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Supercritical fluid chromatography

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ABSTRACT. The characteristic features of supercritical fluid chromatography (SCFC) are examined and there is a brief historical note concerning the development of the method. Information concerning the use of supercritical fluid chromatography in the analysis of objects of different nature is presented in the form of a table. The roles of the mobile and stationary phases in the separation process and the characteristic features of the apparatus and of the use of the method in physicochemical research are discussed.

The bibliography includes 364 references.

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I. Introduction

In the classification of chromatographic methods in terms of the state of aggregation of the mobile phase (MP) employed, one speaks of gas and liquid chromatography. Supercritical fluid chromatography (SCFC) occupies an intermediate position since a supercritical fluid differs in its properties from those of both a liquid and a gas.

Depending on the nature of the eluent and the conditions under which it operates, one can distinguish the following versions of chromatographic separation:[1] gas chromatography proper (the eluent consists of the usual gases at pressures close to atmospheric); barochromatography (the mobile phase consists of the usual gases at elevated pressures); vapour chromatography (using vapours of volatile liquids); supercritical fluid chromatography (the pressure and temperature of the mobile phase exceed somewhat the critical parameters); density chromatography (the pressure amounts to hundreds and thousands of atmospheres).

The transition to fluid chromatography can be achieved also by transforming the liquid eluent by means of the appropriate changes in temperature and pressure. The distinctive features of the SCFC method are determined mainly by the state of the mobile phase. The following may be included among them:

(1) Specificity of the apparatus (possibility of using individual units comprising liquid and gas chromatographs).

(2) The use of additional devices ensuring the transition of the fluid to the liquid state (employing detectors traditional for liquid chromatography) or gas state (employing gas-chromatographic detectors).

(3) The high solvent power of the fluid which limits the number of suitable stationary phases (SP).

(4) The sharp alteration of the properties of the mobile phase in the vicinity of the critical points, which makes it difficult to obtain stable results for small changes in the separation parameters.

(5) The need to attain effective hermetic seals in all parts of the chromatograph and in the connections.

Examination of the driving and inhibiting factors as well as of the elementary step underlying the separation show that in supercritical fluid chromatography the more detailed classification used in gas and liquid chromatography is also possible.[2]

In all cases (gas and liquid chromatography and SCFC) the driving factor is the stream of mobile phase and the inhibiting factor is physical sorption.

Like gas and liquid chromatography, SCFC can be divided into fluid-adsorption and fluid-liquid chromatography.†

II. Historical note

The first study using a mobile phase in the supercritical state was carried out in 1962.[3] Freons (150–170 °C, pressure up to 136 kg cm^{-1}) were used as the mobile phases. Porphyrins, which are not susceptible to gas-chromatographic analysis because of their thermal instability, were eluted under supercritical conditions. Later the range of eluents employed was expanded, making it possible to analyse polynuclear aromatic hydrocarbons with boiling points up to 600 °C.[4] However, the method was not widely used for many years. a sharp increase in interest in SCFC occurred in the 1980's–1990's. Thus, since 1985 about 400 studies have been published, including two monographs[5,6] and about 20 reviews[7–26]. A number of communications were devoted to the use of the method for the analysis of biologically important organic compounds,[27] its advantages and disadvantages,[28] and also its role in analytical chemistry.[22,28–31] Numerous communications[27,32–127] about the method were delivered at the St. Petersburg Conferences starting in 1985. The first symposium on SCFC was held in 1987.[128]

III. The mobile phase

Substances which are thermally stable above the critical temperature, which undergo no changes on contact with the stationary phase (the latter has a large surface area and can exhibit a

† As in other versions of partition chromatography, in fluid-liquid chromatography adsorption by the solid carrier may make a significant contribution to the separation.

catalytic activity), and which have suitable critical parameters (pressure and temperature) can be used as mobile phases in SCFC. There exists a fairly large list of substances which can be employed as eluents in fluid chromatography.[129] However, in practice only a few of them are commonly used (Table 1). Eluents whose transition to the critical state requires a high temperature or pressure (water with P_{cr} = 226.8 kg cm^{-2} and T_{cr} = 374.4 °C; benzene with P_{cr} = 43.8 kg cm^{-2} and T_{cr} = 288.9 °C) are hardly employed in practice. Many hydrocarbons, for example pentane, isomerise or undergo other reactions when adsorbents with a large surace area are used as the stationary phase[1] (changes occur also in the sorbates), which affect significantly the separation characteristics. Being in the supercritical state, the mobile phase acquires a high solvent power and the diffusion coefficients of the substances dissolved in it are also high under these conditions. This makes it possible to treat the fluid as a mobile phase combining the advantages of the solvent in liquid chromatography with those of the carrier gas in gas chromatography. The main requirements which must be met by the mobile phase in SCFC, as in gas and liquid chromatography, are inertness towards the substances analysed, the stationary phase, and the material of the column and the connections and also compatibility with the detector. The most widely used mobile phase is CO_2 (Table 2). Ethane,[211] butane,[145.176] n-pentane,[25,26,138,176,182,187,203,245] nitrogen oxides,[26,184,189,202,205,215,237,290] fluorine derivatives of sulphur,[186,215,241307,320] hydrocarbons,[126,193] and the intert gases[185,267] are more rarely used. The preferential employment of the non-polar CO_2 as the mobile phase can be accounted for both by the low values of its critical parameters (31.3 °C, 72.9 atm), which makes it possible to carry out the analysis at the usual temperatures, and by the possibility of controlling its selectivity by introducing modifying agents of different nature using a number of procedures:[309,311] methanol,[148,170,179,182] isopropyl alcohol,[156,159,163,170,182] chloromethanes,[159] nitromethane,[163] dioxane,[187] etc. Another advantage of CO_2 as the mobile phase is also the possibility of using virtually all the classical types of detector in conjunction with it (the ionisation-flame detector, the UV detector, mass spectrometers, IR spectrometers, etc.—Table 2). The absence of such advantages in other mobile phases is evidently one of the reasons for their limited application. The difficulties arising in the analysis of polar compounds, which are not fully removed even when modifying agents are employed, must be included among the disadvantages of CO_2. The possibility of obtaining inverted micelles in supercritical fluids such as ethane and propane has been investigated.[311–314] The core of the micelle is capable of being solvated by water, which gives rise to the possibility of the solubilisation in it of polar compounds and their subsequent effective separation during partition between the water-solvated micelles and the non-polar stationary phase. Polar compounds (such as a neutral azo-dye and a protein—cytochrome *c*), which do not dissolve in the pure fluid and in the water-saturated fluid, can dissolve in such a mobile phase. The maximum separation in CSFC is attained with programmed temperature and pressure. It is to be expected that the properties of the mobile phase can vary appreciably over a wide temperature and pressure range and the behaviour of the fluid resembles the behaviour of the mobile phase in liquid or gas chromatography. At the critical pressure and temperature, the mobile phase passes from one state of aggregation to another, which is accompanied by a sharp alteration in the nature of the separation. Fig. 1 presents the dependences of the logarithms of the relative retentions of naphthalene and anthracene on the reciprocal of the absolute temperature using hexane as the mobile phase.[315] It is seen that, on attainment of critical conditions, there is a sharp jump in the relative retention, indicating a change in the state of aggregation of the mobile phase. Thus, contrary to the traditional ideas about the passive role of the mobile phase in the gas-chromatographic process, one may claim that the change in the state of aggregation of the mobile phase alters also the selectivity of the separation. The posibility of controlling the selectivity by altering the state of aggregation of the mobile phase was also noted previously. Solid–liquid, mesomorphous, etc. transitions were achieved in this connection.

Table 1. Properties of certain mobile phases used in supercritical fluid chromatography.[129]

Compound	T_b, °C	T_{cr}, °C	P_{cr}, kg × cm^{-2}	ρ^*, g cm^{-3}
Carbon dioxide	—78.5	31.3	72.9	0.448
Nitrous oxide	—89.0	36.5	71.4	0.457
Ethane	103.6	9.9	50.5	0.227
Butane	—0.5	152.0	37.5	0.228
Pentane	36.3	196.6	33.3	0.232
Methanol	64.7	240.5	78.9	0.272
Isopropyl alcohol	82.5	235.3	47.0	0.279
SF_6	—	45.6	37.1	0.750

*ρ = density of supercritical fluid.

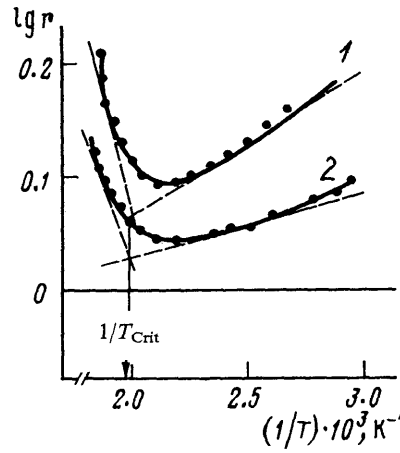


Figure 1. Dependence of the logarithms of the relative retentions of naphthalene (curve *1*) and anthracene (curve *2*) (with benzene as the standard) on the reciprocal of the absolute temperature (average pressure in the column 10 kg cm^{-2}, mobile phase—hexane, 15 × 0.4 cm stainless steel column filled with Silasorb 600).[315]

IV. The stationary phase

Packed columns are used in the fluid-adsorption version and both packed and capillary columns are used in the fluid-liquid version. In the case of capillary columns, cross-linked polysiloxanes are most

often employed as the stationary phase (Table 2): diphenylsiloxane, methylphenylsiloxane, methylsiloxane,[131,153] OC-17,[133,137] OV-225,[137] polysiloxane with grafted *N*-naphthylaminoacid ester,[155] etc. Azo-t-butane[131] or other compounds of a similar type are used as cross-linking agents. Adequate attention has been devoted to problems of the synthesis of stationary liquids for SCFC satisfying the requirements of the virtually complete insolubility in the fluid and thermal stability. Such liquids are cyanoethylphenylvinylmethylpolysiloxane,[316] oligoepoxyethane-containing polysiloxane phases,[317] and chiral stationary phases.[149,166,179] Studies on the swelling of the stationary phases, used in the SCFC with capillary columns, in the fluid and the influence of this process on the retention characteristics are of special interest. In particular, the dissolution of a number of individual mobile phases (pentane, CO_2) and binary mobile phases (methanol–pentane, CO_2–2-propanol) in polysiloxane stationary phases with different ratios of the phenyl and methyl components (OV-1, DV-5, SE-54, OV-17, SE-33) has been investigated.[318–321] In all cases, the soluiblity and adsorbability of the mobile phase diminish with increase in pressure. On raising the pressure above a certain value (which is 260 °C for pentane[320]), the influence of the pressure becomes insignificant. The high solvent power of the mobile phase makes more stringent the requirements as regards the technique of the preparation of the capillary columns.[322–324] Thus it has been shown[322] that the stability of the stationary phase film is directly proportional to the viscosity of the solution. In order to improve the quality of the columns, it is recommended that volatile solvents be employed, raising the temperature of the column during the deposition of the liquid. It is also proposed that a modifying agent can be used to maintain the required viscosity. However, stringent requirements must also be met by such a modifying agent. In experiments with packed columns in the fluid-adsorption version, stationary phases based on silicon dioxide are generally employed: silica gel,[126,180,182,184–186,196,237,255] LiChrosorb Si,[175,183] LiChrosorb Si60,[26,187,197,217,263] LiChrosorb Si 100,[214,224,245,252] PSG porous glass beads,[226] and PRP-I polymeric sorbent.[125] Alumina is hardly used,[295] evidently because of its high catalytic activity under the conditions of the existence of the fluid. In experiments with packed columns, preference is given to grafted sorbents. In this case the sorbents consist of various silica gels with grafted NH_2,[125,173,180,193,233] C_{18},[64,125,175,218] CN,[125,196] and chiral groups,[194,198] as well as others used traditionally in liquid chromatography.

Table 2. Conditions in the separation of mixtures in a stream of supercritical fluid.

System analysed	Mobile phase	Stationary phase, column, detector	Refs
Chlorine-containing compounds, pesticides, n-alkanes, polybutadiene (M = 500), triacylglycerides	Pentane, CO_2	Quartz columns more than 15 m long and with an internal diameter less than 100 μm coated with polymethylphenyl-siloxane ethers (5 or 50% of phenyl)	[Ref. 25]
Polyaromatic hydrocarbons, PS-800 polystyrene	1,4-Dioxane, pentane, C_2H_6, CO_2, N_2O	25 cm × 4.6 mm columns with LiChrosorb Si60; UV detector	[Ref. 26]
Mixture of N,N′-dimethyl aniline, *N*-methylaniline aniline, quinoline, 1,2,3,4-tetrahydroquinoline		IRFT	[Ref. 121]

Table 2 (continued).

System analysed	Mobile phase	Stationary phase, column, detector	Refs
Lipids	CO_2	IRFT	[Ref. 122]
Fluorocarbon grease	CO_2	9.4 m × 30 μm columns with a 0.20 μm layer of DV-1; FID	[Ref. 123]
Various organic substances	Fluid with 1–2% Ar	Chromatographic separation with subsequent condensation on a cooled (12 K) gold-plated cylinder; the component (argon) matrix formed is analysed on an IR spectrometer	[Ref. 124]
Altemaria toxins in produce (grain, fruit, vegetables)	CO_2 + methanol, CO_2 + isopropyl alcohol	Packed columns filled with SG containing grafted C_1, C_8, C_{18}, NH_2, CN, and other groups; UV detector	[Ref. 125]
Ferrocene derivatives, mixtures of metal acetylacetonates	CO_2 and Freon 23 modified with methanol	Packed columns filled with SG, SG containing grafted C_{18} and phenyl groups or PRP-1 polymeric sorbent; UV detector	[Ref. 126]
Polyphenyls: *o*-, *m*-, and *p*-terphenyls, *o*, *o*′-quaterphenyl, *m*, *m*′-quaterphenyl	CO_2	19.5 m × 100 μm quartz columns coated with a 0.4 μm layer of DV-5 (5% phenylmethylsiloxane); IRFT	[Ref. 130]
Napthalene, phenanthrene, pyrene, and benzopyrene	CO_2	5 m × 25(50) μm quartz columns coated with a 0.15 μm layer of cross-linked SE-54; IRFT	[Ref. 131]
Involatile and thermally unstable compounds	CO_2	MS	[Ref. 132]
n-Alkanes, alcohols	CO_2	20 m × 50 μm quartz columns coated with a 0.25 μm layer of OV-17 SP; FID	[Ref. 133]
Lipids, wax, siloxane oligomers, urine extracts	CO_2	10 m × 50(100) μm quartz columns coated with a 0.2 μm layer of DV-1701 (lipids, urine extracts) or a 0.2 μm layer of DV-5(wax); 20 m × 100 μm quartz columns with a 0.4 μm layer of DV-5 (oligomers)	[Ref. 134]
Triglycerol esters	CO_2	10 m × 50 μm quartz columns with a 0.1 μm layer of methyl-phenyl siloxane 50% phenyl) and a 0.2 μm layer of methyl siloxane	[Ref. 135]
Carbamates and acid pesticides, mixtures of alkanes, triacylcylcerides, oils	CO_2	Quartz columns 2–5 m long with an internal diameter less than 75 μm coated by a 0.15 μm layer of cross-linked SE-54	[Ref. 136]
Triglycerides (T_{36}, T_{48}, T_{42}, T_{54})	CO_2	10 m × 100 μm quartz columns (in a steel tube with a 0.2 μm layer of SE-54, RSL-300, OV-225, and poly(ethylene glycol); FID	[Ref. 137]
Azoaniline and anthraquinone dyes	Pentane	20 m × 50 μm quartz columns with a 0.25 μm layer of cross-linked SE-54; UV detector	[Ref. 138]
Labile carboxylic acids, prostaglandins	CO_2	12 m × 50 μm quartz columns with a 0,25 μm layer of cyanopropylpolysiloxane (and 15 m × 50 μm columns); FID	[Ref. 139]
Glycerol tetraesters	CO_2	10 m × 75 μm columns with a 0.25 μm layer of cross-linked methylphenylpolysiloxane; FID	[Ref. 140]
Medicinal preparations (steroids, therapeutic antibiotics, cannabinoids)	CO_2	13–18 m × 50 μm columns with cross-linked SE-33; FID	[Ref. 141]
Polyaromatic nitrocompounds (polar fraction of diesel extracts)	CO_2	15 m × 50 μm columns with a 0.25 μm layer of cross-linked n-octylpolysiloxane and biphenylpolysiloxane; nitrogen-selective detector	[Ref. 142]
Mono, di, and triglycerides	CO_2	5 and 19 m × 100 μm columns with a 0,25 μm layer of dimethyldiphenylpolysiloxane and cyanopropylmethyldiphenylpolysiloxane: FID	[Ref. 143] [Ref. 144]
Napthalene, phenanthrene, chrysene, picene	Butane, CO_2	Quartz columns of different lengths and with different diameters with a 0.5 μm layer of cross-linked methylsiloxane; fluorescent detector	[Ref. 145]
Isomers of antioxidants, caffeine, sodium arachidonate, testosterone, cholesterol	CO_2	3 m × 0.1 mm columns with a 0.4 μm layer DV-5; redox-chemiluminescent detector	[Ref. 146]
Components of wax, metabolites of triazine pesticides, high-molecular-weight polyaromatic compounds, abietic acid	CO_2	10 m × 50 μm columns with a 0.5 μm layer of SB-phenyl-5; MS	[Ref. 147]

Table 2 (continued).

System analysed	Mobile phase	Stationary phase, column, detector	Refs
49 compounds used in agro-chemistry	CO_2 modified with methanol	20 m × 100 μm columns with SE-33 and SB-cyanopropyl-25; UV detector	[Ref. 148]
N-pentafluoro-propionylisopropyl esters and the D- and L-isomers of methionine	CO_2	20 m × 200 μm columns with a 0.15 μm layer of polysiloxane cotaining 7% of a chiral amide; FID	[Ref. 149]
Extract of acid herbicides, mixture of volatile and involatile components	CO_2	19.5 m × 100 μm columns with a 0.4 μm layer of DV-5; FID	[Ref. 150]
Oligo- and poly-saccharides (18 glucose fragments)	CO_2	10 m × 65 μm columns with a 0.2 μm layer of DV-1; FID	[Ref. 151]
Squalane (lipid standard), 1,3-distearin, 1,2-dipalmito-stearin	CO_2	10 m × 75 μm columns with cross-linked methylphenylpoly-siloxane (50% of phenyl); FID and MS	[Ref. 152]
Pyrrolizidine alkaloids	CO_2	10 m × 50 μm columns with SB-biphenyl-30; MS	[Ref. 153]
C_{10}, C_{24}, and C_{36} normal hydrocarbons, crude petroleum, napthalene, hydrogenated triglycerides	CO_2	16.5 m × 50 μm columns with a 0.25 μm layer of SE-54 deactivated by polymethyl-hydrosiloxane	[Ref. 154]
Norephedrine derivatives, amino acids	CO_2	10 m × 50 μm columns with *N*-napthyl--amino acid ester grafted on polymethyl--siloxane; FID	[Ref. 155]
Mixture of hydrocarbons, caffeine, polyethylene-propylene	CO_2	10 m × 50 μm columns with a 0.25 μm layer of SB-biphenyl-30; extraction with supercritical fluid; FID	[Ref. 156]
Mixture of glycerides, mixture of hydrocarbons	CO_2 with $HCOOH + H_2O$	10 m × 50 μm columns with a 0.2 μm layer of polysiloxanes; FID	[Ref. 157]
Pesticides and metabolites, dimpylatodiisocyanato-toluene, Triton X-100, tetrahydrocannabinol	CO_2	15 m × 50 μm columns with a 0.25 μm layer of SB-methyl-100; FID; thermionic detector	[Ref. 158]
Phenanthrene, chrysene, picene, coronene, naphthalene and their derivatives	CO_2, CO_2 + + 2-propanol, $CO_2 + CH_2Cl_2$	10 m × 50 μm columns with a 0.25 μm layer of 100% methylpolysiloxane; UV detector	[Ref. 159]
Coal tar, polymeric additives	CO_2	Columns with methylpolysiloxane (10 m × 50 μm) and SG containing grafted C_{18} groups (25 × 4.6 mm); FID	[Ref. 160]
Pyrethrin	CO_2	IR spectrometer	[Ref. 161]
Caffeine, cocaine, codeine, sulphonamides, pesticide carbamates	CO_2	Columns of different lengths with an internal diameter of 50 μm; MS	[Ref. 162]
Coal tar extract, pyrene, ovalene	CO_2 CO_2 + + 2-propanol, CH_3NO_2	10 m × 50 μm columns with a 0.25 μm layer of 100% cross-linked methylpoly-siloxane; UV detector	[Ref. 163]
Surfactants, polyglycols (M = 1200), dimethyl-polysiloxane	CO_2	3 – 20 m × 50 μm columns with SB-bi--phenyl-30 and SB-methyl-100; FID	[Ref. 164]
Wax, crude petroleum	CO_2	20 m × 100 μm columns with a 0.1 μm layer of cross-linked VR-1; FID	[Ref. 165]
Isopropyl esters of 3,5-dinitrobenzamides	CO_2	5 – 10 m × 50 μm columns with a cross-linked polymeric chiral SB; FID	[Ref. 166]
Sulphur-containing poly cyclic compounds	CO_2, CO_2 + + N_2O	10 m × 50 μm columns with a cross-linked SE-30; plasma detector	[Ref. 167] [Ref. 168]
Explosive (traces)	CO_2	6.8 m × 0.05 mm columns with a 0.25 μm layer of super-cross-linked SB-octyl-50; thermoenergetic detection	[Ref. 169]
Polycyclic aromatic hydrocarbons and their nitro-derivatives	CO_2, CO_2 + + methanol	25 cm × 1.3 mm columns with Spher C_{18}; UV detector	[Ref. 170]
Poly(ethylene oxide), Triton X-305, polycaprolactone diol, epoxy-polymers	CO_2, CO_2 + + methanol, CH_3CN	25 cm × 4.6 mm columns, polystyrene SP, PRP-1, and LiChrosorb Si 100; UV detector	[Ref. 171]
Mixture of polyaromatic hydrocarbons	CO_2, CO_2 + + 7 modifying agents	20 cm × 4.6 mm columns with SG containing grafted diol groups; 15 cm × × 4.5 mm columns with SG containing grafted octyl groups; UV	[Ref. 172]
Polyaromatic hydrocarbons extracted from coal tar	CO_2	Series-connected packed columns filled with silica gel containing grafted amino-groups and octadecyl groups	[Ref. 173]
Coffee extract from roasted coffee grains, coffee grain powder	CO_2	Extraction with supercritical fluid followed by separation; UV detector	[Ref. 174]

Table 2 (continued).

System analysed	Mobile phase	Stationary phase, column detector	Refs
Mixture of polyaromatic hydrocarbons, mixture of phenol derivatives, mixture of unsaturated mono-aromatic hydrocarbons	CO_2, CO_2 + + polar modi-fying agents	15 – 25 cm × 4.6 columns filled with SG containing grafted C_{18} groups and LiChrosorb Si 60; UV detector	[Ref. 175]
Polyaromatic hydrocarbons	Propane, butane pentane, iso--butane	UV detector	[Ref. 176]
High-boiling residues from North Sea petroleums	CO_2	25 cm × 1.3 columns with CP-Spher Si; 30 cm × 2.1 mm columns with Spher-5 containing grafted cyano-groups; 25 cm × 1.3 mm columns with SG impregnated with 1% $AgNO_3$ solution; FID	[Ref. 177] [Ref. 178]
Phosphine oxide enantiomers	CO_2, CO_2 + + alcohols, CO_2 + alcohol mixtures	10 cm × 4.6 mm steel columns filled with the chiral Pirkle phase (LiChrosorb with grafted NH_2 groups); UV detector	[Ref. 179]
Unpurified urine extract, medicinal drugs, multi-component mixtures of polar and non-polar substances	CO_2	20 cm × 2.1 mm columns filled with SG or Spherosorb containing amino- and nitrile groups; MS	[Ref. 180]
Sucrose polyethers in a mixture with aliphatic acids	CO_2	10 m × 65 μm columns with a 0.20 μm layer of DV-1; FID	[Ref. 181]
Aromatic hydrocarbons	CO_2, CO_2 + + methanol	Packed columns filled with SG, Develosil ODS, and a chiral SP; UV detector	[Ref. 182]
Mixture of xanthines, carbamates, sulphon-amides, steroids, and ergot alkaloids	CO_2, CO_2 + + methanol or methoxyethanol	10 cm × 4.6 mm columns filled with LiChrosorb or Spherosorb containing grafed NH_2 groups; MS	[Ref. 183]
Group analysis of petroleum	NO, CO_2	3 columns with Spheri-5-cyano-MPLC, SG CP-Spher, SG impregnated with $AgNO_3$; FID	[Ref. 184]
Polyaromatic hydrocarbons in extracts of aerosol particles in diesel engine exhaust gases	CO_2	Extraction with supercritical fluid followed by separation on 15 cm × 4.6 mm columns with Develosil ODS-5; UV detector	[Ref. 127]
2-Methyl-1, 4-napthoquinone, acenapthenequinone phenanthrenequinone	CO_2 + methanol	25 cm × 1 mm columns filled with SG; IRFT	[Ref. 185]
Group analysis of petrols and petroleum products (up to 350 °C)	SF_6 CO_2	25 cm × 1 mm columns with SG; FID 25 cm × 4.6 mm columns with SG and SG impregnated with $AgNO_3$; FID	[Ref. 186] [Ref. 178]
Oligostyrene PS 800 (M = 810), mixture of napthalene, anthracene, pyrene, and chrysene	Pentane, 1,4-dioxane	25cm × 4.6 mm columns with LiChrosorb Si 60; UV detector	[Ref. 187]
Polyaromatic hydrocarbons from diesel fuel exhaust gases	CO_2, CO_2 + + methanol	Extraction with supercritical fluid followed by gas-chromatographic analysis	[Ref. 188]
Aromatic aldehydes and ketones, polyaromatic hydrocarbons, epoxy-acrylate oligomers	Xenon	17 m × 150 μm columns coated by cross-linked SE-54; IRFT	[Ref. 189, 190, 191]
Mixtures of petroleum and coal origin	CO_2	Semi-preparative SCFC, columns with an internal diameter of 30 – 70 μm filled with SG containing grafted NH_2 groups; UV detector, FID	[Ref. 192]
Mixture of aniline and its derivatives, mixture of phenols, ethers, and alcohol	CO_2, CO_2 + + methanol, Freon-23	25 cm × 4.6 mm columns filled with SG containing grafted NH_2 and phenyl groups; UV detectors, IRFT	[Ref. 193]
Racemic mixtures of t-butyl esters of *N*-acetylamino-acids	CO_2, CO_2 + + methanol, methyl ether	25 cm × 4 mm columns filled with a chiral sorbent (*N*-formyl-L-valylaminopropyl grafted to SG); UV detector	[Ref. 194]
Polydimethylsiloxane, acenapthenequinone	CO_2	19.5 m – 100 μm columns with a 0.4 μm layer of DV-5; IRFT	[Ref. 195]
Polyaromatic hydrocarbons, aromatic amines, alkyl-benzenes, chlorobenzenes, dialkyl phthalates, azo-compounds	CO_2 + modifying agents	Packed columns filled with SG and SG containing grafted diol and CN groups; FID	[Ref. 196]
Oligostyrenes PS 8000	CO_2 + 1,4--dioxane	25 cm × 4.6 mm columns with LiChrosorb Si 60	[Ref. 197]

Table 2 (continued).

System analysed	Mobile phase	Stationary phase, column, detector	Refs
Optical isomers of α-aminoacid derivatives	CO_2, methanol	20 cm × 4 mm columns with a chiral SP (SG with grafted *N*-formylvaline); UV detector	[Ref. 198]
Sulphur-containing heterocyles in vacuum cracking residues	CO_2	Extraction with supercritical fluid followed by gas -chromatographic analysis	[Ref. 199]
Liquid crystal mixtures	CO_2	Packed columns with SG containing grafted C_{18} groups; UV detector	[Ref. 200]
8 esters	CO_2	12.5 cm × 5 mm columns filled with Spherisorb ODS-2; UV detector	[Ref. 201]
Polyaromatic hydrocarbons in ash, dust, and river bottom deposits	N_2O, CO_2, N_2O + methanol	Extraction with supercritical fluid followed by gas-chromatographic determination	[Ref. 202]
Polystyrene oligomers	Pentane	1 m × 260 μm columns with Develosil ODS; UV detector	[Ref. 203]
Polyaromatic hydrocarbons	CO_2	22 cm × 4.6 mm columns filled with SG containing grafted C_{18} groups and 15 cm × 4.6 mm columns with Develosil ODS-5	[Ref. 204]
Polyaromatic hydrocarbons, nicotine, and related compounds in cigarette ash, etc.	CO_2 or N_2O	Extraction with supercritical fluid followed by gas-chromatographic determination	[Ref. 205]
Polyaromatic hydrocarbons	CO_2, CO_2 + + modifying agent	25 cm × 4.6 mm columns filled with LiChrosorb Si 100; UV detector	[Ref. 206]
Anthraquinone in paper and wood	CO_2	Extraction with supercritical fluid followed by HPLC analysis	[Ref. 207]
Styrene oligomers A500 and A1000, components of OU-17 Nonidet P-40 detergent	methanol, diethyl ether	Columns with Develosil-100-5 and Develosil ODS-5; UV detector	[Ref. 208]
Racemic amides and phosphine oxides	CO_2, CO_2 + CH_3OH, C_2H_5OH	25 cm × 4.6 mm columns (SP with grafted β-cyclodextrin); 25 cm × 4.6 mm columns with Pirkle covalent phase [(*R*)-*N*-3, 5-dinitro-benzoylphenylglycine]; UV detector	[Ref. 209]
Ferrocenes	CO_2	25 cm × 1 mm columns with Shimpak Diol-150; detector—emission spectrometer with atomisation in a plasma	[Ref. 210]
Polystyrene standard (M = 1574)	CO_2, ethane	UV detection	[Ref. 211]
n-Alkanes, alkyl aryl ketones, terpenes, polyaromatic hydrocarbons	CO_2	20 cm × 3 mm columns with Spherisorb ODS-2; FID	[Ref. 212]
Polyaromatic hydrocarbons	CO_2	Extraction with supercritical fluid followed by gas-chromatographic analysis	[Ref. 213]
Polyaromatic hydrocarbons	alkanes, CO_2	25 cm × 4.6 mm columns with LiChrosorb Si 100	[Ref. 214]
Aerosols in a stream of eluent	CO_2, N_2O, pentane, benzene, SF_6	Detection by laser light scattering method	[Ref. 215]
Mixtures of docosane and pyrene, triacylglycerides, fructose and sucrose, opium alkaloids	CO_2, CO_2 + polar modifying agents	10 – 20 cm × 4.6 mm columns filled with Sorbax BP Sil, Micropak MCH, Spherisorb containing grafted NH_2 groups, SG containing grafted C_{18} groups	[Ref. 216]
Polyaromatic hydrocarbons, petroleum products	CO_2	15 – 50 cm × 1 mm columns (Sorbax BP Sil); 15 cm × 4.6 mm columns (LiChrosorb Si 60); 15 cm × 4.6 mm columns (Spherisorb ODS-2); 15 cm × 4.6 mm columns (SG XOA 800); FID	[Ref. 217]
Phthalates, styrene oligomers, polyaromatic hydrocarbons	CO_2	10 cm × 0.3 mm columns filled with Develosil ODS-3K and ODS-5K; UV detector	[Ref. 218]
Binary mobile phases	CO_2 with organic modifying agents	20 cm × 4.6 mm columns filed with Sg containing diol groups; UV detector and detection in the visible region of the spectrum	[Ref. 219]
Complex organic compounds on various adsorbents; resins, foil, dust, Spherocarb, etc.	CO_2, isobutane, methanol and binary MP	Extraction with supercritical fluid	[Ref. 220]

Table 2 (continued).

System analysed	Mobile phase	Stationary phase, column, detector	Refs
Baldenon (a steriod preparation), medicinal drugs with a COOH group	CO_2	10 m × 5 μm and 5 m × 25 μm columns with grafted SB-methyl and SB-octyl phases; MS	[Ref. 221]
Napthalene, fluorene, phenanthrene, pyrene	CO_2	25 cm × 4.6 mm columns filled with grafted Spherisorb ODS-2 carrier	[Ref. 222]
Polyaromatic hydrocarbons	CO_2	Packed columns having an internal diameter of 4.6 mm with SG and SG containing grafted C_{18}, diol, diphenyl[biphenyl], and napthyl-ethyl groups; UV detector	[Ref. 223]
Polystyrene standards, mixture of aromatic hydrocarbons	Pentane, dioxane	25 cm × 4.5 mm columns filled with LiChrosorb Si 100; UV detector	[Ref. 224]
Thermolabile herbicides from sandy, loamy soils	CO_2, CO_2 + + methanol	Extraction with supercritical fluid	[Ref. 225]
Styrene and methylphenylsiloxane oligomers	Methanol, diethyl ether	Packed columns with PSG-10 porous glass beads (d = 11.5 μm, pore size 178 Å)	[Ref. 226]
Benzyl chloride	CO_2	15 cm × 4 mm columns with Silasorb 600 Silasorb containing grafted C_{18} groups	[Ref. 227]
Solid samples	CO_2	Extraction with supercritical fluid	[Ref. 228]
"Maoming" oil shale		Extraction with supercritical fluid	[Ref. 229]
Polyethylene PE-70	CO_2	10 cm × 1 mm and 20 cm × 1 mm columns SG containing grafted poly--siloxane	[Ref. 230]
Steroids, benzodiazepines opiates	CO_2	16 m × 100 μm SCFC columns with SPB-1; 30 m × 250 μm gas-liquid chromatographic columns with DV-5; detection based on ionic mobilities	[Ref. 231]
Sulphonoamide preparations and antibiotics	CO_2, CO_2 + isopropyl alcohol	10 cm × 1 mm columns with cyanodeltabond; 15 cm × 1 mm columns with Spherisorb 5ODS2; 7 m column with SB-cyanopropyl-25, SB-methyl-100, and SB-biphenyl-30	[Ref. 232]
Amines, Azaarenes	CO_2	25 cm × 4.6 mm and 25 cm × 1 mm columns with grafted amino-groups and nitrile groups; FID, IRFT	[Ref. 233]
Enantiomers of 3-thienylcyclohexylglycollic acid	CO_2, CO_2 + + methanol	25 cm × 4.6 mm columns with Cyclobond CSP and chiral OB gel; UV detector	[Ref. 234]
Phenmedipham, aldicarb	CO_2	10 m × 100 μm columns with SB-methyl-100; IRFT, FID	[Ref. 235]
Alkaloids from the leaves of *Catharanthus roesus*	CO_2 + methanol	10 cm × 4.5 mm columns with Spherisorb; UV detector, MS	[Ref. 236]
Ketoacids from urine	NO	10 m × 50 μm columns with cross-linked SE-30; thermionic detector	[Ref. 237]
Siloxane liquids, fats	CO_2	10 m × 50 μm columns with a 0.2 μm layer of DV-5 and 25 m × 100μm columns with a 0.2 μm layer of SE-24; FID	[Ref. 238]
Herbicides, pharmaceutical preparations	CO_2	6 m × 50 μm columns with a 0.25 μm layer biphenylyl-siloxane; MS	[Ref. 239, 240]
Group analysis of petrols and middle distillates of fuel	SF_6 + CO_2	25 cm × 1 mm columns with SG; 25 cm × × 2.1 mm columns with $AgNO_3$-treated Nucleosil SA; FID	[Ref. 241]
Hydroxyethylated alcohols	CO_2	Columns 5 m long containing methylpolysiloxane; FID	[Ref. 242]
Polystyrene oligomers, pyridine, phenol	CO_2	Packed columns with SG of diferent porosity (70 – 1100 Å) containing grafted C_{18} groups (2 – 17%); UV detector	[Ref. 243]
Solid samples containing organic compounds		Extraction with supercritical fluid followed by gas-chromatographic analysis	[Ref. 244]
Napthalene, anthracene, pyrene, chrysene	Pentane	24 cm × 4.6 mm columns with LiChrosorb Si 100; UV detector	[Ref. 245]
Group separation of petroleum components	CO_2	8 – 10 and 15 m × 200 μm columns with a 0.15 μm layer of liquid crystal poly--siloxane	[Ref. 246]
Enantiomers of 1,2-aminoalcohols	CO_2 + ASCCl	10 × 30 cm × 4.6 mm columns with CS, GN phase; UV detector	[Ref. 247]
Mixtures of polymers, aldicarb and its metabolites, mixtures of monomers, dimers, and trimers of diisocyanatotoluene	CO_2	15 m × 50 μm columns with SB-biphenyl--30; 12 m × 50 μm columns with 50% cyanopropyl-siloxane; 20 m × 50 μm columns with SE-63;FID	[Ref. 248]
Analysis of traces of organic substances	CO_2	Capillary columns with poly-siloxane SP; all types of detectors	[Ref. 249]

Table 2 (continued).

System analysed	Mobile phase	Stationary phase, column, detector	Refs
Group and individual analysis of petrols	CO_2	SCFC and gas chromatography, 25 cm × 4.6 mm columns with SG; 25 cm × 4.6 mm columns with SG impregnated with $AgNO_3$; 10 cm × × 4.6 mm columns with cation-exhange SG; 25 cm × 4.6 mm columns with SG containing grafted amino-groups; FID	[Ref. 250]
Palladium β-diketonates	CO_2 + methanol	Series-connected 5 cm × 4.6 mm and 30 cm × 4.6 mm columns with LiChrosorb Si 60 and a 25 cm × 4.6 mm column with SG containing grafted C_{18} groups; UV detector	[Ref. 251]
Caprolactonediol and methyl methacrylate oligomers	$CO_2 + CH_3CN$	25 cm × 4.6 mm columns with LiChrosorb Si 100; UV detector	[Ref. 252]
Polyaromatic hydrocarbons in marine deposits	CO_2	25 cm × 1 mm columns with Spherisorb-5; FID photoionisation detector, MS	[Ref. 253]
Oil from lemon peel	CO_2	Extraction with supercritical fluid; MS	[Ref. 254]
8 organophosphorus pesticides	CO_2, CO_2 + + 2-propanol	10 cm × 1 mm columns with SG and SG containing grafted amino-groups and C_{18} groups;MS	[Ref. 255]
Chemical additives to polymers (21 compounds)	CO_2	15 m × 100 μm columns with a 0.5 μm layer of phenylmethylpolysiloxane; FID, IRFT	[Ref. 256]
Components of the smell of natural produce	CO_2	Extraction with supercritical fluid followed by gas-chromatographic analysis	[Ref. 257]
Free aliphatic acids	$CO_2 + H_2O$	10 cm × 1 mm column filled with 7 different SP; FID	[Ref. 258]
Oligosaccharides	CO_2	10 m × 50 μm columns with a 0.2 μm layer of DV-5; MS	[Ref. 259]
Essential oils, petroleum products	CO_2	Extraction with supercritical fluid	[Ref. 260]
Herbicides based on sulphonylurea and their metabolites	CO_2 + polar modifying agents	Extraction with supercritical fluid followed by SCFC analysis	[Ref. 261]
Homologous series of alkylarenes and n-alkanes	CO_2, CO_2 + + methanol, CH_3CN	15 cm × 4.6 columns with styrene–di-vinyl-benzene copolymer (PLRP-S); UV detector	[Ref. 262]
Metal carbonyls, highly viscous motor oils, standard aromatic hydrocarbons	CO_2, CO_2 + + methanol, CH_3CN	Extraction with supercritical fluid followed by SCFC analysis	[Ref. 263]
Ecdysteroids, phytoecdysteroids	CO_2 + methanol	2 cm × 4.6 mm columns with SG; UV detector, MS	[Ref. 264, 265]
Basic nitrogen-containing substances	CO_2, CO_2 + + methanol	25 cm × 1 mm columns with Deltabond; FID	[Ref. 266]
Terpenes	Xenon	40 cm × 100 μm columns with Spherosil-XOA-800 SG; UV detector	[Ref. 267]
Methyl palmitate	CO_2, CO_2 + + 1-hexanol	10 m × 100 μm columns with a 0.5 μm layer of SB-methyl-100; IRFT	[Ref. 268]
Aromatic hydrocarbons	CO_2	10, 15, and 25 cm × 2.1 and 4.6 mm columns filled with SG containing grafted C_{18} groups	[Ref. 269]
Poly(methyl-3,3,3-trifluoropropyl)siloxane	CO_2, CO_2 + + 2-propanol	MS	[Ref. 270]
Mixtures of nitro-derivatives of diphenylamine and aniline	CO_2	10 cm × 1 mm columns with a sorbent containing cyano-propyl groups, 10 m × 100 μm column with a 0.25 μm layer of SB-cyano-propyl-25; IRFT	[Ref. 271]
Diuron and its metabolites	CO_2 + methanol	15 cm × 4.6 mm columns filled Rosil C_{18}; UV detector	[Ref. 272]
Benzene derivatives (6 compounds)	CO_2, CO_2 + + methanol	30 cm × 4.6 mm columns filled with SG containing grafted C_{18} groups; 17.5 cm × 4.6 mm columns with a polydivinyl-benzene sobent containing C_{18} groups; UV detector	[Ref. 273]
Polychlorinated biphenyls, polyaromatic hydrocarbons, heterocycles, $C_{12}-C_{24}$ alkanes	CO_2	Extraction with supercritical fluid from polyurethane foam followed by chromatograph-linked mass-spectrometric analysis	[Ref. 274]

Table 2 (continued).

System analysed	Mobile phase	Stationary phase, column, detector	Refs
Pesticides	CO_2	Extraction with supercritical fluid followed by HPLC analysis	[Ref. 275]
Explosives, side products	CO_2	25 cm × 1 mm columns with Deltabond containing cyano-groups: IRFT	[Ref. 276, 277]
8 nitro-derivatives	CO_2	1.5–2.5 cm × 1 mm columns, Deltabond containing grafted cyano-groups	[Ref. 277]
Aminoacids	$CO_2 + CH_3OH$, H_2O, CH_3NH_2	15 cm × 4.6 mm columns filled with SG of the Nucleosil-100 type	[Ref. 278]
Docosanol and palmitic acid	CO_2 + methanol	15 cm × 4.6 mm columns filled with Sorbax ADS and LiChrosrob RP-18; vaporisation light scattering-based detection	[Ref. 279]
Mixtures of steroids	CO_2	10 m × 100 μm column with SB-cyano-propyl-25;IRFT	[Ref. 280]
α-Pinene and its oxidation products	CO_2	Extraction with supercritical fluid followed by SCFC analysis	[Ref. 281]
Oil triacylglycerides	CO_2	5 m × 50 μm columns with a 0.2 μm layer of DV-5; MS	[Ref. 282]
Anthracene, dichlorobi-phenyl sulphone, triazopan,vitamins, steroids	CO_2	Packed 10 cm × 1 mm and capillary 6 m × 50 μm columns; photoionisation detector	[Ref. 283]
Tocopherols from wheatgerm	CO_2 + alcohol	Extraction with supercritical fluid followed by HPLC analysis of fractions	[Ref. 284]
Complex organic compounds	CO_2 + methanol	15 cm × 4.6 mm columns filled with Nucleosil containing grafted C_{18} groups or with Rosil containing aminopropyl groups; MS	[Ref. 285]
Sulphor-containing antioxidants and heterocycles isolated from objects in the environment	CO_2	3.5 m × 100 columns with a 0.4 μm layer of DV-5; chemiluminescence detector of atomic sulphur	[Ref. 286]
Sesquiterpenes	CO_2	25 cm × 4.6 mm columns filled SG of the Nucleosil-100 or Spherisorb type; IRFT	[Ref. 287]
Ethoxyethylated alcohols, inositol triphosphate, peroxides	CO_2	10 m × 50 μm columns with a 0.5 μm layer SB-methyl-100; FID and MS	[Ref. 288]
Phenylthiohydantoin derivatives of aminoacids (24 compounds)	CO_2 + modifying agent	25 m × 4.6 mm columns filled with Sorbax containing grafted cyano-groups; UV detector	[Ref. 289]
Steroids in plasma and urine	N_2O	10 m × 50 μm columns with polymethyl-hydrosiloxane; thermionic detector	[Ref. 290]
Sulphur-containing organic compounds	CO_2	20 m × 100 μm columns with a 0.2 μm layer of DV-1701; flame-photometric detector	[Ref. 291]
Polyaromatic hydrocarbons	CO_2	10 m × 50 μm columns with a 0.5 μm layer of SB-phenyl-5; MS	[Ref. 292]
Trimethoprim, hexoestrol, diethylstilboestrol, dienoestrol, sulphamethazine in pig kidneys	CO_2	Extraction with supercritical fluid followed by SCFC analysis	[Ref. 293]
Biphenylylmethylsiloxane	CO_2	4 m × 0.5 mm columns with SB-phenyl-5; UV or fluorimetric detector	[Ref. 294]
C_{21}, C_{24}, C_{26}, C_{28}, C_{31} n-alkanes, caffeine	CO_2	10 cm × 1 mm columns filled with Al_2O_3 in the alcoholic form and Deltabond containing grafted cyano-groups	[Ref. 295]
Organic components of river or ground water	CO_2	1.8 mm × 0.25 mm columns with Spheri-sorb ODS, 10 m × 50 μm columns with a 0.25 μm layer of cross-linked SE-30, concentration on Sep-PAK C_{18}; UV detector, FID	[Ref. 296]
Organic isocyanates	CO_2	Columns with an internal diameter of 10 μm SP: SB-methyl-100 (0.5 μm), SB-biphenyl-30 (0.25 μm), SB-octyl-50 (0.5 μm)	[Ref. 297]
Napthalene, biphenyl, phenanthrene, n-alkanes	CO_2	10 m × 100 μm columns with BP-1 and 12 m × 100 m columns with BP-10; FID	[Ref. 298]
Aromatic hydrocarbons from furnace and diesel fuel	CO_2	Columns filled with SG; FID	[Ref. 299]
Azaarenes	CO_2 + methanol	SG with grafted amino-groups UV detector 10 cm × 0.35 mm columns; IRFT	[Ref. 300] [Ref. 301]
Polymethylphenylsiloxane oligomers	Alcohol + C_6H_{14}		
Herbicides and pesticides ($\overline{M}$ = 200–350)		Comparison of the characteristics of the determination by the HPLC and SCFC methods using capillary and packed columns; FID, UV detector , selective detector of nitrogen and phosphorus	[Ref. 302]

Table 2 (continued).

System analysed	Mobile phase	Stationary phase, column, detector	Refs
Aromatic hydrocarbons	CO_2	25 cm × 4.6 mm columns filled with SG containing grafted C_{18} groups; UV detector	[Ref. 303]
Up to C_{90} n-alkanes from Polywax 655, oil, triglycer--ides esters of cholesterol and aliphatic saturated and unsaturated acids	CO_2	5–25 m × 0.2–0.53 mm columns with a 0.1–0.25 μm layer of polymethyl- and polymethylphenyl-siloxanes (comparison with gas-liquid chromatography on capil-lary columns)	[Ref. 304]
Mixtures of mineral oils, polydimethyl-siloxanes, etc	CO_2	10 m × 0.1 mm capillary columns; FID	[Ref. 305]
Benzoic and isophthalic acids and their methyl esters	11 different MP	Capillary columns with internal diam-eters of 77 and 100 μm with DV-5 and Carbowax; UV detector, IRFT	[Ref. 306]
1-Decanol and its deriva-tives (7 compounds)	SF_6	5 m × 100 μm columns with methylpoly-siloxane; FID	[Ref. 307]
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin from specimens of aqueous deposits	CO_2 + methanol	Extraction with supercritical fluid	[Ref. 308]

Note. SG = silica gel; FID = flame-ionisation detector, MS = mass spectrometer, IRFT = IR spectrometer with Fourier transform, ASCCI = acetonitrile solution of the counterion and the $N(C_2H_5)_3$ $[N(C_2H_5)_3H^+?]$ competing ion, HPLC = high performance liquid chromatography.

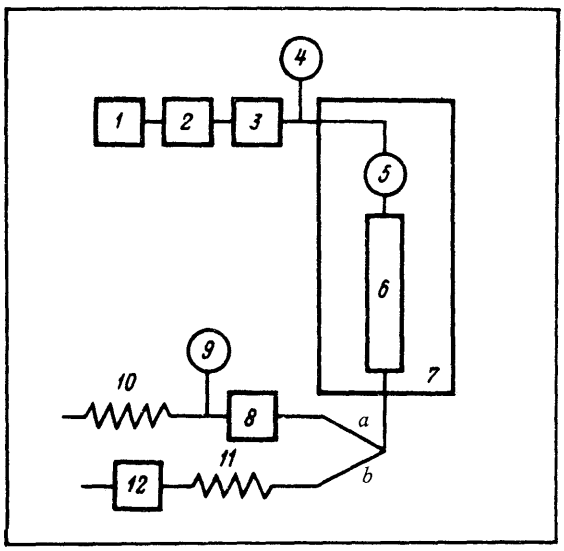


Figure 2. Block diagram of the fluid chromatograph: *1*, cylinder; *2*, pressure reducer; *3*, pump; *4*, manometer; *5*, metering tap; *6*, chromatographic column; *7*, column thermostat; *8*, UV detector; *9*, reference manometer; *10* and *11*, restrictors; *12*, ionisation detector.

V. Apparatus

The formation of the fluid can be regarded as transition from one state of aggregation of the mobile phase to another (from liquid to gaseous and conversely). The separation of various mixture requires the correct combination of individual units comprising liquid or gas chromatographs. Here it is necessary to ensure, on the one hand, a stable high pressure in the system and, on the other, the possibility of detection in the fluid flow. A block scheme of an SCF chromatograph is illustrated in Fig. 2. One may note two principal aspects of the construction of the apparatus: the improvement of the design of the detectors and of the intermediate devices for the connection of the SCF chromatograph to other instruments for physicochemical research and also the development of the restrictor technology and of the technique for the injection of the sample.[325,326] The technique of the injection of the sample in SCFC with capillary columns is approximately the same as in gas chromatography: sample injection with stream splitting, injection with stream splitting and maintenance for a period of time, direct injection, and injection with extraction by the supercritical fluid.[327] In view of the small diameter of the capilliary columns in SFC (50–100 μm compared with 200–500 μm in gas chromatography), the use of automated systems with a programmed sample injection cycle (from 50 μs to 2 s) is promising.[328] The loop-type metering taps with stream splitting generally adopted in high performance liquid chromatography, are widely used.

The high pressure necessary to maintain the mobile phase in the supercritical fluid state hinders the application of detectors traditionally employed in high performance liquid chromatography (HPLC) or gas chromatography. Flame-ionisation detectors (FID) and UV detectors are most often used for detection in SCFC (Table 2). The columns are connected to the detecting systems via a restrictor which is placed before or beyond the detector in order to prevent a sharp change in the pressure in the system. For detection in a stream of liquid, the restrictor is placed beyond the detector (for example, in the case of UV detection). If a FID is used in the chromatograph, the placing of the restrictor beyond the column makes it possible to direct the stream of the mobile phase immediately into the detector. Quartz capillaries (straight capillaries, tapering capillaries,[329] and capillaries coiled into a helix) and partly fused ends of the columns (the so called integral restrictors[134]) can function as restrictors. The study of the effectiveness of capillary restrictors[329–331] showed that the restrictor must be heated, which makes it possible to eliminate the losses of the compounds being analysed and to control the linear flow rate of the mobile phase in the column by programming the temperature. The FID are used in SCFC virtually without any modifications. Certain complications arise when UV detectors are employed because their cell is not always designed for the necessary pressure. A detecting device for SCFC designed for pressures up to 500 kg cm^{-2} has been proposed.[332] Its working cell consists of a section of a capillary with a remote polyimide coating and three optical wave guides perpendicular to its axis. UV beams are directed into the cell through one of them but the other two are used for the simultaneous observation of the fluorescence and the absorption of UV radiation. For the combination of the SCF chromatograph with a mass spectrometer,[333–338] an appropriate interface is essential. Judging from the existing reviews,[334] there is reason to believe that appreciable advances have been made in this field. As in the classical versions of chromatography, in the analysis of sulphur and phosphorus compounds by SCFC a flame-photometric detector is used[339] which makes it possible to detect nanogramme amounts of sulphur and phosphorus. IR spectrometers, as a rule combined with Fourier transformation, play a notable role as detectors.[340–342] Such detectors are most convenient in experiments with CO_2 as the mobile phase. Carbon dioxide is transparent over a wide range,

which permits the determination of many organic compounds. An advantage of the use of CO_2 is also that the sensitivity of the detection can be greatly increased by combining the IR spectrometer with a microcope.[130] The pure sorbate is introduced onto the surface of a ZnSe plate transparent in the IR region (under normal conditions, CO_2 is converted into the gaseous state), after which its IR spectrum is recorded. Plasma detectors,[168,343,344] ion-conducting polymer membranes,[345] ion mobility spectrometers,[346,347] and ^1H NMR spectrometers[348] are less widely used. As in classical gas chromatography, in certain cases double detection is resorted to in order to obtain universal (for example, using a FID) and specific (using a photometric detector) chromatograms.[349] The use of a combination of these detectors is particularly convenient in the analysis of mixtures with a complex composition. Thus the application of equipment traditional for gas and liquid chromatography in SCFC requires only the construction of special units whereby the columns can be connected to the detectors.[344,350]

VI. Qualitative and quantitative analyses

The development of gas chromatography made it possible to achieve considerable advances in the identification of substances: (1) it became possible to compare directly the signal received from the object analysed with the signal from a standard specimen; (2) an identification system based on the determination of the retention indices of the mixture components was developed.

The use of liquid chromatography for qualitative analysis involves problems caused by the difficulty of determining the retention time of the non-sorbed component.

Most of the problems arising in liquid chromatography are retained in the SCFC, occupying an intermediate position, while the achievements of gas chromatography are little used. One of the main disadvantages of SCFC is the difficulty of maintaining reproducible separation conditions, which is associated with the sharp alteration of the properties of the fluid near the critical point. Another disadvantage is caused by the necessity to use adsorbents and sorbents with grafted groups, whose characteristics are not as satisfactorily reproducible as in gas chromatography. Reference specimens are most often employed for the purpose of identification.[150,151,153,157] In the analysis of complex objects of unknown composition, group separation with subsequent individual analysis of the fractions, for example, by gas chromatography with capillary columns[199,213,231] or HPLC,[153,275] is frequently employed. In the latter case, the approaches adpted in HPLC are used in SCFC. Attempts have been made to set up standard retention index scales. In particular, compounds belonging to the homologous series of alkyl aryl ketones (ranging from acetophenone to octaphenone) and normal alkanes (from dodecane to tetracosane) have been used for this purpose.[262] The application of both scales leads to comparable results, but the former must be regarded as more universal because it can be employed when polar modifying agents are added to the mobile phase (for example, CO_2). Modified Kovac indices, calculated from the formula[351]

$$RI = \frac{\lg t'_{R(x)} - \lg t'_{R'(\text{decane})}}{\lg t'_{R'(\text{pentadecane})} - \lg t'_{R(\text{decane})}},$$

where $t'_{R(x)}$ is reduced retention time of the substance analysed, were proposed for estimation of retentions of different kinds.

Smaller difficulties arise in quantitative analysis. The calibrating plot[167,216,230] and internal standard[202] methods are most often used in SCFC for the treatment of the signal. The calculation is based either on the area of the chromatographic peak or on its height.

VII. Extraction by the supercritical fluid

The supercritical fluid has a number of characteristic features as an extractant: (1) its viscosity is virtually identical to that of the gas and its diffusion coefficient is greater and its density is smaller than those of the liquid (this makes the extraction time several times shorter); (2) its solvent power depends greatly on the temperature and pressure, which permits its deliberate alteration.

Such properties of the fluid promote the rapid extraction of a wide range of organic compounds (polyaromatic hydrocarbons, diuron, linuron, caffiene, medicinal drugs, insecticides, herbicides, etc.) from ash, town dust, soil, river and sea bottom deposits, etc.[188,202,205,207,213,220,225,229,244,254,257,260,261,274,275,281,284,308,352]

Table 3 presents certain examples of the use of extraction by a supercritical fluid. As a rule a degree of extraction of 80–95% is attained after only 20–30 min from the start of extraction. The change in pressure and temperature (and hence in the solvent power of the extractant) during the extraction process gives grounds for the assumption that extraction by the supercritical fluid is an additional separation stage during which individual fractions of the substances analysed may be isolated. Thus fractions comprising sulphur-containing heterocycles (with different numbers of rings) have been isolated from the vacuum residues in the catalytic cracking of petroleum,[199] caffeine has been isolated from coffee extract and coffee grains,[174] polyaromatic hydrocarbons have been isolated from town dust,[220] etc. Extraction by the supercritical fluid can be carried out after preliminary concentration of the substance to be analysed on different adsorbents (synthetic resins, polyurethane foil, carbon sorbents, Tenax GT,[188,220,274] and glass wool[275]), which makes it possible to reduce the detection limit. A convenient feature of the use of a supercritical fluid for extraction also consists in the fact that the extract may be analysed not only by SCFC but also by HPLC [174,207,275,284] or gas chromatography.[199,205,213,244,257,281] The gas-chromatographic analysis of the extract as a rule presupposes the cryogenic concentration of the sample at the inlet to the column[205,244,257] or the absorption of the substances present in the sample by an appropriate solvent into which an internal standard has been introduced.[150] The subsequent analysis is performed by the usual gas-chromatographic procedure. In the extraction of mixtures of known composition, the regime permitting the attainment of the maximum extraction and separation can be selected on the basis of preliminary calculations of the solubilities of the substances analysed in the supercritical fluid using the available formulae.[353] The employment of extraction by a supercritical fluid for the automatic preparation of samples for analysis not only by chromatographic but other (for example spectroscopic) methods is likewise promising. Thus extraction by a supercritical fluid can be included in any multistage analytical scheme.

VIII. Physicochemical aspects of the use of supercritical fluid chromatography

The study of the equilibrium in the fluid-sorbent system, which makes it possible to determine the thermodynamic characteristics of the dissolution of a number of substances, is of considerable

interest.[342,353,354] Special versions of fluid chromatographs have been proposed for physicochemical research.[355] They can be used also for analytical purposes. The diffusion coefficients (simple and binary) of compounds such as unsaturated aliphatic acid esters and benzene and its derivatives have been determined in supercritical CO_2 [355,356] and chlorotrifluoromethane and sulphur hexafluoride.[357] The heats of desorption of toluene, phenol, naphthalene, anthracene, and other aromatic hydrocarbons have been determined in the temperature range 307–353 K and at pressures up to 200 kg cm^{-2} using CO_2 as the mobile phase.[358] The heat of desorption increment per C_2H_4 group is $\sim$2.507 kJ mol^{-1}. The effect of density on the enthalpy and entropy of transfer in SCFC has been investigated[359] using CO_2 as the mobile phase and the cross-linked SE-54 and OV-17 stationary phases. The change (decrease) in the enthalpy of transfer of the test substance with increase in the density of the mobile phase (CO_2) has been confirmed for sorbates such as normal alcohols and normal alkanes. The enthalpies found by the authors[359] (−24.7 to −35.2 kJ mol^{-1} for OV-17 and −16.3 to −36.0 kJ mol^{-1} for SE-54) agree with the literature data obtained by liquid chromatography (for high densities) and gas chromatography (for low densities). The intermediate position of SCFC was yet again confirmed. An attempt was made to devise a single theory of adsorption chromatography using homogeneous adsorbents and adsorbents characterised by a discrete distribution on their surface of energetically or structurally different adsorption centres.[264,360–363] The mobile phase can be a gas, a liquid, or a supercritical fluid.

Table 3. Extraction with supercritical fluid.

Object analysed	Isolation and determination conditions, extractant	Refs.
Plastic materials, corn ears, control mixtures of hydrocarbons	CO_2, subsequent analysis—SCFC (10 m × 50 μm columns with a 0.25 μm layer of SB-biphenyl-30)	[Ref. 156]
Coffee extract (roasted grains)	CO_2, subsequent analysis—HPLC (SG and SP) with grafted C_{18} groups, $CH_3OH + H_2O$ as MP	[Ref. 174]
Contaminants in the environment preadsorbed on TENAX GC (SRM 1650 standard and polyaromatic hydrocarbons from diesel fuel up to coronene inclusive)	CO_2 and $CO_2 + CH_3OH$. Direct extraction from adsorbing cartridge (30 min); subsequent analysis—gas chromatography (cryogenic concentration at inlet to 30 m × 320 μm column with a 1 μm layer of DV-5)	[Ref. 188]
Polyaromatic hydrocarbons from ash, town dust, and river bottom deposits	Ethane, CO_2 and N_2O, CO_2 and N_2O with CH_3OH, the extract is collected in a vessel with a solvent containing the internal standard; analysis on 60 m × 250 μm columns with a 0.25 μm layer of DV-5	[Ref. 202]
Anthraquinone from kraft-paper, pine wood fillings	CO_2 (20 min), analysis–HPLC using 15 cm × 3.5 mm columns with Bondapak C_{18}, CH_3CN–pH 6.8 buffer mixture as MP	[Ref. 207]
Polyaromatic hydrocarbons (SRM 1649 standard)	CO_2; possibility of extraction of all the substances from the matrix, quantitative extraction and concentration of traces, selective extraction of individual fractions, and multistage extraction. Analysis—gas chromatography (15 m × 250 μm column with a 0.25 μm layer of SE-54)	[Ref. 213]
Chrysene, benzanthrone, 1-nitro-pyrene, dibenzocarbazole, coronene etc, SRM 1649 standard)	CO_2, isobutane, and $CH_3OH - CO_2$ from adsorbents (KhAD-2, polyurethane foil, Spherocarb); desorption of polar compounds with $CO_2 + CH_3OH$ mixture and desorption of high molecular-weight compounds with isobutane; analysis—gas chromatography (15 m × 250 μm with cross-linked SE-54)	[Ref. 220]

Table 3 (continued).

Object analysed	Isolation and determination conditions, extractant	Refs.
Herbicides from loamy soils	CO_2, $CO_2 + CH_3OH$; analysis—SCFC (capillary columns with SB-cyanopropyl-25 and packed columns with Partisil-5, ODS-3)	[Ref. 225]
Natural products, aromatic hydrocarbons	CO_2; automatic isolation of substance from matrix and sample preparation (Milton Roy SPA system)	[Ref. 228]
"Maoming" oil shale	Supercritical liquid in the presence of H_2O and toluene with subsequent collection of individual fractions (soluble in cyclohexane, toluene, etc)	[Ref. 229]
Polyaromatic hydrocarbons (in impregnated wood, town dust, river deposits), phenols from aerosols in forest fires, nicotine from tobacco, scent components, biological markers	CO_2, N_2O, ethane; subsequent analysis—gas chromatography (30 m × 320 μm columns with a 1 μm layer of DV-5 and 60 m × 250 μm columns with a 0.25 μm layer of DV-5); cryogenic concentration of the sample is carried out at the inlet to the column	[Ref. 244]
Oil from lemon peel	CO_2; extractor—empty 35 mm × 4.6 mm column; analysis—gas chromatography (25 m × 200 μm column with CBP 20)	[Ref. 254]
Components of the smell of natural products	CO_2, extractor (0.1 ml) combined with the gas chromatograph evaporator, after reduction of pressure, the extract is subjected to cryogenic concentration at the inlet to a 30 m × 320 μm column with a 1 μm layer of DV-5	[Ref. 257]
Standard aromatic hydrocarbons (in heptane)	CO_2, $CO_2 + CH_3OH$; extractor connected to a 6-way metering tap in place of metering loop and is provided with autonomous heating; no "memory" effect	[Ref. 263]
Polyaromatic hydrocarbons (from napthalene to perylene), polychlorinated biphenyls	CO_2; sample extracted from filter, extract concentrated to 1 ml and analysed (20 m × 250 μm columns with a 0.25 μm layer of DV-5)	[Ref. 274]
Pesticides from glass wool (5 substances)	CO_2; CO_2 passed through extractor, the eluate being directed to series-connected 18 × 1.5 mm column with RP-18 or 14 × 1.5 mm columns with Si 60 on which the sample is fractionated	[Ref. 275]
Tocopherols from wheat germ	CO_2 + alcohol; extract concentrated on a 50 × 10 mm column with SG from which it is directed to seperation (20 cm × 20 mm column); the collected fractions are analysed by HPLC	[Ref. 284]
2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDBD)	CO_2, NO, and their mixtures with CH_3OH; 100% extraction from bottom TCDBD deposits achieved, gas chromatographic analysis (30 m × 250 μm columns with a 0.17 μm layer of cross-linked SE-54)	[Ref. 308]

Note. SG = silica gel.

The development of the SCFC method confirms the view that chromatographic separation is a single process occurring over a broad spectrum of experimental conditions (with a gas, a supercritical fluid, or a liquid as the mobile phase). The chromatographic separation of any objects can be achieved using the same apparatus. By varying the experimental conditions (pressure and temperature), it is possible to select an effective procedure for the solution of a specific analytical problem.

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