Chapter 29 Supercritical Fluid Chromatography and Extraction

The critical temperature of a substance is the temperature above which a distinct liquid phase can not exist, regardless of pressure.

The vapor pressure of a substance at its critical temperature is the critical pressure of the substance.

At temperatures and pressures above its critical temperature and pressure (its critical point), a substance is called a supercritical fluid.

TABLE 29-1 Comparison of Properties of Supercritical Fluids with Liquids and Gases (all of the data are order-of-magnitude only)

	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})	$(1–3) \times 10^{-4}$	$(1–3) \times 10^{-4}$	$(0.2–3) \times 10^{-2}$

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_2O	36.5	71.7	0.45	0.94
NH_3	132.5	112.5	0.24	0.40
n-Butane	152.0	37.5	0.23	0.50

*From M. L. Lee and K. E. Markides, *Science*, 1987, *235*, 1345. With permission.

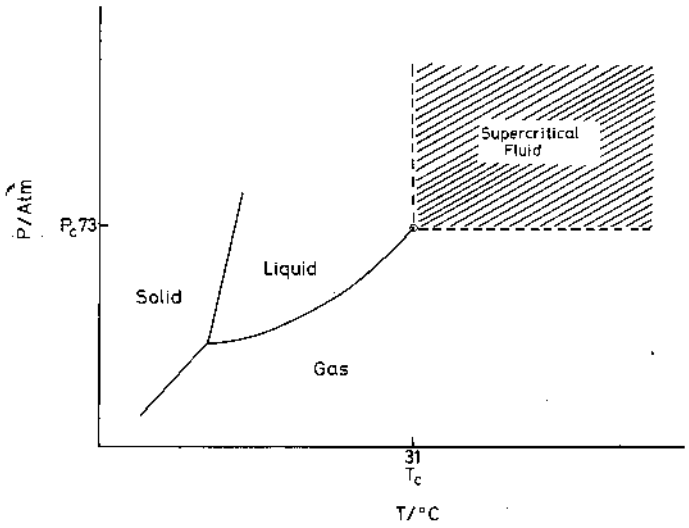


Figure 1 *Carbon dioxide phase diagram*

1. Concepts

2. Instrumentation

Question: What are the differences (major) between GC and SFC ?

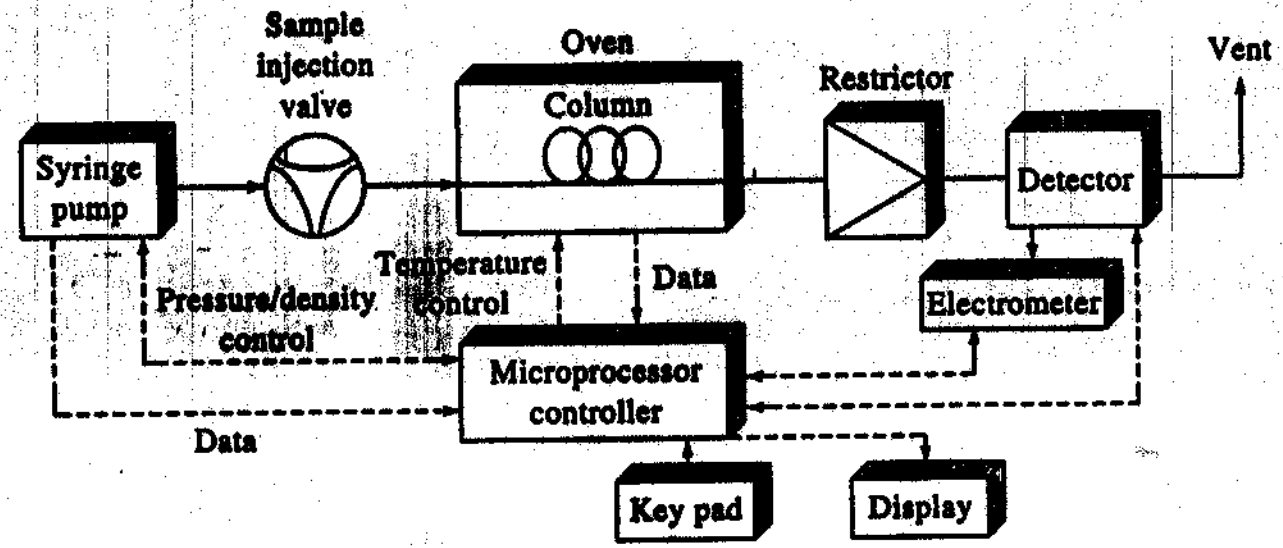


Figure 29-1 Schematic of an instrument for supercritical fluid chromatography.

3. Example of SFC

Question: What are the techniques used in GC and LC that are based on similar rationale as pressure programing in SFC ?

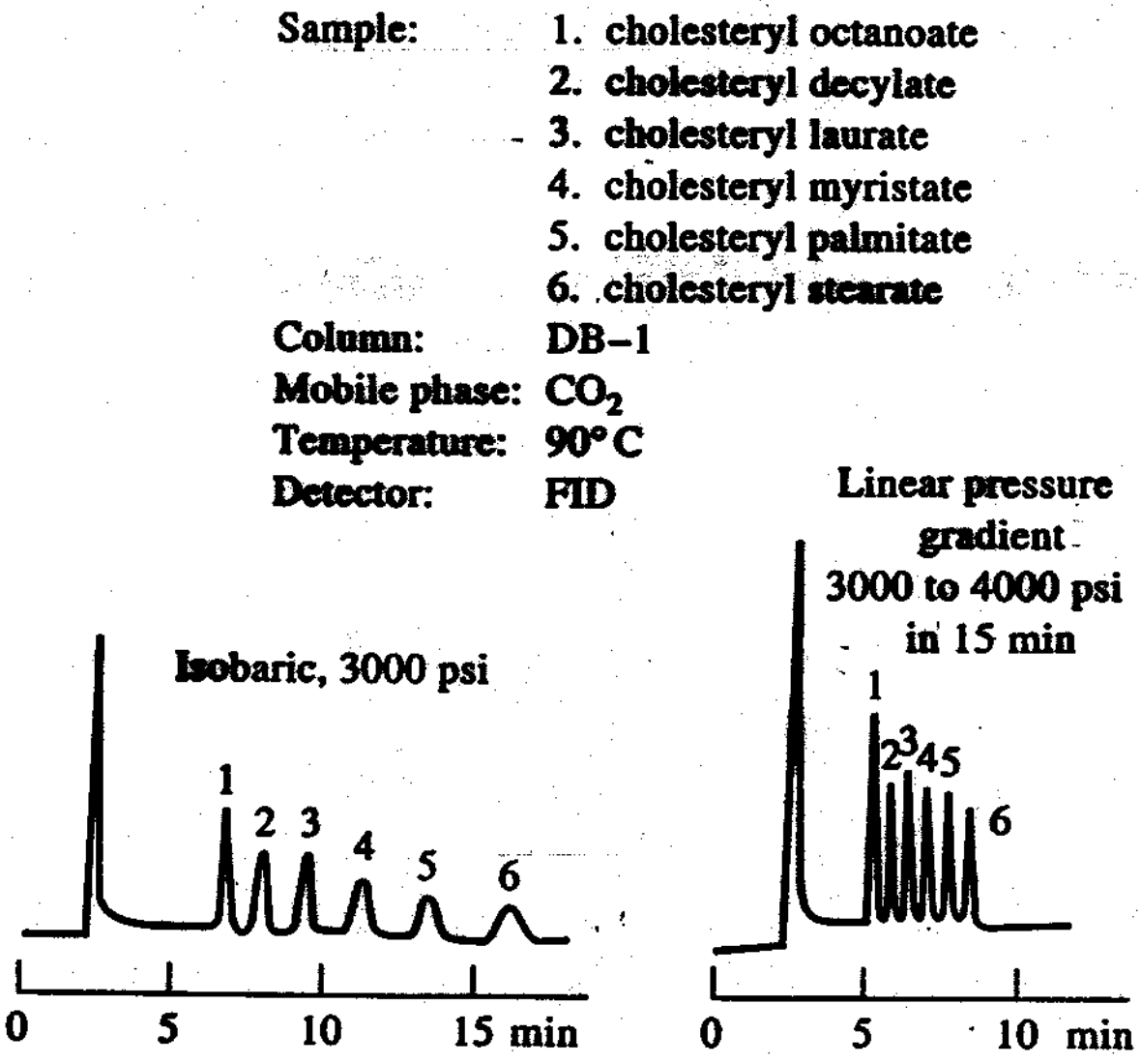


Figure 29-2 Effect of pressure programming in supercritical fluid chromatography. *(Courtesy of Brownlee Labs., Santa Clara, CA.)*

4. Supercritical Fluid Extraction

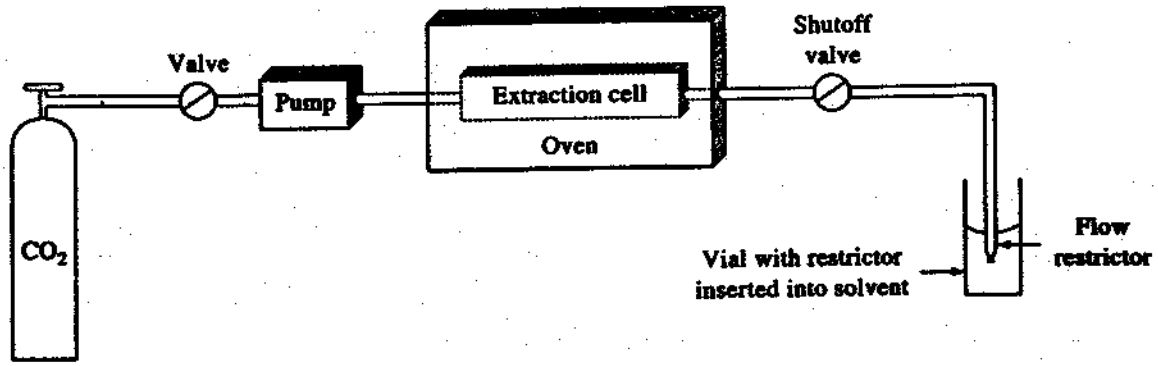


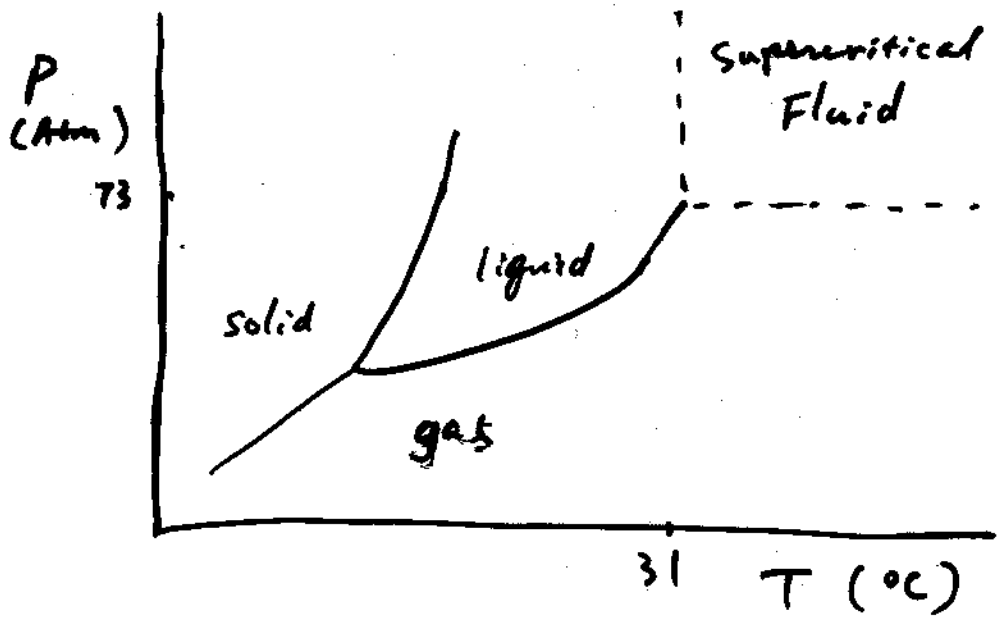
Figure 29-9 A typical arrangement for off-line SFC. The shutoff valve is required for static SFC but not dynamic SFC.

TABLE 29-3 Some Typical Applications of Supercritical Fluid Extraction

Material	Analyte*	SF	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	Fat	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 = polycyclicaromatic hydrocarbons; PCBs = polychlorinated biphenyls.

Carbon dioxide phase diagram



Advantages of Supercritical Fluid Extraction

1. Fast (high diffusion rate, low viscosity)
2. Solvent strength can be varied by changing pressure and sometimes, T.
3. Many supercritical fluids are gases at ambient conditions.
4. Inexpensive, inert, and nontoxic.