

Chapter 29

Supercritical Fluid Chromatography and Extraction

29A Properties of supercritical fluids

A supercritical fluid is formed whenever a substance is heated above its critical temperature.

TABLE 29-1 Comparison of Properties of Supercritical Fluids with Liquids and Gases

Property	Gas (STP)	Supercritical Fluid	Liquid
Density, g/cm ³	$(0.6-2) \times 10^{-3}$	0.2-0.5	0.6-2
Diffusion coefficient, cm ² /s	$(1-4) \times 10^{-1}$	$10^{-3}-10^{-4}$	$(0.2-2) \times 10^{-5}$
Viscosity, g cm ⁻¹ s ⁻¹	$(1-3) \times 10^{-4}$	$(1-3) \times 10^{-4}$	$(0.2-3) \times 10^{-2}$

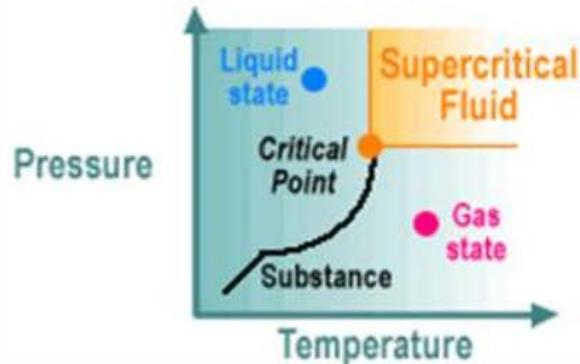
Note: All data are to an order of magnitude only.

TABLE 29-2 Properties of Some Supercritical Fluids

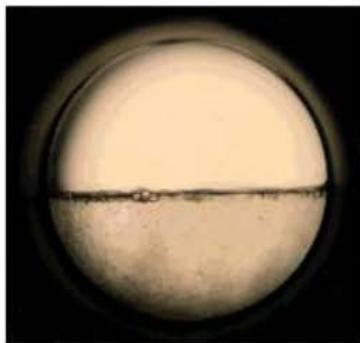
Fluid	Critical Temperature, °C	Critical Pressure, atm	Critical Point Density, g/mL	Density at 400 atm, g/mL
CO ₂	31.3	72.9	0.47	0.96
N ₂ O	36.5	71.7	0.45	0.94
NH ₃	132.5	112.5	0.24	0.40
<i>n</i> -Butane	152.0	37.5	0.23	0.50

Supercritical Fluids

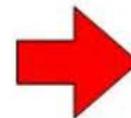
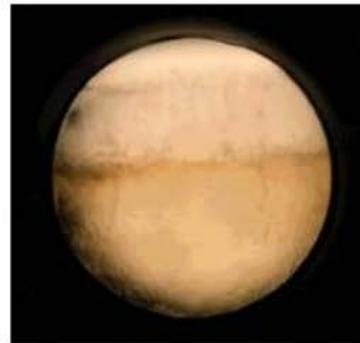
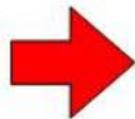
A substance becomes a supercritical fluid above its critical point of temperature and pressure



Moves like a gas and dissolves things like a liquid



Subcritical



Supercritical

Increasing pressure, phase boundary disappears

http://www.suflux.com/EN/products/scf_img/scf01_img01.jpg

<http://www.buykorea.org/product-details/supercritical-fluid-system-supercritical-extraction-system--3014692.html>

supercritical fluids

29B Supercritical fluid chromatography

29B-1 Instrumentation and Operating Variables

As shown in Fig 29-1, instruments for SFC are similar in most aspects to the instruments for HPLC described in Section 28C.

As shown in Fig 29-1, in a commercial instrument for SFC, such instrument variables as pumping pressure, oven temperature, and detector performance are computer controlled.

* **Effects of Pressure**

Pressure changes in SFC have a pronounced effect on the retention factor k and thus the retention time t_R .

* **Stationary Phases:**

OT and PC in GC are used- Bonded and cross linked siloxanes.

* **Mobile Phases:** Most widely used one is CO_2

* **Detectors:** FID in GC, Mass spec.

Fig. 29-3 Performance characteristics of ODS column with HPLC and SFC

Fig. 29-1 Supercritical Chromatography Schematic of an instrument

Comparison of gradients

GC, HPLC, and SFC each has some sort of gradient control

GC : Temperature

HPLC : Solvent nature and polarity

SFC : Pressure

Temperature

Solvent nature and polarity

SFC offers the widest range of possible control,
but longest development time.

Pressure programming

Two types of pressure programming are available.

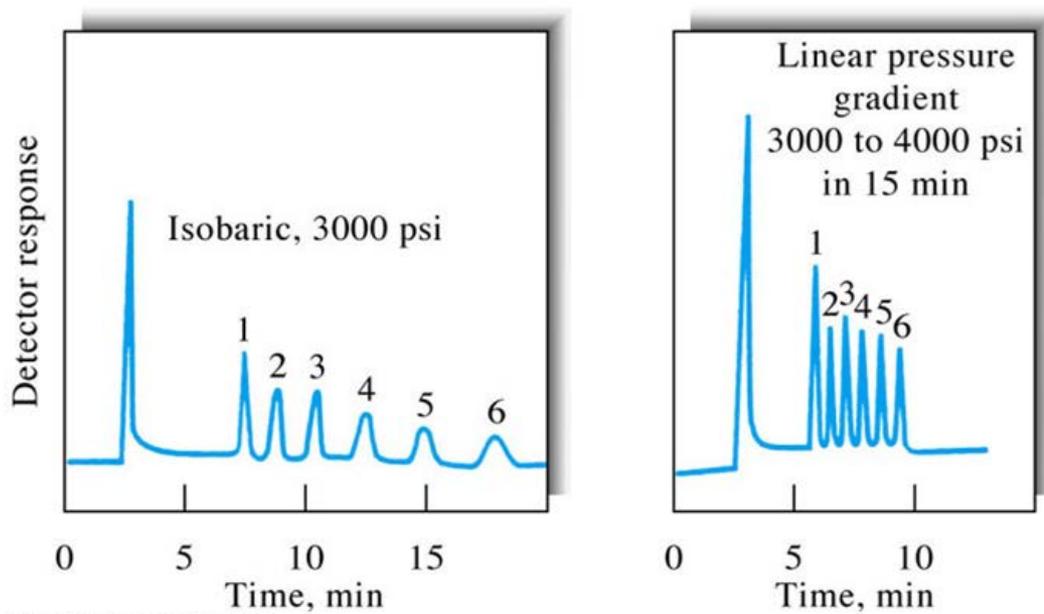
Linear --- like temperature programming where pressure is increased
at a fixed rate.

Asymptotic --- rate is decreased linearly as it approaches the maximum.

Fig. 29-2 Effect of pressure programming in SFC

Sample: 1. cholesteryl octanoate
2. cholesteryl decylate
3. cholesteryl laurate
4. cholesteryl myristate
5. cholesteryl palmitate
6. cholesteryl stearate

Column: DB-1
Mobile phase: CO₂
Temperature: 90°C
Detector: FID Flame ionization



29B-2 Comparison to other types of chromatography

The data in Tables 29-1 and 29-2 reveal that several physical properties of supercritical fluids are intermediate between gases and liquids.

Fig 29-3. Performance characteristics of a 5- μm octadecyl (C_{18}) bonded silica column when elution is supercritical carbon dioxide SFC.

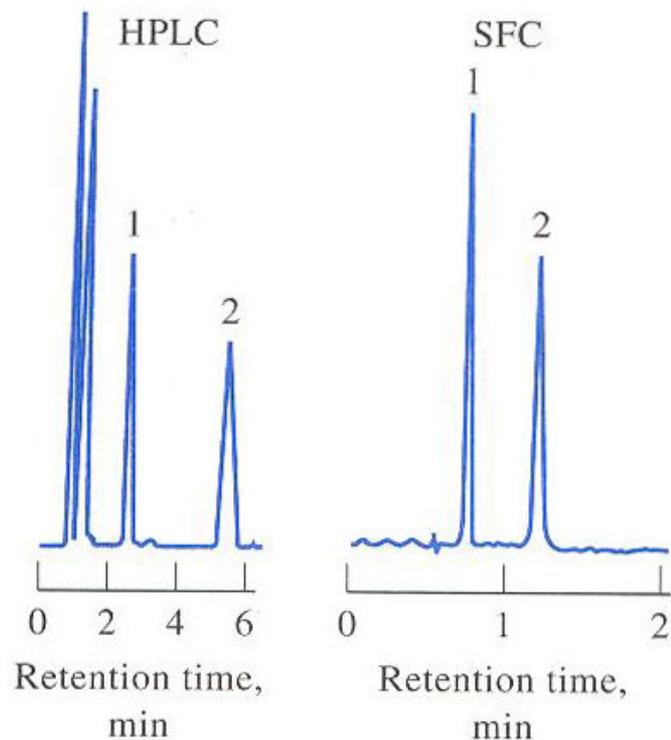


FIGURE 29-4 Comparison of chromatograms obtained by conventional partition chromatography (HPLC) and SFC. Column: 20 cm \times 4.6 mm with 10- μ m reversed-phase bonded packing. Analytes: (1) biphenyl; (2) terphenyl. For HPLC: mobile phase, 65% CH₃OH to 35% H₂O; flow rate, 4 mL/min; linear velocity, 0.55 cm/s; sample size, 10 μ L. For SFC: mobile phase, CO₂; flow rate, 5.4 mL/min; linear velocity, 0.76/s; sample size, 3 μ L. (From D. R. Gere, T. J. Stark, and T. N. Tweeten, *Application Note 800-4*, Hewlett-Packard Corp., Palo Alto, CA, 1983. With permission.)

Fig. 29-5 Range of molecular weight(daltons) and size (um)

29B-3 Applications

Fig 29-6 shows the separation of the enantiomers of metoprolol, a beta-blocking drug, by both HPLC and SFC.

FIGURE 29-6 Separation of enantiomers of metoprolol by HPLC (a) and SFC (b) on a Chiralcel OD stationary phase. In (a) the mobile phase was 20% 2-propanol in hexane with 1% diethylamine; selectivity $\alpha = 2.67$ and resolution $R_s = 4.8$. In (b), CO_2 was used containing 20% methanol with 0.5% isopropylamine; $\alpha = 2.77$ and $R_s = 12.7$.

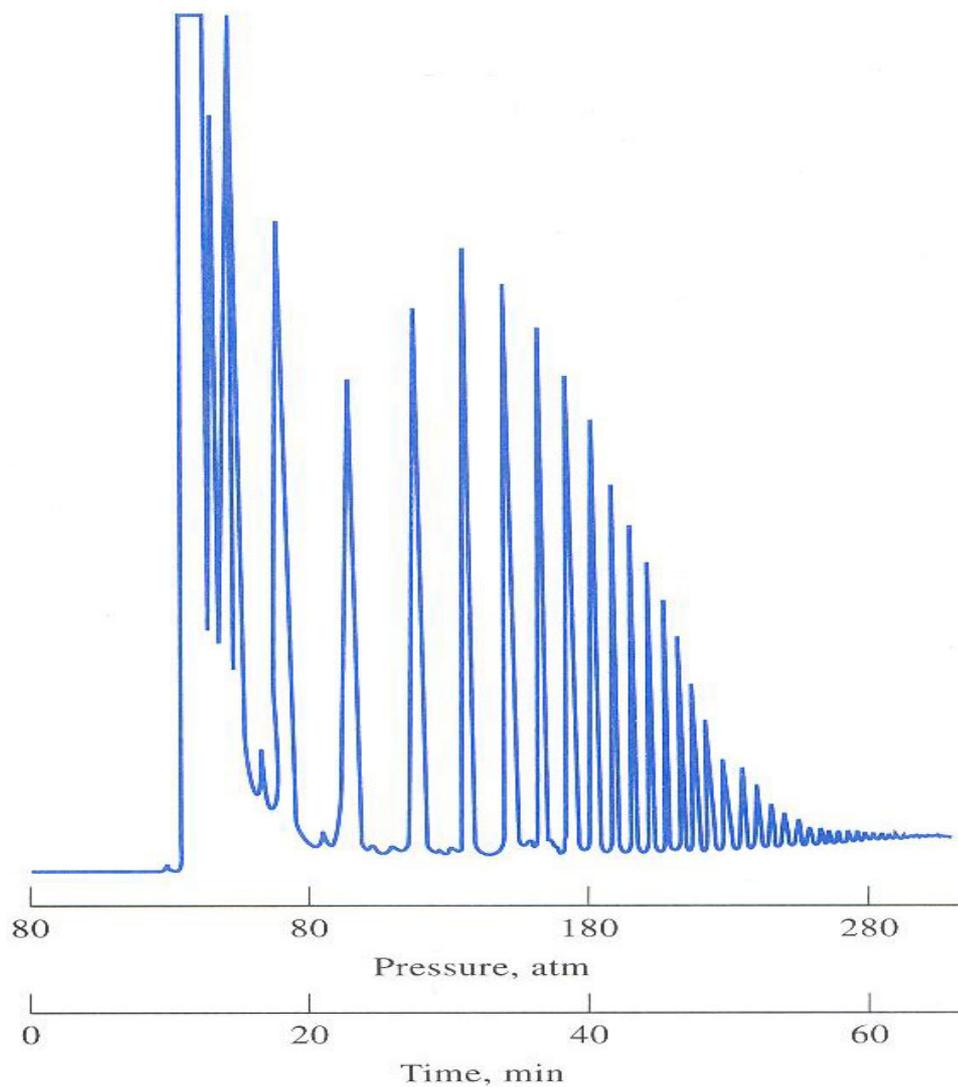
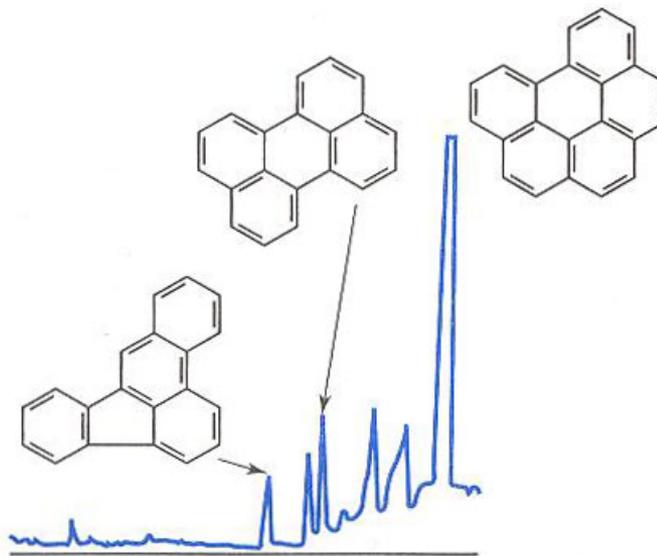


FIGURE 29-7 Separation of oligomers of dimethylpolysiloxane by SFC. (From C. M. White and R. K. Houck, *HRC&CC*, **1986**, 9, 4. With permission.)

400 nm
Excitation



335 nm
Excitation

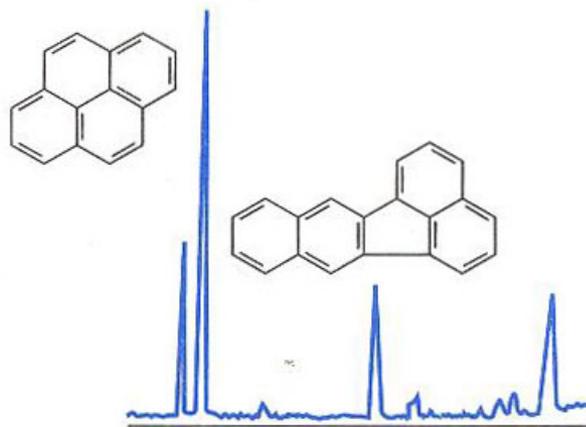


FIGURE 29-8 Portions of the supercritical fluid chromatograms of polycyclic aromatics in a carbon-black extract, illustrating the selectivity achieved by fluorescence excitation at two wavelengths. (From C. M. White and R. K. Houck, *HRC&CC*, **1986**, 9, 4. With permission.)

Fig. 29-9 SF extraction (Off line SFC)

Typical Supercritical Solvents

Compound	T _c ° C	P _c atm	d*
CO ₂	31.3	72.9	0.96
C ₂ H ₄	9.9	50.5	---
N ₂ O	36.5	72.5	0.94
NH ₃	132.5	112.5	0.40
n-C ₅	196.6	33.3	0.51
n-C ₄	152.0	37.5	0.50
CCl ₂ F ₂	111.8	40.7	1.12
CHF ₃	25.9	46.9	---
H ₂ O	374.1	218.3	---

* Density in g/ml at 400 atm.

29C Supercritical fluid extraction

Often, the analysis of complex materials requires as a preliminary step separation of the analyte or analytes from a sample matrix.

29C-1 Advantages SFE

1. SFE is generally fast.
2. The solvent strength of a supercritical fluid can be varied by changes in the pressure and to a lesser extent in the temperature.
3. Many supercritical fluids are gases at ambient conditions.
4. Some supercritical fluids are cheap, inert, and non-toxic.

29C-2 Instrumentation

The instrumentation for SFE can be relatively simple as shown in Fig 29-10.

29C-3 Supercritical Fluid Choice

Fig 29-11 demonstrate the improved efficiency achieved by the presence of a small amount of methanol in the extraction of various materials from soil samples.

29C-4 Off-Line and On-Line Extractions

Two types of methods have been used to collect analytes after extraction: *off-line* and *on-line*.

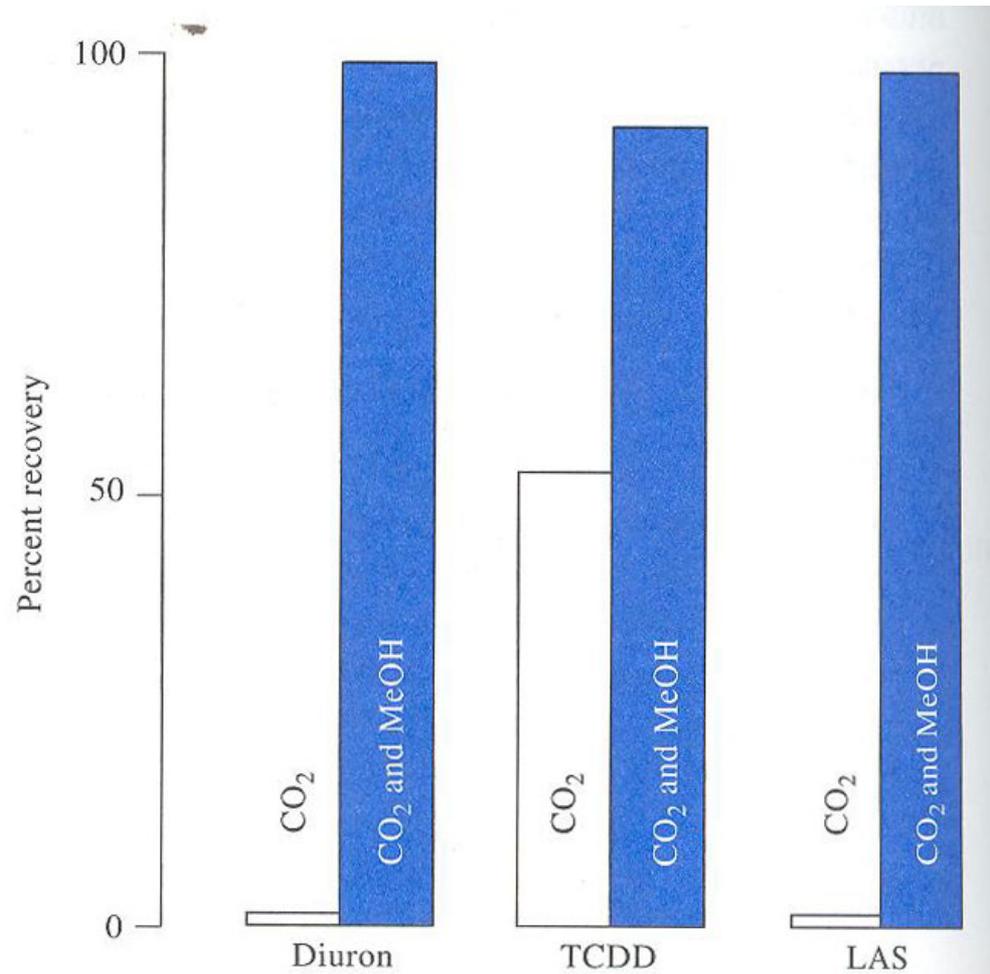


FIGURE 29-11 Comparison of extraction efficiencies obtained by using CO₂ and CO₂ modified with methanol. A soil sample was used. All extractions were for 30 min. Diuron is a common herbicide that is an aromatic substituted derivative of urea. TCDD is 2,3,7,8-tetrachloro-dibenzo-*p*-dioxin. LAS is linear alkylbenzenesulfonate detergent.

29C-5 Typical Application of SFE

Table 29-3 provides a few typical applications of off-line and on-line SFE.

TABLE 29-3 Some Typical Analytical Applications of SFE

Material	Analyte*	Supercritical Fluid	Extraction Time, min	Off-line (1), On-line (2)
Soils	Pesticides	CO ₂	20	1
River sediments	PAHs	CO ₂ /5% MeOH	120	1
Smoke, urban dust	PAHs	CO ₂	15	2
Railroad bed soil	PCBs, PAHs	CO ₂ /MeOH	45	1
Foods	Fats	CO ₂ /MeOH	12	1
Spices, bubble gum	Aromas and fragrances	CO ₂	10	2
Serum	Cholesterol	CO ₂	30	1
Coal, fly ash	PCBs, dioxins	CO ₂	15	2
Polymers	Additives and oligomers	CO ₂	15	2
Animal tissue	Drug residues	CO ₂	9	1

*PAHs = polycyclic aromatic hydrocarbons; PCBs = polychlorinated biphenyls.

Industrial applications

The special properties of supercritical fluids bring certain advantages to chemical separation processes. Several applications have been fully developed and commercialized.

Food and flavouring

SFE is applied in food and flavouring industry as the residual solvent could be easily removed from the product no matter whether it is the extract or the extracted matrix. The biggest application is the decaffeination of tea and coffee. Other important areas are the extraction of essential oils and aroma materials from spices. Brewery industry uses SFE for the extraction of hop. The method is used in extracting some edible oils and producing cholesterol-free egg powder.

Petrolchemistry

The distillation residue of the crude oil is handled with SFE as a custom large-scale procedure (ROSE Residum Oil Supercritical Extraction). The method is applied in regeneration procedures of used oils and lubricants.

Pharmaceutical industry

Producing of active ingredients from herbal plants for avoiding thermo or chemical degradation.
Elimination of residual solvents from the products.

Other plant extractions

Production of denicotined tobacco.

Environmental protection

Elimination of residual solvents from wastes. Purification of contaminated soil.