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GAS CHROMATOGRAPHY 1988

by

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MANAGEMENT PERSPECTIVE

The manuscript was prepared in response to a standing request for Dr. F.I. Onuska to make a bi-yearly contribution on the subject of column technology and gas chromatographic techniques, open tubular column gas chromatography, and supercritical fluid chromatography for a review published by the Journal of Analytical Chemistry. This review covers the period between 1986 - 1988. This contribution together with contributions from Dr. R.E. Clement from Ontario Ministry of the Environment, Prof. G.A. Eiceman, New Mexico State University and Prof. H.H. Hill, Jr., Washington State University, provides a comprehensive review of the fundamental developments in the field of gas chromatography which is published in Anal. Chem. 1988, 60, 279R-294R.

This review is a useful compendium of international achievements for analytical chemists and managers. It should be of interest to researchers in Canada and overseas and will help to avoid duplication in research areas covered in separation sciences during the review period.

Dr. J. Lawrence
Director
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PERSPECTIVES DE GESTION

Le document a été préparé en réponse à une demande de contribution bisannuelle par F.I. Onuska à une étude publiée par le Journal of Analytical Chemistry et portant sur les sujets suivants : technologie sur colonnes et techniques de chromatographie en phase gazeuse, chromatographie gazeuse avec colonne tubulaire ouverte, chromatographie sous pressions hypercritiques. L'étude couvre la période de 1986 à 1988. Cette contribution avec d'autres faites par R.E. Clement du ministère ontarien de l'environnement, G.A. Eiceman, qui enseigne à l'université du Nouveau-Mexique, et H.H. Hill, Jr., professeur à l'université de l'État de Washington, couvrent tous les progrès fondamentaux accomplis dans le domaine de la chromatographie gazeuse (Anal. Chem. 1988, 60, 279R-294R).

L'étude constitue un recueil très utile de toutes les réalisations internationales à l'intention des chimistes et des gestionnaires dans le domaine de l'analyse. Elle devrait être d'un grand intérêt pour les chercheurs du Canada et d'outre-mer, et permettra d'éviter les recherches faites en double dans le domaine des techniques de séparation pendant la période visée.

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ABSTRACT

A review is made of chromatographic techniques and methodologies based on an extensive literature search covering principal separation sciences and gas chromatography. This is updated every two years for the biennial review and covers all analytical journals available to the reviewer.

RÉSUMÉ

Revue des techniques et des méthodes chromatographiques grâce à des recherches étendues dans la documentation traitant des principales sciences et techniques de séparation ainsi que de la chromatographie gazeuse. Elle est mise à jour tous les deux et couvre toutes les publications analytiques accessibles.

COLUMN THEORY AND TECHNIQUES

A monography describing the properties of adsorbents and catalysts has been published by Paryjczak (1A), and an excellent text covering quantitative analysis of gas chromatography by Novak and Leclercq (2A) and a practical volume by Grob (3A) describes methodological aspects of making and manipulating capillary columns for gas chromatography. New developments in gas chromatography and open tubular column chromatography have appeared (4A, 5A).

The retention mechanism was studied for n-alkanes with a cross-linked polydialkyl siloxane stationary phases having different alkyl chain lengths (C8 to C18). Model stationary phases were prepared with these phases and the specific retention volumes of the analytes measured within the range of 8 to 160 °C. The thermodynamic calculations indicate that bulk dissolution appears to be the dominant mechanism for their retention within these stationary phases (6A). The distribution of elution peaks expressed in Gram-Charlier series were derived by means of Melling's transformation for OTCs gas chromatography. The effect of pressure drop on parameters such as skewness was also discussed. For linear non-ideal chromatographic process, the skewness of a peak is inversely proportional to the square root of its number of theoretical plates (7A). Dose (8A) investigated the computational simulation of temperature programmed GC behavior of two series of analytes. The approach presented accounts for both retention time and peak width behavior over diverse temperature programs. Simulation accuracies are generally 1 % for retention time data

and 10 to 15 % for peak width data. The isothermal retention time data used as input, are most conveniently reduced to 2 quantities S_v and H_v , which are proposed as a new class of retention indices. A technique using inverse GC for accurately measuring polymer-solute diffusion coefficients was developed by Pawlisch (9A) The validity of the technique was demonstrated by measuring the diffusivity and activity of benzene, toluene and ethylbenzene in polystyrene between 110 and 140 °C. The diffusion coefficients obtained were consistent with existing vapor sorption measurements. Leclercq and Cramers (10A) demonstrated that for a given separation problem, vacuum outlet operation of columns with a constant inner diameter always yields the shortest analysis times under min. plate height conditions. The comparison of vacuum vs. atm. outlet operation is broadened to columns with different dimensions. It appears that vacuum outlet operation is beneficial only in terms of speed of analyses, if low maximum plate numbers are required. The gain in speed of analysis is more pronounced for wide-bore than for narrow-bore columns. Characterization of peak asymmetry with overloaded capillary columns based on the solution of the mass-balance equations with a parabolic expansion of the isotherm equation is in good agreement with the experimental peak profiles observed (11A). The asymmetry depends greatly on the magnitude of the second derivative of the isotherm at the origin. It is due to overloading and is independent on column length and flow rate. It increases with decreasing column diameter and with decreasing film thickness. Thermodynamic functions such as heat of adsorption and entropy of analytes were

determined for 2 bonded stationary phases by Lu *et al.* (12A). The reaction between these functions and surface properties and resolution performance of the bonded stationary phases were discussed. Purnell *et al.* (13A) discussed theory and practice of coupled columns of any kind. An example is presented of its use in the optimization of a sample analysis with serial columns which further establishes the quantitative validity of the theory and illustrates its practicality and simplicity in use. Guiochon and Gutierrez (14A) derived an equation for the prediction of the plate height on a serial combination of capillary columns in GC. The equation together with an equation for the apparent capacity factor can be used to optimize the system parameters in resolving a mixture. Procedures are described (15A) for the calculation of programmed temperature GC retention times, elution temperatures, retention indices, and two kinds equivalent temperatures from isothermal data. These procedures involve the determination of upper integral limits using numerical integration and root-trapping methodology. Computer programs were written for both single ramp/multiplateau temperature programs. Experimental verification of the theory of serially coupled GC-columns indicates it to be entirely valid and free of all assumptions other than that of carrier gas ideality (16A). Selectivity tuning in OTC GC is presented by Sandra *et al.* (17A). Selectivity tuning can be performed in 3 different ways, namely by synthesizing a tuned stationary phase, by mixing the basic phases, or by coupling OTCs of different selectivities. Pretorius and Lawson (18A) derived equations to predict the extent to which the sample size may be

increased, without decreasing the column performance by stationary phase focusing at subambient temperatures. Berezkina *et al.* (19A) discussed dynamic and impulse chromatographic methods for the equilibrium study of heterogenous reactions in gas-condensed phase systems. Nygren and Olin (20A) derived equations for predicting the results of exponentially flow programmed separations in gas chromatography. Zolotarev *et al.* (21A) derived equations for calculating parameters in capillary column formed from two coaxial cylinders. Ceulemans (22A) evaluated the correlation between column efficiency, resolving power, and analysis time based on the quasi-linear relation between peak width and retention times. On the basis of the equations derived, a much more rational choice of columns and operating conditions becomes possible.

High oven temperature on-column injection at column temperatures well above the b.p. of the solvent, is highly attractive for rapid analyses at elevated temperatures (23B). Movements of the solute within the column inlet are described, from which technical requirements are derived. Avoidance of peak distortion is also discussed (24A). Roeraade (25A) discussed the advantages of at-column injection technique which include quantitative transfer of sample, no dead volume, and direct transfer of sample to a narrow bore column or a pre-column. The application of the cooled needle technique to split and splitless sampling onto OTCs to simulated distillation analyses was described by Schomburg and Haeusing (26A). Boeren and Gerner described an automatic sample introduction onto narrow bore

columns with a splitter as well as the splitless injection of both solids and gases (27B). The speed of analysis in OTCs can be substantially increased by reduction of the column inner diameter. However, special demands are then posed upon instrumental design. The sampling system is highly critical because it has to be capable of delivering small injection band widths which must be compatible with the column inside diameter (28A). A simple backflushing, peak-cutting method was developed for the determination of trace components present in the tail of a major component peak by Guan *et al.* (29A). Alexander *et al.* (30A) described a method for coupling glass and fused silica OTCs by using PTFE shrinkable tubings. Kaiser *et al.* (31A) reviewed current status of high resolution column technology for GC. Ettre (32A) reviewed the interrelations between tube diameter and film thickness, their influence on the efficiency and resolution, and their influence on sample capacity in OTCs. Large diameter OTCs in GC analysis provide the packed column chromatographer with a simple route to higher resolution GC. The columns seem fully compatible with all common modes of detection (33A). The theory which predicts the retention time, retention temperature and peak width for any kind of multi-step temperature programming and the principle of optimization is described by Lu *et al.* (34A). The optimization of GC temperature programs using simulated retention times and peak widths is described by Dose (35A). A time/resolution compromise term is included in the chromatographic response function and the effects of changing the weight of that term are investigated. Convergence to the

experimental optimum temperature program is demonstrated in one case by searching the setting space about the determined optimum. Freeman and Jennings (36A) optimized GC separations based on the use of stationary phases specifically designed to maximize solute alphas. Selectivity can be further tuned by differential variations in the carrier gas velocity through dissimilarly coated coupled columns or temperature variations in columns of at least moderate polarity. Hyver and Phillips (37A) evaluate chromatographic theories for enhancing resolution, speed and sensitivity in HRGC and HRGC-MS. Optimum performance of HRGC columns as a function of tube diameter and film thickness under various operating conditions were studied (38A) and a computer program was written for calculation of H-u curves and minimum analysis time. Saxton (39A) describes a simultaneous parameter compensation in the replication of programmed GC retention measurements. Golay (40A) discusses the problem of optimizing the capacity ratio of an OTC for a selected presumably most critical component, and it is considered as a function of the diffusion time in the stationary phase. The essential column parameters are derived for given inlet pressure and analysis time. A double advantage can be derived from the use of high inlet pressures. Lin *et al.* (41A) described conditions to select the optimal operation conditions for GC. A basic software is described to obtain the whole imitating chromatogram at any given temperature and to predict the peak's separation in relation to temperature. Optimization of stationary phase selectivity for the GC separation of C_n cyclic and aromatic hydrocarbons using squalane

and liquid crystal glass capillary columns in series is described by Krupcik *et al.* (42A). The optimization criterion used was derived from the Kovats retention indices of the solutes. The use of multichannel chromatographic detectors that produce spectra characteristic of the eluents permits the deconvolution of partially overlapping peaks without any assumptions about peak shape or prior knowledge of the spectra of the individual compounds (43A). Crilly utilized numerical deconvolution of gas chromatographic peaks using Jansson's method (44A). The max. peak amplitude of the instrument and peak non-negativity serve as constraints to improve the peak estimation. Super-resolution is achieved without significantly degrading the chromatogram signal-to-noise ratio. Application of chemometrics in homolog-specific analysis of PCBs based on SIMCA 3B algorithms was evaluated by Onuska *et al.* (45A). The objective of utilizing SIMCA 3B was its evaluation for a possible identification, classification and categorization of Aroclors in environmental samples (46A). Parameters affecting the quantitative performance of cold on-column and splitless injection systems was evaluated by Snell *et al.* (47A). Analytical results were evaluated as based on the interlaboratory reproducibility of gas chromatographic data obtained with capillary columns by Stoev (48A). The study was carried out on a mixture of n-alkanes.

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LIQUID PHASES

A triangular plot of relative retention indices suggested 3 groupings of stationary phases : polar, nonpolar and intermediate polarities. Three solute probes containing butanol, pyridine and octyne were selected to check these indices. Their ratios proved more consistent than their absolute values (1B). Fine *et al.*(2B) described a preparation and GC-characterization of some crown-ether stationary phases. Blomberg (3B) reviewed commercial vs. laboratory made columns. Stationary phases, aspects of retention index determination, selectivity in OTCs, and new types of selectively separating stationary phases are discussed. The ladder-type siloxane polymer was investigated as a high temperature stationary phase. Its application to the separation of different classes of compounds demonstrated possibility of selective separation of high boiling compounds (4B). Hawkes (5B) stated that the traditional advice to avoid stationary phases with high viscosity is unsound and is being based on a model that is inapplicable to polymers or other long chain molecules. Diffusion in polymers is not related to conventional viscosity. A series of polar substituted phenylalkyl dimethoxymethylsilanes was prepared by Brashaw *et al.*(6B). The 4-methoxy- and 3,4-dimethoxyphenylethylsilanes demonstrated different selectivities for polar solutes than could be obtained with other available stationary phases. Ogden *et al.*(7B) described synthesis of phenyl and cyanoethyl, phenyl siloxane phases suitable for preparation of OTC in GC and supercritical fluid chromatography. Bartle *et al.*(8B) discussed Rayleigh instability of stationary phase films in capillary column GC. The film of stationary phase on the wall

of a capillary column and that of the the phase solution during both static and dynamic coating is subject to Rayleigh instability, which is quite independent of wettability. Bradshaw *et al.* (9B) reported a new moderately polar phase containing the 3-(4-methoxyphenyl)propyl group. Good temperature stability was achieved. A temperature program of up to 280 ° gave little column bleed. Mixed stationary phases of OV-101 and OV-25 and OV-101 and OV-17 were prepared by placing both phases on the same support (10B). Experimental retention indices on mixed stationary phases agree with predicted values. Giesbrecht (11B) described the use of window-diagrams and reviewed mixed phase column applications. Horka *et al.* (12B) studied OTCs coated with acid-modified poly(ethylene glycol) type immobilized stationary phases. The thermostability and chromatographic behavior of the columns and the stability of the coated films after washing with different solvents were investigated. Pesek *et al.* (13B) studied presence of the double bond on the allyl moiety as a site for additional reactions which could produce new stationary phases by bromination. Lakszner and Szepesy (14B) investigated the major factors influencing the analytical results namely film thickness, amount of water injected and temperature effects. Rokushika *et al.* (15B) reported synthesis and preparation of new polyacrylate liquid crystalline stationary phases suitable for GC and SFC open tubular columns. The wide working range of the capillary column was extended below the glass-nematic transition temperature. Smirnov and Shcherbakova (16B) studied selectivity factors of liquid crystal stationary phases. The selectivity is

determined by two factors : 1) functional groups of their molecules causing specific sorbent-sorbate interactions, and 2) orientation order of the liquid crystalline state. Schomburg *et al.* (17B) performed crosslinking experiments for immobilization of polymeric chiral compounds. Mesomorphic biphenylcarboxylate esters were coupled via flexible aliphatic hydrocarbon spacers to a polysiloxane backbone by Markides *et al.*(18B). Unique selectivity and good efficiency over a wide temperature range for these phases were demonstrated by the separation of various isomeric polycyclic compounds. Martire (19B) presented a molecular theory based on a lattice model. The results are discussed in terms of the calculated orientational order of the solute molecules and other molecular level effects. Disk-like liquid crystals comprising alkyl esters of p-alkylphenyl esters of benzene hexacarboxylate have been synthesized by Witkiewicz *et al.* (20B). Preparation and application of glass capillary columns deactivated with polyethylene glycol isophthalate was described by Fu *et al.* (21B). Prospectives of polymeric liquid crystal stationary phases for OTC separation offer unique selectivity for priority pollutants along with other compounds (22B). Matisova *et al.* (23B) studied the dependence of the properties of liquid crystals on the film thickness and surface quality of OTCs. It was verified that the capacity factors, retention indices, and selectivity significantly depend upon the thickness of the liquid crystalline stationary phase film and the quality of the tubing. Six new polysiloxanes containing chiral amide side-chains were prepared by the hydrosilation of appropriate

amide-containing alkenes onto polyhydromethylsiloxane (24B).

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OPEN TUBULAR COLUMN GAS CHROMATOGRAPHY

The capillary rise method was used to obtain contact angle measurements on untreated fused silica and fused silica treated with a variety of deactivating reagents. The contact angle data were used in the construction of Zisman plots which allowed characterization of the wettability of the surfaces by their critical surface energies. The wettability of raw fused silica was found to be widely variable which adversely affects attempts to fully deactivate the surface. Hydrothermal treatment of the fused silica with HNO_3 was found to be adequate for cleaning and hydroxylating the silica surface so as to allow complete deactivation. Simple silylating reagents, cyclic siloxanes, and polysiloxanes covering a wide range of polarity were used and evaluated as deactivating reagents (1C). Berlizov *et al* (2C) studied properties of Pyrex glass and quartz capillary columns before and after deactivation with OV-101. Heeg (3C) observed various capillary materials under the electron microscope and a comparison was made with those capillaries leached with inorganic acids. Berezkin *et al*. (4A) investigated the role of adsorption at the stationary phase interface in capillary columns prepared with crosslinked and non-crosslinked phases. It seems that deactivation of fused silica tubing is still causing significant problems especially with more polar stationary phases. Wolley *et al*. (5C) described reaction conditions for surface deactivation of fused silica columns with polymethylhydrosiloxanes, and phenylhydrosiloxanes (8C). Van de Ven *et al*. (6C,7C) studied deactivation processes with silazanes. Ogden (9C) used tetrakis(3-

cyanoethyl)tetramethylcyclotetracyclo- siloxane for GC and supercritical fluid chromatography columns. Markides *et al.*(10C) described a method for surface deactivation of fused silica capillary columns with a cyanopropylhydrosiloxane reagent at 250 °C. A procedure was developed to remove acidic impurities that are present in polar stationary phases. Woolley *et al.*(11C) deactivated small diameter fused silica columns with a mixture of polymethylhydrosiloxanes and several low molecular weight organosilicon hydrides. Rohwer *et al.*(12C) deactivated nickel tubing by chemical vapor deposition of silica from silane gas and subsequent treatment with cyclooctamethyltetrasiloxane. The technique of spontaneous coating of capillary columns employing liquefied butane and ethylene chloride as solvents of the stationary phase was described by Janak *et al.*(13C,15C). Grob and Grob (14C) provided hints for statically coating capillary columns. The hints include pressurizing before pumping as a repair technique for breakthrough by using a compressed gas at 4 to 5 bar for 15 minutes to every freshly filled column, the addition of methylene chloride to pentane solvent to reduce pumping time and the use of vacuum reservoirs as vacuum source instead of the water pump.

Wickramanayake and Aue (16C) described preparation of a bonded polyoxyethylene phase. There is circumstantial evidence the the nonextractable layer is held by multiple hydrogen bonding. Horka *et al.*(17C) described a procedure for the preparation of an immobilized stationary phase based on Carbowax 20M for capillary column GC. The stationary phase crosslinking was carried out with

Desmodur N 75, pluriisocyanates. The properties of the prepared capillary columns are compared. A simplified method for Carbowax 20M immobilization on capillary glass columns for GC, based on leaching the capillaries followed by static coating of Carbowax 20 M and 40 % dicumyl peroxide was published by Bystricky (18C).

The efficiency of fused silica OTCs coated with thick films of polyphenylmethyl siloxane was compared to thin apolar and medium polarity coatings. Experimental data demonstrate a significant loss in chromatographic efficiency of thick films of medium and polar siloxane stationary phases. The low diffusion coefficients in the liquid phase is responsible for this behavior. The influence of the temperature and the nature of the efficiency was also studied (19C).

Blum (20C-22C) provided detailed procedures for the preparation of inert and high temperature apolar, moderately polar and polar glass capillary columns using OH-terminated polysiloxane stationary phases. Intensively leached silica surfaces with OH-terminated phases provide a new way of producing capillary columns with substantially increased inertness and thermostability. All processes involved in their preparation are discussed, and detailed working directions are given for the following phases : OV-1701-OH, OV-31-OH, OV-61-OH, OV-17-OH, OV-240-OH and PS-347.5 and PS-086. There is no doubt so far that the principle of terminal silanol groups is applicable to all silicone phases, and may replace the traditional endcapped stationary phases in the future. Duquet *et al.* (23C) synthesized a cyanopropylsilicone stationary phase for fused silica OTCs. Wide

bore columns coated with this phase were tested with respect to efficiency, activity, and thermal stability. The selectivity of the phase for fatty acid methyl esters is very good. A simple method is described by Eddib *et al.* (24C) for preparing thermally stable and highly efficient capillary columns coated with highly polar cyanosilicone phases over previously deposited silica layer. Aerts *et al.* (25C) described preparation of a narrow-bore (50 μm) and wide-bore (320 μm) OTCs for immobilized cyanopropyl-substituted silicones containing 60 and 88 percent cyanopropyl substitution. The polarity of polar columns appeared to be greatly dependent on column temperature and is completely different for wide and narrow-bore columns. Immobilization of stationary phase films using gamma radiation was studied by Borek *et al.* (26C). Columns were irradiated with 2 to 10 Mrad dose to study the immobilization of stationary phases. An immobilization of 83 to 100 % was obtained with SE-30 and SE-54 but less than 14 percent for Carbowax and Silar 10C. Chuang *et al.* (27C) achieved immobilization of OV-1701 vinyl and OV-225 vinyl using ozone as an initiator. Farbrot *et al.* (28C) polymerized stationary phases in 12 to 50 μm open tubular columns used in LC and GC. Melda *et al.* (29C) discussed thick film capillaries and their applications for process gas chromatography in comparison with packed columns.

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SUPERCRITICAL FLUID CHROMATOGRAPHY

The present state of supercritical fluid chromatography (SFC) has been reviewed by many authors (1D-7D). The principles, instrumentation and applications of SFC are discussed.

Schwartz *et al.* (8D) compared separation efficiency and speed of packed and capillary columns for SFC by using plate height equations and van Deemter plots. Three hypothetical molecules that require progressively higher fluid density for their migrations were selected. When solvent viscosities and solute mol. weights are large, packed columns with regard appear to have a distinct advantage over capillary columns with regard to the number of plates generated per unit time. Similar subject was discussed by Caude *et al.* (9D).

The preparation of immobilized polysiloxane coated on packings or capillaries were discussed with regard to their efficiency (10D), speed, pressure drop (11D), deactivation, polarity and thermal stability (12D) and kinetic column effects and chromatographic performance (13D). Unified molecular theory of chromatography and its application to supercritical fluid mobile phases has been described by Martire *et al.* (14D). Hydrodynamic description of SF flow through the porous packing of analytical high performance column is founded on Darcy's law, the Peng-Robinson equation of state and viscosity correlation. This model fits results with a very good accuracy for both pressure drop of several eluents such as CO_2 , N_2O , CF_2H_2 , CBrF_3 , and SF_6 through various types of columns and eluent residence time measurements. These results show that it is possible to describe supercritical

fluid properties with relatively simple correlations. Fields and Lee studied effects of density and temperature on efficiency in capillary SFC (16D). Yonker and Smith (17D) investigated effects of density on enthalpy and entropy of transfer for SFC. The results demonstrate the independence of enthalpy and entropy of transfer with supercritical fluid density during chromatographic separations. The simultaneous calculation of pressure, density and temperature profiles for packed columns used in SFC is described (18D). The results show that pressure profiles over packed columns are approx. linear. The density decreases along the column length and so does the temperature of the eluent. Both the variations in density and in temperature are enhanced by using smaller particles or higher flow-rates. The pressure and the temperature dependent behavior of the chromatographic parameters for binary eluent mixture containing pentane and 1,4-dioxane was studied (19D). Yonker *et al.* (20D) studied effects of pressure on retention in SFC, and an effect of solute concentration on retention. The optimum pressure conditions can be obtained for max. resolution of two solutes during pressure programming or isobaric separations (21D). Christensen (22D) described on-line multidimensional chromatographic separation, which makes use of the unusual properties of supercritical mobile phase. Leyendecker *et al.* (23D, 24D) studied properties of various low boiling eluents. Kuei *et al.* (25D) assembled an instrumentation that allows the use of supercritical ammonia as mobile phase. In addition, the stabilities of various polysiloxane stationary phases were examined. The effects of

modifiers in supercritical fluid chromatography was examined (26D, 27D, 28D). Using carbon dioxide as the primary mobile phase, the modifiers investigated included methanol, 2-methoxyethanol, 1-propanol, THF, dimethyl sulfoxide, acetonitrile, SF₆ and freon 11. Mourier *et al.* (29D) studied the effect of the physical state of the supercritical fluid on solute retention. French and Novotny (30D) evaluated xenon as a unique mobile phase which is due to its optical transparency and is highly suitable for SFC/Fourier transform IR spectrometry.

Various studies of retention processes in SFC with binary (32D) and multiple gradients by programming eluent composition and temperature (31D) and pressure (33D) were studied. They appear promising for extending the range of amenable separations. Similarly, retention and resolution in density-programmed SFC was studied by Linnemann *et al.* (34D). By using pentane and 1,4-dioxane as a binary eluent system and silica as the stationary phase, three dimensional network plots of capacity ratios, selectivities, effective plate numbers and resolutions for PAHs vs. column temperature and eluent composition at constant pressure were obtained (35D). The dependence of reduced plate height on reduced velocity in carbon dioxide SFC with packed columns was studied using Knox model and supplementary coefficients with a parabolic dependence on velocity were added (36D).

A sample introduction system for capillary SFC, which allows the dissolution of the sample in the supercritical mobile phase before being introduced into the column was described by Jackson

et al. (37D). The potential of such an injection system was demonstrated but further developments are needed to make the technique of practical utility.

Performance of capillary restrictors in SFC was examined (38D). The transport of low volatility analytes is facilitated by heating the fluid prior to the restrictor or less effectively, by heating in the restrictor. The successful transport and detection of nonvolatile compounds by FID with SFC were demonstrated. An integral restrictor for capillary SFC was designed by Guthrie *et al.* (39D). The device is reproducible, mechanically stable and can be easily altered to produce a specific mobile phase flow rate.

The properties of a double-chamber pneumatically driven piston pump (40D), syringe pumps and reciprocating piston pumps in SFC were compared (41D). A computer controlled pumping system for SFC was designed based on a pneumatic amplifier pump by Pariente *et al.* (42D).

The current status and developmental trends in detection for SFC were reviewed by Novotny (43D). A dual-flame photometric detection system having the detection limit 25 ng for the sulphur and 0.25 ng for the phosphorus when CO₂ was used as the mobile phase was discussed by Markides *et al.* (44D). Holzer *et al.* (45D) described a simple interface between a capillary SFC and mass spectrometer. The system is equipped with a splitting device which allows simultaneous EI/MS and flame ionization detection when CO₂ is used as the mobile fluid. A similar system was designed by Smith *et al.* (46D). Capillary SFC with both FID and

electron impact MS provide detection limits in the picogram range and significantly improve sensitivity compared to HPLC (47D). Arpino *et al.* (48D) reviewed SFC/MS coupling and they claim that better performance may be obtained for some types of substances or when complex mixtures must be analyzed. The use of SFC with packed columns for the analysis of polar compounds, and with capillary columns for the analysis of complex mixtures, and its combination to a mass spectrometer were discussed by Berry *et al.* (49D).

The hyphenated analytical methods are among the most powerful techniques available to the analytical chemist for the identification and quantitation of the components of complex mixtures. An automated interface was demonstrated for SFC and Fourier transform IR spectrometry (50D) using a capillary column in which the mobile phase is rapidly eliminated and the diffuse reflectance spectrum of the solute is measured. Design considerations for the high pressure IR cell were given by Hughes *et al.* (51D, 52D). The coupling of SFC with Fourier-transform MS has been accomplished by using standard commercially available equipment (53D). Jinno (54D) reviewed interfacing between SFC and IR spectrometry. He states that 2 types of interfacing approaches have been introduced : direct flow cell and solvent elimination. An application to polycyclic aromatic hydrocarbons or sesquiterpenes was performed (55D). The coupling of SFC with a light-scattering detector was investigated by Carraud *et al.* (56D). With packed columns, LSD is complementary to the FID.

A very attractive technique emerging from utilization of a suitable supercritical fluid separation is supercritical fluid extraction. Nagahama reviewed the principle, applications and future trends of this novel technique (57D). Saito *et al.* (58 D) reviewed supercritical fluid extraction (SFE) and SFC and their directly coupled systems. Gmuer *et al.* (59D) designed a prototype for direct coupling of SFE and capillary SFC. Smith *et al.* (60D) discussed SFC, SFC-MS and microscale SFE by supercritical ammonia combined with chromatographic methods. Campbell *et al.* (61D) studied semi-preparative SFC which permits high quality separation of coal tar with easy solvent removal. Saito and Hondo (62D) reviewed on the historical background and applications SFE and SFC and their applications in food processing. Tanaka (63D) reviewed the SFE in pharmaceutical industry. An elegant method for the SFC in environmental samples using SFE-GC-MS was published by Hawthorne *et al.* (64D, 65D). An apparatus and procedures for direct coupling of SFE to capillary SFC was described by Gmuer (66D). The method can be used for monitoring cheese ripening, rancidity development in dairy products and for detecting aroma defects in butter.

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