Supercritical Fluid Chromatography

1. What is supercritical fluid
2. Supercritical Fluid Extraction
3. Supercritical fluid chromatography (SFC)
4. Theory of SFC
5. Instrumentation
6. Applications

Supercritical Fluid Chromatography

1. What is supercritical fluid

Supercritical fluid is a state of matter that is intermediate between a gas and liquid in its properties. This state formed when a gas or liquid solvent is subjected to temperature and pressure condition exceeding a particular critical point. The temperature and pressure at which this pint Occurs are known as the Critical temperature and Critical pressure and are Characteristic of the solvent. Beyond this point, the solvent Will be neither a gas or liquid, but will possess properties of both phases . Whether this supercritical fluid acts more like a gas or liquid will depend on the pressure and temperature

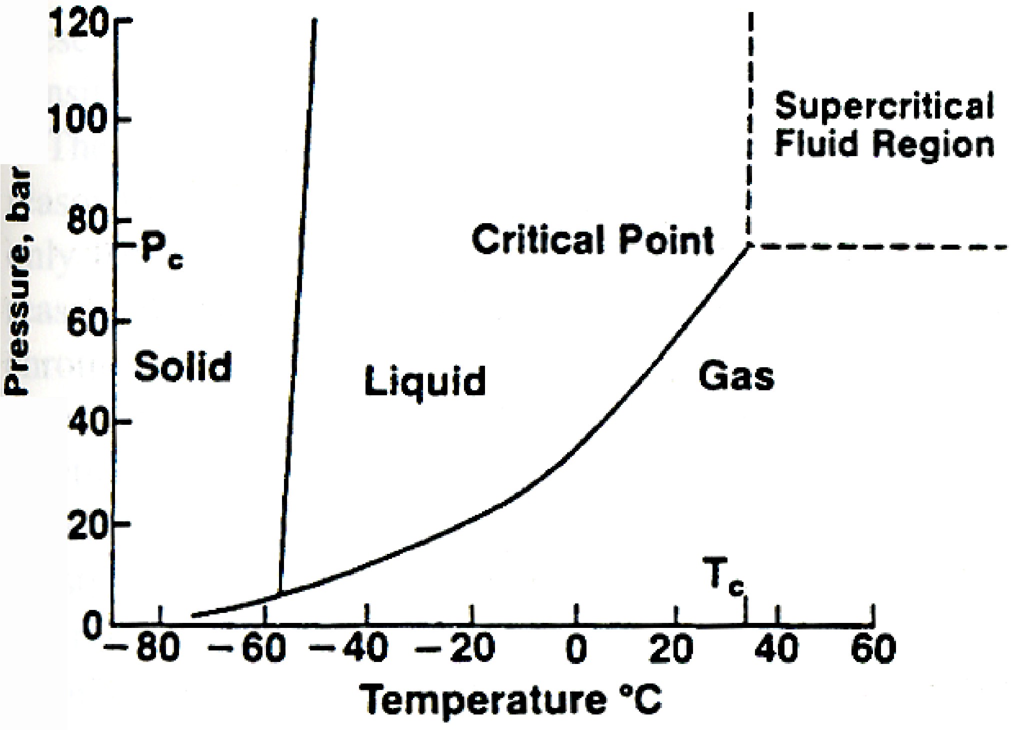


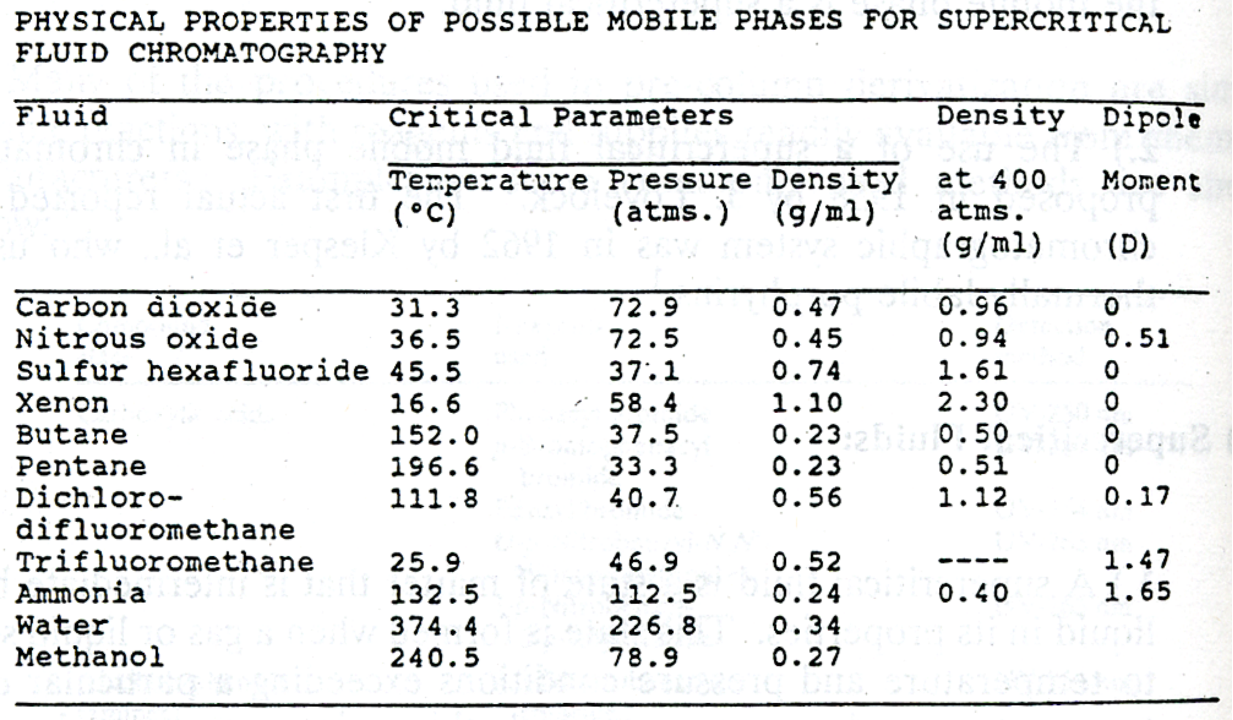
Figure 7.1. Phase diagram for carbon dioxide

Table 7.1
Change in density of supercritical fluid carbon dioxide with pressure and temperature

Temperature (°C)	Pressure (atm)	Density (g/ml)
40	72	0.22
	400	0.96
60	72	0.17
	400	0.90
80	72	0.14
	400	0.82
100	72	0.13
	400	0.76
120	72	0.12
	400	0.70
140	72	0.11
	400	0.64

Table 7.2
Representative properties of typical chromatographic mobile phases

Mobile phase	Temperature (°C)	Pressure (atm)	Density (g/ml)	Diffusivity (cm^2/s)	Viscosity (cP)
Helium	200	1.5	$2x10^{-4}$	0.1-1	0.02
Carbon dioxide					
low density	100	80	0.15	10^{-3}	0.02
high density	35	200	0.8	10^{-4}	0.1
Water	20		1.0	10^{-5}	1.0



PHYSICAL PROPERTIES OF POSSIBLE MOBILE PHASES FOR SUPERCRITICAL FLUID CHROMATOGRAPHY

Fluid	Critical Parameters			Density at 400 atms. (g/ml)	Dipole Moment (D)
	Temperature (°C)	Pressure (atms.)	Density (g/ml)		
Carbon dioxide	31.3	72.9	0.47	0.96	0
Nitrous oxide	36.5	72.5	0.45	0.94	0.51
Sulfur hexafluoride	45.5	37.1	0.74	1.61	0
Xenon	16.6	58.4	1.10	2.30	0
Butane	152.0	37.5	0.23	0.50	0
Pentane	196.6	33.3	0.23	0.51	0
Dichloro-difluoromethane	111.8	40.7	0.56	1.12	0.17
Trifluoromethane	25.9	46.9	0.52	----	1.47
Ammonia	132.5	112.5	0.24	0.40	1.65
Water	374.4	226.8	0.34		
Methanol	240.5	78.9	0.27		

2. Supercritical Fluid Extraction

There are several advantages of supercritical fluid extraction (SFE):

a. SFE is generally fast**. The rate of mass transfer between a sample matrix and an extraction fluid is determined by the rate of diffusion of a species in the fluid and the viscosity of the fluid—the greater the diffusion rate and the lower the viscosity, the greater will be the rate of mass transfer.**

b. The solvent strength of a supercritical fluid **can be varied by changes in the pressure and to a less extent in the temperature.**

c. Many supercritical fluids are gases at ambient condition.

d. Some supercritical fluid are cheap, inert, and nontoxic.

3. Supercritical fluid chromatography (SFC)

a. SFC is **a chromatographic technique in which the mobile phase is a supercritical fluid.**

b. The use of a supercritical **fluid mobile phase in chromatography was first proposed in 1958 by J. Lovelock. The first actual report use of this in a chromatographic system was in 1962 by Klesper et al, who used it to separate thermally-labile porphyrins.**

c. SFC is of importance because it permits the separation and determination of *a group of compounds that are not conveniently handled by either GC or LC*. **These compounds (1) are either non-volatile or thermally labile so that the GC are in-applicable, and (2) contain no functional groups that make impossible detection by spectroscopic or electrochemical techniques employed in LC.**

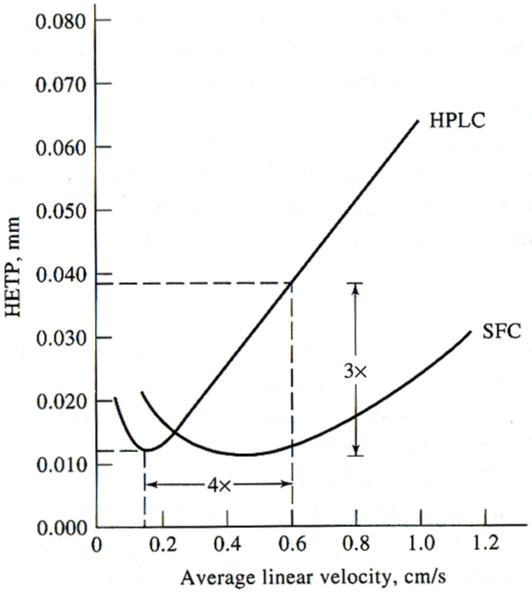
4. Theory of SFC

Since supercritical fluids have properties between those of gases and liquid, their use as a mobile phase offers several advantages. Typical physical properties of liquid, gases and supercritical fluids are shown below:

Phase	density	Diffusion coefficient	Viscosity
Gas	10^{-3}	10^{-1}	10^{-4}
SL	0.3-0.9	$10^{-3} \sim 10^{-4}$	$10^{-3} \sim 10^{-4}$
Liquid	1	$<10^{-5}$	10^{-2}

a. One of advantages is that supercritical fluid have lower densities and viscosities than liquids. This results in larger diffusion coefficients for solutes is SFC than LC. This results in Better efficiencies and higher optimum linear Velocities in SFC than LC. The plate height of a SFC System is given by the van Deemter equation.

$$H = A + B/u + Cu$$



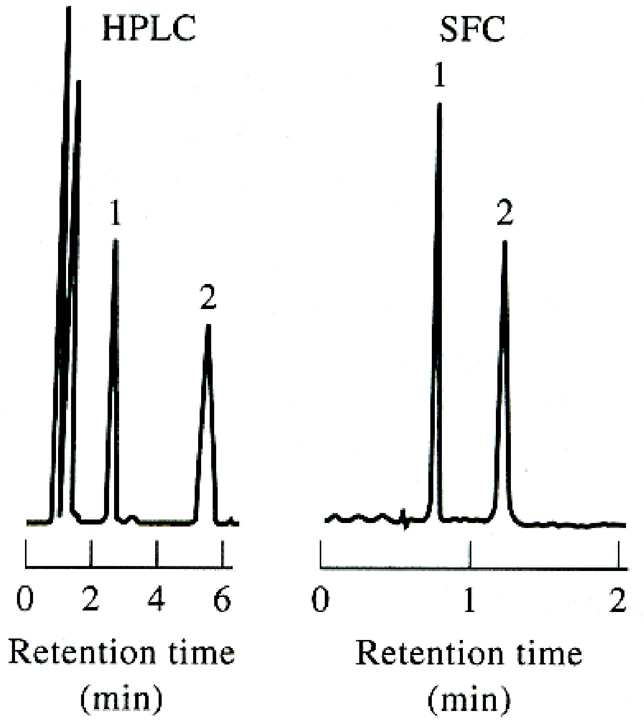


Figure 29-4 Comparison of chromatograms obtained by conventional partition chromatography (HPLC) and supercritical fluid chromatography (SFC). Column: 20 cm × 4.6 mm packed with 10 µm reversed-phase bonded. Analytes: (1) biphenyl; (2) terphenyl. For HPLC: mobile phase, 65/35% CH_3OH/H_2O; flow rate, 4 mL/min; linear velocity, 0.55 cm/s; sample size, 10 µL. For SFC: mobile phase, CO_2; flow rate, 5.4 mL/min; linear velocity, 0.76/s; sample size, 3 µL. *(From D. R. Gere, T. J. Stark, and T. N. Tweeten,* Application Note 800-4. *Hewlett-Packard Company, 1983. With permission.)*

b. SFs have higher densities than gas, so that mobile phase has a greater chance of interacting with the solute than that in GC (i.e., carrier gas). This makes the mobile phase important in determining the retention of solutes on the system and give more flexibility in optimizing the separation. For example, retention of solutes in SFC can be changed by using a different column (i.e. different stationary phases) as in GC, or by changing the mobile phase strength as in LC.

isobaric **Flow-rate programming** **Pressure programming**

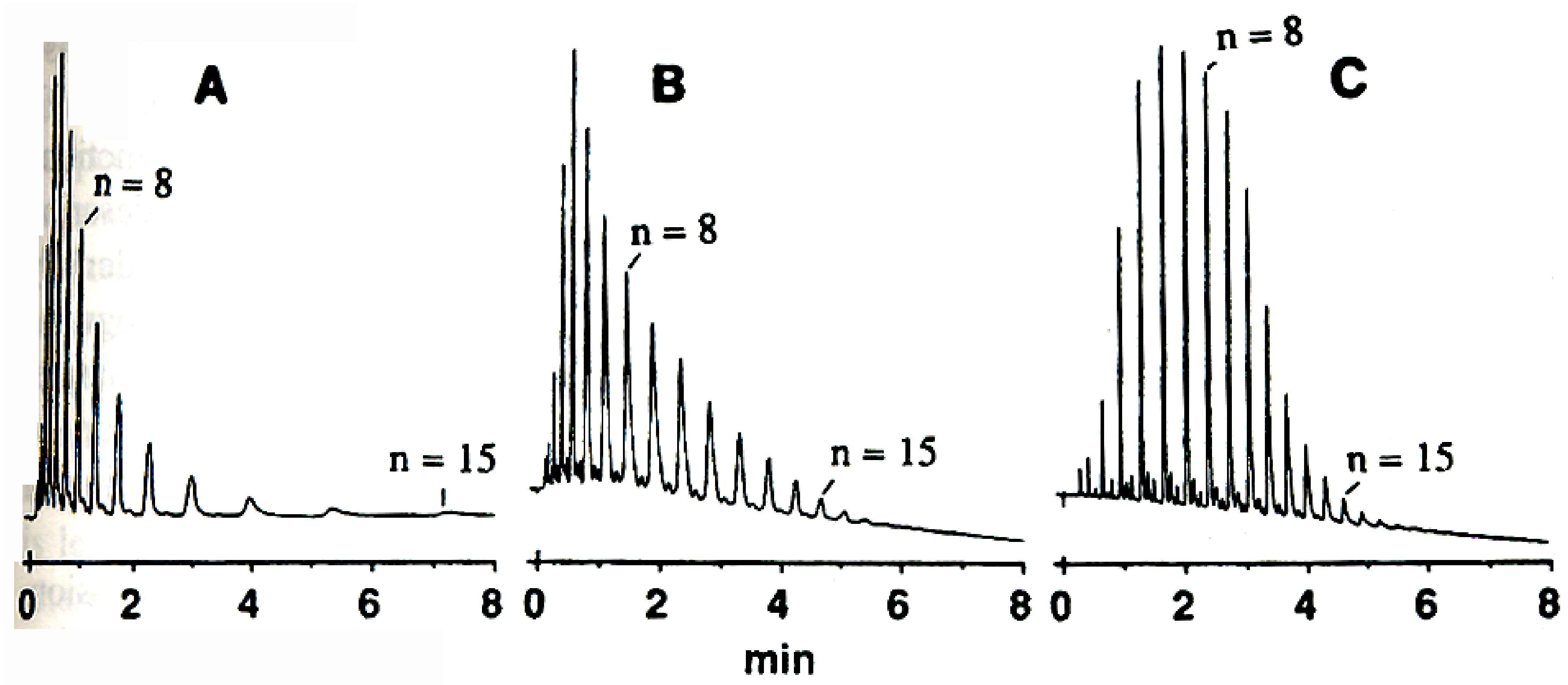


Figure 7.8. Separation of Triton X-114 by SFC using programmed elution on a 10 cm x 2 mm I.D. Nucleosil C_{18} column, 3 µm packing, at 170°C with UV detection at 278 nm. Separation on the left: isobaric conditions at 210 bar with a mobile phase of carbon dioxide and methanol (2 + 0.125) ml/min. Center separation: composition gradient from 0.025 to 0.4 ml/min methanol over 8 min with other conditions as above. Separation on the right: pressure program from 130 to 375 bar over 8 min with the same mobile phase used for the isobaric separation. (From ref. [137]; ©Copyright Preston Publications, Inc.)

c. One major advantage of SFC is its ability to use detector available for either GC or LC, such as FID, UV-Vis, and Fluorescence detectors. This gives it a wide range of both universal and selective detections for use in either analytical or preparative-scale work.

GC detectors:

Thermal conductivity detector (TCD): 10^{-7} M (10^{3}-fold range)

Flame Ionization detector (FID): 10^{-10} M (a 10^{5}-fold range)

Nitrogen-phosporus detector (NPD): 10^{-10} M (a 10^{6}-fold range)

Electron capture detector (ECD): $10^{-14} \sim 10^{-16}$ M (a 10^{3}- 10^{4} fold range)

Flame photometric detector (FPD):10^{-14} M (P, S)

Electrochemical detector (S, halogen,nitrogen-)

LC detectors:

Refractive Index Detector (10^{-5} to 10^{-6} M)

Absorption Detector (UV/Vis)

(10^{-8} M)

Fluorescence Detector (10^{-10} M)

Conductivity Detector

(10^{-6} M)

Electrochemical Detector

(10^{-11} M)

d. Depending on which supercritical fluid is used, it is also possible to use SFC at lower T than GC. This makes it more useful in the separation of thermally unstable compounds.

e. The stationary phases used in SFC can be similar to those in LC as well as GC. Either packed or open-tubular columns may be used.

Because of these advantages, SFC is commonly viewed as a technique which is complementary to both LC and GC.

5. Instrumentation

a. Instrumentation for SFC can be obtained commercially or adapting system used for either LC and GC.

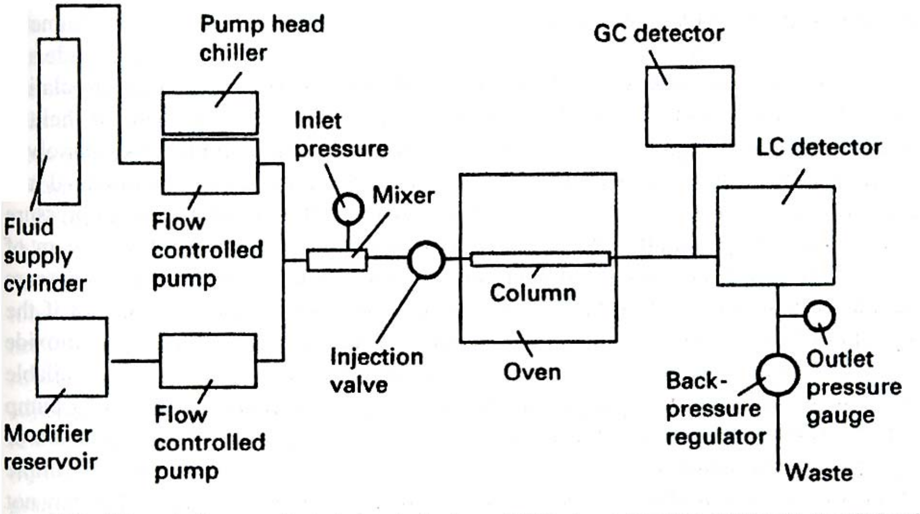


Figure 7.9. Schematic diagram of a typical packed column SFC instrument capable of pressure (density) and composition mobile phase programming. (From ref. [146].©Academic Press).

b. The main difference of a SFC than a LC or GC system is the need to control bother temperature and pressure of mobile phase. This must be done to keep the mobile phase as a Supercritical fluid. Control of the pressure (density) of the supercritical fluid can also used to vary strength of mobile phase during the gradient elution in SFC .

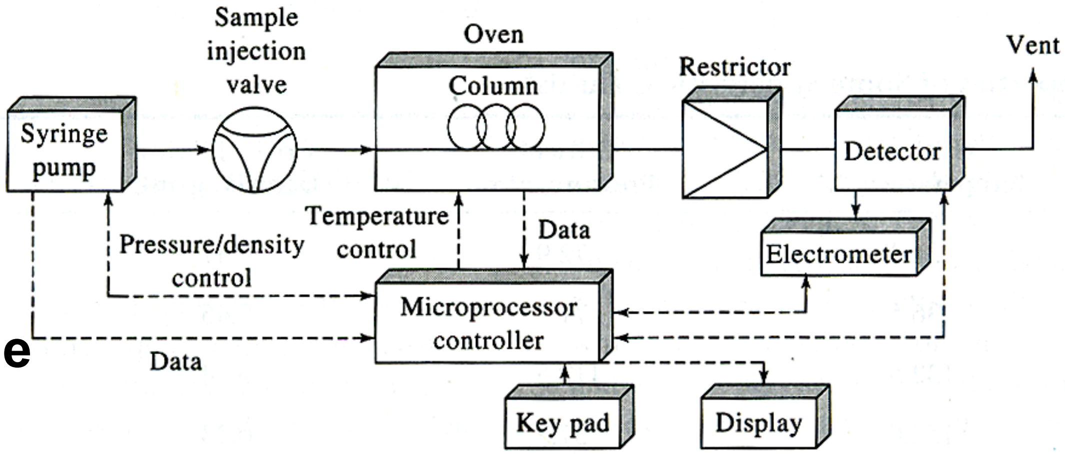


Figure 29-1 Schematic of an instrument for supercritical fluid chromatography.

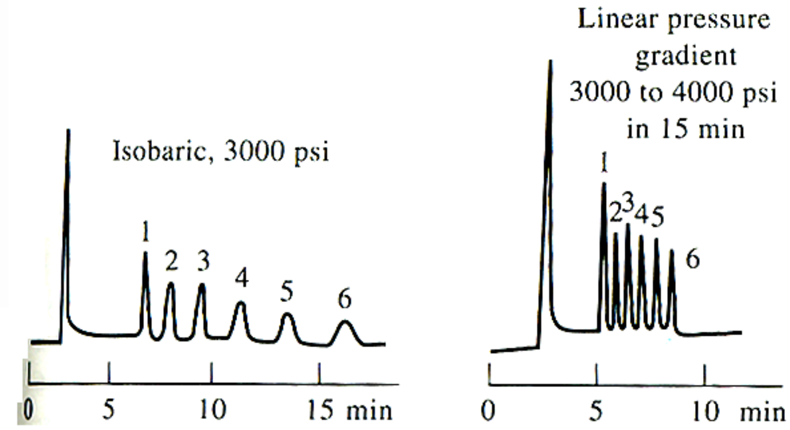
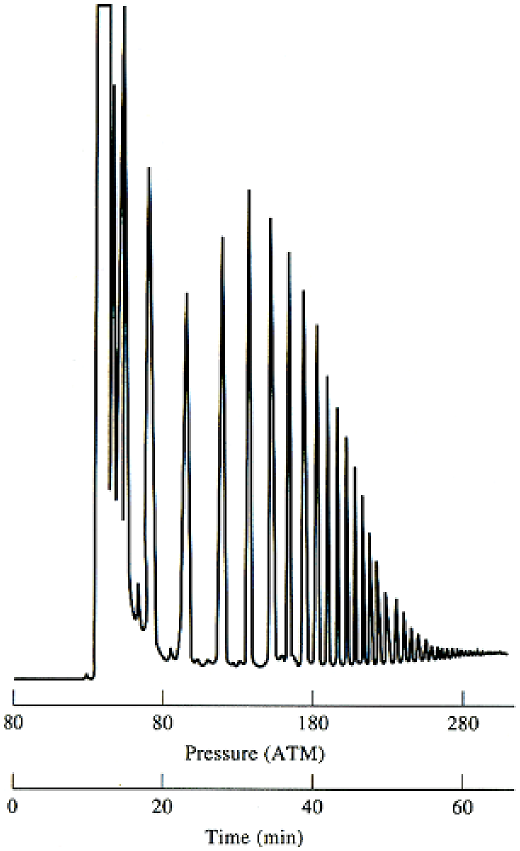


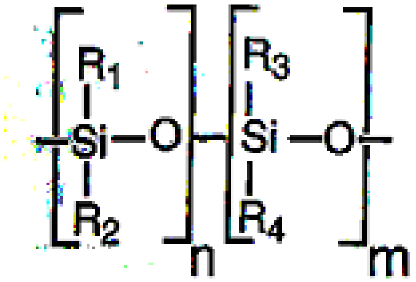
Figure 29-2 Effect of pressure programming in supercritical fluid chromatography. *(Courtesy of Brownlee Labs., Santa Clara, CA.)*

Sample:	1. cholesteryl octanoate 2. cholesteryl decylate 3. cholesteryl laurate 4. cholesteryl myristate 5. cholesteryl palmitate 6. cholesteryl stearate
Column:	DB–1
Mobile phase:	CO_2
Temperature:	90° C
Detector:	FID

6. Applications

By now, SFC has been applied to a wide variety of materials, including Natural products, drug, foods, pesticides and herbicides, surfactants polymers, and polymer additives, fossil fuels, and explosives and Propellants.





Dimethylpolysiloxane: non-volatile and special function groups

Figure 29-6 Separation of oligomers of dimethylpolysiloxane by supercritical fluid chromatography. *(From C. M. White and R. K. Houck, HRC & CC, 1986, 9, 4. With permission.)*

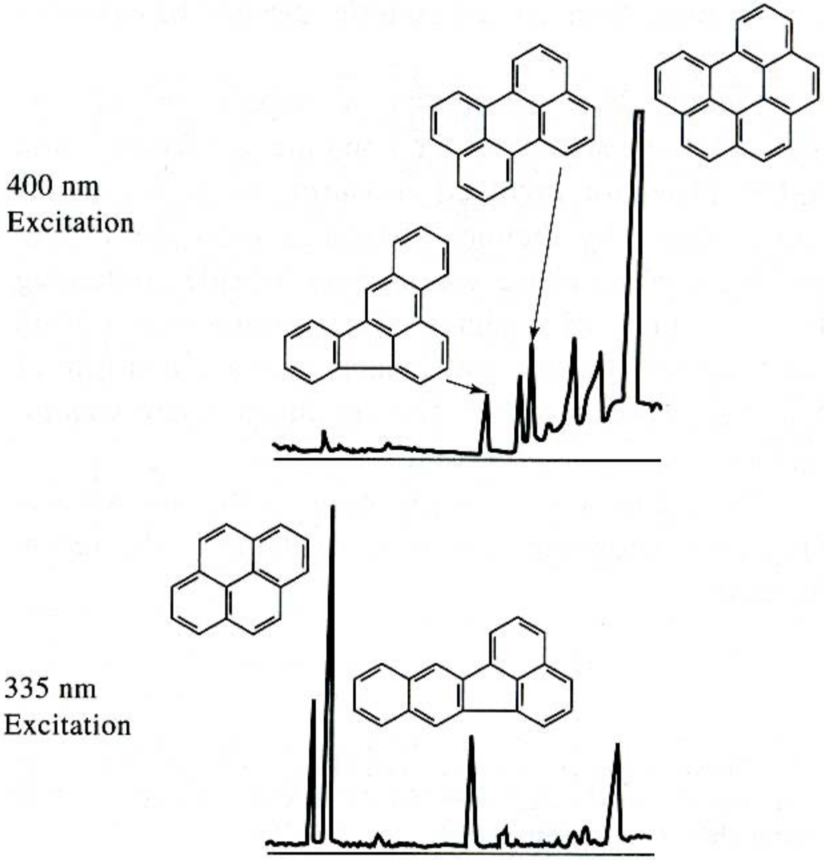


Figure 29-7 Portions of the supercritical fluid chromatograms of polycyclic aromatics in a carbon-black extract, illustrating the selectivity achieved by fluorescence excitation at two wavelengths. *(From C. M. White and R. K. Houck,* HRC & CC, ***1986****, 9, 4. With permission.)*

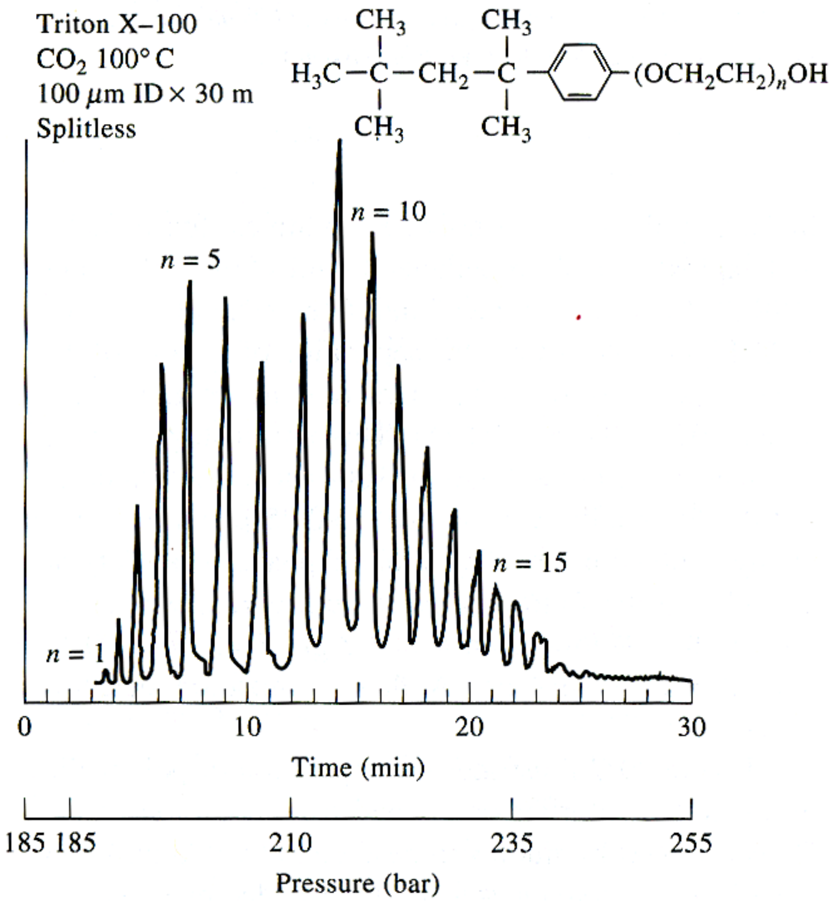


Figure 29-8 Chromatograms for the nonionic surfactant Triton X-100 with total current mass spectrometric detection. *(Reprinted with permission from R. D. Smith and H. R. Udseth,* Anal. Chem., ***1987****, 59, 17. Copyright 1987 American Chemical Society.)*

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