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The Present Status of Dense (Supercritical) Gas Extraction and Dense Gas Chromatography: Impetus for DGC/MS Development

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The Present Status of Dense (Supercritical) Gas Extraction and Dense Gas Chromatography: Impetus for DGC/MS Development

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ABSTRACT

Dense (supercritical) gas chromatography and the related rapidly growing field of dense gas extraction are reviewed and an extensive compilation detailing the dense gas systems (solvent gases, solutes, temperatures, pressures) that have been studied is presented. Furthermore, dense gas chromatography is compared to both gas and high performance liquid chromatographies with emphasis on mass spectrometric detection in all three. It is concluded that a dense gas chromatograph/mass spectrometer, a new instrument, is both a complement to existing techniques and a timely development for use with dense (supercritical) gas systems.

1. INTRODUCTION

The main purpose of this paper is to review the area of dense gas chromatography and the related (broader) area of dense gas extraction--particularly since there has been intense renewed interest in these areas in the last six years. A secondary purpose is to present the motivation for developing a new instrument, a dense gas chromatograph/mass spectrometer (DGC/MS), which is capable of directly interfacing high pressure systems to a mass spectrometer, a powerful selective and universal detector.

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In compiling data to create a directory of the experimental conditions that had been studied in DGC and that would be pertinent to the operation of a DGC/MS, the author became keenly aware of the abundant, very recent work with dense gases as extractive solvents. Because of the intimate overlap of the areas of dense gas chromatography and dense gas extraction, it was obvious that a useful compilation would have to include data from all the related work of DGC, dense gas extraction and solubility studies.

The resulting compilation is presented after first describing the properties which make dense gases so attractive as solvents, then outlining the reported work in dense gas extraction and DGC, and finally comparing GC/MS, HPLC/MS and DGC/MS to determine the possible advantages of DGC/MS. The author hopes that the reader will gain an appreciation of 1) dense gases as viable alternatives to liquid solvents and 2) the potential of the DGC/MS technique--a timely development which promises to be applicable to a wide variety of high pressure processes.

2. PROPERTIES OF DENSE GASES

A dense gas (also referred* to as a supercritical fluid, high pressure gas, hyperpressure gas, ultra high pressure gas) is a gas at temperatures and pressures such that its density is comparable to normal liquid densities of the substance. As shown in Figure 1**,

*The various terms are used in different areas by different authors with some effort to define pressure regions. This author prefers the term "dense gas" to emphasize the fact that the most important parameter in the work to be described is the density and not either the absolute pressure or the temperature alone.

**From van der Waal's Law of Corresponding States one would expect that the relationship between the reduced parameters shown in Figure 1 is applicable for all substances (4). Similar curves for ethylene, methane, nitrogen, acetylene, carbon monoxide, propane, and argon within the reduced temperature range $1.000 \leq T_R \leq 1.049$ fall remarkably close to the curve shown in Figure 1.

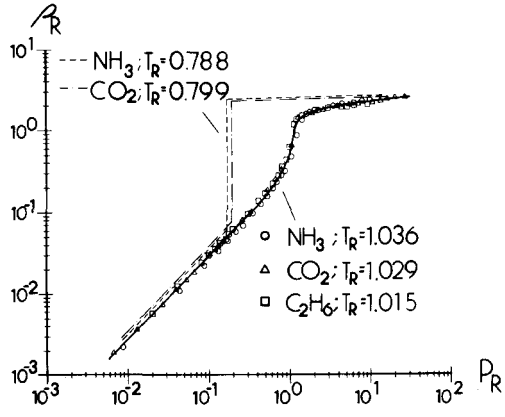

FIGURE 1. Reduced density (ρ_R) as a function of reduced pressure (P_R) for three gases at reduced temperatures (T_R) close to 1. (Throughout this paper, "reduced" means the value of a parameter divided by its value at the critical point.) Reduced isotherms for carbon dioxide (T_R = 0.799) and ammonia (T_R = 0.788) show density as a function of pressure for subcritical gas and liquid phases. (Data from References 1 and 2.)

for a gas at temperatures just above the critical temperature (T_c) of the substance, liquid-like densities are rapidly approached with modest increases in pressure in the range of 0.7 to 2 times the critical pressure (P_c). Higher pressures are required to attain liquid-like densities for temperatures further above critical, as demonstrated by the three isotherms in Figure 2.

It is interesting to compare the density near the critical point to densities of common solvents at room temperature, i.e., conditions far from critical but typically encountered in high performance liquid chromatography and perhaps in some liquid solvent extraction procedures. A survey of six common solvents--benzene, cyclohexane, carbon tetrachloride, chloroform, n-pentane, and isobutane--shows that for these solvents a temperature of 300°K is equivalent to reduced temperatures of 0.53 to 0.74. Hence, as shown by the isotherms in Figure 1 for CO_2 and NH_3 at reduced temperatures of about 0.79--slightly high for the room temperature

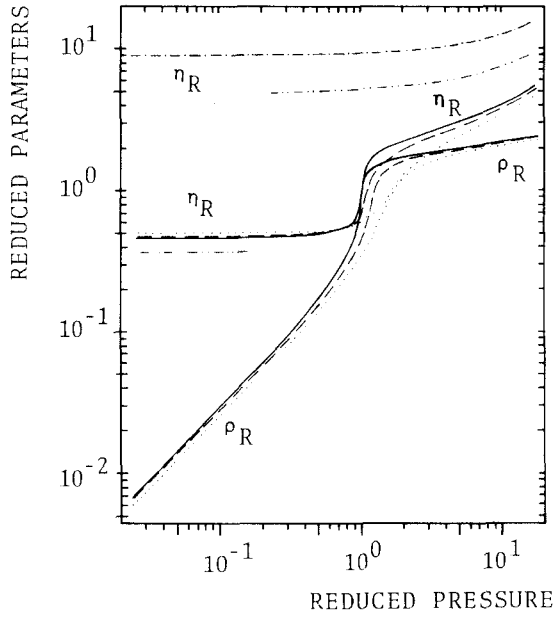

FIGURE 2. Reduced viscosity (η_R) and density (ρ_R) as functions of reduced pressure at various reduced temperatures (T_R). (Ethylene data, Ref. 2; n-pentane data, Ref. 3.)

— . — . — . — n-Pentane, $T_R = 0.63$ (i.e., 25°C)

— .. — .. — .. n-Pentane, $T_R = 0.789$

——————— Ethylene, $T_R = 1.002$, (T_c + 0.50°C)

— — — Ethylene, $T_R = 1.037$, (T_c + 10.50°C)

. . . . . Ethylene, $T_R = 1.108$, (T_c + 30.50°C)

range, the densities at room temperature are only a factor of about two times the dense gas density at $2P_c$ and T_c. For further comparison between dense gases and liquid, the viscosity data displayed in Figure 2 show that the viscosity of a common liquid solvent (n-pentane) is a factor of four times that of dense ethylene for $2P_c$ and T_c (and a factor of ten times that of the gas at P_c and T_c). Also it can be seen that the gas viscosity approaches the liquid value more slowly (with increasing pressure) than does the density.

The curves in Figure 2 also illustrate the difference in temperature dependence between viscosity and density: an increased temperature leads to an increased viscosity for a gas and a decreased viscosity for a fluid (dense gas or liquid) but to a decreased density for all states.

It is also of interest to explore the values of the diffusivity in the critical region versus the gaseous and liquid states. The reduced diffusivity (for self-diffusion), D_R--as well as the reduced

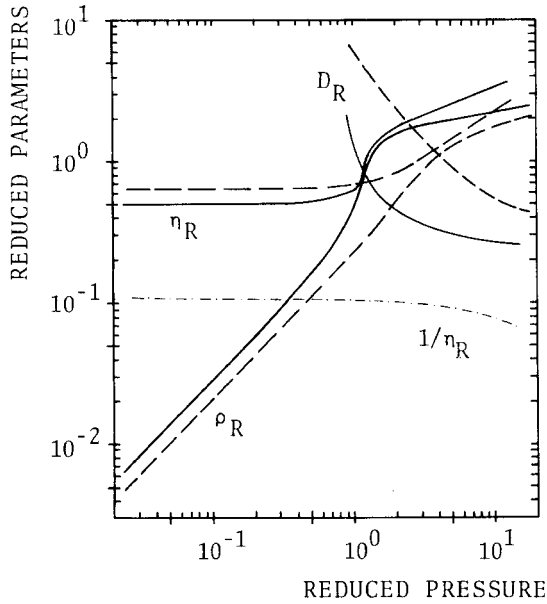

FIGURE 3. Reduced viscosity (η_R), density (ρ_R), self-diffusivity (D_R) as functions of reduced pressure for methane at two reduced temperatures (T_R). The inverse of the n-pentane reduced viscosity (at T_R = 0.63) is presented as an approximation to liquid diffusivities at room temperature. (Density, viscosity data from Ref. 2, n-pentane data from Ref. 3, diffusivity data from Ref. 5.)

———— Methane: T_R = 1.05 for ρ_R,η_R; T_R = 1.02 for D_R

— — — Methane: T_R = 1.42 for ρ_R,η_R; T_R = 1.43 for D_R

·—·—· $1/\eta_R \sim D_R$ for n-Pentane at T_R= 0.63

viscosity, η_R, and the reduced density--as a function of reduced pressure is shown in Figure 3. Since D is equal to η/ρ for dilute gases (6) and the viscosity, η, is essentially independent of pressure in that region, the diffusivity is inversely proportional to density. The diffusivity of liquids is inversely proportional to viscosity. As an approximation to liquid diffusivity behavior, the inverse of the n-pentane reduced liquid viscosity data (Figure 2) is graphed in Figure 3. While the ordinate placement of the complete curve is not exact and may vary by a small factor, the shape of the curve is valid and shows the relative insensitivity of the diffusivity of a liquid to pressure. The value for the reduced diffusivity for liquid methane at $T_R = 0.62$ and $\rho_R = 2.56$ (corresponds to $P_R \sim 1.1$) is about 0.1. Hence, it can be seen that the diffusivity of a dense gas at $\sim P_c$ and $\sim T_c$ is at least a factor of ten larger than that of a liquid.

The following data are presented for order-of-magnitude comparisons of the three important parameters:

	ρ (g/mL)	η (g/cm s)	D^a (cm^2/s)
Gas 1 atm, ~15-30°C	$(0.6 - 2) \times 10^{-3}$	$(1 - 3) \times 10^{-4}$	0.1 - 0.4
Dense Gas			
T_c, P_c	0.2 - 0.5	$(1 - 3) \times 10^{-4}$	0.7×10^{-3}
$\sim T_c$, $4P_c$	0.4 - 0.9	$(3 - 9) \times 10^{-4}$	0.2×10^{-3}
Liquid (organic solvents, water) ~15-30°C	0.6 - 1.6	$(0.2 - 3) \times 10^{-2}$	$(0.2 - 2) \times 10^{-5}$

[a]Self diffusion for Gas and Dense Gas; binary mixture for Liquid.

Consequential Benefits of Dense Gas Properties

The liquid-like densities of dense gases result in liquid-like solvent powers. This property and the faster mass transport capability due to the dense gas viscosity and diffusivity make dense gases very attractive as solvents. Bailes (7) has reviewed liquid

solvent extraction in organic and petrochemical industries and noted that solvent extraction is particularly important in the food and pharmaceutical industries because many products are thermally labile and cannot be separated by distillation. Obviously, major considerations in liquid extraction processes are the choice of solvent including the operating temperature range and its toxicity and the solvent/solute separation. Incomplete solvent recovery must be minimized because of expensive solvent loss and possible contamination of the product with the solvent. Often distillation is required to improve solvent recovery. As an alternative separation method which typically uses biologically safe gases such as CO_2, dense gas extraction combines the separation processes of liquid extraction and distillation and it has been proposed (8) that this process be called destraction. Compared to the other separation techniques dense gas extraction (or destraction) has several important characteristics: 1) temperatures are usually close to critical temperatures so mild conditions can be used for thermally labile compounds, 2) dense gases can dissolve involatile compounds, 3) compounds can be selectively dissolved by changing the density of the gas, 4) three dense gas parameters, density as well as temperature and composition, can be easily varied, 5) essentially complete separation of solvent/solute with high solvent recovery can be accomplished by isothermal decompression or isobaric heating, and 6) the solutes can be fractionated during the solvent/solute separation. Since chromatography is a multistage phase-transfer process, the above comments also apply to the use of dense gases in chromatography.

Even though the liquid-like solvent powers of dense gases have been recognized for over 100 years (9,10), there was relatively little application of dense gas solvents until about twenty years ago with the early experiments in dense gas chromatography. Within the last ten years and particularly this last year there has been intense interest in high pressure fluid mixtures and dense gas extraction processes (11-22, 137-150) especially in the food,

pharmaceutical, and coal industries.* Papers presented at three recent symposia (8,23-36,154-159) outline the rapid growth of work in this area. Subjects discussed included dense gas extraction of raw food and drug materials, industrial plant design, energy consumption compared to conventional separation techniques, dense gas chromatography, and phase equilibria.

Theoretical Approaches to Solubility Predictions

Irani and Funk (37) have outlined several of the theoretical approaches used to estimate phase equilibria--many of which involve empirical or semi-empirical equations of state. The equation of state descriptions of phase equilibria of compressed gas mixtures have dealt with a variety of solutes ranging from light gases (160-164) to heavy solid hydrocarbons (165-171) and have generated data (e.g., binary interaction parameters (172)) useful for describing dense gas systems including those dense gas systems where the solvent is the gas plus an entrainer. Prausnitz (173), Oellrich et al (172), and Peter (174) compare several of the equation-of-state approaches. Furthermore, Rowlinson (38,39) has discussed the thermodynamics of (super)critical binary solutions as has Schneider who has also presented data for many systems (15,16,31,40,175-179) and reviewed the experimental methods used (41).

An in-depth discussion of any of these methods will not be pursued here; many of the cited references contain comprehensive discussions and literature lists as do several of the papers in this Special Topics issue. Another approach mentioned by other authors in this issue is the use of the Hildebrand solubility parameter developed by Giddings et al (42-44). This scheme will be briefly outlined to permit easy comparison.

*In the area of supercritical extraction/liquefaction of coal, the supercritical extraction process has become commonplace enough that the emphasis is on the extract analysis and not on the extraction procedure (e.g., References 151-153).

The Hildebrand solubility parameter, δ, originally defined as the square root of the molecular cohesive energy per unit volume (the internal pressure), is admittedly a general quantity not based on a precise model (45); however, it has been found to be quite useful for solubility predictions for a wide range of compounds. Generally, if component solubility parameter values agree to within ± 1 $(cal/cc)^{\frac{1}{2}}$, those components will probably be mutually soluble. Various methods have been devised to calculate solubility parameters for liquids and solids and also for compounds which form non-regular solutions because of polarity and hydrogen bonding (46,47). An expression for the solubility parameter for a gas is obtained in the following manner.

From elementary considerations, the internal pressure (P_i) is given by:

$$P_i = (\partial E/\partial V)_T. \tag{1}$$

Thus, for a van der Waals gas,

$$P = RT/(V-b) - a/V^2, \tag{2}$$

the internal pressure, $(\partial E/\partial V)_T$, is found to be

$$(\partial E/\partial V)_T = a/V^2 \tag{3}$$

so that the gas solubility parameter is given by

$$\delta_g = a^{\frac{1}{2}}/V. \tag{4}$$

The parameter, a, in the van der Waals equation can be evaluated in terms of the critical pressure (P_c) and critical volume (V_c); upon substitution one obtains

$$\delta_g = (3P_c)^{\frac{1}{2}}\rho_g/\rho_c \tag{5}$$

where δ_g is the solubility parameter of the gas, P_c is the critical pressure (units of cal/cc), ρ_g is the gas density, and ρ_c is the gas critical density. It was found (42) that experimental results were represented better by

$$\delta_g = 1.25 P_c^{1/2} \rho_g / \rho_\ell \tag{6}$$

where units of P_c are atmospheres and units of δ_g are $(\text{cal/cc})^{1/2}$. In the above equation ρ_ℓ is the liquid density of the substance and is chosen such that the reduced liquid density (ρ_ℓ/ρ_c) is about 2.66--i.e., about 1 atm pressure and boiling point temperature (42). Assuming a regular, saturated (zero free energy of mixing) solution, one obtains

$$\ln X_o/X_g = -\Phi_g^2 V_o(\delta_g^2 - 2\delta_o\delta_g + \delta_o^2)/RT \tag{7}$$

where X_o is the solute mole fraction of the solution, X_g is the gas mole fraction, Φ_g is the volume fraction of the gas, V_o is the molar volume of the solute, δ_o is the solute solubility parameter and δ_g is the gas solubility parameter. Experimentally, it has been found that:

$$\log X_o = A\delta_g^2 + B\delta_g + C \tag{8}$$

(or substituting for δ_g,

$$\log X_o = A'\rho_g^2 + B'\rho_g + C) \tag{9}$$

where A, B, and C are least square fit parameters for a parabolic equation. The derivations of the above relationships have been presented in detail by Bowman (46).

Several important properties of dense gas solutions are embodied in the equations for the solubility parameter and the solute solubility:

1. The gas solubility parameter can be separated into two terms, $1.25P_c^{\frac{1}{2}}$ and ρ_g/ρ_ℓ. The first is referred to as the chemical effect. It depends upon the identity of the gas--specifically the intermolecular forces of that compound. The second term is a state effect.

2. As $\rho_g \to \rho_\ell$, a maximum value is obtained for δ_g. Hence, while there is a maximum value at high pressures, the dense gas solubility parameter can assume a whole range of values below that maximum. The maximum value of δ_g is determined by gas identity while all other values depend upon the chosen physical state. (A diagram comparing the maximum δ_g for many gases to the liquid solubility parameters of common solvents has been presented in several places (42,46,48,49).)

3. There is a threshold density below which a solute is not soluble in the dense solvent gas. (from $|\delta_g - \delta_o| \leq 1\ (\text{cal/cc})^{\frac{1}{2}}$)

4. Because of the parabolic solute solubility-dense gas density relationship, there is a maximum solubility at some density so that at even higher densities the solubility decreases. The location and magnitude of the maximum is different for different solute/solvent gas pairs. (Several systems have been studied and are presented in Reference 46.) It should be emphasized that the solubility function is a parabolic density function and not necessarily a parabolic pressure function because of the very nonlinear pressure-density relationship in the vicinity of the critical point.

These properties are important in extraction processes as well as in the more specialized dense gas chromatography. Examples of the use of dense gases as solvents in extractions are now presented.

3. DENSE GAS EXTRACTION

Extraction using dense gas solvents has been used in a variety of fields--e.g., the processing of food, pharmaceuticals, petroleum

products, and coal. Probably the method is being actively developed to an even greater extent than presented here or in two recent reviews (180,181). Unsurprisingly, details are not readily available since these are competitive industrial processes. Several examples will be presented in this part to indicate the direction of the current work in dense gas extraction and related high pressure systems.

Industrial Applications

One of the earliest industrial applications was that of Katz and Whaley (50) where natural gas at pressures above 68 atm and temperatures up to 200°C was used to separate liquid hydrocarbon mixtures. T.P. Zhuze et al have used supercritical gases for the de-asphalting and deresination of petroleum, the extraction of lanolin from wool grease, and the extraction of ozocerite from its ores (51-53). Desalination of water has been accomplished using liquid organic solvents at elevated temperatures (often just below critical) pressures (51,54). Zosel has patented a process for the separation of mixtures of aluminum trialkyls having alkyl groups of different chain lengths using supercritical ethane or ethylene (55). Several other processes patented by Zosel are important to the food industry: deodorization of plant oils (soybean, palm and peanut) with simultaneous removal of free fatty acids (56) using CO_2; oil extraction from soybean flakes, corn, and bones using propane, ethane, CO_2, or N_2O (57); simultaneous hydrogenation and deodorization of fats and/or oils with a CO_2/H_2 gas mixture (58); and decaffeination of coffee with supercritical CO_2 (59) and supercritical humid CO_2 (60). O. Vitzthum et al have also patented similar extractions: fats and oils from plant seeds with subcritical gases (CO_2, SF_6, $CClF_3$, CHF_2Cl, CF_3Cl, CF_2CH_2, C_3F_8, N_2O, C_2H_6, C_2H_4 and various mixtures of these gases) (61); hops extraction with supercritical CO_2 (62); cocoa butter and aroma components (with identification) from cocoa beans with CO_2 (63,64); spice (black pepper)

extraction with CO_2 (65); oil (containing flavor components) and caffeine from coffee with CO_2 (66-68); and nicotine from tobacco using CO_2, N_2O, Ar, SF_6 or halogenated hydrocarbons (69,70). They have also extracted black tea aroma constituents with supercritical CO_2 and then identified the volatile components of the extract using GC/MS (71).

Many of the extraction processes have developed beyond "bench-top models." The dense gas extraction of petroleum and ozocerite cited above was used industrially in Russia as early as 1960. The Kerr-McGee Refining Corporation has operated a semicommercial plant (750 b/d) for de-asphalting of residuum oil (72). In this plant supercritical solvent recovery resulted in a utility savings of 50% over the usual solvent recovery methods of evaporation; also cited were typical investment savings of about 20%. Even more recently Kerr-McGee (138,139) has developed to the pilot plant level (163 kg/h) a critical solvent deashing (CSD) process to separate ash from liquefied coal (i.e., the more familiar solvent refined coal). Here, the critical solvent is used to remove coal liquefaction products from vacuum still bottoms leaving insoluble coal and mineral matter as a dry flowable ash concentrate. The coal components dissolved in the solvent gas can be fractionated (oils, asphaltenes, and multifunctional compounds) to lighter products and a heavier molten low-ash (<0.09%) fluid which can be solidified to the product coal. It is estimated that this process coupled with a conventional solvent refining plant will be more cost effective than similarly sized filtration or anti-solvent plants. Eggers (30,73) has described the development and planning of large-scale industrial plants for extraction of natural products--particularly with regard to component design, thermodynamic calculations, power consumption (see also Reference 37) and economic optimization. Zosel (8) has recently described three extraction schemes to remove caffeine from green coffee beans using dense CO_2; the schemes will soon be put into commercial production.

Peter and Brunner have also been granted patents for the decaffeination of coffee by two high pressure processes (74,75). In one process (74) the dense solvent gas consists of a mixture of an entraining agent (alcohols, esters, ketones, chlorinated lower hydrocarbons, formaldehyde dimethylacetal) and a compressed gas (N_2, N_2O, CO_2, $CClF_3$, lower hydrocarbons). The second process utilized only liquid solvents (ethanol, methanol, ethylacetate, acetone, and formaldehyde dimethylacetal) at temperatures of 35-50°C and pressures of 100-500 bar. While this process is not a dense gas extraction, the amount of caffeine extracted increased as a function of pressure as often reported for liquid extractions at elevated pressures.

An example of a pharmaceutical application (76) is the patented dense gas extraction of camomile (Matricaria chamomilla) using CO_2 or N_2O at pressures at least 1.2 times critical pressure and temperatures less than 50°C. The products selectively extracted are bisabolol, its oxides, proazulenes, coumarins and fragrant components while polysaccharides, acids, and flavenoids are not extracted. Many other examples of dense gas extraction of components from raw materials are given in Table 1.

Several authors (77-88), particularly Gangoli and Thodos (89), have discussed the very real advantages of supercritical extraction of coal to liquid fractions, a hydrogen-rich and mineral-free solid, and a porous non-caking char residue which may be subsequently gasified. As in the cases of natural products and the very similar application of critical solvent deashing of (conventional) solvent refined coal, supercritical coal extraction/liquefaction is rapidly developing from bench-scale reactor tests. A small pilot plant (10 lb/h, or 4.5 kg/h, coal) has already been constructed in the United Kingdom (87). Again, as in the other examples, the economic factors in this type of coal processing are important; in this respect Maddocks and Gibson (82) have shown that dense gas extraction compares favorably with solvent refining and thermal decomposition processes.

TABLE 1

Summary of Work in Dense Gas Extraction and Dense Gas Chromatography

Dense Gas [a b c]	Compounds Dissolved/Separated	Stationary Phase	Det.[d]	Ref.
Argon (Ar)				
20°C 325 atm	One-step extraction of nicotine from tobacco (with adjusted water content of 25%); recovery by expansion and cooling. (Here, reduced density ∿ 0.9.)	--	--	1 (1970) 2 (1971)
Carbon dioxide (CO_2)				
20°C 120-750 psig (8-50 atm)	Step-wise fractionation/precipitation of heavier oil phases of Coalinga residual oil dissolved in propane.	--	--	3 (1940)
100°C 265-1250 psig (18-83 atm)	Step-wise pressure fractionation/precipitation of heavier oil phases of Coalinga residual oil dissolved in butane. Patented process for separating a liquid high molecular weight mixture into fractions using a compressed gaseous precipitating agent.			
35-55°C 60-320 atm	Solubility of naphthalene.	--	--	4 (1964)
40-50°C 90-120 kg/cm^2	Component separation from following: 1-dodecene/1-tetradecene/1-hexadecene; 2-ethyl-1-hexanol/benzyl alcohol.	--	--	5,6 (1964)
40°C 300 atm	Extraction (∿70%) of bitumens contained in argillaceous rock.	--	--	7 (1966)

(continued)

TABLE 1 (continued)

Dense Gas[a b c]	Compounds Dissolved/Separated	Stationary Phase	Det.[d]	Ref.
Carbon dioxide, cont.				
40 °C 1-81 kg/cm^2	Capacity ratio studies with n-alkanes (n = 3 to 13), toluene, n-octane, cumene, sec-butylbenzene,benzene, p-xylene, cis-decalin	25% w Squalane on Sil-O-Cel	FI	8 (1966)
-16-260 °C 29-1500 bar	Phase equilibria of CO2 with n-octane, n-undecane, n-tridecane, n-hexadecane.			9 (1967)
15-35 °C 709-919 psi (47-61 atm)	Phase equilibria studies to investigate compressed gases as salting out agents for separation of components in liquid mixtures using the CO2/water/n-propanol system. (Other compressed gases studied--subcritical C2H6, CClF3, CHF3, and supercritical C2H4.)	--	--	10 (1967)
40 °C 90-1350 atm	Solubility studies with Gum rubber, waxes, and oils: Apiezon L; Carbowax 20M, 400, 1000, 4000; squalane; squalene; SE-30 (400,000 Mw); dinonyl phthalate; DC-200. Purines: adenine. Terpenes: alpha,beta-carotenes; lycopene. Amino acids: glycine. Nucleosides: adenosine, guanosine, uridine (all slightly soluble). Corticol steroids: cortisone, hydrocortisone (both slightly soluble). Sterols: cholesterol, ergosterol, lanosterol. Sugars: ribose, arabinose, glucose, maltose, xylose, fructose, mannose, sorbose. Alkanes: n-octadecane, n-docosane, n-cctacosane. Misc.: officinilic acid, polyvinyl chloride.	--	FI	11,12 (1968) 13 (1969)
	Separation of alpha,beta-carotenes.	15% Ucon	FI	12 (1968)

Carbon dioxide, cont.

40 °C 1-1000 bar	Initial high pressure capillary experiments to separate alkanes and aromatics and to measure retention volumes. Additionally at pressures over 100 bar, squalane and dinonyl phthalate can be separated on Apiezon L.	Squalane, Silicone Oil, Apieson L/ Capillary	FI (M)	14 (1969)
50-70 °C 250-1000 atm	One-step extraction of nicotine from tobacco (with adjusted water content of 15-25%); recovery is by expansion and cooling.	--	--	1 (1970) 2 (1971)
45-50 °C 315-400 atm	Extraction of resins, ethereal oil, alpha-acids, beta-acids somewhat selectively with no extraction of tannins from air-dry hops. Moist CO2 can be used to extract tannins. Mixture separation is by expansion (isothermal or at liquid temperatures--with lower separation temperatures resulting in more water separating). Patented; other gases cited--SF6, CHF3, CHF2Cl, CF3Cl, CF2CH2, C3F8, N20, C2H6, C2H4.	--	--	15 (1971) 16,17,18 (1972) 19 (1976)
50-60 °C 280-400 atm	Extraction of odor components (essential oils) with dry CO2 followed by extraction of flavor components with wet CO2 perhaps followed by water extraction from natural spices: piperine from ground black pepper (350 atm), eugenol and aceteugenol from ground cloves (280 atm), cinnamaldehyde and eugenol from crushed cinnamon sticks (300 atm), and vanillin from crushed vanilla pods (400 atm). Separation by decompression --either isothermally or at liquid CO2 temperatures. Separation temperatures < Tc results in precipitation of H2O when using moist CO2 so extract moisture content can be controlled. Patented.	--	--	20 (1971) 21,22,23 (1972)

(continued)

TABLE 1 (continued)

Dense Gas [a b c]	Compounds Dissolved/Separated	Stationary Phase	Det.[d]	Ref.
Carbon dioxide, cont.				
50-150 °C 150-1740 atm	Extraction of aromatic oils from ground roast coffee (caffeinated and decaffeinated) with the oil color and aroma characterization (aroma number ~ 4 times that of pressed oil; also high antioxidant content) dependent on extraction temperature, pressure and presence of caffeine. Patented; other gases cited--SF6, CHF3, CHF2Cl, CF3Cl, C3F8.	--	--	24 (1971)
60 °C 60-330 atm	Extraction of aroma components from Brazillian tobacco with dry CO2 (330 atm) with component separation by decreasing pressure and temperature (63 atm, 25 °C) followed by extraction of nicotine from aroma-free tobacco with moist CO2 (60 atm) with removal of nicotine as a sulfuric acid salt (or picric acid or silico-tungstic acid salt) by circulating the compressed solution at constant (i.e., extraction) temperature and pressure through a container with acid. Tobacco is re-impregnated with aromatic components by reversing the first extraction step. (Alternatively, nicotine can be removed by an activated carbon bed or by expansion to subcritical conditions of the solvent gas.) Patented; other gases cited--N2O, SF6, Ar, CClF3.	--	--	25 (1971)
45-50 °C 280-350 atm	Extraction of butter from crushed coconuts (350 atm), oil from sunflower seeds (320 atm), oil from crushed soybeans (280 atm), and oil from peanuts (300 atm) with precipitation from dense mixture by pressure reduction accompanied by any temperature control (increase, decrease, isothermal) which will assure that water originating from the plant material does not co-precipitate. Patented; other gases cited--SF6, CHF3, CHF2Cl, CF3Cl, CF2CH2, C3F8, N2O, C2H6, C2H4.	--	--	26 (1971) 27 (1972)

Carbon dioxide, cont.

40-50 °C 180-350 atm	Extraction of aromatic oils from coarsely crushed roasted coffee with dry CO2. Separation is achieved by isothermal pressure reduction followed by extraction of caffeine from moistened oil-free coffee with moist CO2 with either an isothermal expansion or a lowering of temperature and pressure to liquid conditions (in the latter the water also precipitates and must be replenished) or an expansion at an elevated temperature. The oil- and caffeine-free coffee is water extracted (preferably using the same extraction vessel) followed by spray or freeze drying of the extract with impregnation of the powder by the aromatic oils obtained in the first extraction. (Alternatively, components dissolved in the solvent gas may be removed by liquefaction by lowering the temperature or the temperature and pressure followed by adsorption on columns of activated carbon or kieselguhr with the adsorbed materials removed by supercritical dry or moist CO2 or conventional organic solvents.) Patented.	--	--	28 (1972)
40 °C 10-115 atm	Pressure dependence of the capacity factor for mesitylene, n-decane, bromobenzene, 2-butanol, and fluorene and of the HETP for mesitylene and n-decane using supercritical fluid chromatography.	Carbowax 400/ Porasil C	FI (M)	29 (1972)
40 °C 63-95 atm PP	Isobaric and pressure-stepped chromatograms of cyclic hydrocarbons: azulene, acenaphthalene, diphenylmethane, diphenyl, naphthalene, 1,5,9-cyclododecatriene, tetralin, indene, mesitylene, dicyclopentadiene, cis-decalin, trans-decalin, p-xylol, camphene, toluene, benzene, cyclohexane, cyclopentane.	OPN/Porasil C		
40 °C 53-80 atm PP	Pressure programmed separation of n-alkanes (n = 5 - 22) with n = 16, 18, 20 not separated here as on Carbowax 400/Porasil C.	OPN/Porasil C		

(continued)

TABLE 1 (continued)

Dense Gas [a b c]	Compounds Dissolved/Separated	Stationary Phase	Det.[d]	Ref.
Carbon dioxide, cont.				
40 °C 55-117 atm PP	Separation of primarily oxygen-containing compounds: anise alcohol, 1-decanol, anisaldehyde, diacetone alcohol, iso-amylalcohol, 1-butanol, iso-butanol, 2-butanol, tert-butanol, methyl ethyl ketone, acetic acid ethyl ether, benzene, cyclohexane.	Carbowax 400/		
40 °C 41-115 atm PP	Chromatographic separation of a rose oil (having at least 30 individual substances) with 10 recognizable peaks indicating different substance groups.	OPN/Porasil C		
40 °C 60-93 atm PP	Chromatographic separation of a lemon oil with 12 peaks.	OPN/Porasil C or Carbowax 400/ Porasil C		
40 °C 58-85.5 atm PP	Chromatographic separation of thermally labile cyclohepatatriene organic acid methylesters (CCME): 1,3,6-CCME, 1,4,6-CCME, 1,3,5-CCME, phenylacetic acid ester, 2,4,6-CCME.	OPN/Porasil C		
33-40 °C 1000-3000 psi (68-204 atm) PP	Separation of thermally unstable (at GC conditions) compounds: ferrocene, cyclopentadienyl Mn(CO)3, dicyclpentadienyl TiCl2. n-alkylbromides (n = 8 to 22).	Carbowax 400/ Porasil F	UV (HP)	30 (1972)
40 °C 51-134 atm PP	Studies of temperature and pressure effects: n-alkanes (n = 5 to 22).	Carbowax 400/ Porasil C Acid Alumina	FI (M)	29,31 (1972) 32 (1973)
	Cyclic hydrocarbons: fluoranthene, phenanthrene, naphthalene, 1,3,5-trimethylbenzene, 1,4-dimethyl-benzene, benzene, cyclohexane, cyclopentane, toluene, cumene, fluorene, acenaphthylene, biphenyl, tetralin, indene.	Carbowax 400/ Porasil C		

Carbon dioxide, cont.

	Cyclic hydrocarbons: triphenylmethane, diphenylmethane, 1,2,4,5-tetramethylbenzene, phenylacetylene, cyclohexane, cyclopentane, benzene, toluene, camphene, azulene, 1,5,9-cyclododecatriene.	Oxidipropionitrile/ Porasil C		31 (1972) 32 (1973)
	Decaffeination of tea leaves:	--	--	33 (1972)
45 °C 400 atm	Extraction of aroma components from black tea leaves with dry CO2 followed by extraction of caffeine from the leaves with moist CO2 at same temperature, pressure. Isothermal expansion for solute precipitation. Then impregnation of de-caffeinated, de-aromatized leaves with extracted aroma components by decreasing pressure, temperature of CO2 over tea (10°C, 45 atm).			
	Preparation of decaffeinated instant tea:			
45 °C 400 atm	Extraction of aroma components from black tea leaves.			
50 °C 240 atm	Extraction of caffeine from de-aromatized leaves followed by aqueous extraction of leaves to make aqueous spray powder.			
10-45 °C 45-350 atm	Impregnation of aqueous extract powder with aroma components by decreasing CO2 temperature, pressure to liquid conditions. Patented process; other gases cited--N2O, SF6, CHF3, CC1F3, CHF2C1, CF2CH2, C2H6, C2H4, C3F8.			
40 °C 20-150 bar PP	Capacity ratio studies with n-decane, 1-decine, trans-5-decene, fluorene.	OPN/Porasil C Carbowax 400/ Porasil C	FI	32 (1973)
90-200 °C 200-245 atm	Deodorization with fatty acid removal to yield odor- and taste-free products by countercurrent extraction of the plant materials pumped through a glass bead bed with removal of the extracted products from the CO2 in an activated carbon bed at the circulating temperature and pressure: soy oil (90°C, 200 atm), palm fat	--	--	34 (1973)

(continued)

TABLE 1 (continued)

Dense Gas [a b c]	Compounds Dissolved/Separated	Stationary Phase	Det.[d]	Ref.
Carbon dioxide, cont.				
	(150°C, 220 atm)--palm fat previously deacidified and bleached, and peanut oil (200°C, 245 atm). Patented			
18-80 °C 73 atm	Extraction of oil from soy flakes at subcritical temperatures with separation of dissolved oil at supercritical temperatures; always ∿ critical pressure. Patented.	--	--	35 (1973)
40-60 °C 200-400 atm	Extraction of cocoa butter from cocoa mass or crushed cocoa nibs to obtain 74-99% extractable fat fraction leaving a powdery residue. Recovery of butter is effected by pressure reduction with a temperature above or below critical. Cocoa fat is less soluble in liquid CO2 than in supercritical CO2. Patented process; other solvent gases cited were N2O, SF6, CHF3, C2H4, C2H6, CF3Cl, CF2CH2, C3F8.	--	--	36 (1973)
55.5 °C 170 atm	Removal of 70% phenol adsorbed on activated carbon bed. Patented process to regenerate adsorbents with supercritical fluids at temperatures < Tc + 50°C.	--	--	37 (1974)
7-150 °C 1-100 MPa	Fluid phase equilibria in binary mixtures of CO2 + 2,6,10,15,19,23-hexamethyltetracosane (squalane) for alkane weight fractions of 0.069 to 0.930.	--	--	38 (1975)
30-70 °C 30-170 bar	Capacity ratios as a function of supercritical fluid density using decane, hexadecane, eicosane, squalane.	Carbowax 400/ Porasil C	FI	39 (1975)
33-39 °C 1500-3000 psi (102-204 atm) PP	Automobile exhaust: triphenylene, chrysene, benzo(ghi)-fluoranthene, naphthacene, benz(a)anthracene, pyrene, benzo(b)fluorene, 7-methylbenz(a)anthracene, 7,12-dimethylbenz(a)anthracene, benzo(c)phenanthrene, 1-methylpyrene, 3-methylpyrene, 1,3-dimethylpyrene,	Permaphase ETH	UV	40 (1976)

Carbon dioxide, cont.	perylene, benzo(e)pyrene, benzo(a)pyrene, benzo(k)-fluoranthene.			
35 °C 1400-1800 psi (95-123 atm) PP	Automobile exhaust: 6-methylchrysene, naphthacene, chrysene, triphenylene, benz(a)anthracene, benzo(c)-phenanthrene, benzo(b)fluorene, 7,12-dimethylbenz(a)-anthracene, 7-methylbenz(a)anthracene, 1,3-dimethyl-pyrene, benzo(c)phenanthrene, 1-methylpyrene, 3-methylpyrene, pyrene, benzo(a)fluorene.	Vydac Reverse Phase	UV	40 (1976)
40 °C 0-350 atm DP	Solubility and density programming studies with decane, phenylstearate, pentadecylphenol, eicosanoic acid, hexadecane, 1,3,5-triphenylbenzene, Antioxidant #330, pentacene, polystyrene 900 and 2100, diethylstilbestrol dipalmitate, eicosane, di-2-naphthylsebacate, 1,1-diphenylethyl-1-adamantane carboxylate, 1,1,2-triphenyleicosanate.	--	UV FI	41 (1976)
	Separation of 9,10-diphenylanthracene, benzene, naphtha-lene, phenanthrene, anthracene, 2,3-benzanthracene, polystyrene 600 oligomers.	Carbowax 400/ Porasil C		
50, 100 °C 20-250 bar	Isothermal P,x-diagrams of the quasibinary glyceride mixture/CO2 system. (Glyceride mixture: triglyceride, diglyceride, monoglyceride, glycerin.)	--	--	42 (1976)
100 °C 100-300 atm	A pressure-concentration isotherm of CO2/squalane with comparison of predictions using a modified Redlich-Kwong equation of state to experimental values.	--	--	43 (1976)
40 °C 70-400 bar PP	Dense gas extraction/thin layer chromatography (TLC) of Fat soluble dye mixture: guajazulene, azobenzene, Ceres Red, Ceres Blue, Sudan Red, indophenol. Pyrone mixture: umbelliferone, flavone, coumarin. Raw coffee: fatty oils, caffeine.	--	TL	44 (1976)

(continued)

TABLE 1 (continued)

Dense Gas [a b c]	Compounds Dissolved/Separated	Stationary Phase	Det.[d]	Ref.
Carbon dioxide, cont.				
40 °C 20-200 bar PP	Fat soluble dye mixture: Fat Orange, Indophenol (not extracted), Ceres Black (not extracted), Sudan Red, Sudan Blue, Ceres Red, Ceres Orange, Ceres Green, Sudan Yellow, Sudan Yellow liquid, Sudan Orange.			45 (1980)
40 °C 70-90 bar	Dense gas extraction/thin layer chromatography (TLC) of Caraway seeds: limonene, carvone, fatty oils. Sage leaves: eucalyptol, thujone, camphor. Peppermint leaves: mentnol, menthone. Ginger root: gingerone. Camomile flowers: herniarin (7-methoxycoumarin), tyrothricin, diclyoether. Lemon leaves: eucalyptol, santonin. Unrefined coffee: caffeine, fatty oils. Pepper: piperine. Chilies: capsaicine. Hops flowers: humulon, lupulon. Marijuana: cannabidiol, cannabinol, tetrahydroxy-cannibinol. Sunflower seeds: squalene, cholesterol, fatty oils.	--	TL	46 (1976) 45 (1980)
40 °C 80-200 bar PP	Sunflower seeds (with 0.5% squalene added): sterols, diglycerides, triglycerides with epoxy acids, steryl esters, squalene. (Ref. 45 only)			
40 °C 70-300 bar	Solubility studies with Polyaromatics: naphthalene, phenanthrene, anthracene, pyrene, 1,2-benzanthracene, chrysene, tetracene. Phenols: phenol, catechol, resorcinol, hydroquinone, pyrogallol, phloroglucinol. Aromatic organic acids: benzoic, cinnamic, salicyclic, anisic, veratric, 3-hydroxy-4-methoxyphenylacetic, ferulic, vanillic, coumaric, gentisic, syringic, sinapic, caffeic. Anthraquinones: anthraquinone, 4-hydroxyanthraquinone, chrysophanic acid, 1,8- and 1,5-dihydroxyanthraquinone, 1,2,4-trihydroxyquinone, emodin, alizarin.			

Carbon dioxide, cont.

	Pyrones: coumarin, flavone, umbelliferone, fraxetin. Lipids: myristyl alcohol, cholesterol, alpha- and gamma-distearin, triolean.			
40 °C 80-300 bar PP	Dense gas extraction/thin layer chromatography (TLC) of Vitamin-oil mixture: cholesterol, vitamins D3, K3, and A, alpha-tocopherol, triglyceride, alpha-tocopherol-acetate, steryl ester. Alkaloid drug (Strychnos nux vomica): brucine, strychnine, fatty oils.	--	TL	47 (1977)
38-121 °C 100-4890 psi (7-32 atm)	Solubility of CO2 in reservoir crude oils as a function of temperature and pressure with volatilization of significant amounts of oil near system critical points for oil recovery by CO2 injection.	--	--	48 (1977)
35-50 °C 80-160 bar	Extraction of active components of camomile flowers (bisabolol, bisabolol oxides A and B, proazulene as matricin, ene-yne dicycloethers, (-)-alpha-bisabolol) as well as typical odor components. States that polysaccharides and plant acids (chlorogenic acid and other forerunners of flavone) and flavonoids are not extracted. Furthermore, extraction (not over 50 °C for thermally labile compounds) and solute precipitation (-10 to 50 °C, 10-65 bar) can be chosen to minimize extraction of lipids (waxes, fats), carotenoids, and chlorophylls. Reference outlines pressure stepped extractions, pressure-stepped separations, and combinations thereof for selective active ingredient extraction/fractionation. (Subcritical separation temperatures result in recovery of water, volatiles, and odor components.) Patented; other gases cited--N2O, SF6, C2H4, C2H6, CC1F3, CHF3, C2F4, C2F6, C2HC15,C2H2F2.	--	--	49 (1977)

(continued)

TABLE 1 (continued)

Dense Gas [a b c]	Compounds Dissolved/Separated	Stationary Phase	Det.[d]	Ref.
Carbon dioxide, cont.				
31-80 °C 72-500 bar	Extraction of camomile flowers followed by TLC analysis: matricin, (-)-alpha-bisabolol, bisabolol oxides A and B, ene-yne dicycloethers (cis-, trans-spiroethers).	--	TL	50,51 (1978)
40 °C 80-200 bar	Extraction of samples deposited on quartz wool followed by analysis by thin layer chromatography (TLC). Alkaloids: arecoline, quinine, cinchonidine, colchicine, coniine, ephedrine, emetine, o-methylpsychotrine, nicotine, codeine, narcotine, papaverine, thebaine, yohimbine, reserpine, tropanol, atropine, scopolamine, vincristine, vinblastine, vincamine. Alkaloid salts: arecoline hydrochloride, coniine hydrobromide. Extraction of alkaloids from plant materials followed by TLC analysis. Belladonna leaves: hyoscyamine and scopolamine. Cinchona bark: quinine and cinchonidine. Conium fruit: coniine. Ephedra: ephedrine. Ipecacuanha roots: emetine. Opium (crude): codeine, thebaine, narcotine, papaverine. Rauwolfia roots: yohimbine, reserpine. Nicotiana leaves: nicotine.	--	TL	50,52 (1978) 45 (1980)
40 °C 500-2000 bar	Solubility studies with Amino acids: glycine, phenylalanine, L-tryptophan, leucine. Sugars: D-glucose, D-xylose, sucrose. Natural products: frangulin A, emodin, 6,7-dihydroxycoumarin (esculetin).	--	UV	53 (1978)
40 °C 40-110 bar	DGC capacity ratio studies with naphthalene and fluorene.	Perisorb A	NS	54 (1978)

Carbon dioxide, cont.

40 °C 73-87 bar	DGC retention time studies of hexadecane.	Carbowax 400/ Porasil C		
90 °C 160-220 atm	Extraction of caffeine from green coffee beans.	--	--	55 (1978)
30-100 °C 300 bar	Extraction of nicotine from raw tobacco.	--	--	56 (1978)
54-128 °C 51-334 bar	Phase equilibria of oleic acid/CO2 showing gas phase enhancements of ten-to-the-seven for some conditions.	--	--	57 (1978)
50-125 °C 25-257 bar	Phase equilibria for oleic acid glyceride mixture (mono-, di-, and triglycerides, glycerin) in CO2.			
75 °C 202-572 bar	Phase equilibria for palm oil.			
40-153 °C 32-303 bar	Phase equilibria for several binary modifier/CO2 solutions: glycerin (100 °C, 149-201 bar), benzene (80 °C, 51-100 bar), methylene chloride (55-129 °C, 53-56 bar), squalane (70-153 °C, 34-303 bar), dimethylformamide (54-100 °C, 32-255 bar), acetone (54-124 °C, 51 bar), tetrahydrofuran (56-101 °C, 49-148 bar), ethanol (50-130 °C, 52-56 bar), formaldehyde dimethyl acetal (40-70 °C, 54-94 bar).			
35-50 °C 90-170 bar	SFC study of the influence of temperature, pressure, stationary phase, and solvent gas density on the capacity ratio using naphthalene and fluorene. Partial molar volume of naphthalene, fluorene in CO2 and ethane as a function of pressure (compared to the pressure dependence of the isothermal compressibility).	Silica gel (Perisorb A, LiChrosorb) Perisorb RP-8	UV	58 (1978)

(continued)

TABLE 1 (continued)

Dense Gas [a b c]	Compounds Dissolved/Separated	Stationary Phase	Det.[d]	Ref.
Carbon dioxide, cont.				
40 °C 20-120 bar	Diffusion coefficient of benzene as a function of density.			
50-70 °C 100-265 atm	Regeneration of granular activated carbon with supercritical CO2.	--	--	59 (1978)
140 °C 10 MPa	Chromatographic separation of n-alkanes (n = 9 - 20) using the moment method to evaluate retention times.	Molecular Sieve 5A	FI	60,61 (1979)
20-200 °C 0.5-20 MPa PP	Chromatographic studies to determine: Pressure dependence of the retention times of n-paraffins (n = 9 to 14) and the partition coefficients of paraffins (2,4-dimethylheptane, n-nonane, n-tridecane) at isothermal conditions. Temperature dependence of the second virial coefficient (B22) as a function of temperature. Quantitative group separation of n-paraffins (C10-C20) from isoparaffins by pressure programming.			
30-40 °C 75-250 atm	Split introduction (∿ 0.2%) of DGC effluent via hot tubing (450 °C) into Nuclide Model 1290 G mass spectrometer. Synthetic mixture: phenanthrene, fluoranthene, pyrene, benzanthracene, benzo(ghi)perylene, anthanthrene, dimethylnaphthalene. Synthetic mixture: C9-C13 n-paraffins, naphthalene, methylnaphthalene, decalin, anthracene. Hiawatha coal oil: C9-C13 n-paraffins; naphthalene; C1, C3, C4, C5-alkylnaphthalenes; decalin.	Permaphase ETH	MS	62 (1979)
35 °C 275 atm	Solubility studies of stigmasterol (0.03 wt %), estrone (0.10 wt %), delta9-tetrahydrocannabinol (0.10 wt %). Extraction of cytotoxic species from seven plant mater-	--	--	63 (1979)

Carbon dioxide, cont.	ials containing potential antineoplastic agents. (Plant materials: Citharexylum Caudatum, Maytenus Rothiana, Maytenus Putterlickoiades, Gypsophilia Paniculata, Maytenus Senegalensis, Maquire Calophylla, Rollinia Papillionella. Extracted compounds not identified; total extracts tested for cytotoxicity.)			
	Measured solubilities of compounds as a function of pressure with spectrophotometric detection/quantitation after expansion of the dense gas solution.	--	--	64 (1979)
40 °C 80-200 bar	Aromatic organic acids: benzoic acid, p-hydroxybenzoic acid ethyl ester, salicylic acid, trans-cinnamic acid, gentisinic acid, and p-hydroxybenzoic acid.			
40 °C 80-200 bar	Pyrone derivatives: coumarin, flavone, umbelliferone.			
40 °C 80-2000 bar	Hydrophillic substances: gentisic acid, p-hydroxybenzoic acid, umbelliferone.			
21-60 °C 50-200 bar	Pressure dependent solubility isotherms of caffeine.			
40 °C 80-160 bar	Determination of binary diffusion coefficients of benzene, n-propylbenzene, and 1,3,5-trimethylbenzene in CO2 as a function of pressure with SFC via the chromatographic broadening technique.	Open tubular diffusion	UV (HP)	65 (1979)
35-55 °C 110,130 bar	Determination of binary diffusion coefficients of benzene, n-propylbenzene, and 1,3,5-trimethylbenzene in CO2 as a function of temperature.			
37.8 °C 16-73 atm	Calculated isothermal pressure-mole fraction phase equilibria compared to experimental values with decane.	--	--	66 (1979)

(continued)

TABLE 1 (continued)

Dense Gas [a b c]	Compounds Dissolved/Separated	Stationary Phase	Det.[d]	Ref.
Carbon dioxide, cont.				
36 °C 80-250 atm	Solubilities of 3 common waste-water pollutants as a function of pressure: phenol, p-chlorophenol, and 2,4-dichlorophenol.	--	--	67 (1980)
60 °C 112-240 atm	Solubility of phenol as a function of pressure.			
-- --	Studies of the adsorption of these compounds from the CO2 solution on activated carbon (AMOCO GX-31) and a polymeric adsorbent (Rohn and Haas XAD-2).	--	--	68 (1980)
90 °C 200-210 bar	Selective extraction of caffeine from coffee beans (treated to have 40% water content) with removal of caffeine from CO2 by 1. adsorption in charcoal pellets mixed with the coffee beans (with regeneration of the pellets by chloroform extraction), 2. adsorption in active charcoal in a reactor vessel separate from the extraction vessel, 3. washing the supercritical solution with water (UV monitoring of the water extract).	--	--	69 (1980)
40 °C 220 bar	Extraction of oil from ground soybeans with decompression to 40 bar in the separator. (CO2 extraction yields an extract of oil plus water; C2H6 extraction yields an oil extract and a water-containing residue.)			
55 °C 100-150 bar	Extraction of lignite tar in reflux column (stainless steel packing) with heated head (95 °C; hot-finger, destraction effect) to dissolve creosote plus lower hydrocarbons up to C20; higher paraffins, olefins (soluble in dense ethane) remain in the residue.	--	--	70 (1980)
35-65 °C 84-484 atm	Solubility studies with naphthalene, biphenyl over wide pressure range to find upper critical end points.	--	--	71 (1980)

Carbon dioxide, cont.

40 °C 100-130 bar	Extraction of didrovaltrate and valtrate from Valeriana wallichi roots. Also shows the extraction time is dependent upon the macerated particle size and compares yields of supercritical and Soxhlet extractions.	--	--	72 (1980)
17-50 °C 90-700 bar	Extraction of oils from soybeans, sunflower seeds, and rapeseeds to study 1. fractionation by step-wise pressure reduction, temperature increase and/or both with qualitative description of fraction differences; 2. liquid vs supercritical CO2 as solvent; 3. oil solubility as a function of pressure; 4. effect of solvent gas flow rate on oil concentration in the gas; 5. size and shape of ground plant material particles.	--	--	73 (1980)
20-75 °C 90-250 bar	Extraction of Pyrethrin I and II, Cinerin I and II, and Jasmolin I and II (pyrethrolone, cinerolone esters of chrysanthemum mono-, dicarboxylic acids) from pyrethrum flowers as a function of extraction parameters with comparison to extraction with liquid CO2, petroleum ether.	--	--	74 (1980)
40 °C 60-200 bar	Quantitative solubility studies of opium alkaloids as a function of solvent gas pressure: codeine, thebaine, noscapine, papaverine, morphine. (Also liquid CO2 solubilities for codeine, thebaine, papaverine,noscapine.)	--	--	75 (1980)
35-50 °C 40-140 bar	Use of supercritical fluid chromatography to determine partial molar volumes of naphthalene and fluorene at infinite dilution in CO2 near its critical point showing a strong correlation between that parameter and the isothermal compressibility of CO2.	Perisorb A Perisorb RP8	NS	76 (1980)
20-40 °C 60-200 bar	Solubility studies of thebaine as a function of pressure with specific comparison to other solvents (liquid	--	--	77 (1980)

(continued)

TABLE 1 (continued)

Dense Gas [a b c]	Compounds Dissolved/Separated	Stationary Phase	Det.[d]	Ref.
Carbon dioxide, cont.				
	CO_2, liquid and supercritical CHF_3) with off-line analysis by TLC and spectrophotometry. Thebaine was also extracted from the macerated plant material Papaver bracteatum Lindl. at various solvent pressures and moisture contents of plant material with all solvents. CHF_3 (liquid, supercritical) is better solvent for thebaine (by a factor > 5 at 150 bar) with with selective extraction of thebaine vs fatty oils at 100 bar CHF_3. For the plant material, ammonia pretreatment is necessary and a water content of 30-40% is desirable.			
15-40 °C 50-300 bar	Solubility of alpha-tocopheryl acetate (Vitamin E acetate) from subcritical to supercritical conditions.	--	--	78 (1980)
50 °C 5000-8000 psi (333-533 atm)	Extraction of oil from full-fat soyflakes (soybeans) to a residual oil content of < 0.5% with separation of oil from gas by pressure reduction. Oil extract was similar to hexane extract except for much lower phosphorous content --comparable to a degummed crude and indicating lower solubility of phopholipids. Oil solubility in CO_2 ~ 1.3% (w).	--	--	79,80 (1981)
35-65 °C 80-280 bar	Solubility of 2,3- and 2,6-dimethylnaphthalene, phenanthrene, benzoic acid and hexachloroethane at various temperatures and pressures with correlation of the data with the Peng-Robinson equation of state.	--	--	81 (1981)
70 °C 100-200 bar	Comparison of solvent gases for the pressure-dependent separation factor between hexadecanol and octadecane.	--	--	82 (1981)
55 °C 200 bar	Ethane "destraction" of brown coal tar (55 °C, 200 bar) with pressure reduction to yield creosote oil and	--	--	172 (1981)

Carbon dioxide				
	paraffins followed by selective, quantitative removal of the creosote oil and lower hydrocarbons (< C26) from the ethane destract using CO2 (optimal conditions --55 °C, 135 bar) in a rectifying apparatus (packed bed with hot-finger at 90 °C). (Moist CO2--~8% (w) H2O at destraction conditions--will selectively remove creosote oil compounds leaving behind lower paraffins (< C26).)			
(Carbon dioxide)/Hydrogen				
190 °C 200 atm	Countercurrent simultaneous hydrogenation and deodorization of ground nut oil (mixed with finely divided nickle) in a glass-ball filled column with 1.5 atm partial pressure of H2. Oil impurities dissolved in the solvent gas are removed in a bed of active charcoal maintained at the same temperature, pressure as the extractor. No decompression in this process.	--	--	83,84 (1974)
200 °C 220 atm	Hydrogenation/deodorization of a sunflower oil (with finely divided nickle catalyst) with 2 atm partial pressure H2 as above except here separator bed temperature is 80 °C to allow a heavier charging of the active charcoal. Continuous operation at high pressure.			
210 °C 235 atm	Hydrogenation/deodorization of whale oil (mixed with nickle catalyst) with 3 atm partial pressure H2. Here solvent gas is expanded to < Pc (~70 atm) in an intermediate separation chamber where most impurities precipitate; then it is passed through the active charcoal separator. Both separators are held at 80 °C.			
	Patented; states that fish, cottonseed, rape, and soya oils can be hardened and deodorized in this manner.			

(continued)

TABLE 1 (continued)

Dense Gas [a b c]	Compounds Dissolved/Separated	Stationary Phase	Det.[d]	Ref.
(Carbon dioxide)/Water				
40-80 °C 120-180 atm	Decaffeination of coffee beans with supercritical CO2 saturated with water with deposition of the extracted caffeine in an activated charcoal bed by lowering the solvent gas temperature to liquid conditions. Some water is imparted to the beans as caffeine is dissolved; therefore, dry supercritical CO2 is again passed through the beans to remove the water. Patented; states that liquid CO2 extraction removes caffeine and aroma-related components.	--	--	85 (1970) 86 (1971)
70 °C 160 atm	Moist CO2 is continuously circulated at constant temperature and pressure to remove caffeine from raw coffee; caffeine is removed from the dense solution by multiple treatments with water--vs activated carbon bed design.	--	--	87 (1972)
(Carbon dioxide)/Ammonia				
70 °C 250 atm	One-step extraction of nicotine from tobacco (with adjusted water content of 20%) with 5% NH3 in CO2; recovery by expansion and cooling.	--	--	1 (1970) 2 (1971)
(Carbon dioxide)/Methanol				
50-125 °C 11-238 atm	Phase equilibria of system oleic acid mixture/methanol/CO2. (Mixture: mono-, di-, triglycerides, glycerin.)	--	--	57 (1978)
30-40 °C 75-250 atm	Split introduction ($\sim$ 0.2%) of DGC effluent via hot tubing (450 °C) into Nuclide Model 1290 G mass spectrometer with 1.5% methanol in CO2. Synthetic mixture: phenanthrene, fluoranthene, pyrene, benzanthracene, benzo(ghi)perylene, anthanthrene, dimethylnaphthalene.	Permaphase ETH	MS	62 (1979)

(CO2)/Methanol, cont.

	Synthetic mixture: C9-C13 n-paraffins, naphthalene, methylnaphthalene, decalin, anthracene. Hiawatha coal oil: C9-C13 n-paraffins; naphthalene; C1, C3, C4, C5-alkylnaphthalenes; decalin.			

(Carbon dioxide)/Acetonitrile

102 °C 149-254 bar	Phase equilibria of the system oleic acid/stearic acid/acetonitrile/CO2 for several concentrations of modifier and solute.	--	--	57 (1978)

(Carbon dioxide)/Acetaldehyde

102 °C 21-207 bar	Phase equilibria of the system oleic acid/stearic acid/acetaldehyde/CO2 for four pressures.	--	--	57 (1978)

(Carbon dioxide)/Ethanol

50-110 °C 50-210 bar	Concentration of involatile components (glyceride mixture) in the gas phase as function of temperature and pressure for a range of modifier concentrations. Presents interaction parameters of solutes, entrainers as a function of temperature.	--	--	57 (1978)
35 °C 275 atm	Use of ethanol-saturated CO2 for the extraction of cytotoxic species from seven plant materials containing potential antineoplastic agents. (Plant materials: Citharexylum Caudatum, Maytenus Rothiana, Maytenus Putterlickoiades, Gypsophilia Paniculata, Maytenus Senegalensis, Maguire Calophylla, Rollinia Papillionella. Extracted components not identified; total extracts tested for cytotoxicity.)	--	--	63 (1979)

(continued)

TABLE 1 (continued)

Dense Gas [a b c]	Compounds Dissolved/Separated	Stationary Phase	Det.[d]	Ref.
(CO2)/Ethanol, cont.				
70-110 °C 135 bar	Countercurrent column separation of free fatty acids from palm oil with precipitation of entrainer and component from solvent gas stream in a separating column heated to 110 °C.	--	--	82 (1981)
(Carbon dioxide)/Acetone				
102 °C 155 bar	Variable solvent gas mixture composition for solubility studies of oleic and stearic acids.	--	--	88 (1974) 89 (1979)
69.6 °C 132.5 bar	Separation of oleic acid from a glyceride mixture in countercurrent columns with 0-15 wt% acetone/CO2. Ref. 42 evaluates separation of mono- and di-glycerides as a funtion of entrainer concentration, residence time, contact surface, and influence of the circulating gas stream upon the mixture and entrainer streams.	Bubble plate column (NW 65)	--	90 (1976) 42 (1976)
75-125 °C 98-248 bar	Gas phase concentrations of glyceride mixture (mono-, di-, triglycerides, glycerin) as a function of temperature and pressure as well as phase equilibria of the quasi-ternary system (with mole% acetone from 0 to 23%) showing specific separation factors for each of the glyceride mixture components.			
77-127 °C 103-157 bar	Phase equilibria of oleic acid/stearic acid/acetone/CO2 over a range of solute, modifier concentrations. Shows the separation factor of oleic, stearic acids as a function of temperature. Also presents interaction parameters of solutes and entrainer with CO2 as a function of temperature.	--	--	57 (1978)

(CO2)/Acetone, cont.

70-110 °C 130 bar	Variable mole ratio in phase equilibria studies of quasi-ternary system CO2/acetone/oleic acid glycerides.	--	--	91 (1978)

(Carbon dioxide)/Dimethylformamide

75 °C 198 bar	Phase equilibria for the system (stearic acid, oleic acid, linoleic acid, linolenic acid)/dimethylformamide/CO2 for various modifier concentrations.	--	--	57 (1978)

(Carbon dioxide)/Propane

101 °C 103-151 atm	Phase equilibria for the system oleic acid/stearic acid/propane/CO2 for three propane/CO2 ratios.	--	--	57 (1978)

(Carbon dioxide)/Formaldehyde dimethylacetal

45 °C 90 bar	Extraction of caffeine from raw coffee (water content ~ 50%) with water-vapor-saturated entrainer(17% wt)/CO2 solvent gas with removal of the caffeine by condensing/washing of caffeine plus azeotrope-former (or entrainer) from the circulating gas in a countercurrent column at 80 °C. Patented; other gases--N2, N2O, C2H6, C2H4, CH4, CClF3, C3H6; other entrainers--ethanol, methanol, dimethyl ether, diethyl ether, acetone, acetylacetone, ethyl malonate, ethyl acetate, methyl acetate, methylene chloride, dichloroethylene, trichloroethylene.	--	--	92 (1977)

(Carbon dioxide)/Tetrahydrofuran

70 °C 151 bar	Phase equilibria of the system (stearic acid, oleic acid, linoleic acid, linolenic acid)/THF/CO2 for various modifier concentrations.	--	--	57 (1978)

(continued)

TABLE 1 (continued)

Dense Gas [a b c]	Compounds Dissolved/Separated	Stationary Phase	Det. [d]	Ref.
(Carbon dioxide)/Methyl ethyl ketone				
70 °C 151-155 bar	Phase equilibria of (oleic, stearic acids)/methyl ethyl ketone/CO2 for a range of modifier concentrations.	--	--	57 (1978)
(Carbon dioxide)/Acetylacetone				
123 °C 143-147 bar	Phase equilibria of the system (oleic and stearic acids)/ acetylacetone/CO2 for a few modifier concentrations.	--	--	57 (1978)
(Carbon dioxide)/Methyl malonate				
159 °C 213-217 bar	Phase equilibria of (oleic, stearic acids)/methyl malonate/CO2 for various modifier concentrations.	--	--	57 (1978)
(Carbon dioxide)/Benzene				
70 °C 135-138 bar	Phase equilibria of oleic acid in benzene/CO2; also interaction parameters of solute, entrainer with CO2.	-	--	57 (1978)
100 °C 160 bar	Partition coefficient and separation factor of oleic, stearic acids as a function of benzene mole fraction.			
(Carbon dioxide)/n-Hexane				
102 °C 149-259 bar	Phase equilibria of oleic and stearic acids over a range of modifier concentrations.	--	--	57 (1978)
71-134 °C 1120-1308 psig (77-90 atm)	Separation of glycerides in distillation column: mono-, di-, and tri-oleate with 36-47% (w) n-hexane.	Stainless Steel KnitMesh	--	93 (1978) 94 (1980)

(Carbon dioxide)/Methylene chloride				
75-126 °C 94-203 bar	Phase equilibria of (oleic, stearic acids)/CH2Cl2/ CO2 for various solute, modifier concentrations.	--	--	57 (1978)
50 °C 140 bar	Investigations with a semi-commercial apparatus with plate columns for separating linseed oil fatty acids to fatty acids of different degrees of saturation. Separation followed by GC analysis of products: linolenic, linoleic, oleic, stearic, palmitic acids. Concentration of modifier not stated.	Plate column	--	89 (1979)
(Carbon dioxide)/Carbon tetrachloride				
70-135 °C 1220-1450 psig (84-100 atm)	Separation of glycerides in distillation column: mono-, di-, and tri-oleate with 43-69% (w) CCl4. This dense gas mixture resulted in equipment corrosion.	Stainless Steel KnitMesh	--	93 (1978) 94 (1980)
Water (H2O)				
∿374 °C ∿220 atm	Reforming of organic materials (glucose, cellulose, maple sawdust) to produce fuel gases and low MW products (alcohols, aldehydes, furans) without producing char or solid residue (prevented by high solubility of organics in supercritical H2O).	--	--	95 (1980)
Nitrogen (N2)				
40-60 °C 51-153 bar	Phase equilibria of formaldehyde dimethylacetal in N2.	--	--	57 (1978)

(continued)

TABLE 1 (continued)

Dense Gas [a b c]	Compounds Dissolved/Separated	Stationary Phase	Det.[d]	Ref.
(Nitrogen)/Formaldehyde dimethylacetal				
40 °C 200 bar	Extraction of caffeine from raw coffee (moisture content about 46%) with a compressed gas mixture of water vapor saturated entrainer (3% wt)/N2 with the removal of the caffeine by condensing/washing of caffeine plus azeotrope-former (entrainer) from the circulating gas in a countercurrent column held at 20 °C. Patented; other gases cited--CO2, N2O, C2H6, C2H4, CH4, CClF3, C3H6; other entrainers cited--ethanol, methanol, dimethyl ether, diethyl ether, acetone, acetylacetone, ethyl malonate, ethyl acetate, methyl acetate, dichloroethylene, trichloroethylene, methylene chloride. (For N2 alone at these conditions, reduced density is ∿ 0.68.)	--	--	92 (1977)
(Nitrogen)/Benzene				
102 °C 50-206 bar	Phase equilibria for the system oleic acid/stearic acid/benzene/N2.	--	--	57 (1978)
Nitrous oxide (N2O)				
40-45 °C 100 kg/cm^2	Solubility of hexadecene (0.08 mL/NL N2O); component separation of 1-tetradecene/1-hexadecene/1-octadecene.	--	--	5,6 (1964)
28 °C 65 atm	One-step extraction of nicotine from tobacco (adjusted water content of 25%) with subcritical N2O; recovery by expansion and cooling.	--	--	1 (1970) 2 (1971)
50 °C 200 atm	Extraction of resins, ethereal oil, alpha-acids, beta-acids somewhat selectively with no extraction of tannins from air-dry hops. Mixture separation is by expansion (isothermal or at liquid temperatures--with lower separation temperatures resulting in more	--	--	15 (1971) 16,17,18 (1972) 19

Nitrous oxide, cont.	water separating). Patented; other gases cited--SF6, CHF3, CHF2Cl, CF3Cl, CF2CH2, C3F8, CO2, C2H6, C2H4.			(1976)
20-75 °C 72 atm	Extraction of oil from soy flakes at subcritical temperatures with separation of dissolved oil at supercritical temperatures; always ∿ critical pressure. Patented.	--	--	35 (1973)
40 °C 80-200 bar	Extraction of samples deposited on quartz wool followed by analysis by thin layer chromatography (TLC). Alkaloids: arecoline, quinine, quinidine, cinchonine, cinchonidine, colchicine, coniine, ephedrine, psychotrine, cephaeline, emetine, o-methylpsychotrine, nicotine, morphine, codeine, thebaine, narcotine, papaverine, ajmaline, yohimbine, reserpine, tropanol, atropine, scopolamine, vincristine, vinblastine, vincamine. Alkaloid salts: arcoline hydrochloride, coniine hydrobromide, ephedrine hydrochloride. Extraction of alkaloids from plant material followed by TLC analysis. Areca nuts: arecoline. Belladona leaves: hyoscyamine, scopolamine. Cinchona bark: quinine. Conium fruit: coniine. Ephedra: ephedrine. Ipecacuanha roots: psychotrine, cephaeline, emetine, o-methylpsychotrine. Opium (crude): morphine, codeine, thebaine, narcotine, papaverine. Rauwolfia roots: ajmaline, yohimbine, reserpine. Nicotiana leaves: nicotine.	--	TL	50,52 (1978) 45 (1980)
31-80 °C 72-500 bar	Extraction of camomile flowers followed by TLC analysis: matricin, (-)-alpha-bisabolol, bisabolol oxides A and B, ene-yne dicycloethers (cis-, trans-spiroethers).	--	TL	50,51 (1978)

(continued)

TABLE 1 (continued)

Dense Gas [a b c]	Compounds Dissolved/Separated	Stationary Phase	Det.[d]	Ref.
Nitrous oxide, cont.				
70 °C 100-350 bar	Partition coefficient of components of a glyceride mixture (free fatty acids and mono- and diglycerides) as a function of pressure.	--	--	57 (1970)
40 °C 60-200 bar	Quantitative solubility studies of opium alkaloids as a function of solvent gas pressure: codeine, noscapine. (Also includes solubilities of both in liquid N2O.)	--	--	75 (1980)
70 °C 100-200 bar	Comparison of solvent gases for the pressure-dependent separation factor between hexadecanol and octadecane.	--	--	82 (1981)
Ammonia (NH3)				
160-170 °C 350 atm	Solubility of paraffin oil. Anhydrous glycerol is readily soluble in supercritical NH3; insoluble in nonpolar hydrocarbons. Solution of aluminum alcoholate after removal of hydrocarbon compounds with supercritical ethylene.	--	--	5 (1964)
140 °C 200 atm	Solubility studies with Gum rubber, waxes, and oils: Carbowax 4000 and 20M, squalane, squalene, OV-17. Nucleosides and nucleotides: adenosine, guanosine, uridine, adenylic acid. Corticol steroids: cortisone, hydrocortisone. Sterols: cholesterol, ergosterol, lanosterol. Sugars: ribose, arabinose, glucose, galactose (slight), maltose, lactose, xylose, fructose, mannose, sorbose. Purines: caffeine. Amino acids: glycine, leucine, alanine, trytophan, tyrosine, arginine, lysine, glycylglycine, glycyl-L-leucyl-L-tyrosine. Proteins: cytochrome C. Misc.: quercitin, alpha-glucose pentaacetate.	--	FI	11,12 (1968) 13 (1969)

Ammonia, cont.

	Separation of glycine, glycylglycine, glycylleucyl-tyrosine.	Porasil B	FI	13 (1969)
Sulfur hexafluoride (SF6)				
70 °C 300 atm	One-step extraction of nicotine from tobacco (with adjusted water content of 20%); nicotine removal by diverting 20% gas flow to a sorption bed (alumina, silica gel, activated carbon, ion exhange, impregnated infusorial earth or molecular sieves).	--	--	1 (1970) 2 (1971)
50 °C 39 atm	Threshold solubility of 600 MW polystyrene.	--	UV	41 (1976)
Methane (CH4)				
20 °C 30-130 atm	Fractionation of Potok oil (alphalt- and wax-free) in a solvent of propane/butane/isobutane and Grabowinica residue crude in a solvent of propane/butane by pressure-stepping CH4 (99%). Patented process for gas fractionation of high molecular mixtures.	--	--	96 (1936)
40 °C 20-80 MN/m^2	Cited in a monograph review of gas extraction: extraction of a Russian crude oil.	--	--	97 (1971)
38 °C 45-363 atm	Calculated isothermal pressure-mole fraction phase equilibria compared to experimental values with decane.	--	--	66 (1979)
190-430 °C 20-250 atm	Solubility of 9,10-dihydrophenanthrene at high temperatures and pressures.	--	--	98 (1980)

(continued)

TABLE 1 (continued)

Dense Gas [a b c]	Compounds Dissolved/Separated	Stationary Phase	Det.[d]	Ref.
(Methane)/Ethane				
100 °C 150 atm	Separation of a solution of a topped crude in liquid propane/butane (formation of that solution caused precipitation of asphaltic substances) into heavy and light oil fractions. Patented process for gas fractionation of high molecular mixtures.	--	--	96 (1936)
(Methane)/Natural gas mixture				
50-100 °C 200-550 atm	Solubility of crude oil in natural gas (C1-71%, C2-14%, C3-7.6%, C4-4.6%, C5-3.2%--wt%'s) at high pressures with paraffin (C1-C19), naphthenic (C1-C22), and aromatic (C1-C21) components. Authors outline seven parameters (system and hydrocarbon) which influence the partition coefficient and measure the convergence pressure as a function of temperature for mixtures.	--	--	99 (1981)
Methanol (CH4O)				
335 °C --	Extraction/liquefaction of coal to obtain pyridine soluble material.	--	--	100 (1978)
250 °C 100 bar	Liquefaction of wood with flow apparatus (1mL/min) to remove non-lignin and lignin components selectively according to choice of solvent.	--	--	101 (1979)
Acetonitrile (C2H3N)				
	Influence of the stationary and mobile phases on separation:		DRI (AMB)	102 (1977)
282-289 °C 86-100 atm	Hydrocarbons and esters (no separation effect).	Tenax		

Acetonitrile, cont.

285-300 °C 50-55 atm	Capacity ratios for naphthalene, phenanthrene, pyrene, squalane, di-tridecylphthalate. (No signal other than sample solvent, THF, detected for polystyrol, chrysene, coronene; there was swelling of the packing.)	Chromosorb 101		
298-308 °C 45-60 atm	Only phenanthrene and squalane gave second signal after sample solvent peak (THF).	Florisil		
288-305 °C 58-61 atm	The pressure and flow rate of this combination could not be controlled well enough for capacity ratio measurements of hydrocarbons and polystyrol.	Merckogel SI 200		
-- --	A strong ammonia odor with acetonitrile on Alox T; author states as a precaution acetonitrile should not be used with aluminum oxide.	LiChrosorb Alox T		
Ethylene (C_2H_4)				
13-31.5 °C 31-101 atm	Solubility of p-chloroiodobenzene.	--	--	103 (1953)
12-60 °C 40-270 atm	Solubility of naphthalene.	--	--	104 (1953)
10.5-19.5 °C 300-1500 psi (20-100 atm)	Phase equilibria studies (showing Types 1,2, and 3 behavior) with decane, cetane, hexaldehyde, propyl-propionate, toluene, capronitrile, o-dichlorobenzene, p-dichlorobenzene, propanol, hexanol, decanol, propionic acid, caproic acid, capric acid, and oleic acid to demonstrate the possibility of supercritical gas extraction.	--	--	105 (1955)
5-25 °C 0-1000 psig	Qualitative and quantitative phase equilibria for supercritial-ethylene/water/organic-liquid systems	--	--	106 (1959)

(continued)

TABLE 1 (continued)

Dense Gas [a b c]	Compounds Dissolved/Separated	Stationary Phase	Det.[d]	Ref.
Ethylene, cont.				
(0-67 atm)	exhibiting "salting out" behavior with acetone, acetaldehyde, acetonitrile, acetic acid, sec-butyl alcohol, t-butyl alcohol,ethanol,ethyl acetate,ethylenediamine, ethylene glycol, formaldehyde, formic acid, glyoxal, methanol,methyl ethyl ketone,methyl Cellosolve,methylal, morpholine, isopropanol, n-propanol, propionaldehyde, propionic acid, pyridine, triethylamine, triethanolamine, triethylphosphate with hydrogen bonding and phase behavior classifications. The supercritical component is analogous to conventional salting out agents in liquid-liquid-solid systems.			
12-45 °C 50-300 atm	Solubility of naphthalene.	--	--	4 (1964)
12-80 °C 200 atm	Extraction of paraffin oil with solubilities 0.32 mL oil/g C2H4 at 12 °C to 0.072 mL oil/g C2H4 at 70 °C and of aluminum butylate (0.37 mL/g at 20 °C, 0.26 mL/g at 80 °C).	--	--	5 (1964)
25 °C 200 kg/cm^2	Selective extraction of paraffin oil from ammonium chloride suspension.			
23 °C 200 kg/cm^2	Solvation of sulfuric acid dimethyl ester (0.48 g/mL C2H4) and non-solvation of sulfuric acid.			
20 °C 200 kg/cm^2	Pure paraffin oil solubility 0.19 mL/NL C2H4; paraffin oil/dodecene mixture (3/1), solubility of 0.53 mL/NL C2H4 for paraffin oil, 0.18 mL/NL C2H4 for dodecene.			
20 °C 75-100 atm	Extracted products of paraffin oil/dodecene mixture to give 70% olefins at 100 atm and 90% olefins at 75 atm.			
20 °C 200 kg/cm^2	Solubility of dibutyl ether, methyl ethyl ketone, formic acid; extraction of used (black) gear oil to yield product of light yellow color (90% oil recovered); extraction of fat (0.0022 mL/NL C2H4) from rich milk;			

Ethylene, cont.	extraction of fat from yolk of fresh hen's eggs; solvation of vegetable oil (0.0033 mL/NL C2H4).
20-25 °C 75-115 kg/cm^2	Solubility of 2-ethyl-1-hexanol, aniline, cyclohexylamine, cyclohexanol, 1,5-pentanediol, nitrobenzene.
20 °C 30-50 kg/cm^2	Selective, quantitative extraction, by increasing pressure, of butanol from butanol/glycerol mixture and propanol from propanol/glycerol mixture.
25 °C 200 kg/cm^2	Solvation of both chlorophyll and paraffin oil from a chlorophyll/paraffin oil mixture.
25 °C 60 kg/cm^2	Solubility of camphor; selective separation of naphthalene from naphthalene/methylene blue mixture; selective solvation of naphthalene then anthracene when pressure increased to 140 kg/cm2.
18-35 °C 60-140 kg/cm^2	Component separation of following mixtures: n-dodecane/n-tetradecane, 5-methylundecane/7-methylpentadecane, n-hexadecane/n-eicosane, n-1-hexadecene/n-1-octadecene, 2-hexyl-1-decene/1-octyl-1-dodecene, 2-hexyl-1-decene/n-eicosane, 1-phenyldecane/1-phenyltetradecane, 1-octanol/1-decanol/1-dodecanol, 2-ethyl-1-hexanol/benzyl alcohol, n-octylacetate/n-dodecylacetate/n-hexadecylacetate, n-octylacetate/n-dodecylbutyrate, 3-octanone/2-decanone, di-n-butylether/diphenylether, cyclohexylamine/aniline,nitrobenzene/3-nitro-o-xylene. (Also quoted in Ref. 6.)
20 °C 100-200 kg/cm^2	Solubility experiments with aqueous solutions of alcohols (methanol, ethanol, propanol, butanol, 1,3-butanediol, ethylene glycol) which show that the hydroxyl group/hydrocarbon radical proportion is important to solubility--only propanol and butanol were soluble. Similarly with a 1/1 acetone/water mixture, no acetone dissolved in supercritical ethylene. Similarly "pure" cutting oil has a solubility of 0.25 mL/g C2H4; solubility of cutting oil from a 1/1 oil/water mixture

(continued)

TABLE 1 (continued)

Dense Gas [a b c]	Compounds Dissolved/Separated	Stationary Phase	Det.[d]	Ref.
Ethylene, cont.				
	is 0.002 mL/g C2H4; and cutting oil from a 1/10 oil/ water mixture is less than 0.001 mL/g C2H4.			
75 °C 200 atm	Removal of hydrocarbon by-products from aluminum alcoholate (prepared by oxidation of a growth product from aluminum triethyl and ethylene) which had been previously freed from all separable olefins and by-products by distillation. Treatment with supercritical NH3 dissolves the purified aluminum alcoholate.			
20 °C 120 kg/cm^2	Extraction of a crude petroleum oil with fractionation into 4 fractions either by successive step-wise pressure reductions in 4 pressure separators or by step-wise temperature increases in 4 pressure separators. (Also quoted in Ref. 6.)			
	Feasibility studies of extracting tar acids, tar bases neutral oils from coal tar by studying model compounds with 2,4-xylenol for tar acid, quinoline for tar base, and benzene, ethanol, n-dodecane for neutral oil:	--	--	107 (1966)
75 °C 300-3050 psi (20-203 atm)	Phase equilibria of the binary systems of benzene, ethanol, dodecane, 2,4-xylenol, and quinoline in C2H4.			
24-75 °C 750-3400 psi (50-227 atm)	Phase equilibria of the multicomponent systems: quinoline/ dodecane/C2H4; 2,4-xylenol/dodecane/C2H4; 2,4-xylenol/ quinoline/C2H4; quinoline/2,4-xylenol/dodecane/C2H4 as well as the pressure dependence of the relative volatility of components of these systems. (May be a reaction product between xylenol, quinoline with low C2H4 solubility giving decreased recovery of either.			
25-100 °C 2500-3000 psia (167-200 atm)	Extraction of coal tar, pitch and coal with 2-5% (w) of the samples soluble in C2H4 to yield nearly colorless, mainly volatile compounds such as aliphatic hydrocarbons, aromatics, polar compounds.(No identification.)			

Ethylene, cont.

25 °C 77-98 atm	Extraction/fractionation of products of preparative disproportionation of Al(C2H5)1.5(C8H15)1.5 in supercritical ethylene using countercurrent washing (with enriched extracted product) in an unheated packed exchange column with pressure stepping to obtain fractions enriched in trioctenylaluminum.	--	--	108 (1966)
20 °C 59-105 atm	Extraction/fractionation of products of preparative disproportionation of dipropyl-9-decenylaluminum with supercritical ethylene using a hot-finger (38 °C) at the top of a packed exchange column with pressure stepping to obtain fractions enriched in tridecenylaluminum or tripropylaluminum.			
15 °C 100-810 psi (7-54 atm)	Phase equilibria studies to investigate compressed gases as salting out agents for separation of components in liquid mixtures using the ethylene/water/n-propanol system. In the water/ethylene binary there was formation of a solid ethylene hydrate (469 psi, C2H4·7H2O); in the n-propanol/ethylene binary, a minimum in gas phase solubility was observed. (Other compressed gases studied--subcritical C2H6, CClF3, CHF3, and sub- to supercritical CO2.)	--	--	10 (1967)
20 °C 72-120 kg/cm^2	Destraction of a mixture of aluminum tri-n-butyl and aluminum tri-n-octyl with step-wise pressure increase and maximum condensing hot-finger temperature of 50 °C.	--	--	109 (1969)
25 °C 3000 psig	Separation of a coal tar into pitch and oil fractions and of a pitch into volatile oils and solid residue with fractionation by step-wise pressure reduction. Extraction of anthracene paste with relatively pure anthracene and naphthalene recovered. Patented process for extraction of part of carbonaceous content from carbonaceous material using fluids above critical	--	--	110 (1969)

(continued)

TABLE 1 (continued)

Dense Gas [a b c]	Compounds Dissolved/Separated	Stationary Phase	Det.[d]	Ref.
Ethylene cont.				
	temperatures; other gases cited--CH4, C2H6, C3H8, C2H4, C3H6, NH3, Cl2, CO2, benzene, toluene, pyridine, dimethylamine, ethylamine, methylamine, hydrocarbons from C4 to C12.			
	Cited in a monograph review of gas extraction:	--	--	97 (1971)
25 °C 10-30 MN/m^2	Extraction of a coke oven tar to a 40% pitch residue.			
75 °C 5-20 MN/m^2	Solubility studies of dodecane, quinoline, 2,4-xylenol.			
12-45 °C 6-30 MN/m^2	Solubility studies of naphthalene (these solubility vs temperature isobars often reproduced; origin Tsekhanskaya et al, Zh. Fiz. Khim. 38 (1964) p. 2166).			
19 °C 6.9-8.1 MN/m^2	Extraction of involatile liquids: capric acid, caproic acid, cetane, hexyl alcohol.			
105 °C 20-50 MN/m^2	Extraction of Russian fuel oil residue.			
20-173 °C 50-300 bar	Solubility studies of oleic and stearic acids. (Other dense gases were studied, but no data presented: propane, CO2, Freon 13B1 and Freon 13.)	--	--	88 (1974)
23-70 °C 1-200 atm	Pressure, temperature effects upon paraffin oil solubility in solvent gas. (Very small solubility until pressure range 50-200 atm at 23 °C.)	--	--	55 (1978)
25 °C 50-70 atm	Visual observation of solubility of alpha-olefins (C14-C20) in solvent gas "destraction" experiments.			

Ethylene, cont.				
20-173 °C 52-313 bar	Phase equilibria of oleic acid/C2H4 showing gas phase enhancement of almost ten-to-the-twelve for some conditions.	--	--	57 (1978)
77-127 °C 68-323 bar	Phase equilibria of stearic acid/C2H4 showing gas phase enhancement of almost ten-to-the-sixth for some conditions.			
77-127 °C 68-248 bar	Phase equilibria for the ternary system of oleic acid/stearic acid/C2H4.			
50-125 °C 26-208 bar	Phase equilibria for oleic acid glyceride mixture (mono-, di-, triglycerides, glycerin) in C2H4.			
70 °C 103-293 bar	Isothermal phase equilibria for palm oil in C2H4.			
35-65 °C 80-280 bar	Solubility of 2,3- and 2,6-dimethylnaphthalene, phenanthrene, and benzoic acid at various temperatures and pressures with correlation of the data with the Peng-Robinson equation of state.	--	--	81 (1981)
70 °C 100-200 bar	Comparison of solvent gases for the pressure-dependent separation factor between hexadecanol, octadecane.	--	--	82 (1981)
(Ethylene)/Methanol				
50-156 °C 108-254 bar	Phase equilibria of the system oleic acid mixture/methanol/C2H4. (Mixture: mono-, di-, triglycerides, glycerin.)	--	--	57 (1978)
(Ethylene)/Acetone				
54-127 °C 59-198 bar	Phase equilibria of the system of oleic acid/stearic acid/acetone/C2H4 over a range of solute and	--	--	57 (1978)

(continued)

TABLE 1 (continued)

Dense Gas [a b c]	Compounds Dissolved/Separated	Stationary Phase	Det.[d]	Ref.
(C2H4)/Acetone, cont.	modifier concentrations. Also gives the separation factor of an oleic and stearic acid mixture as well as solute/C2H4 interaction parameters as a function of temperature.			
(Ethylene)/Dimethylformamide				
70 °C 200 bar	Phase equilibria for the system (stearic acid, oleic acid, linoleic acid, linolenic acid)/dimethylformamide/ C2H4. Interaction parameters of modifier and some solutes with C2H4 as a function of temperature presented.	--	--	57 (1978)
(Ethylene)/Propane				
102 °C 105-153 bar	Phase equilibria studies of oleic and stearic acids in propane/ethylene.	--	--	57 (1978)
(Ethylene)/Formaldehyde dimethylacetal				
75 °C 200 bar	Phase equilibria of oleic, stearic, and linoleic acids at various modifier concentrations.	--	--	57 (1978)
(Ethylene)/Benzene				
54-102 °C 54-155 bar	Phase equilibria of the ternary system of stearic acid/ benzene/C2H4 over a range of modifier and solute concentrations.	--	--	57 (1978)
102-124 °C 151-196 bar	Phase equilibria of the system oleic acid/stearic acid/ benzene/C2H4; also gives the separation factor of an oleic and stearic acid mixture as a function of temperature.			

(Ethylene)/Toluene				
130 °C 130 bar	Separation of fine solid particles (micron size) suspended in a solvent (or entrainer) using a supercritical gas to make a ternary fluid solution having a density greater than that of the pure supercritical component at the same conditions and less than that of the original viscous solid suspension. Example given of the oil and particle separation of shale oil (suspended in toluene) using 40% (w) toluene in ethylene (1 part gas plus entrainer to 3 parts shale oil) in 4 minutes.	--	--	82 (1981)
(Ethylene)/n-Heptane				
50-125 °C ? bar	Separation factor of an oleic and stearic acid mixture as a function of temperature at various modifier concentrations.	--	--	57 (1978)
100.7 °C 150.8 bar	Phase equilibria of oleic and stearic acids in n-heptane/ethylene.			
(Ethylene)/Methylene chloride				
103 °C 158 bar	Phase equilibria of (oleic, stearic acids)/CH2Cl2/ C2H4 for a few concentrations of solutes, modifier.	--	--	57 (1978)
Ethane (C2H6)				
40 °C 60-160 kg/cm^2 PP	Selective extraction/fractionation of individual alpha-olefins (95-99% pure fractions) from a mixture of C16H32, C18H36, C20H40, C22H44, C24H48, C26H52. Component separation of the following mixtures: n-hexadecane/n-eicosane; n-tetradecane/n-octadecane; 2-ethyl-1-hexanol/benzyl alcohol; n-1-octanol/n-1-decanol/n-1-dodecanol; n-1-dodecene/n-1-tetradecane; 1-hexadecene/paraffin oil; di-n-butylether/paraffin oil.	--	--	5,6 (1964)

(continued)

TABLE 1 (continued)

Dense Gas [a b c]	Compounds Dissolved/Separated	Stationary Phase	Det.[d]	Ref.
Ethane, cont.				
40 °C 56-70 atm PP	Extraction/fractionation of products from preparative disproportionation of diethyl-7-octenylaluminum in supercritical ethane using countercurrent washing (with enriched extracted product) in an unheated packed exchange column and pressure-stepping to obtain triethylaluminum-rich and trioctenylaluminum-rich fractions.	--	--	108 (1966)
40 °C 60-92 kg/cm^2 PP	Destraction of a growth product of aluminum triethyl and ethylene to obtain free olefins (C14-C20) in the first fraction and thereafter aluminum tributyl, aluminum trihexyl, aluminum trioctyl in separate fractions which also contain smaller amounts of higher free olefins. Pressure is step-wise increased; maximum condensing hot-finger temperature is 95°C.	--	--	109 (1969)
50 °C 75-100 atm PP	Destraction to separate a mixture of hexadecene, octadecene, eicosene, olefins to C30, and aluminum tridodecyl with step-wise pressure increase and maximum hot-finger temperature of 98 °C to yield an olefin-free aluminum growth product.			
40 °C 60-100 atm PP	Destraction to separate a mixture of aluminum triisobutyl and aluminum trioctenyl with pressure stepping and a hot finger temperature of 60°C. Patented.			
20-80 °C 48 atm	Extraction of oil from soy flakes at subcritical temperatures with separation of dissolved oil at supercritical temperatures; always ~ critical pressure. Patented.	--	--	35 (1973)
40 °C 63-150 atm	Threshold solubilities of Antioxidant #330, diethylstilbestrol dipalmitate, 2030 and 4000 MW polystyrene, hexaphenylbenzene.	--	UV	41 (1976)

Ethane, cont.

45 °C 60-110 atm	Fractionation (by pressure change) of mixture of alpha-olefins (C14, C16, C18, C20) in "destraction" work.	--	--	55 (1978)
27-50 °C 100-160 atm	Fractionation of cod-liver oil into 50 fractions in "fractional destraction" experiments.			
40 °C 40-120 bar	Chromatographic study of the influence of pressure, stationary phase, and solvent gas density on the capacity ratio using naphthalene and fluorene.	Silica gel (Perisorb A) Perisorb RP-8	UV	58 (1978)
40 °C 40-90 bar	Partial molar volume of naphthalene as a function of pressure.			
40 °C 220 bar	Extraction of oil from ground soybeans with decompression to 40 bar in the separator. (CO_2 extraction yields an extract of oil plus water; C_2H_4 extraction yields an oil extract and a water-containing residue.)	--	--	69 (1980)
55 °C 200 bar	Extraction of lignite tar in reflux column (stainless steel packing) with heated head (destraction, hot-finger effect) to dissolve many tar components (but not selective separation of creosote, hydrocarbons) leaving ash and high MW (>C40) substances. Suggests ethane-extract be further extracted by CO_2 to separate higher paraffins and olefins (C20-C40) from creosote.	--	--	70 (1980)
35-60 °C 49.7-62.4 atm	Solubilities of n-heptane. Data shows behavior of partial molar volume of n-heptane as a function of n-heptane mole fraction which implies that "solubilities in the critical region are not only sensitive to pressure but that the pressure dependence itself is sensitive to composition changes in the critical region" so assuming ideal Henry's law behavior is inappropriate.	--	--	111 (1981)

(continued)

TABLE 1 (continued)

Dense Gas [a b c]	Compounds Dissolved/Separated	Stationary Phase	Det.[d]	Ref.
Ethane, cont.				
70 °C 100-200 bar	Comparison of solvent gases for the pressure-dependent separation factor between hexadecanol and octadecane.	--	--	82 (1981)
55 °C 200 bar	Ethane destraction of brown coal tar with pressure reduction to yield creosote oil and paraffins followed by selective, quantitative removal of the creosote oil, lower hydrocarbons (< C26) from ethane destract using CO2 (55 °C, 135 bar) in a rectifying apparatus (packed bed with hot finger at 90 °C). (Moist CO2--∿8% (w) H2O at destraction conditions--will selectively remove creosote oil components leaving behind lower paraffins (< C26).)	--	--	172 (1981)
Ethanol (C_2H_6O)				
250 °C 100 bar	Liquefaction of wood with flow apparatus (1mL/min) to remove non-lignin and lignin components selectively according to choice of solvent.	--	--	101 (1979)
(Ethanol)/water				
265-275 °C 150 bar	Use of a continuous flow reactor for degradation (with product extraction) of white peat with a yield of 75-85% (w) extract (mainly water soluble solid) and of black peat (15% yield, considerable fraction of volatile products). No characterization of compounds in extracts. Water/ethanol = 7/3 (v/v).	--	--	112 (1979)
250 °C 100 bar	Liquefaction of wood with flow apparatus (1mL/min) to remove non-lignin and lignin components selectively according to choice of solvent and composition of water/ethanol mixture (6-70% water).			101 (1979)

Propylene (C_3H_6)				
110 °C 125 kg/cm^2	Component separation from a mixture of 1-hexadecene/1-octadecene/1-eicosene.	--	--	5,6 (1964)
105 °C 5-20 MN/m^2	Cited in a monograph review of gas extraction: extraction of a Russian fuel oil residue.	--	--	97 (1971)
Acetone (C_3H_6O)				
350-550 °C 1500 psig (100 atm)	Extraction of oil shales and tar sands with only 5-25% organic matter remaining in the shale or sand. Patented.	--	--	119 (1975)
250 °C 80 atm	Dense gas extraction of spruce wood followed by silica-gel and gel permeation chromatography or NaOH extraction and GC/MS: o- and p-cresol, guaiacol, 4-ethylphenol, 3,4-dimethylphenol, 4-methylguaiacol, p-isopropylphenol, 4-ethylguaiacol, 6-isopropylguaiacol, eugenol, 4-n-propylguaiacol, vanillin, isoeugenol, 6-isopropenylguaiacol, coniferyl alcohol.	--	--	120 (1978)
250-340 °C 250 bar	Extraction of thermal degradation products of cellulose and chitin followed by analysis by GC, GC/MS, and TLC. Cellulose (98% liquefied): 1,6-anhydro-beta-D-glucopyranose (glucosan), 1,6-anhydro-beta-D-glucofuranose, 1,4:3,6-dianhydro-alpha-D-glucopyranose, and 1,6-anhydro-3,4-dideoxy-beta-D-glycero-hex-3-enopyranos-2-ulose. Chitin: 2-acetamido-1,6-anhydro-2-deoxy-beta-D-glucopyranose, acetamide, diacetamide, and 1,6-anhydro-3,4-dideoxy-beta-D-glycero-hex-3-eno-pyranos-2-ulose.	--	--	121 (1978)
270 °C 100 bar	Liquefaction of wood with flow apparatus (1mL/min) to remove non-lignin and lignin components selectively according to choice of solvent.	--	--	101 (1979)

(continued)

TABLE 1 (continued)

Dense Gas [a b c]	Compounds Dissolved/Separated	Stationary Phase	Det.[d]	Ref.
Propane (C_3H_8)				
110 °C 125 kg/cm^2	Component separation from a mixture of 1-hexadecene/1-octadecene/1-eicosene.	--	--	5,6 (1964)
120 °C 200 kg/cm^2	Anhydrous glycerol not dissolved (insoluble in ethylene, soluble in NH_3).			
105 °C 5-20 MN/m^2	Cited in a monograph review of gas extraction: extraction of a Russian fuel oil residue.	--	--	97 (1971)
80-150 °C 50 atm	Extraction of fats and oils from ground corn to produce a powder containing less than 0.01% fat; the obtained powder is further treated with aqueous solutions of various pH's to obtain alpha-amylase, amyloglucosidase, and glucose. Patented process; other gases cited--CO_2 and SO_2.	--	--	113 (1973)
20-140 °C 42 atm	Extraction of oil from soy flakes, ground corn, crushed peanuts, sunflower seeds, olives, olive pits, linseed, cotton seeds, coconuts at subcritical temperatures with separation of dissolved oils at supercritical temperatures; throughout, approximately critical pressures. This method for cotton seeds eliminates toxic impurities accompanying pressing. Patented.	--	--	35 (1973)
100 °C 6-10 MPa	Extraction of lanolin from wool grease.	--	--	114 (1974) 115 (1977)
140 °C 130 atm	Deasphalting of petroleum to yield products lower in vanadium (0.15 ppm vs 2.4 ppm) and lower in involatile materials (1.3 vs 2.0 Conradson number) than liquid extraction.	--	--	55 (1978)

Propane, cont.				
108-128 °C 21-340 bar	Phase equilibria of oleic acid/propane showing gas phase enhancement of about ten-to-the-third.	--	--	57 (1978)
110 °C 200 bar	Isothermal "destraction" of Athabaska tar sands to yield dark-red, viscous oil (with separation of oil by pressure reduction) followed by toluene Soxhlet extraction of asphaltenes from destraction residue.	--	--	172 (1981)
(Propane)/SO2				
80-150 °C 50 atm	Extraction of fats and oils from ground corn to produce a powder containing less than 0.01% fat. Patented process; other gases cited CO2 and SO2.	--	--	113 (1973)
(Propane)/Ethane				
12 °C 400 psig (27 atm)	Extraction of pure water from sea water (3% (w) NaCl) using ∿ 8% (w) ethane in propane and forming water /organic hydrate crystals (e.g., C3H8·18H2O) from which water and solvents are recovered upon pressure decrease and/or temperature increase. Patented; claimed temperature and pressure ranges are sub to supercritical for some of the cited gases--propane, ethane/propane, methane/propane.	--	--	116 (1960)
(Propane)/Propylene				
100 °C 90-110 atm	Deasphalting of petroleum and removal of ozocerite from ores with 6-27% propylene in propane.	--	--	117 (1960)
(Propane)/n-Butane				
140 °C 110-120 atm	Deasphalting of a heavy, highly resinous crude petroleum residue with a high aromatic hydrocarbon content (70%)	--	--	118 (1969)

(continued)

TABLE 1 (continued)

Dense Gas [a b c]	Compounds Dissolved/Separated	Stationary Phase	Det.[d]	Ref.
(C3H8)/Butane, cont.	with separation of dissolved hydrocarbon material by pressure reduction with a 1/1 (w) ratio of butane/ propane. Patented process; propane alone is less effective than butane or propane/butane.			
(Propane)/Hexane				
115 °C 55 bar	Countercurrent column separation of free fatty acids from palm oil with precipitation of entrainer and component from solvent gas stream in a separating column at a different temperature.	--	--	82 (1981)
1-Propanol (C3H8O)				
250 °C 100 bar	Liquefaction of wood with flow apparatus (1mL/min) to remove non-lignin and lignin components selectively according to choice of solvent.	--	--	101 (1979)
Isopropanol (C3H8O)				
245 °C 40-51 kg/cm^2	di-n-Alkylphthalates (n = 2 to 16).	10% (w) Polyethylene/ Sil-O-Cel	UV	122,123 (1967)
	2-n-hexylnaphthalene, 2-n-dodecylnaphthalene, 2-phenylnaphthalene, 1,1'-binaphthyl, naphthalene, phenanthrene, 1,2-benzanthracene, picene, biphenyl, o- and p-terphenyl, 2,2'-binaphthyl, anthracene, pyrene, 2-naphthyl hexadecyl ether, 2-naphthyl pentadecyl ketone, m-terphenyl, m-quinquephenyl, coronene, decacylene.	Untreated alumina		124 (1967)
	In Ref. 125, noted that isopropanol especially with alumina may not be completely stable at all temperatures used (possibly dehydration with solid adsorbent).			125 (1970)

Isopropanol, cont.

335 °C --	Extraction/liquefaction of coal and lignite to obtain pyridine soluble material.	--	--	100 (1978)
250 °C 100 bar	Liquefaction of wood with flow apparatus (1mL/min) to remove non-lignin and lignin components selectively according to choice of solvent.	--	--	101 (1979)

Tetrahydrofuran (C_4H_8O)

310 °C 1500 psig (100 atm)	Extraction of Athabasca tar sands with only 9.3% organic matter remaining in the shale. Patented.	--	--	119 (1975)
	Influence of the stationary and mobile phases on separations (Tenax dissolves).		DRI (AMB)	102 (1977)
272-276 °C 60-140 atm	Aromatics (no separation effect; gel swells).	Chromosorb 101		
274-280 °C 34-125 atm	Capacity ratio of polystyrol (Avg MW 10,000) as a single broad peak.	Florisil		
283-300 °C 53-61 atm	Capacity ratios of naphthalene, phenanthrene, anthracene, pyrene, chrysene.	Merckogel SI 200		
292 °C 60 atm	Capacity ratios of naphthalene, phenanthrene, anthracene, pyrene, anthracene oil (from a coal tar fraction, Avg MW 200, 270-340 BP range), squalane, Kirkuk GVD (crude oil from Kirkuk, MW 410) with a selection of temperature and pressure so that (P/Pcr)/(T/Tcr) = 1.09.	Merckogel SI 200		
280-284 °C 40-150 atm	Hydrocarbons (no separation effect).	Spherosil XOA 500		

(continued)

TABLE 1 (continued)

Dense Gas [a b c]	Compounds Dissolved/Separated	Stationary Phase	Det.[d]	Ref.
Tetrahydrofuran, cont.				
275-286 °C 120-200 atm	Aromatics (no separation effect).	LiChrosorb Alox T		
290 °C 80 atm	Dense gas extraction of spruce wood followed by silica-gel and gel permeation chromatography or NaOH extraction and GC/MS: o- and p-cresol, guaiacol, 4-ethylphenol, 3,4-dimethylphenol, 4-methylguaicol, p-isopropyl-phenol, 4-ethylguaiacol, 6-isopropylguaicol, eugenol, 4-n-propylguaiacol, vanillin, isoeugenol, 6-isopro-penylguaiacol, coniferyl alcohol.	--	--	120 (1978)
Ethylacetate ($C_4H_8O_2$)				
	Influence of the stationary and mobile phases on separation:		DRI (AMB)	102 (1977)
255-260 °C 50-52 atm	Aromatics (no separation effect).	Tenax		
270-280 °C 50-100 atm	Hydrocarbons, polystyrol (no separation effect).	Florisil		
262-284 °C 100-110 atm	Hydrocarbons with weak separation effect (hexadecane, anthracene, phenanthrene).	Merckogel SI 200		
273-280 °C 95-100 atm	Hydrocarbons, polystyrols (no separation effect).	LiChrosorb Alox T		
270 °C 100 bar	Liquefaction of wood with flow apparatus (1mL/min) to remove non-lignin and lignin components selectively according to choice of solvent.	--	--	101 (1979)

n-Butane (C_4H_{10})				
160 °C 50-80 atm	Deasphalting of a heavy, highly resinous crude petroleum residue with a high aromatic hydrocarbon content (70%) with separation of dissolved hydrocarbon material by pressure reduction. Patented process; propane alone is less effective than butane or propane/butane.	--	--	118 (1969)
Isobutane (C_4H_{10})				
120-180 °C 37 atm	Extraction of oil from bone at subcritical temperatures with separation of dissolved oil at supercritical temperatures; always ~ critical pressure. Patented.	--	--	35 (1973)
Isobutanol ($C_4H_{10}O$)				
280 °C 100 bar	Liquefaction of wood with flow apparatus (1mL/min) to remove non-lignin and lignin components selectively according to choice of solvent.	--	--	101 (1979)
2-Butanol ($C_4H_{10}O$)				
270 °C 100 bar	Liquefaction of wood with flow apparatus (1mL/min) to remove non-lignin and lignin compounds selectively according to choice of solvent.	--	--	101 (1979)
Diethyl ether ($C_4H_{10}O$)				
200 °C 39-50 kg/cm^2	Phenols: phenol,hydroquinone,phloroglucinol,pyrogallol. Oxidation/polymerization inhibitors: Topanol A, TBC, Ionol, Lubad J. Quinones: anthraquinone, 1,2-benzanthraquinone, 6,13-pentacenequinone, phenanthrenequinone. Pharmaceuticals and alkaloids: aspirin, phenacetin, caffeine, cinchonine, brucine. Epoxy resin out to a 1478 molecular weight.	Porapak Q	UV	126 (1969) 125 (1970)

(continued)

TABLE 1 (continued)

Dense Gas [a b c]	Compounds Dissolved/Separated	Stationary Phase	Det.[d]	Ref.
Diethyl ether, cont.				
250 °C 100 bar	Supercritical liquefaction of wood with flow apparatus (1 mL/min) to remove non-lignin or lignin components selectively according to choice of solvent.	--	--	101 (1979)
Pyridine (C5H5N)				
440 °C 1500 psig (100 atm)	Extraction of Colorado oil shale with only 8% organic matter remaining in the shale. Patented.	--	--	119 (1975)
n-Pentane (C5H12)				
210-213 °C 30-50 kg/cm^2	2-n-hexylnaphthalene, 2-n-dodecylnaphthalene, di-n-alkylphthalates, dimyricyl phthalate, diphenyl phthalate, benzene, phenanthrene, 9,9'-bifluorenyl, 9-phenylanthracene, 1,2-benzpyrene, biphenyl, m-triphenyl, m-quinquephenyl, 1-dodecyl-4-octadecylbenzene, 2-phenylnaphthalene, 1,1'- and 2,2'-binaphthyl, 2-naphthyl pentadecyl ketone, 2-naphthyl hexadecyl ether, 1-phenylhexadecenal, 1-phenyl-1-hexadecenol.	23%(w) PEG 6000/ Sil-O-Cel	UV	122,123 (1967) 125 (1970)
213 °C 36-40 kg/cm^2	Naphthalene, phenanthrene, anthracene, pyrene, benz(a)-anthracene, chrysene, naphthalene, perylene, picene, di-n-alkylphthalates.	5-10% (w) Alkathene /Sil-O-Cel		
	1,3-dimethylnaphthalene	23% PEG 1000/ Sil-O-Cel		
200-300 °C 40-50 kg/cm^2	Anthracene, 1,1'-binaphthyl, pyrene, 2-phenylnaphthalene, phenanthrene, 9-phenylanthracene, 2-n-hexanaphthalene, 2-n-dodecylnaphthalene, benz(a)anthracene, picene, 1,2-benzpyrene, 3,4-benzpyrene.	Untreated alumina	UV	124 (1967)

n-Pentane, cont.

200-210 °C 26-50 kg/cm^2	Alkylbenzenes (up to C18 plus C12 chains); pressure programming of these in Ref. 125. Fat soluble vitamins: A1, E1, K1. Steroids: benzoate esters of cholesterol and pregenolene, propionate ester of testosterone, testosterone. Organo-metal complexes: ferrocene, 1-acetylferrocene, 1,1'-diacetylferrocene.	Porapak Q	UV	126 (1969) 125 (1970)
-- --	Distillation with supercritical pentane of a heavy coal tar to various fractions (colors, clear...dark... brilliant red--with last having MW 1500-1600). Distillation with supercritical n-pentane: triethylene glycol is very soluble in supercritical n-pentane and not very soluble in liquid n-pentane.	--	--	125 (1970)
220 °C 80 atm	Carbowax 20M as a stationary phase was dissolved and transported.	--	--	127 (1970)
203 °C 50 atm	Separation of a mineral oil distillation cut according to chemical type: substituted benzenes, benzothiophenes, naphthalenes, dibenzothiophenes, phenanthrenes, and highly substituted phenanthrenes.	Alumina	UV	128 (1970)
	Study of the influence of a number of variables (flow rate, packing particle size and shape, polar active sites of the support, pressure drop) on column efficiency:		UV	129 (1971) 130 (1973)
198-228 °C 30-70 atm	Isothermal pressure dependence of k' of biphenyl, durene, naphthalene and isobaric temperature dependence of k' of naphthalene and biphenyl.	Alumina (Basic)		
220 °C 34-54 atm	Effect of pressure on elution times of benzene, phenanthrene, chrysene.	Porasil C		

(continued)

TABLE 1 (continued)

Dense Gas [a b c]	Compounds Dissolved/Separated	Stationary Phase	Det.[d]	Ref.
n-Pentane, cont.				
20-220 °C 27-41 atm	HETP as a function of flow rate for various temperatures, pressures and column packings using benzene, chrysene, naphthalene, biphenyl, triphenylmethane, phenanthrene bibenzyl, benzophenone, benzyl phenyl ketone, benzil.	Corasil I (37-50μm) Porasil C (120/150;80/100) Durapak Chromosorb P AW, DMCS (80/100) Chromosorb P (60/80 mesh)		
190-202 °C 37 atm	Comparison of a separation (benzene, naphthalene, phenanthrene) at sub- and supercritical conditions.	Alumina	UV (AMB)	131 (1972)
173 °C 18-26 atm PP	Vapor phase separation of benzene, naphthalene, phenanthrene, anthracene, pyrene at subcritical conditions mild enough to avoid the isomerization of n-pentane discussed in this reference.	Porapak Q		
206 °C 30-36 atm PP	DC-710 polysiloxane polymer (MW 2600).	Porasil C n-C8H18/Porasil C Porapak Q Alumina	UV	132 (1975)
350-550 °C 1500 psi (100 atm)	Extraction of oil shales and tar sands with only 5-25% organic matter remaining in the shale or sand. Patented.	--	--	119 (1975)
	Influence of combinations of stationary and mobile phases on separations:		DRI (AMB)	102 (1977)
206-218 °C 40-44 atm	Capacity ratio of naphthalene, hexadecane, squalane, and decalin.	Spherosil XOA 500		
221 °C 47.5 atm	Capacity ratios of naphthalene, phenanthrene, pyrene, anthracene oil (from a coal tar fraction, Avg MW 200,	Spherosil XOA 500		

n-Pentane, cont.

	270-340 C BP range), squalane, Kirkuk GVD (crude oil oil from Kirkuk, Avg MW 410) with a selection of temperature and pressure so that (P/Pcr)/(T/Tcr) = 1.29.			
205-218 °C 65-77 atm	Capacity ratio of naphthalene, heptane, hexadecane, squalane.	LiChrosorb SI 100		
205 °C 54-60 atm	Capacity ratios of naphthalene, phenanthrene, pyrene, heptane, hexadecane, squalane, hexatriacontane.	LiChrosorb Alox T		
210-220 °C 60-75 atm	Hydrocarbons and esters but no separation effect.	Tenax		
200-215 °C 55-90 atm	Hydrocarbons and esters but no separation effect.	Florosil		
218-225 °C 20-25 atm	Capacity ratios of aromatics (showed a separation effect; however, subcritical pressure and a second liquid phase, possibly water, was observed).	Porasil C		
221-225 °C 400-820 psi (27-55 atm)	Analytical and preparative scale separation of DC-710 oligomers for preparation of GC capillary column stationary phases. (See Ref. 134 for the characterization of the bulk and SFC-obtained oligomers.) Ref. 133 also describes a computer automated system for (multi-ramp) pressure and temperature programming for supercritical fluid chromatography.	Porasil C	UV	133 (1976) 134 (1977)
140-290 °C 280-1200 psig (19-80 atm) PP TP	Selective extraction of maltenes, low-molecular weight (2500-4000) asphaltenes and high molecular weight (up to 10,000) asphaltenes from Athabasca tar sands using a chromatographic adsorption effect (but with readily desorbed adsorbate) in carbon columns and sub- and supercritical n-pentane along with sub- and supercritical benzene. (95% yield of extractable material with n-pentane under pressure vs 75% yield with n-	Carbon Adsorption Columns	--	135 (1977) 136 (1978) 94 (1980)

(continued)

TABLE 1 (continued)

Dense Gas [a b c]	Compounds Dissolved/Separated	Stationary Phase	Det.[d]	Ref.
n-Pentane, cont.				
	pentane at atmospheric pressure with comparable extraction rates.)			
158-218 °C 815-846 psig (54-56 atm) TP	Selective extraction of peat wax and low-, medium-, and high-molecular weight asphaltenes from peat using a chromatographic adsorption effect in carbon columns and sub- and supercritical pressurized n-pentane and subcritical pressurized benzene and benzene/ethanol. Yields and extraction rates with increased pressure and temperature are greater than with conventional atmospheric extracton.			
230 °C 56 bar	Extraction rate studies of mono-, di-, and triglycerides from celite and silica supports which showed a selective support effect and glyceride-hydrolysis by silica.			
220 °C 20-80 bar PP	Styrene oligomers (n = 1 to 40).	Porasil A	UV	137 (1977)
208-241 °C 375-1700 psi (26-116 atm) PP	Polystyrene oligomers (Mw 2200, 4000).	n-C18/Porasil C Phenyl Bondapak CPG-10-170	SP	138 (1977) 139 (1978)
220 °C 125 psi (9 atm)	Column efficiency studies with naphthalene, phenanthrene, pyrene.	Porasil A	UV	140 (1978)
250 °C 100 bar	Supercritical liquefaction of wood with flow apparatus (1 mL/min) to remove non-lignin and lignin components selectively according to choice of solvent.	--	--	101 (1979)

n-Pentane, cont.

243 °C 73 bar PP (neg) TP	In situ loading of gas chromatographic column packings using a supercritical solution of OV-3 in n-pentane (with negative pressure programming and positive temperature programming to effect deposition).	--	--	141 (1979)
210 °C 32 atm	Capillary supercritical fluid chromatography with separation of a model mixture: anthracene, pyrene, benzo[k]fluoranthene, benzo[e]pyrene, dibenz[a,c]-anthracene, benzo[ghi]perylene, and coronene. (Column I.D., 0.2 and 0.3 mm)	Phenylmethyl-polysiloxane (bonded)/glass capillary	FM	142 (1981)
180-210 °C 3.5-10.3 MPa	Extraction/liquefaction of carbonaceous materials with on-line UV monitoring to give "destractograms" followed by UV, IR, NMR, GC (FID,FPD), and GC/MS analysis of collected fractions: High Purity Graphites--large, polycyclic aromatics (and no extractable sulfur). Technical Grade Graphites--alkanes and alkylbenzenes, alkylnaphthalenes, alkyl-substituted thiophenes and benzothiophenes. Active Carbons--alkanes, dienes, small amounts of alkylbenzenes, thiols, smaller amounts of alkyl-substituted thiophenes. Charcoals--(released the smallest amount of material) almost entirely alkanes in small amounts with small quantities of large thiols.	--	UV	143 (1981)

(n-Pentane)/Methanol

205 °C 600-900 psi (41-61 atm) PP	Polystyrene oligomers with 5% methanol.	n-Octyl/ Porasil C	UV	144 (1969)

(continued)

TABLE 1 (continued)

Dense Gas [a b c]	Compounds Dissolved/Separated	Stationary Phase	Det.[d]	Ref.
(C5H12)/Methanol, cont.				
208-214 °C 570-1075 psi (39-73 atm)	Cyclic hydrocarbons: phenanthrene, fluoranthene, chrysene, 7,12-dimethylbenz(a)anthracene, benzo(a)pyrene, coronene. Polystyrene (MW 900, 2100), polyphenyl ethers (MW>522). (All with 5% methanol.)	Alumina n-C8H18/ Porasil C	UV	145 (1970)
212 °C 42.7 atm	Separation of polystyrene oligomers (Mw 266 to 994) with 10% methanol.	n-Octyl bonded/ Porasil	UV (AMB)	131 (1972)
192-214 °C 540 psi (37 atm)	DC-710 polysiloxane polymer with 5% methanol.	Porasil C	UV	132 (1975)
180-260 °C 20-110 bar PP, TP	Styrene oligomers with 5% methanol.	Porasil A	UV	137 (1977) 146,147 (1978)
220-235 °C 20-330 bar PP	Styrene oligomers (Mw 900, 2200, 4000) with 10% methanol.			148,149 (1977)
(n-Pentane)/Isopropanol				
220 °C 40.8 atm	Study of the influence of a number of variables (flow rate, packing particle size and shape, polar active sites of the support, pressure drop) on column efficiency with 0-0.5% isopropanol.	Porasil C	UV (AMB)	129 (1971) 130 (1973)
203 °C 37.6 atm	Effect of isopropanol (0.1-10%) upon retention times of naphthalene, phenanthrene, anthracene.	Alumina	UV (AMB)	131 (1972)
198-216 °C 30-36 atm	DC-710 polysiloxane polymers with 0-20% isopropanol.	Porasil C	UV	132 (1975)

(C5H12)/Isopropanol cont.

	Influence of combinations of stationary and mobile phases on separations:		DRI (AMB)	102 (1977)
204-225 °C 42-56 atm	Capacity ratios of naphthalene, phenanthrene, pyrene, chrysene, anthracene, diethyl phthalate, didecyl-phthalate, cholesteryl acetate, cholesteryl palmitate with 1% isopropanol.	LiChrosorb Alox T %		
217-232 °C 76-85 atm	Capacity ratios of naphthalene, phenanthrene, pyrene, chrysene with 2% isopropanol.	Lichrosorb Alox T		
213-217 °C 53-75 atm	Capacity ratios of alkanes with 0.2% isopropanol.	LiChrosorb SI 100		
172-260 °C 500-1300 psi (34-88 atm) PP,TP	Capacity ratio studies of polystyrene oligomers (MW 2200, 4000) with 5-10% isopropanol.	CPG-10-75 CPG-10-170 CPG-10-240 Porasil C	SP	138 (1977) 139 (1978)
240 °C 3.5-7.6 MPa PP	Effects of column length, particle size, flow rate, and pressure programming on resolution in pressure programmed supercritical fluid chromatography with 5% isopropanol using monodisperse polystyrene (Avg MW = 800).	Porasil C,270/325 Porasil C,100/150 Porasil C, 80/100 Controlled pore glass, 60/80	UV	150 (1980)
(n-Pentane)/Cyclohexane				
208 °C 600-1300 psi (41-88 atm) PP	Capacity ratio studies of polystyrene oligomers (MW 2200) with 0.1-10% cyclohexane.	n-C18/Porasil C	SP	138 (1977) 139 (1978)

(continued)

TABLE 1 (continued)

Dense Gas [a] [b] [c]	Compounds Dissolved/Separated	Stationary Phase	Det.[d]	Ref.
Benzene (C6H6)				
300 °C 1750 psi (119 atm)	Extraction of coal to yield an ash-free or reduced-ash coal. Patented process for extraction of part of carbonaceous content from carbonaceous material using fluids above supercritical temperatures; other gases cited--CH4, C2H6, C3H8, C2H4, C3H6, NH3, Cl2, CO2, toluene, pyridine, dimethylamine, ethylamine, methylamine, or hydrocarbons from C4 to C12.	--	--	110 (1969)
140-290 °C 400-820 psi (27-55 atm) PP TP	Selective extraction of maltenes, low MW (2500-4000) asphaltenes and high MW (up to 10,000) asphaltenes from Athabasca tar sands using a chromatographic adsorption effect (but with readily desorbed adsorbate) in carbon columns and sub- and supercritical n-pentane along with sub- and supercritical benzene.	Carbon Adsorption Columns	--	135 (1977) 136 (1978) 94 (1980)
158-218 °C 815-846 psig (54-56 atm) TP	Selective extraction of peat wax and low, medium, and high MW asphaltenes from peat using a chromatographic adsorption effect in carbon columns and sub- and supercritical pressurized n-pentane and subcritical pressurized benzene and benzene/ethanol. (Extraction rates, yields with increased pressure, temperature are greater than with conventional extraction.			
305-335 °C 3400-4100 psig (232-280 atm)	Extraction/liquefaction of coal to obtain pyridine soluble material.	--	--	100 (1978)
Cyclohexane (C6H12)				
	Influence of combinations of stationary and mobile phases on separations--however, no separation effect observed here.		DRI (AMB)	102 (1977)
295 °C 80-90 atm	Aromatics, esters, polymers, nitrogen-containing compounds.	Tenax		

Cyclohexane, cont.				
297-303 °C 40-56 atm	Hydrocarbons and esters.	Florisil		
294-303 °C 90-95 atm	Aromatics.	Merckogel SI 200		
295 °C 100 atm	Hydrocarbons.	LiChrosorb Alox T		
Hexane (C_6H_{14})				
230-259 °C 18-80 kg/cm^2	Polynuclear aromatics: triphenylene, naphthalene, phenanthrene, pyrene, chrysene. Coal tar: 8 unidentified compounds.	Corasil (II)	NS	151 (1975)
Di-isopropyl ether ($C_6H_{14}O$)				
	Influence of combinations of stationary and mobile phases on separations (Tenax dissolves):		DRI (AMB)	102 (1977)
235-250 °C 50-160 atm	Hydrocarbons and esters (no separation effect).	Porapak Q Chromosorb 101 Chromosorb 102		
234-237 °C 52-54 atm	Aromatics (no separation effect).	Florisil		
247-255 °C 42-60 atm	Hydrocarbons and esters (no separation effect).	Porasil C		
233-250 °C 55-85 atm	Capacity ratios of diethyl phthalate, didecyl phthalate, ditridecyl phthalate, cholesteryl acetate, cholesteryl palmitate, naphthalene, phenanthrene, anthracene, pyrene, chrysene, perylene, adamantane, hexadecane, squalane, hexatriacontane, three polyphenols (one of which was terphenyl).	LiChrosorb Alox T		

(continued)

TABLE 1 (continued)

Dense Gas [a b c]	Compounds Dissolved/Separated	Stationary Phase	Det.[d]	Ref.
Toluene (C_7H_8)				
350 °C 10 MN/m^2	Extraction/liquefaction of a series of bituminous coals ranging in rank from 18-45% volatile content.	--	--	152 (1975)
350 °C 10 MPa	Extraction/liquefaction of a coal yielding products of Aliphatics: phytane, pristane, norpristane, farnesane, 2,6,10-trimethyltridecane, 2,6,10-trimethylundecane, n-alkanes (up to C31). Oxygen compounds: quinones, benzofurans, dibenzofurans, diphenyl ethers, aromatic ethers. Aromatics: alkyl (C1-C4), hydroaromatics, naphthenics.	--	--	153 (1975)
350-550 °C 1500 psi (100 atm)	Extraction of oil shales and tar sands with only 5-25% organic matter remaining in the shale or sand. Patented.	--	--	119 (1975)
350-450 °C 17 MPa	Dense gas extraction/liquefaction of coal to yield Aliphatics: n-C13 to n-C34. Aromatics: bibenzyl, anthracene, 9,10-dialkylanthracene, pyrene, benzo(a)pyrene, dibenzo(def,mno)chrysene, perylene, dibenzo(b,def)chrysene, coronene, aromatic hydroxyl compounds.	--	--	154 (1977)
340 °C 80 atm	Dense gas extraction of spruce wood followed by silica-gel and gel permeation chromatography or NaOH extraction and GC/MS: o- and p-cresol, guaiacol, 4-ethylphenol, 3,4-dimethylphenol, 4-methylguaiacol, p-isopropylphenol, 4-ethylguaiacol, 6-isopropylguaiacol, eugenol, 4-n-propylguaiacol, vanillin, isoeugenol, 6-isopropenylguaiacol, coniferyl alcohol.	--	--	120 (1978)
400 °C 16 MPa	Dense gas extraction/liquefaction of two lignites to give paraffins, alkylated hydrocarbons, and phenolic and oxygenated compounds.	--	--	155 (1978)

Toluene, cont.

305-375 °C 2400-4800 psia (164-328 atm)	Solvent gas temperature and density effects on extraction/liquefaction of coal and lignite to obtain pyridine soluble material.	--	--	100 (1978)
350-450 °C 17 MPa	Pyrolysis of toluene at supercritical conditions of toluene finding the product yield and distribution as a function of temperature and residence time.	--	--	156 (1978)
440 °C 100 atm	Extraction of Wyodak coal to yield a low ash extract (21% (w) dry coal) with a higher hydrogen content than original coal leaving a char with 27% (w) volatile content, high reactivity to CO2 (∿ original coal).	--	--	157 (1979)
340-450 °C 8-17 MPa	Dense gas extraction/liquefaction of coal to study paraffinic hydrocarbons as organic geochemical markers.	--	--	158 (1979)
400 °C 10.2 MPa	Low temperature pyrolysis with simultaneous dense gas extraction of products of a British coal with a yield of 26.7% followed by NMR analysis of the (ordinary organic) solvent fractionated fractions for structural analysis of the aromatic fractions: pentane-solubles, 2-3 aromatic rings/average molecule; asphaltenes, 5-8 aromatic rings/molecule;benzene insolubles,8-9 aromatic rings/molecule. The substituents were alkyl, naphthenic, phenolic hydroxyls with aromatic ether linkages but no carbonyls.	--	--	159 (1979) 160 (1979)
340 °C 8 MPa	Dense gas extraction of two Turkish lignites with yields of 14-16% (w) of dry, ash-free coals followed by GC/MS, NMR analysis of solvent fractionated fractions (paraffins, aromatics, polars, asphaltenes/asphaltols).	--	--	161 (1979)

(continued)

TABLE 1 (continued)

Dense Gas [a b c]	Compounds Dissolved/Separated	Stationary Phase	Det.[d]	Ref.
Toluene, cont.				
450°C 20 MPa	Supercritical gas extraction/liquefaction of a bituminous coal to study experimental procedures (batch vs continuous reactors, H2, SnCl2) followed by (ordinary organic) solvent fractionation and IR, phosphorescence, NMR, thermogravimetric, x-ray fluorescence, and GLC analyses. Thermal breakdown of toluene was observed. Compared to hydropyrolysis at the same temperature and pressure, dense gas extraction was shown to be milder.	--	--	162 (1980)
360°C 11.6-29.4 MPa	Extraction of a Turkish coking coal followed by (ordinary organic) solvent fractionation of the extracts with analysis by GC, GC/MS: 1- and 2-methylnaphthalene; 1,2- and 2,3-dimethylnaphthalene; isopropylnaphthalene; trimethylnaphthalene; C16-C25 straight chain alkanes; 1,1-diphenyl-1-heptene; phenanthrene; o- and p-xylene; 1,3,5-, 1,2,4- and 1,2,3-trimethylbenzenes; allylbenzene; indene; naphthalene; methyldiphenyl; 3,3'-, 4,4', 3,4'- and 3,4-dimethyldiphenyl; 3-methylphenol; p-isopropylphenol; 3-ethyl-5-methylphenol; o- and p-sec-butylphenol; 2,5-diisobutylthiopene; 1- and 2-ethylnaphthalene; 1,4-dimethylnaphthalene; biphenyl; bibenzyl; 2- and 4-methylfluorene; 2,3-dimethylfluorene; anthracene; 3,3',4,4'-tetramethyldiphenyl; 2- and 3-methylphenanthrene; 2,5- and 9,10-dimethylphenanthrene; 2,3,5-trimethylphenanthrene; hexadecahydropyrene; pyrene; 1,2- and 1,3-benzofluorene; methylpyrene; 1,2- and 1,3-diphenylbenzene; chrysene; pentaethylstyrene;5,8-dimethylbenzo(c)phenanthrene; 9,10-dimethylbenzoanthracene.	--	--	163 (1981)
(Toluene)/Hydrogen				
400°C 10 MPa	Extraction/liquefaction of a coal yielding products of Aliphatics: phytane, pristane, norpristane, farnesane, 2,6,10-trimethyltridecane, 2,6,10-trimethylundecane, n-alkanes (up to C31).	--	--	164 (1978)

(C7H8)/Hydrogen, cont.

	Oxygenated compounds: quinones, benzofurans, dibenzofurans, diphenyl ethers, aromatic ethers. Aromatics: alkyl (C1-C4), hydroaromatics, naphthenics.			
400 °C 13 MPa	Low temperature pyrolysis with simultaneous dense gas extraction in the presence of hydrogen and zinc chloride catalyst of a British coal with a yield of 47.5% followed by NMR analysis of the (ordinary organic) solvent fractionated fractions for aromatic structural analysis. Compared to toluene extraction at 400 °C, 10.2 MPa of a British coal, "extract consisted of smaller molecules with much lower oxygen and sulfur contents, more naphthenic substituents, and few alkyl groups and methylene and biphenyl linkages."	--	--	159 (1979) 160 (1979)
450 °C 20 MPa	Supercritical gas extraction/liquefaction of a bituminous coal to study experimental procedures (batch vs continuous reactors, H2, SnCl2) followed by (ordinary organic) solvent fractionation and IR, phosphorescence, NMR, thermogravimetric, x-ray fluorescence, and GLC analyses. While thermal breakdown of toluene was observed, the presence of hydrogen helped to suppress it. Hydrogen in the dense solvent gas led to more aromatic, lower MW asphaltenes. However, dense gas extraction with H2/toluene was still a milder process than hydropyrolysis at the same temperature, pressure.	--	--	162 (19800
(p-Cresol, C7H8O)/H2O				
440 °C 100 atm	Extraction of Wyodak coal to yield a low ash extract (~40% (w) dry coal) with 10% (w) H2O in p-cresol. p-Cresol apparently decomposed or reacted with the coal to yield additional extract-like material.	--	--	157 (1979)

(continued)

TABLE 1 (continued)

Dense Gas [a b c]	Compounds Dissolved/Separated	Stationary Phase	Det.[d]	Ref.
Methylcyclohexane (C_7H_{14})				
440 °C 1500 psig (100 atm)	Extraction of Colorado oil shale with only 8% organic matter remaining in the shale. Patented.	--	--	119 (1975)
Tetralin ($C_{10}H_{12}$)				
380-450 °C 10-30 MPa	Extraction of coal to yield an extract (75 wt% daf coal) containing some high MW material which was insoluble in THF and could not be fully characterized by gel permeation chromatography (exclusion limit 9000).	--	--	165,166 (1981)
Fluoroform (CHF_3)				
40 °C 53-76 atm	Threshold solubilities of Antioxidant #330, diethylstilbestrol dipalmitate, di-2-naphthyl sebacate.	--	UV	41 (1976)
40 °C 60-200 bar	Quantitative solubility studies of opium alkaloids as a function of solvent gas pressure: papaverine, thebaine, noscapine, codeine, morphine. (Solubilities in liquid CHF_3 for codeine, thebaine, papaverine, noscapine.)	--	--	75 (1980)
30-40 °C 70-80 bar	Extraction of dihydrovaltrate and valtrate from Valeriana wallichia roots with fractionation by decompression (2 steps); also shows the extraction time is dependent upon the macerated particle size and compares supercritical and Soxhlet extraction yields. Solubility in CHF_3 is 30 mg/NL (70 bar, 30 °C) vs 12 mg/NL (100 bar, 40 °C) in CO_2.	--	--	72 (1980)
19-40 °C 60-200 bar	Solubility studies of thebaine as a function of pressure with specific comparison to other solvents (liquid CO_2, liquid and supercritical CHF_3) with off-line	--	--	77 (1980)

Fluoroform, cont.

	analysis by TLC and spectrophotometry. Thebaine was also extracted from the macerated plant material Papaver bracteatum Lindl. at various solvent pressures and moisture contents of plant material with all indicated solvents. CHF_3 (liquid and supercritical) is a better solvent for thebaine (by a factor of over 5 at 150 bar) with selective extraction of thebaine vs fatty oils at 100 bar CHF_3. For the plant material, pretreatment with ammonia is necessary and a water content of 30-40% is desirable.			
Chlorotrifluoromethane ($CClF_3$)				
42 °C 70-75 kg/cm^2	Slight solubility of paraffin oil; upon increasing pressure from 70 to 75 kg/cm2, it was observed that phase layers reversed with the paraffin oil on top at 75 kg/cm2.	--	--	5 (1964)
25-60 °C 28-250 atm	One-step extraction of nicotine from tobacco (with adjusted water content of 12%) with either sub- or supercritical solvent gas; recovery of nicotine was effected by expansion and cooling.	--	--	1 (1970) 2 (1971)
54-127 °C 48-364 bar	Phase equilibria of oleic acid/CF_3Cl showing gas phase enhancement of ~ ten-to-the-eighth for some conditions.	--	--	57 (1978)
70 °C 100-350 bar	Partition coefficient of components of a glyceride mixture (free fatty acids and mono- and diglycerides) as a function of pressure.			
70 °C 100-200 bar	Comparison of solvent gases for the pressure-dependent separation factor between hexadecanol and octadecane.	--	--	82 (1981)

(continued)

TABLE 1 (continued)

Dense Gas [a] [b] [c]	Compounds Dissolved/Separated	Stationary Phase	Det.[d]	Ref.
Bromotrifluoromethane (CBrF3)				
76-128 °C 29-151 atm	Phase equilibria of oleic acid/CF3Br showing gas phase enhancement of ~ ten-to-the-eighth for some conditions.	--	--	57 (1978)
Chlorodifluoromethane (CHClF2)				
150-170 °C 800-2300 psi (54-157 atm)	Ni etioporphyrin II, Ni mesoporphyrin IX dimethyl ester.	33% Carbowax 20M or Narflex 370/ Chromosorb W	--	167 (1962)
Dichlorodifluoromethane (CCl2F2)				
150-170 °C 800-2300 psi (54-157 atm)	Ni etioporphyrin II, Ni mesoporphyrin IX dimethyl ester.	33% Carbowax 20M or Narflex 370/ Chromosorb W	--	167 (1962)
130 °C 925-1000 psi (63-68 atm)	Salicylaldoximates: Ni(II), Cu(II), Zn(II). Thenoyltrifluoroacetonates: Sc(III), Y(III), Eu(III), Al(III), Zr(IV), VO, Fe(III), Co(III), Ni(II), Pd(II), Cu(II), Zn(II), Th(IV), UO2.	2% Kel-F/Chromosorb W AW HMDS	SP	169 (1968)
140-153 °C 1000-2700 psig (68-184 atm) PP	Porphyrins and metalloporphyrins: etioporphyrins of Cu, Ni, VO and Mg; etioporphyrin II; mesoporphyrin IX dimethyl ester; mesoporphyrin IX diethyl ester; deuteroporphyrin IX dimethyl ester; desoxophyllerythroetioporphyrin.	20% XE-60 or 12% Versamid 900 + 0.2% Mg phthalocyanine or 10% Epon 1001/ Chromosorb W	SP	170 (1968)
115 °C 950-1100 psi (65-75 atm)	Acetylacetonates which often decompose at GC temperatures: Li(I), Na(I), K(I), Be(II), Mg(II), Ca(II), Sr(II), Ba(II), Al(III), Ga(III), In(III), Tl(I), Sc(III), Y(III), La(III), Ce(III), Pr(III), Nd(III), Tb(III), TiO, TiCl2, Zr(IV), VO, Cr(III), MoO2, UO2, Mn(II,III), Fe(III), Ru(III), Co(II,III), Rh(III),	10% Epon 1001/ Chromosorb W or 5% Epon 1009/ Chromosorb P AW HMDS	UV	171 (1970)

Dichlorodifluoromethane, cont.

	Ir(III), Ni(II), Pd(II), Pt(II), Cu(II), Zn(II), Cd(II), Pb(II), Th(IV), U(IV)			

1,1-Difluoroethane ($C_2H_4F_2$)

118°C 50 atm	Threshold solubility of hexaphenylbenzene.	--	UV	41 (1976)
118°C 1088 atm	Exclusion chromatography of toluene, polystyrene 600 and 4000, biphenyl, polyvinylpyrolidine, acetone.	Porous silica glass	UV	41 (1976) 168 (1977)

[a]Conditions: PP-pressure programming, DP-density programming, TP-temperature programming

[b]Units: 1 atm = 1.0133 bar = 0.10133 MPa = 0.10133 MN/m^2 = 1.0332 kg/cm^2 = 14.696 psi

[c]Critical temperature (°C) and critical pressure (atm) of pure gases: Argon, (-122.3, 48.3); Carbon dioxide, (31.1,72.9); Water, (374, 220); Nitrogen, (-146.9, 33.5); Nitrous oxide, (36.4, 71.5); Ammonia, (132.4, 113.3); Sulfur hexafluoride, (45.5, 37.1); Methane, (-82.6, 45.4); Methanol,(239.9, 78.5); Acetonitrile, (274.5, 47.7); Ethylene, (9.5, 50.1); Ethane, (32.3, 48.2); Ethanol, (243.1, 63.0); Propylene, (91.6, 45.5); Propane, (96.7, 41.9); Acetone, (235.5, 47.0); 1-Propanol, (263.6, 51.0); Isopropanol, (235.3, 47.0); Tetrahydrofuran, (267, 51.9); Ethyl acetate, (250.1, 37.8); n-Butane, (152.0, 37.5); Isobutane, (134.9, 36.7); Isobutanol, (274.6, 42.4); 2-Butanol, (262.8, 41.4); Diethyl ether, (193.6, 36.3); Pyridine, (346.8, 55.6); n-Pentane, (196.6, 33.3); Benzene, (288.4, 47.9); Cyclohexane, (281, 40.4); Hexane, (234.7, 29.9); Di-isopropyl ether, (228, 26.8); Toluene, (320.8, 41.6); p-Cresol, (431.4, 50.8); Methylcyclohexane, (298.9, 34.3); Tetralin, (426, 34.7); Fluoroform, (25.6, 47.7); Chlorotrifluoromethane, (28.8, 38.1); Bromotrifluoromethane, (67, 39.4); Chlorodifluoromethane, (96, 48.7); Dichlorodifluoromethane, (112,40.6); 1,1-Difluoroethane, (113.5, 46.9).

[d]Detectors: FI-flame ionization, UV-ultraviolet, SP-spectrophotometer, TL-thin layer plate, MS-mass spectrometer, DRI-differential refractometer, FM-fluorimetric, NS-not stated, HP-high pressure, M-modified, AMB-ambient

Geological Applications

Dense gas extraction could be used to good advantage in geological studies of rock composition. For example, Petersilie and Sörensen (90) describe first the separation and GC analysis of entrained hydrocarbon gases followed by the liquid solvent extraction and IR analysis of bituminous substances in their samples. Dense gas extraction with on-line analysis would considerably simplify the process. This type of extraction/analysis procedure would be particularly helpful in oil-shale sample characterization (typical procedure in Reference 91). Geologists are not only interested in sample analysis but also in simulating formation-reaction conditions (92,93)--often at elevated pressures and temperatures. These geological interests then are analogous to high pressure chemical reaction studies, many of which have industrial applications: polymerization, hydrogenation, cracking, and aldehyde, acid and alcohol production.

High Pressure Reactions

Comments about high pressure reactions may seem inappropriate within a section dealing expressly with extraction. However, it has been postulated that in high pressure systems, fluids act both as reactant and solvent in some processes. In these systems some of the reactants and products will certainly be in the gas (fluid) phase and so on-line analysis would be a great aid for studies of high pressure reactions as well as the described extractions. Weale (94) has pointed out that utilization of high pressure reactions has been hampered by the lack of detailed studies of reaction kinetics and mechanisms and thermodynamic data at high pressures. Reactions are studied in different ways: 1) removal of a sample after some definite reaction time, 2) continuous removal of a sample during a reaction (difficult at high pressures) and 3) continuous monitoring of parameters such as volume change, electrical conductivity, and spectrophotometric (useful only with well characterized reactions, which are rarely found). In addition to being

difficult, sample removal for monitoring in small-scale research studies may constitute removal of an appreciable amount of the reaction species and thereby disrupt the system under study (95). Young has discussed experimental methods for studying phase behavior of mixtures at high temperatures and pressures and also mentioned sampling difficulties (96).

Often high pressures not only eliminate the need for high temperatures (thereby avoiding decomposition) but also provide new reaction schemes. Luft (97) and particularly Thies (98) have discussed the kinetic aspects of high pressure reactions including rate constant dependence on compressibilities, molar volumes, solvation effects, and viscosity. Also, Thies describes the reaction path/product selectivity that is possible with pressure as the controlling factor. Among the several examples presented were the reaction of CO_2 and aniline to give 3-phenyl-2,4-quinozoline dione (vs diphenylurea), Diels-Alder reactions, the synthesis of hexamethylacetonoxime from hexamethylacetone, and the increased yield of 2-nitro-1,3-xylol from m-xylol. Irani and Funk (37) have briefly outlined some systems in which the supercritical solvent is not inert and influences the reaction products: isomerization of normal paraffins, decrease in asphaltene products in coal liquefaction, and conversion of sulfur and nitrogen to H_2S and NH_3 in the treatment of hydrocarbons. Similarly, Menshutkin type reactions, $(C_2H_5)_3N + C_2H_5I \rightleftarrows (C_2H_5)_4N^+ + I^-$, in supercritical isopropanol and methanol at various conditions have been studied to ascertain the dependence of the volume of activation upon temperature and pressure (99). Metal amides, imides, and nitrides have been synthesized using supercritical ammonia and metals and metal salts (100).

DGC/MS as an On-Line Detector for High Pressure Gas Systems

Dense gas chromatography, discussed in the next section, would be applicable for product analysis in many of the extraction and kinetics applications of dense gases. In particular, a DGC/MS instrument as described in Section 5 could be used to separate,

identify, and monitor continuously the various species in the dense gas phase at high pressures, eliminating the decompression followed by extra sample handling for analysis by GC, HPLC, IR, etc.

4. PRIOR DENSE GAS CHROMATOGRAPHY STUDIES

Six reviews of the work done in DGC detail the theory, instrumentation, chromatographic materials and performance, and analytical and physicochemical applications of DGC (48, 101-103, 176, 182). All systems and conditions studied to date are outlined in Table 1.

DGC Compared to GC and LC*

As expected from the properties of solvent dense gases, DGC combines characteristics of both gas and liquid chromatographies. A GC-type advantage is the speed of separation due to the low viscosity and high diffusivity of the gas. In a packed column across which there is a constant pressure drop, the velocity of the fluid is inversely proportional to the viscosity so lower viscosities lead to faster flow rates. If the fluid velocity is constant, the pressure drop is directly proportional to viscosity and so lower viscosities require less pressure drop to obtain a given flow rate. However, a high diffusivity as in GC contributes to longitudinal zone spreading so lower diffusivities improve resolution but also increase separation times. Diffusivities intermediate between those of liquids and gases should result in faster separations (i.e., faster than LC) and less zone spreading (i.e., less than GC). Both parameters are incorporated in the dimensionless Reynolds number: $Re = \rho v d_p/\eta$ (ρ, density; v, velocity; d_p, diameter of packing particles; η, viscosity). For a packed bed a change from laminar to turbulent flow--and improved mass transport--occurs for

*DGC-dense gas chromatography; GC-gas chromatography; LC-liquid chromatography; HPLC-high performance liquid chromatography; MS-mass spectrometer.

values of the Reynolds number in the range of 1-10 to 1-100 (104). For typical DGC conditions (say, CO_2 at 40°C) with a density of 0.8 g/mL, a velocity of 10 cm/s, a packing particle diameter of 30 μm, and a viscosity of 8×10^{-4} poise, the Reynolds number is 30 and so the flow probably has become turbulent.

Usually in gas chromatography the mobile gaseous phase serves one purpose: zone movement. However, there has been some work in GC in which steam and organic vapors are used as the mobile phase. A review by Rudenko et al (49) outlines the work in this area and considers the effects on the chromatographic HETP (plate height) as well as reviewing dense gas chromatography as an extension to these studies. Various characteristics of these systems as detailed by Rudenko et al are 1) column efficiency is increased, 2) it is possible to chromatograph (analytically and preparatively) highly polar, involatile compounds at temperatures of 50-100°C and upward, 3) there is no need for column deactivation, 4) analysis time is reduced, and 5) the method is very useful for analysis of aqueous solutions and dispersions. Nonaka (105) has presented an extensive review considering steam and steam mixtures as the mobile phase. He maintains that there is probably little interaction between solute and mobile phase molecules because of the low density of the mobile phase and states that straightforward evidence of interaction has not yet been obtained. However, the mobile phase probably deactivates the stationary phase in gas-solid chromatography and any active, uncoated sites in gas-liquid chromatography. Stationary phase modification has been further studied by Parcher and Westlake (106): the polarity of a liquid stationary phase is altered by the mobile phase composition. Hence, these GC studies with steam and organic vapors are pertinent to DGC since they emphasize the interaction of the mobile phase with the column stationary phase and may indicate the interaction (to an undetermined extent) of the mobile phase with the solute.

In liquid chromatography the mobile phase serves two purposes: zone movement and solvation. Hence, DGC is similar to LC in that

DGC may be used to dissolve and elute high molecular weight compounds, polymers, biological molecules, thermally unstable molecules, and involatile* molecules because of the solvent-solute interactions. The dense gas solvent power is a function not only of the particular solvent gas used (LC property) but also of the gas density. One manifestation of the density-dependent solvent power is the existence of a threshold pressure as shown by the work of Giddings et al (42,44) and Klesper et al (107). Below the threshold pressure of a given solvent/solute system, there will be no solution of the solute. The density variable is an advantage unique to DGC. In DGC the solvent power may be quickly and easily varied by density (42,44,46)--pressure (108-114)--programming as well as by temperature programming (typical in GC) and possibly solvent composition programming (typical in LC).

Pressure Programming

Bartmann (113) has published chromatograms of n-alkanes (n = 5 to 20) and cyclic hydrocarbons at 40 and 55°C for various column packings and CO_2 pressure programming in the range of 51 to 134 atm. He notes that the pressure-dependent solvent power of the mobile phase is the decisive factor in determining the migration rate and resolution. Nieman and Rogers (114) have found that there is an optimum temperature which depends upon the molecular weight range when linear pressure programming is applied to separating the oligomers of the silicone polymer, DC-710, with n-pentane as the mobile phase. Klesper and Hartmann (108) have studied the effect of

*When a molecule is dissolved by a dense gas, the process is often described as volatilization since the solute has become part of the gas phase. Because of the action of the dense gas, the solute concentration in the gas phase can increase by more than a factor of 10^{10} compared to the expected vapor pressure at a given temperature (29). Hence, molecules considered involatile at typical GC conditions may be volatilized at temperatures significantly lower than GC conditions.

pressure programming of various mixtures of n-pentane and methanol mobile phase upon the resolution of styrene oligomers for analytical and preparative scale DGC. Jentoft and Gouw (109) note that the pressure programming elution time (95% n-pentane/methanol) of coronene is one-third that of the isobaric conditions. Their studies show that polystyrene oligomer elution times are also up to three times as long with isobaric conditions as with pressure programming. Finally, work by Bowman (46) indicates that linear density programming is superior to linear pressure programming because of the large change in density caused by a small change in pressure near the critical temperature (see Figure 1).

Capacity Ratio Temperature Dependence

Sie and Rijnders (115,116) first noted the strong temperature dependence of the capacity ratio, a modified partition coefficient (stationary phase solute/gas phase solute), in the region close to and above the critical temperature of the gas. The same behavior was also observed by Nieman and Rogers (114) in their experiments which included mixed solvent gases. Just above the critical temperature, because of the high density and the strong intermolecular forces of the dense solvent gas, more solute is dissolved by the dense gas resulting in a low value for the partition coefficient. As the temperature is increased, the density of the gas decreases with a simultaneous lessening of its solvent power so more solute is partitioned in the stationary phase and the partition coefficient increases. At even higher temperatures the partition coefficient may remain essentially constant or decrease again. Beyond this maximum (or leveling point) in the partition coefficient-temperature dependence the behavior is determined by the temperature-dependent volatility of the solute as in conventional GC. If both the temperature and the pressure are increased so that a liquid-like density is maintained, solute concentration in the dense gas phase may increase from the solvent interaction and from the increased solute vapor pressure. Therefore, temperatures need not

be limited to a range near critical as long as the pressure can be sufficiently increased. While higher temperatures and pressures may be advantageous in some cases (28), such conditions will not be suitable for thermally labile compounds.

Stationary Phases

Since dense gases are such powerful solvents for large, involatile molecules, the stationary phase in dense gas-liquid chromatography must be chosen with care (101). However, this problem may have been alleviated by the new bonded phase packings developed for HPLC. The bonded phase packings and the pellicular or superficially porous glass beads appear to be well-suited for DGC: the small particle diameters in narrow ranges yield lower theoretical plate heights (117-119) as shown in GC and HPLC; however, the lower viscosity of a dense gas compared to liquids causes a lower pressure drop across the column than in HPLC (117).

In the above discussion, no differentiation has been made between liquid and solid stationary phases. In dense gas-solid chromatography (116) the dense gas is adsorbed onto the solid adsorbent modifying it in situ, thereby eliminating the need for the usual deactivation treatments. The solute peaks are sharp and symmetrical with none of the typical GSC tailing. It has been proposed that the dense fluid coats the solid surface so that the mechanism is actually a fluid-liquid partition. In typical GSC the operating temperatures are 100-300^{o}C above the boiling points of the solutes to be separated, far higher than is required for the same solutes in GLC where a temperature giving a vapor pressure on the order of 10 Torr (120) may be used. Dense gas-solid and -liquid chromatographies can effect separations at significantly lower temperatures since the minimum operating temperature is determined only by the critical temperature of the solvent dense gas. Advantages of dense gas-solid chromatography are the easier separations of close-boiling isomeric hydrocarbons than with dense gas-liquid chromatography

and the faster separations than with liquid-solid chromatography (116).

Chromatograph System Selectivity

Selectivity in DGC is determined not just by the choice of the solvent gas (and its temperature and pressure) alone but by the combination of the solvent gas and the column packing (101). In dense gas-solid chromatography, type selectivity is achieved with a polar support and a non-polar dense gas while light/heavy selectivity is achieved with a polar support and a polar gas (116). In dense gas-liquid chromatography, type selectivity is similarly best obtained with a polar stationary phase and a non-polar dense gas, but better light/heavy selectivity is obtained with a non-polar stationary phase and a polar dense gas (111-115). The parabolic solute solubility-solvent density relationship affects the selectivity. Lower densities may show typical GC boiling point selectivity with a non-polar dense gas and a polar stationary phase while increasing the density results in type selectivity (101).

5. GC/MS, HPLC/MS AND DGC/MS

While the examples given in the last section and those cited in Table 1 clearly show the wide range of possible applications of DGC, progress in this area has been hampered by the lack of a sensitive and selective detector even though some attempts have been made to overcome detection problems (121,122,183). Ultraviolet detection limits the solute class, flame ionization detection limits the solvent gas, and thermal conductivity detection as well as the first two methods lacks specificity. Thus, research was initiated in view of the demonstrated possibilities of DGC and the great extensions of DGC that would be possible with a mass spectrometer serving as a highly sensitive and selective detector.

An interface between a mass spectrometer and a dense gas chromatograph is made instrumentally difficult by the necessary large pressure drop (200-300 atm to 10^{-5} Torr) and the sensitive density-dependent stability of dense gas/solute mixtures. Thus, it is reasonable to investigate the limitations of both GC/MS and HPLC/MS to establish the fact that DGC/MS is possibly superior to the other techniques for a large range of compounds.

GC/MS

The ability of a modern gas chromatograph/mass spectrometer/computer system (GC/MS/COM) to separate complex mixtures, perform on-line mass analysis, and usually determine the composition by searching files, all in perhaps half an hour, has tremendously aided research in a wide variety of fields, including the areas of health, pollution, and synthetic fuel development. However, GC/MS can be used only with substances having some volatility (a vapor pressure of 10 to 60 Torr) without thermal decomposition and, as observed by Gouw et al (35), only about 10% of the two million compounds known can be thus classified. While derivatization of involatile or thermally labile compounds often permits their analysis by GC/MS, this technique is very difficult to apply to a mixture of compounds of unknown composition and structure. Also there can be difficulties in derivatization of known compounds: non-quantitative conversion, formation of mixed products, and unexpected reactions (123).

HPLC/MS

Modern HPLC separates many mixtures that cannot be analyzed by GC because the moving phase serves two purposes: solvation and zone movement. Because of the mobile phase interaction with the solute and the mild operating temperatures of HPLC, this area of chromatography is suitable for analysis of involatile and/or thermally labile compounds ("the other 90%"). HPLC, like DGC, is

limited by the lack of a sensitive and selective detector except in the recently developing area of HPLC/MS. Several reviews (124,184, 185) describe and evaluate the various HPLC/MS interfaces and outline representative applications. Often high vaporization temperatures for both the solute and solvent (125,126) are used particularly with probe insertion and moving belt/wire transport designs. Other HPLC/MS interfaces have utilized eluent splitting techniques which decrease sensitivity (127), high pressure chemical ionization techniques which may have a variable chemical ionization agent due to solvent gradient elution (128-131), a silicone rubber membrane separator which enriches the eluent in solute but limits the type solvents used (132), or high temperature hydrogenation of solutes which may result in complex mass spectra (133). Games et al (123) have also reviewed HPLC/MS interfaces specifically comparing the split system using the HPLC solvent as a chemical ionization (CI) reagent gas and the belt transport system since these two methods are most capable of routine application in their opinion. The first method has as its disadvantages: 1) 1% of eluate introduced to the mass spectrometer, 2) variable CI reagent gas, and 3) limitation to CI mode mass spectrometry. While the belt transport system has a higher transmission to the mass spectrometer (30-40%) and can be used with either electron impact (EI) or CI mass spectrometer modes, this interface is still limited in its applicability to involatile species. Later work by Games et al (186) exclusively with the belt transport system showed its use with a wide range of compounds; however, there were still problems with thermally labile compounds, compound class dependent sensitivity, and ion source pressure fluctuations with aqueous solutions.

An extensive review of HPLC/MS interfaces is that of Dawkins and McLafferty (134). The authors outline currently used non-MS detectors for HPLC, the advantages/disadvantages of MS detection, and design considerations for HPLC/MS interfaces and evaluate the various presently used interfaces. The major disadvantage or in-

strumentation limitation for MS detection is the volatility requirement: a vapor pressure of 10^{-5} Torr is required for ionization in a conventional ion source. Several methods--rapid heating, field desorption, and direct chemical ionization (DCI)--have been used to obtain spectra of involatile species and are described in this reference. Thus far, only DCI with direct solution introduction (now commonly called direct liquid introduction, DLI), has been applied to a continuously operating HPLC/MS instrument. The method (which was developed commercially at the same time as the preliminary feasibility studies of the DGC/MS (187,188) were completed) appears to give a high sensitivity and has a lower volatility requirement than other HPLC/MS systems. The interface is quite similar to the DGC/MS interface in that the column effuent is expanded as a jet (here, of liquid droplets) into vacuum at mild temperatures. There is, however, some loss of sensitivity due to eluent splitting and there is also a requirement of some thermal stability. (See Reference 189 for a discussion of the optimization of this kind of interface.)

A recently described interface combines the advantages of direct liquid injection and the moving belt technique (190). Here the liquid stream is concentrated by flow along a heated wire (with 95% evaporation of the solvent) with direct introduction of the concentrated solution via a fine needle valve.

Another related direct-liquid-introduction-type interface is the crossed-beam HPLC/MS where the HPLC effluent is introduced into a vacuum region via a capillary tube, the end of which acts as a supersonic nozzle (135). A skimmer downstream of the expanding effluent permits extraction of a molecular beam for sample introduction into the mass spectrometer. Originally, a laser beam crossed with the expanding jet was used to vaporize the solute/solvent mixture. A modified design employs the laser (or alternatively, a flame vaporizer) to heat the capillary tip to vaporize the mixture before expansion through the capillary orifice. Ionization may be

by either EI or CI. Problems initially encountered with this interface include a somewhat low sensitivity (~1 μg) to involatile compounds, some pyrolysis of thermally labile compounds, and incomplete vaporization and/or condensation of species within the molecular beam. However, the system has been further refined (191) resulting in an improvement in sensitivity (60 pg/s) with lessening of pyrolysis and condensation.

DGC/MS

An alternative and similar procedure to HPLC is DGC because of its applicability to the same compounds as HPLC. The possibility that a direct coupling of a mass spectrometer to a dense gas chromatograph would yield an instrument combining the advantages of GC/MS and HPLC was first discussed by Giddings, Myers and Wahrhaftig in 1970 (136). The proposed interface depended upon the very rapid expansion of the solution into a vacuum to form a supersonic molecular beam which would carry the vaporized solute directly, with minimal collision, into the mass spectrometer ion source. Thus, no heating of the dense gas solution would be required, the temperature being determined only by the critical temperature of the solvent gas selected. There would be no volatility requirement; instead, there would be the requirement of solubility in a dense gas, but all systems soluble in a liquid should also dissolve in an appropriate dense gas. The proposed interface--with the inherent advantageous supersonic molecular beam characteristics of fast expansion, nearly collisionless transport (i.e., after molecular flow is established), high-to-low pressure capability, centerline concentration of heavy components in light/heavy mixtures, and low temperatures--seemed suited to the instrumentation problem. Elementary calculations indicated that while solute aggregation might be too fast for detection of isolated solute, several nonequilibrium effects, difficult even to estimate, might well make the rate of aggregation slow enough so that the coupling would be feasible. While the use of supersonic molecular beams has become very widespread in recent

years, this application is unique in the conditions imposed in the beam system; the first DGC/MS instrument is described in detail elsewhere (187,188).

Gouw et al (35) also have proposed the coupling of a mass spectrometer and a dense gas chromatograph and have presented results obtained with their preliminary design. While very few details were given about the actual interface design, it does not appear to be useful for involatile compounds. Column effluent is split so that approximately 0.2% is expanded through a small capillary tube from an external tee to the mass spectrometer sample inlet system. The interface tee is stated to be wound with heating tape and heated to as high a temperature as 450°C. This implies that the entire sample inlet system must also be at this temperature so that solute volatility and thermal stability approaching that required for GC/MS is necessary.

The need for a DGC/MS instrument should be ascertained. Obviously, it will be useful for compounds for which GC analysis is not possible. However, because DGC is so similar to HPLC in terms of applicability to solutes and in light of the rapid development of HPLC/MS, one wonders if a DGC/MS is superfluous. Actually, all of the direct-liquid introduction HPLC/MS interface designs operate similarly to the supersonic beam DGC/MS interface. Comparison of the design is more a question of where the vaporization and concentration processes take place. Certainly DGC/MS will have to be compared to HPLC/MS is terms of both chromatography (DGC vs HPLC) and the interface/detector performance (sensitivity, dynamic range, compound class, yield, enrichment, chemical effect, integrity of the chromatographic profile). There is no obvious area (except, perhaps, the range of compound classes that can be chromatographed) where DGC/MS should not compare favorably and in some cases even show superiority. Moreover, the molecular beam interface for dense gas to a mass spectrometer with or without the chromatography can certainly be used for studying and monitoring dense gas systems.

DGC/MS is a complement to, not a replacement for, GC/MS and HPLC/MS; it seems to be the method most amenable for use in dense (supercritical) gas work.

6. COMPILATION OF WORK IN DENSE GAS EXTRACTION AND DENSE GAS CHROMATOGRAPHY

Some comments about the purpose, contents, and organization of Table 1 are necessary. The purpose was to make a working summary which would give a current listing of the dense gas/solute systems that have been studied along with the temperature and pressure ranges used with a particular combination of dense gas and solute. The table is ordered by solvent gas. Each gas is assigned to one of three groups--inorganic, organic (C,H,O), and halogenated organic. The first is ordered alphabetically then numerically: Ar, CO_2, H_2O, N_2, N_2O, NH_3, SF_6; for the second group the order is based upon the number of carbon, then hydrogen, atoms. The order for the halogenated organics is more arbitrary: CHF_3, $CClF_3$, $CBrF_3$, $CHClF_2$, CCl_2F_2 and $C_2H_4F_2$. The entries for a particular gas are arranged chronologically. Dense gas mixtures follow the data for the pure major component with the following notation: (Major solvent gas)/Modifier, with the mixtures ordered by modifier according to the scheme used for the major solvent gases including placing halogenated organic modifiers (CH_2Cl_2, CCl_4) last.

Phase behavior of dense binary and ternary solutions is often readily applicable to dense gas extraction and chromatography. Whenever this appeared to be the case, the information was included in Table 1. Moreover, there is a related large body of work reporting solute solubilities in compressed gases (e.g., References 192-196) but at temperatures often much higher than critical and often with rather small, volatile solute molecules (e.g., acetone) that are easily analyzed by GC. Perhaps these systems would provide useful information for those interested in possible dense gas/modifier

solvents but since they do not directly concern the solvation of heavy, involatile species, they are not usually included here. Often, two rather subjective criteria were applied: 1. is the gas phase density > $0.7(\rho_c)$ and 2. how does the solute size and complexity compare to naphthalene which is easily dissolved by several dense gases. Some simple systems studying solute solubility in dense gases, e.g., naphthalene/ethylene, are included for historical perspective but many have been omitted because they are often quoted and regularly duplicated.

However, all references that could be found describing actual dense gas extraction and chromatograph conditions are included. When the references were patents, only the specifically described examples were used; extensions to other gases and broader operating conditions that are typically claimed in patents are not listed here. The discussion about dense gas chromatography in Section 4 was an overview. More references are entered in Table 1 than were cited in that section. It is hoped that the reader will find Table 1 to be a current, extensive compilation that is somewhat informative about the chronological development of the area of solute solubility in dense gases while providing background information on which to base experimental selection of the solvent gas and operating conditions.

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