-Q system (Millipore, Molsheim, France). CO_2 (quality 4.5) was supplied by Messer (Mitry-Mory, France).

The test solutes were constituted of polycyclic aromatic hydrocarbons, naphthalene (Acros, Halluin, France), dodecylbenzene (Fluka, Saint Quentin Fallavier, France), 1,2,3,4,5,6,7,8-octahydroanthracene (Aldrich, Saint Quentin Fallavier, France), *tert*-butyl-2-anthracene (Aldrich), fluoranthene (Aldrich), anthracene (Aldrich), toluene (SDS, Peypin, France), propylbenzene (Fluka), pentylbenzene (Aldrich), octylbenzene (Merck, Fontenay-sous-bois, France), hexamethylbenzene (Aldrich), chrysene (Aldrich), 1,2-benzanthracene (Aldrich), 1,25,6-dibenzanthracene (Aldrich), benzo(ghi)perylene (Aldrich) and alkanes (Polywax 655 from Restek, Lisses, France).

Samples were prepared either in dichloromethane (SDS) or *n*-heptane (Acros).

2.2 Apparatus

2.2.1 SFC

A Berger SFC FCM-1200, Mettler-Toledo AutoChem (Viroflay, France) was used with minor modifications. It was equipped with: a dual-pump fluid control module for delivering carbon dioxide and, when required, a modifier, a HP5890 gas chromatograph equipped with a FID, a computer-controlled backpressure regulator. Column outlet pressure was controlled by the instrument backpressure regulator, and injections were made using a high-pressure Valco injection valve (15 000 psi, 2 μL loop) instead of the Rheodyne Model 7413 valve initially available. The injector was air actuated to enable time-split injections. The column was placed in the HP5890 oven. Detection was carried out with both a FID and a multi-wavelength photodiode array detector (DAD) HP 1050 (acquisition frequency 20 Hz, 1.7 μL cell volume); for dual FID/UV detection, the column effluent was split via a T-piece placed in the oven between the column outlet and the UV detector [10]. The T-piece was connected both to a laboratory made integral restrictor (50 μm id deactivated fused silica capillary tubing from S.G.E., Villeneuve St. Georges, France) for transferring ca. 1% of column effluent to the FID, and ca. 99% of column effluent to the diode array UV detector.

For the comparison purpose, a Jasco model X-LC 3075 UV detector for UHPLC (Jasco France, Nantes, France) was equipped with a Jasco SFC high-pressure cell of 2.6 μL volume.

System control and data acquisition of the Berger UV and FID signals were performed by 3D-SFC Chemstation 3.4, whereas the acquisition of the Jasco detector UV signal was carried-out using Azur 4.0.2.0 software (Datalys, Saint-Martin d'Hères, France).

Connection volumes between the injection valve, the column, the restrictor and the detectors were all minimised to reduce the dead volumes for the implementation of 3 mm id columns. However, compared with UHPLC operation, longer tubings were required between the injection valve mounted on the top of the GC oven, the column placed in

the GC oven and the UV detector placed on the top of the GC oven. When FID/UV detection was performed, the T-piece volume could not be neglected for UV operation. For FID operation, the volume of the 50 μm id restrictor had also to be considered.

2.2.2 UHPLC

The UHPLC system consisted of a Jasco model X-LC 3185PU pump, a high-pressure Valco injection valve (15 000 psi, 1 μL loop), a HPLC Croco-cil (CIL, Ste Foy la Grande, France) column oven set at 40°C, a Jasco model X-LC 3075 UV detector (Jasco, France) equipped with a 1- μL low-pressure UV cell. Again, taking advantage of modular system, all the connections from the injector to the detector were as short as possible using a reduced id tubing to minimise extra column volumes; data acquisition was performed using Azur 4.0.2.0 software (Datalys); acquisition frequency was 100 Hz.

2.2.3 Columns

Two types of packed columns were used: 100/50 mm \times 3 mm id, 1.8 μm (Nucleodur Gravity C₁₈, Macherey Nagel, Hoerd, France) and 50 mm \times 4.6 mm id, 1.9 μm (SepaxGP-C₄, from Sepax Technologies, Jasco, France).

3 Results and discussion

3.1 Behaviour of sub-2 μm LC column in SFC: comparison to UHPLC

A Nucleodur Gravity column was tested in SFC and UHPLC conditions using anthracene as the test compound; selected conditions allowed obtaining similar retention factors for both the techniques. The 10-cm long column was used to minimise the impact of extra column band broadening on the measured column efficiency in SFC (it is supposed to be negligible in UHPLC using our 'optimised' modular system). Efficiency was estimated by the number of theoretical plates (N) calculated using Eq. (1)

$$N = \left(\frac{t_r}{\sigma}\right)^2 = 5.54 \left(\frac{t_r}{w_h}\right)^2 \quad (1)$$

where t_r is the retention time of the test solute and w_h the peak width at half peak height.

Plate height (H) and reduced plate height (h) were deduced from N values using Eqs. (2) and (3), respectively, where L is the column length and d_p the particle diameter.

$$H = \frac{L}{N} \quad (2)$$

$$h = \frac{H}{d_p} \quad (3)$$

Kinetic evaluation is presented by plotting the reduced plate height (h) versus the linear velocity (u) as shown in Fig. 1. It

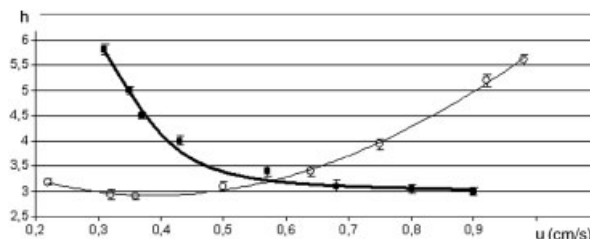


Figure 1. Comparison of kinetic features in SFC (in bold) and UHPLC using 1.8 μm packed columns. Column: Nucleodur gravity C₁₈ 10 cm \times 0.3 cm, 1.8 μm ; liquid mobile phase: water/ACN 40:60 (v/v), $T = 40^\circ\text{C}$, $\lambda = 205\text{ nm}$; SFC: outlet pressure = 200 bar, $T = 50^\circ\text{C}$, test compound: anthracene.

was obtained by varying the linear velocity of the mobile phase in a way that column inlet pressure remained within the specifications of our SFC (400 bar) and UHPLC (1000 bar) instruments.

Using both the techniques, the reduced plate height was close to 3 (2.9 for UHPLC). This means the column gave similar and good efficiencies in both conditions. This fact is not surprising as LC columns, including chiral columns used in routine analysis in pharmaceutical companies, can reach the same performances in LC and SFC. The same conclusion can be drawn from our experiments. However, better h values were reported in UHPLC (see, for example, references [1, 4]) and SFC [12] using columns of different manufacturers packed with similar size particles and tested in different conditions. Maybe the column used for this work could not exhibit better efficiency than that was found; the similarity of the h values reported here in SFC and UHPLC seems to support this conclusion because great attention was paid to the reduction of extra column volumes of our UHPLC apparatus compared with our SFC system. Explanations of lower efficiency could also be found in the following points: SFC report in [12] used quite different conditions as a polar modifier was added to the CO_2 . Radial thermal gradient in the columns have been shown to be responsible for the degradation of efficiency using sub-2 μm particles [14]; their effect is higher for high inner diameter column [15]. The column used here was 3-mm id compared with 2.1 mm id column used by Berger in [12].

As expected from the literature [1], UHPLC optimum linear velocity was higher than in HPLC and a value of 4 mm/s was obtained, it must be pointed out that this value is quite similar or lower than the values of optimum velocity reported more than 20 years ago [16] or very recently [17] in SFC using C₁₈ columns packed with 5 μm particle diameter. This value also confirmed that column, UHPLC system and operating conditions were suitable for a valuable comparison with SFC.

SFC is performed using a mobile phase having a low viscosity leading to higher diffusion coefficients of solutes in the mobile phase (D_m) [18]; as a consequence, higher optimum velocities are obtained according to general Eqs. (4)–(6) describing plate height (H), mass transfer (C)

and optimum velocity

$$H = Au^{1/3} + \frac{B}{u} + Cu \quad (4)$$

$$C = f(k) \cdot d_p^2 / D_m \quad (5)$$

$$u_{\text{opts}} = \frac{D_m}{d_p} \left(\frac{B}{C} \right)^{1/2} \quad (6)$$

where $f(k)$ is a function of retention factor.

Again, the results presented in Fig. 1 are consistent with expectations from the theory: u_{optS} was higher than 9 mm/s, twice the value obtained in UHPLC and ca. 20% more than the value one can estimate from Berger's plots of plate height versus the flow rate of the mobile phase reported in [12] using modified CO₂; as expressed in Eq. (6), this is the consequence of the increased D_m in supercritical CO₂ compared with a liquid mobile phase used in LC or modified CO₂ in SFC. A very flat curve is obtained around the optimum velocity; unfortunately, the part of the curve at high linear velocity that should be flatter in SFC than in UHPLC (increased value of D_m , Eq. (5)) could not be drawn: using the 10-cm length column at higher velocities than 9 mm/s, column inlet pressure exceeded the maximum pressure allowed by the SFC system.

Nevertheless, it could be concluded that the column could deliver the same number of theoretical plates two times faster than in UHPLC; for example, at a linear velocity of 9 mm/s the column could almost deliver 66% more plates in SFC than in LC at the same flow rate. It is worth to note that in investigated pressure/temperature conditions, pressure drop in the column did not perturb the column efficiency as opposed to the behaviour described in some publications [19–21]: compared with UHPLC results, neither an apparent peak deformation nor a significant loss of efficiency occurred. As described in [19], conditions were selected to keep the density gradient in the column lower than 0.1 g/cm³.

Thus, very fast and efficient separations can be obtained in packed column SFC using sub-2 μm particles with neat carbon dioxide as the mobile phase.

3.2 Examples of separations

Figures 2 and 3 show the separation of aromatic hydrocarbons in isoconfertic conditions; two chromatograms of hydrocarbons of various sizes and volatilities are presented. Five-centimetre-long Nucleodur C18 column (Fig. 2) or Sepax C4 column (Fig. 3) was used to allow a reduction in the column pressure drop and high linear velocities to be selected to obtain the fastest separations as possible. Depending on the pressure drop in the column, the backpressure applied and the linear velocity could be varied from one chromatogram to another to obtain proper retention, elution and separation of investigated compounds. The higher the backpressure, the lower the

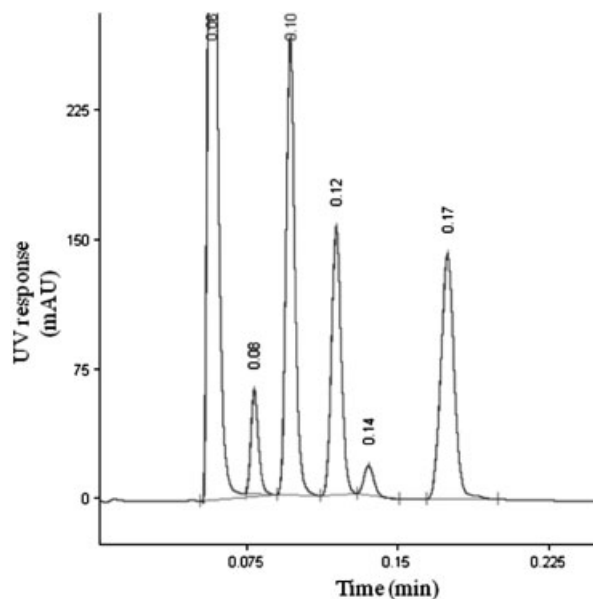


Figure 2. Fast isoconfertic SFC separation of hydrocarbons. Column: Nucleodur gravity C₁₈ 5 cm × 0.3 cm, 1.8 μm; flow rate: 5 mL/min; UV detection at 205 nm. Solutes: 0.08: naphthalene; 0.10: dodecylbenzene; 0.12: 1,2,3,4,5,6,7,8-octahydroanthracene; 0.14: *tert*-butyl-2-anthracene; 0.17: fluoranthene; solvent: dichloromethane $P_{\text{in}} = 330$ bar, $P_{\text{out}} = 150$ bar, $T = 50^\circ\text{C}$, $u = 13.8$ mm/s.

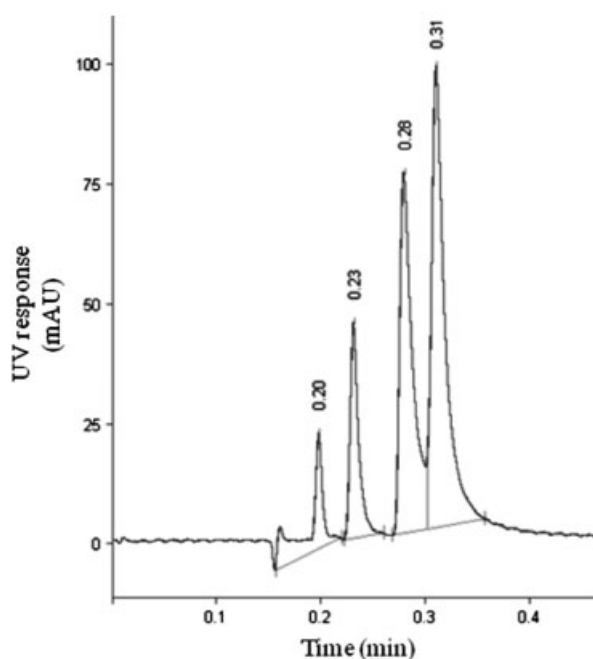


Figure 3. Fast isoconfertic SFC separation of heavy polycyclic hydrocarbons. Column: Sepax C₄ 5 cm × 0.46 cm, 1.9 μm; $P_{\text{in}} = 230$ bar, $P_{\text{out}} = 150$ bar; $T = 50^\circ\text{C}$; flow rate: 5 mL/min, $u = 0.52$ mm/s, UV detection at 254 nm. Solutes: 0.20: chrysene; 0.23: benzanthracene; 0.28: dibenzanthracene; 0.31: benzo(ghi)perylene; solvent: dichloromethane.

retention and the higher the fluid viscosity and the pressure drop in the column. The chromatograms demonstrate, as expected from Fig. 1, that very fast separations (10–15 s) are easily obtained with a peak capacity of 11 using linear velocities above 10 mm/s. This separation can be viewed as ultra high performance SFC (UHPSFC). Such fast separations may not have a major interest for routine analysis as many autosamplers are not fast enough to prepare the injection of the next sample during such a short run; however, owing to the fact that the field of application of neat CO₂ SFC is mainly devoted to the separation of hydrocarbons, UHPSFC could be a good alternative to GC for implementation in comprehensive techniques such as LC × UHPSFC or SFC × UHPSFC where a fast separation can be required in the second dimension if one wants to mimic comprehensive 2D GC (GC × GC) conditions. Such bi-dimensional analytical systems would extend the range of compounds amenable to a FID for detailed analysis of petroleum cuts containing hydrocarbons having more than 60 carbon atoms that are, at the moment, very difficult to elute in high temperature GC × GC [22].

Similarly, Fig. 4 shows a separation of a mixture of alkanes (Polywax 655) spiked with nC 60 paraffin. The analysis was performed using the Nucleodur C18 column, and FID was used for the detection. A density gradient was applied by varying the backpressure from 80 to 300 bar at 60 bar/min; the elution of C60 hydrocarbon was obtained in 4 min at 300 bar and the elution of C80 within 6 min at the same pressure. To our knowledge, using fast GC conditions for simulated distillation, the only report of such a fast separation of heavy alkanes was done at the 29th International Symposium on Capillary Chromatography in Riva Del Garda by Frank Di Sanzo; elution of C60 was obtained in 4 min but elution of higher boiling points hydrocarbons was not shown. Here, UHPSFC results could compete with GC results owing to the very fast analysis obtained using sub-2 μm particles; as opposed to GC, the solvent strength of the supercritical CO₂ facilitated elution of heavy compounds; in GC, for simulated distillation purpose, the

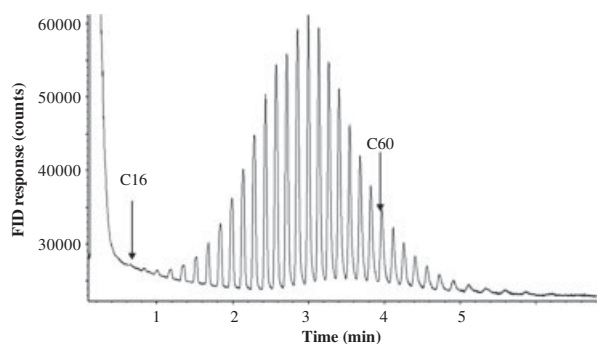


Figure 4. Fast pressure gradient SFC separation of *n*-alkanes (Polywax 655). Column: Nucleodur C₁₈ gravity 5 cm × 0.3 cm, 1.8 μm; flow rate: 2 mL/min; *T* = 100 °C. Pressure gradient from 80 to 300 bar (60 bar/min); FID solutes: Polywax 655, solvent C₇.

elution of heavy hydrocarbons is obtained at very high temperature [23].

To speed up the separation, the C18 column was replaced by a C4 column; assuming similar bonding density a reduction of retention is expected by reducing the length of the bonded alkyl chain. Compared with conditions of Fig. 4, the CO₂ flow rate was increased from 2 to 2.5 mL/min: the pressure ramp was 99 bars/min, the maximum rate available using the ‘Berger’ system; the final backpressure was raised to 370 bars to increase the eluent strength of the mobile phase and to decrease the retention of the heaviest compounds; the high final backpressure was the reason why the flow rate had to be restricted to 2.5 mL/min to reduce the column pressure drop and to keep the column inlet pressure within the specifications of the SFC chromatograph. Figure 5 shows that the elution of light hydrocarbons was faster than in Fig. 4. This result confirmed the expected reduction of retention. Thus, elution of C60 was obtained in 1.7 min at 230 bar and C80 eluted at ca. 310 bar in <2.3 min. The last eluting alkane was C86 or 88. As expected, the lower pressure required for the elution of C60 and C80 also confirmed the lower retention when the C18 column was replaced with the C4 column. However, the reduction in resolution due to the fast pressure ramp is the price to pay for this fast separation. For simulated distillation purpose, this is not a problem: the separation of alkanes is only used for the identification and calibration of retention times [23]. For quantitative analysis of alkanes, the resolution should be improved; otherwise, the separation obtained on the C18 column should be preferred.

It must be pointed out that the elution of heavier hydrocarbons would require at the same time higher temperatures (ca. 160 °C) and backpressures to be applied as it has been described elsewhere using capillary or packed column SFC for simulated distillation purpose [9, 24]. At such temperatures, high backpressure is necessary to keep the density at a quite high value (ca. 0.5 g/cm³) to maintain a high solvent strength of the mobile phase.

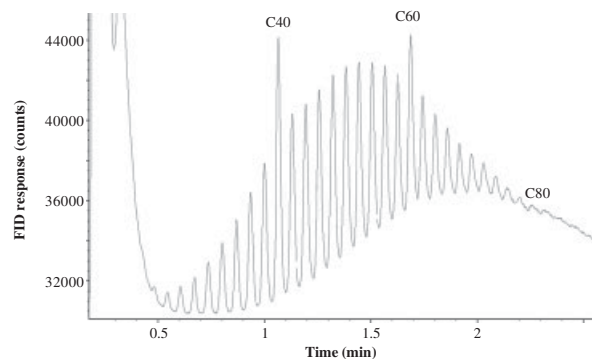


Figure 5. Very fast pressure gradient SFC separation of *n*-alkanes (Polywax 655). Same conditions as in Fig. 4 except column: Sepax C₄ 5 cm × 0.46 cm, 1.9 μm; flow rate: 2.5 mL/min; pressure gradient from 80 to 370 bar (99 bar/min); *T* = 100 °C.

4 Concluding remarks

The feasibility of UHPSFC using neat CO₂ as the mobile phase was demonstrated: a regular packed column SFC system could handle UHPLC columns of 10 cm length and, for very fast separations, of 5 cm length. Very fast separations of hydrocarbons were achieved; a separation of linear alkanes exceeding C80, faster than in GC, is also reported. The fast separations reported here meet the requirements of speed for the application of SFC as a second dimension separation in comprehensive 2D chromatography; the use of a dense mobile phase would be an advantage for the elution of low volatility material.

Work is in progress to extend the use of UHPSFC: higher operating pressures are desirable to implement longer columns, to increase both the CO₂ eluent strength and the mobile phase flow rate. The development of SFC × UHPSFC is in progress.

The authors have declared no conflict of interest.

5 References

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