Gas Chromatography

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INTRODUCTION

This review of fundamental developments in the field of gas chromatography (GC) covers the years 1986–1987. As for the previous review of this series, the principal method of literature review was by use of the biweekly Chemical Abstracts Service CA Selects for GC. Added to the coverage this time are recent developments in GC/MS. Again, CA Selects for Mass Spectrometry were employed for the literature review. To reflect the increasing work in serially coupled column GC and in HPLC/GC, these areas are discussed with multidimensional GC under the new heading of multicolumn chromatography.

The principal developments in liquid phases and solid supports relate to their manufacture and use to improve selectivity for more directed separations, while liquid crystals have gained acceptance as unique phases for certain applications. Liquid phase theory was used to develop predictive tools for PTGC based on isothermal data bases. Less work was reported concerning structure prediction from retention data, while surprisingly little work was performed in the area of solution thermodynamics. Supercritical fluids continue to be extensively studied as were detectors for SFC, including SFC/MS. Important new work was also performed in the areas of serially connected columns and in GC optimization on a theoretical basis. As observed in the previous review in this series, FT-IR continues to receive a great deal of attention as a GC detector. Although extensive applications of GC/MS were reported, especially to biomedical and biochemical problems, there were few fundamental developments in the now well-established GC/MS technique.

COLUMN THEORY AND TECHNIQUES

A monograph describing the properties of adsorbents and catalysts has been published by Paryjczak (A1), an excellent text covering quantitative analysis of gas chromatography was written by Novak and Leclercq (A2), and a practical volume by Grob (A3) describes methodological aspects of making and manipulating capillary columns for gas chromatography. New developments in gas chromatography and open tubular column chromatography have appeared (A4, A5).

The retention mechanism was studied for n-alkanes with different alkyl chain lengths (C8 to C18). Model stationary phases were prepared with these phases and the specific re
tention volumes of the analytes measured within the range of 8 to 160 °C. The thermodynamic calculations indicate that high-resolution appears to be the dominant mechanism for their retention within these stationary phases (A46). The distribution of elution peaks expressed in Gram–Charlier series were derived by means of Melling’s transformation for OTC gas chromatography. The effect of pressure drop on parameters such as the retention times was also investigated. For a mixture of columns and operating conditions becomes possible.

High oven temperature on-column injection at column temperatures well above the boiling point of the solvent, is highly attractive for rapid analyses at elevated temperatures (A25). Movements of the solute within the column inlet are described, from which technical requirements are derived. Avoidance of peak distortion is also discussed. While (A25) discussed the advantages of the at-column injection technique which includes quantitative transfer of sample, no dead volume, and direct transfer of sample to a narrow bore column or a precolumn. The application of the cooled needle technique to split and splitterless sampling onto OTCs to simulated distillation analyses was described by Schomburg and Haeusing (A36). Boeren and Gerner described an automatic sample introduction onto narrow bore columns with a splitter as well as the splitterless injection of both solids and gases (A27). The speed of analysis in OTCs can be substantially increased by reduction of the column inner diameter. However, special demands are then posed on the instrumentation. The sampling system is highly critical because it has to be capable of delivering small injection bandwidths which must be compatible with the column inside diameter (A28). A simple backflushing, peak-cutting method was developed for the determination of trace components present in the tail of a main component peak by Guan et al. (A29). Alexander et al. (A30) described a method for coupling glass and fused silica OTCs by using PTFE shrinkable tubings. Kaiser et al. (A31) reviewed current status of high-resolution column technology for GC. Ettre (A32) 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 (A33). The theory that predicts the retention time, retention temperature, and peak width for any kind of multistep temperature programming and the principle of optimization is described by Lu et al. (A34). The optimization of GC temperature programs using simulated retention times and peak widths is described by Dose (A35). A time/resolution compromise term is included in the chromatographic response function, and the effects of changing the right of this term investigated. The experimental optimum temperature program is demonstrated in one case by searching the setting space about the determined optimum. Freeman and Jennings (A36) 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. Hyder and Phillips (A37) evaluate chromatographic theories for enhancing resolution, speed, and sensitivity in HRGC and HRGC/MS. Optimum performance on a column as a function of tube diameter and film thickness under various operating conditions was studied (A38) and a computer program was written for calculation of $H-u$ curves and minimum analysis time. Saxton (A39) describes a simultaneous parameter compensation in the replication of programmed GC retention measurement (A40) with the aid of a method 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 results from the use of high inlet pressures. Lin et al. (A41) described conditions to select the optimal operation conditions for GC. Basic software is described to obtain the whole imitating chromatogram at any given temperature and to predict the performance of stationary phase selectivity for the GC separation of C$_2$ cyclic and aromatic hydrocarbons using squalane and liquid
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LIQUID PHASES

In general, advances with liquid phases in gas chromatography were aligned toward materials that exhibited specific solute–solvent interactions for improved resolution over general dispersion forces. Several different types of stationary phases were investigated and included liquid crystals (B1–B8), modified silicones (B9–B12), crown ethers (B13, B14), organic salts (B15–B17), and other polymers (B18, B19). The emphasis with liquid crystals was on separation of positional or geometric isomers which was influenced by ratios of length-to-breadth dimensions in solutes (B3–B6) and terminal or lateral substituents in the liquid crystal phases (B4). Separation factors were dependent more on liquid crystal structure than on nematic range (B1), thermocapillary effects were combined with chromatographic methods for improved characterization of liquid crystals (B7), and binary mixtures of liquid crystals were evaluated by using thermochromical parameters (B8). With polysiloxanes, methods for functional group elutriation in existing columns were described (B9) and a family of polar alkylxyphenyl derivatives were evaluated (B10–B12) for high-temperature separations of analytes based on specific intermolecular interactions. Polarity was also introduced into bonded capillary columns through crown ethers that were chromatographically comparable to Carbowax-20M (B19) and exhibited thermal stability (B14). Specificity was added to liquid phases with liquid melts including alkylated ammonium tetrafluoroborates (B15) or thiocyanates (B16) and chromatographic aspects of such substances were reviewed (B17). Dispersive forces were weak in salt–solvent interactions and dipole moments were better indicators of retention. Other developments with liquid phases were made by using more conventional polymers and included assessment of polyethylene in two forms (low density branched and high density linear) for separations of alkenes and aromatic hydrocarbons (B18) and simple addition to OV-101 of N-acetyl capped valinamide for chiral amino acid separations (B19).

The chemistry of liquid phases for GC was explored for the effects of cross linking in bonded phases (B20–B22), identification of structural rearrangements in stationary phases (B23), degredation and oxidation of liquid phases (B24, B25), synthesis of materials for use in 400 °C+ columns (B26), and modification of phases with complexes or polar moieties (B27). Cross-linking was probed for contribution to immobilization of Carbowax-20M (B20), retention by adsorption at the gas–liquid interface (B21), and immobilization of chiral stationary phases (B22). Abnormally large retention volumes for polar solutes with certain polyesters (B29) were attributed to density and hydrogen bonding with the liquid phases. Structural rearrangements that were temperature induced, Consequences of temperatures were also examined with analysis of degradation products from immobilized silicone phases (B24). Cyclic compounds were found in both SE-52 and SE-54 while the cyanopropyl(phenyl)siloxy unit in OV-1701 exerted a destabilizing effect on the liquid phase. In a remarkable development, a column containing OV-1 was heated under oxygen carrier gas flow and a new phase was produced which showed improved peak symmetry of many polar compounds with no ill effect on nonpolar compounds (B28). Changes in the retention index and a reduction in polarity via the McReynolds values were observed. A final investigation related to temperature was the report of methyl polysiloxanes in Al-clad flexible fused silica capillary columns which were suitable for programming to 440 °C with separation of alkanes comprised of carbon numbers from 90 to 100 (B30). Specific interactions were also central in the development of liquid phases modified with lanthanide β-diketonates for complexation interaction (B27) and in the reports on liquid
exchange GC (B28, B29) commonly associated with liquid chromatography. In liquid exchange GC, a copper steareate stationary phase was combined with an ammonia-containing mobile phase for separation of dialkyl (B28) and alkyl aryl (B29) disulfides. Temperature and mobile phase composition were adjusted to effect separations. Thiol-bonded silicas were used to retain copper ions that interacted specifically with organic and aromatic hydrocarbons through complexation.

Two developments in this subject were not easily inserted into categories discussed and will be mentioned individually. The organosilicon chemistry for preparation of capillary columns was reviewed (B31) and the International Union of Pure and Applied Chemistry issued guidelines in six categories for characterization of liquid phases by using uniform procedures (B32). This last reference should greatly facilitate comparisons of new liquid phases in a systematic framework.

**SOLID SUPPORTS AND ADSORPTION**

Natural materials were emphasized in recent studies on solid supports for GC separations and greatly overshadowed the use of synthetic organic polymers. In accord with patterns from the last decade and with developments in liquid phases, modifications of materials for improved specificity were emphasized and were based on mostly empirical models of GSC interactions. Particularly noteworthy is the huge interest from European investigators, all of which were not included here.

Studies on adsorptive and chromatographic properties of zeolites were directed toward effects from cations (C1-C9) and water in the carrier gas (C4). Small hydrocarbons were the central concern in most of these reports and separations were improved with addition of water vapor to the carrier gas. Zeolites were modified with alkali or alkaline-earth metal deposits, and exhibited trends in retention for metal families or groups which differed between saturated and unsaturated hydrocarbons (C1). Cation–hydrocarbon interactions were recognized as dominant absorptive mechanisms in N-A-type zeolites (C2). The adsorption of a binary mixture of carbon dioxide and water on CaA zeolites was successfully modeled to existing equations of adsorption (C6). Methods were described to chromatographically determine OH and adsorbed water on Zeolite surfaces (C5).

Chemical modification of other conventional adsorbents was also a major thrust for nonorganic synthetic materials and included modified silica (C7-C11), altered carbon black (C12-C14), titane-coupled aluminas (C15), plasma-modified silochrome and carbon black (C16), and volatile modifiers with supporting theory (C17). A common theme for all these investigations was user-directed selectivity in adsorption or separation using specific analyte–solvent interactions introduced through the modifying process (D1). Gas-solid chromatography was used to explore the properties of two other natural materials not usually associated with GSC such as lactose (C18), cyclodextrin (C19), cellulose (C20), asbestos (C21), and salt-modified adsorbents (C22). Cyclodextrin was used as a stereospecific material for resolution of substituted aromatic hydrocarbons.

Synthetic organic polymers were the subject of a few studies including thermodynamics of retention for alkanes/alcohols on Porapaks (C23), modifications of styrene–DVB (C24-C27), and chromatographic effects from bead sizes (C28). These studies were aimed at further elucidating the properties of porous polymers, such as effects of number of methylene groups in homologous series of adsorbates, and the consequences from size distributions among various batches of porous polymers. Other organic compounds used as adsorbents were tributyramine salts (C29), molten salts (C30), and metal–vinylpyridine complexes (C31).

A very few physicochemical studies were made as evident from only three reports on the measurement of effective diffusion coefficients in porous packing (C32), determination of the surface acidity of solid catalysts (C39), and sorption-diffusion in molecular sieves (C54). Interesting applications of 1H to quadrupole interactions in homonuclear diatomic molecules (C39) and target factor analysis (C36) were noteworthy. Otherwise, theoretical treatments in GSC were weakly represented and eclipsed easily in numbers alone by applied GSC not cited here.

Two articles of general interest were a historical account of Schuflan's work in GSC (C37) and a review of adsorbents (C38). An interesting combination of GSC with GLC can be found in two reports of capillary columns packed with barium sulfate (C39, C40) for improved resolution of positional/substitutional isomers of olefins and aromatic hydrocarbons.

**SORPTION PROCESSES AND SOLVENTS**

In comparison to the last review in 1986, a surprising amount of activity has occurred in this subject and included some significant advances in describing the molecular basis for chromatographic processes. However, the breadth of investigations was narrow and nearly 85% of all of references abstracted in this category can be placed in equal numbers into two divisions, namely retention indices predictions and thermodynamic measurements in GC. Noteworthy developments have been occurring principally in laboratories from Europe and Asia. Discussion will be organized into the three subjects of retention indices, thermodynamic aspects in GC, and general or isolated subjects.

One issue concerning retention indices (RI) is the prediction of RI values for temperature programmed conditions using data from isothermal chromatography (D1–D8). Advances have been centered on the development of appropriate coefficients for use in linear equations. Presently, precision is only slightly better than 0.5 unit for predicted programmed RI. Predictive capabilities for solution processes with a slightly different emphasis were addressed through the use of mathematical models for calculation of RI units under completely new temperature or column conditions (D9–D21). This was commonly approached by using a single family of compounds for preparation of equations with physicochemical parameters or with solute–solvent energies of interactions. Compounds investigated since 1986 include substituted aromatic hydrocarbons (D9–D12, D15, D20, D81), alcohols (D22), carboxylic acids or esters (D13, D17), quinoline bases (D14), ketones (D16), dialkylamidamidines (D19), amines (D20), and nitroaromatic hydrocarbons (D18). These investigations were not restricted only to a relatively uncomplicated methyloloxanes but also included a wide range of aromatic and nonaromatic phases. Examples of each approach were models from parameters such as boiling point, refractive index, or others (D11, D12, D16, D23, D24) and models from molecular moieties or interaction energies (D6, D12, D14, D17, D25). Finally, the effects from concurrent mechanisms of retention were explored (D26) and limitations on attempts to model and predict retention were critically reviewed (D27).

An equal number of studies were devoted to the determination of terms of interaction in physical chemistry using GLC and included activity coefficients (D28–D31), interaction/solubility parameters (D32–D35), solute–solvent interactions (D36), thermodynamic binary liquid mixtures (D37), entropy of solution (D38), and partition coefficients (D40). The goal in each of these investigations was to explore solute–solvent processes by using the advantages of speed and convenience of GC. Other equilibria such as formation of complexes (D41) or solubility in complexing solvents (D42) were also explored by using GC. Perhaps the most remarkable development recently has been the adaptation of advanced multivariate data analysis to address longstanding difficulties in chromatography, namely systematic interpretation of large amounts of retention information (D43–D47). These techniques may become powerful tools in recognizing various molecular contributions to retention mechanisms (D48) and should be considered seriously in future investigations. Other pertinent articles were found in the determination of nonadditivity (D48) and the role of kinetic coefficients in retention (D49), a description of thermodynamic studies using volatile stationary phases (D50), a mathematical determination of dead time (i.e., void volumes (D51)), a discussion of the choice of concentration scales (D52), a proposed extension of the Kovats RI system (D53), a new liquid phase classification scheme (D54), and a brief review of thermodynamic measurements in GC (D55).

In the category of general subjects, the influence of column effects as related to stationary phases was also considered for chromatographic importance from several perspectives. Studies included the behavior of molecules at interfaces or thin films (i.e., mixed retention mechanisms (D56–D60), overload phenomena (D61), liquid phase swelling (D62), and thermal stability of liquid phases (D63). A general critical
review on liquid phase selection was given by Yancey (D64). Liquid organic salts were examined from consideration of the anion effects on solute retention (D65) and retention mechanisms (D66).

**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 HNO₃ was found to be adequate for cleaning and hydroxylation of 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 (E21). Berlizov et al. (E22) studied properties of Pyrex glass and quartz capillary columns before and after deactivation with OV-101. Heeg (E3) observed various capillary materials under the electron microscope and a comparison was made with those capillaries leached with inorganic acids. Berezkin et al. (E4) investigated the role of adsorption at the stationary phase-interface in capillary columns prepared with cross-linked and non-cross-linked phases. It seems that deactivation of fused silica tubing is still causing significant problems especially with more polar stationary phases. Wolley et al. (E53) described reaction conditions for surface deactivation of fused silica columns with polydimethylsiloxanes, and phenylsilicones-siloxanes (E89). Van de Ven et al. (E86, E77) studied deactivation processes with silazanes. Ogden (E99) used tetrakis(3-cyanoethyl)tetramethycycloctrasiloxane for GC and supercritical fluid chromatography columns. Markides et al. (E101) 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. Wolley et al. (E111) deactivated small diameter fused silica columns with a mixture of polymethylhydrosiloxanes and several low molecular weight organosilicon hydrides. Rohwer et al. (E121) deactivated nickel tubing by chemical vapor deposition of silica from silane gas and subsequent treatment with cyclotetra-methyltetrasiloxane. 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. (E132, E133). Grob and Grob (E141) provided hints for statically coated capillary columns. The hints include pressurizing before pumping and a regular technique for breakthrough by using a compressed gas at 4–5 bar for 15 min 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 (E161) described preparation of a bonded polyoxyethylene phase. There is circumstantial evidence the nonextractable layer is held by multiple hydrogen bonding. Horka et al. (E171) described a procedure for the preparation of an immobilized stationary phase based on Carbowax 20M for capillary column GC. The stationary phase cross-linking was carried out with Desmodur N75, phenylcarbonates. The properties of the prepared capillary columns are compared. A simplified method for Carbowax 20M and 40% dicumyl peroxide was published by Bystricky (E181). The efficiency of fused silica OTCs coated with thick films of polysiloxanes and hydroxyethyl and ethyl vinyl ethers was assessed with 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 plate packing of analytical high-performance columns 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 CO₂, N₂O, C₂F₆, CBr₃F, and SF₆ through various types of columns and eluent residence time measurements. 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 (E161). Yonker and Smith (E171) investigated effects of density on pressure drop over packed columns and entropic contribution to the pressure drop. Their results demonstrate the independence of entropy and enthalpy of transfer with supercritical fluid fluid density during chromatographic separations. The simultaneous calculation of pressure, density, and temperature profiles for packed columns used in SFC is described (E181). The results show that pressure profiles over packed columns are approximately 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 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-OD, OV-31-OD, OV-61-OD, OV-17-OD, OV-240-OD, 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 end-capped stationary phases in the future. Duquet et al. (E225) synthesized a new non-cross-linked 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. (E226) for preparing thermally stable and highly efficient capillary columns coated with highly polar cyanosilicone phases over previously deposited silica layer. Aerts et al. (E225) described preparation of a narrow-bore (50 μm) and wide-bore (320 μm) OTCs for immobilized cyanopropyl-substituted silicones containing 60 and 88% 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 γ radiation was studied by Borek et al. (E225). Columns were irradiated with 2–10 Mrad dose to study the immobilization of stationary phases. An immobilization of both OV-1701 and SE-30 and SE-54 but less than 14% for Carbowax and Silar 10C. Chuang et al. (E271) achieved immobilization of OV-1701 vinyl and OV-225 vinyl using ozone as an initiator. Farbrot et al. (E281) polymerized stationary phases in 12–50 μm open tubular columns used in LC and GC. Melda et al. (E291) described thick film capillaries and their applications for process gas chromatography in comparison with packed columns.

**SUPERCritical FLUID CHROMATOGRAPHY**

The present state of supercritical fluid chromatography (SFC) has been reviewed by many authors (F11–F7). The principles, instrumentation, and applications of SFC are discussed.

Schwartz et al. (F8) 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 molecular weights are large, packed columns appear to have a distinct advantage over capillary columns with regard to the number of plates generated per unit time. A similar subject was discussed by Caude et al. (F9).

The preparation of immobilized polysiloxane coated on packings or capillaries was discussed with regard to efficiency (F10), speed, pressure drop (F11), deactivation, polarity and thermal stability (F12), and kinetic column effects and chromatographic performance (F13). Unified molecular theory of chromatography and its application to supercritical fluid mobile phases have been described by Martire et al. (F14). Hydrodynamic description of SF flow through the thus packing of analytical high-performance columns is based 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 CO₂, N₂O, C₂F₆, CBr₃F, and SF₆ through various types of columns and eluent residence time measurements. 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 (F16). Yonker and Smith (F17) investigated effects of density on pressure drop over packed columns. Their results demonstrate the independence of entropy and enthalpy of transfer with supercritical fluid fluid density during chromatographic separations. The simultaneous calculation of pressure, density, and temperature profiles for packed columns used in SFC is described (F18). The results show that pressure profiles over packed columns are approximately 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 SFC are discussed.
binary eluent mixture containing pentane and 1,4-dioxane was studied (F79). Vonk et al. (F30) studied effects of pressure on retention in SFC and an effect of solute concentration on retention. The optimum pressure conditions can be obtained for maximum resolution of two solutes during pressure programming or isobaric separations (F21). Christensen (F22) described off-line multidimensional chromatographic separa- tion which used all of the physical properties of a critical mobile phase. Leyendecker et al. (F23, F24) studied properties of various low boiling eluents. Kuei et al. (F25) assembled instrumentation that allows the use of supercritical ammonia as mobile phase. In addition, the stabilities of various polyoxazoline stationary phases were examined. The effect of modifier in supercritical fluid chromatography was examined (F26–F28). With 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. (F29) studied the effect of the physical state of the supercritical fluid on solute retention. French and Novotny (F30) 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 (F32) and multiple gradients by programming eluent composition and temperature (F33) were studied. Density-programmed SFC were studied by Linnemann et al. (F34). With pentane and 1,4-dioxane as a binary eluent system and silica as the stationary phase, three-dimensional nomograph plots of capacity ratios, selectivities, effective plate numbers, and resolutions for PAHs vs column temperature and eluent composition at constant pressure were obtained (F35). The dependence of reduced plate height on reduced velocity in carbon dioxide SFC with packed columns was studied by using the Knox model and supplementary coefficients with a parabolic dependence on velocity were added (F36).

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. (F37). 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 (F38). 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 PID with SFC were demonstrated. In an integral restrictor SFC was designed by Guthrie et al. (F39). The device is reproducible and 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 (F40), syringe pumps, and reciprocating piston pumps in SFC were compared (F41). A computer-controlled pumping system for SFC was designed based on a pneumatic amplifier pump by Pariente et al. (F42).

A very attractive technique emerging from utilization of a suitable supercritical fluid separation is supercritical fluid extraction. Nagahama reviewed the principle, applications, and literature of this novel technique (F40). Wenzel and Bunde (F44) reviewed supercritical fluid extraction (SFE) and SFC and their directly coupled systems. Gmuere et al. (F45) designed a prototype for direct coupling of SFE and capillary SFC. Smith et al. (F46) discussed SFC, SFC/MS, and mic- roscale SPE as complementary techniques combined with chromatographic methods. Campbell et al. (F47) studied semipreparative SFC which permits high-quality separation of coal tar with easy solvent removal. Saito and Hondo (F48) reviewed on the historical background and applications SPE and SFC and their applications in food processing. Tanaka (U) developed a device for on-line use of SPE in SFC. An elegant method for the application of SFC to environmental samples using SFE-GC/MS was published by Hawthorne et al. (F50, F51). An apparatus and procedures for direct coupling of SFE to capillary SFC was described by Gmuere (F52). The method can be used for monitoring cheese ripening, rancidity development in dairy products, and detecting aroma defects in butter.

**INSTRUMENTATION AND DETECTORS**

Detectors and injectors for high-resolution capillary gas chromatography were the focus of instrumental research and development over the past two years. Of specific interest was the quantitative introduction of mid to high molecular weight components into high-resolution gas chromatographic columns. Also the explosion of supercritical fluid chromatography led to rapid developments in SFC detectors and instrumentation.

**Sample Introduction**

As the efficiency of chromatographic columns have continued to improve, the importance of injecting narrow bands onto the column while maintaining the quantitative integrity of the sample has increased. Thus the improvement of on-column injection methods has received considerable attention. Two designs for inexpensive on-column injectors were reported (G1, G2). Although efforts were made to increase injection volume, Grob and Neukom (G3) found that phase soaking effects of large volume injections (e.g., 70 μL) reduced peak areas from that expected in comparison with submicroliter injections while Termonia et al. (F44) reported good quantitative data for large on-column injections and Lawson et al. (F45) reported on an apparatus which could be used for SFE injections with a 1% relative standard deviation. Along with injection volume, temperature effects were also investigated. A multipurpose cold injector was reported which could not only be used for on-column injections but could also be modified for split/splitless or solvent vented injections (G6). Grob and Laeubli (G7) described two independent on-column injectors, described technical requirements for on-column injections into columns maintained at high temperatures.

To accurately control injection temperatures, Bruno and Shepherd (G8) developed a miniature mercury contact switch that could be placed inside the injector or other components of a chromatograph. Another temperature control device to aid injection was reported by Pretorius et al. (G9). With operation on the principle of Joule-Thomson cooling, it can be used for thermal focusing of volatiles in a capillary column. Cryofocusing is, of course, a common aid in the injection of volatile compounds. Kolb et al. (G10) investigated this method for sample enrichment during equilibrium headspace sampling.

Although direct injection techniques were employed using a retention gap (G11), sampling of volatiles from fluids was commonly accomplished by stripping and trapping methods. Both repetitive (G12) and automated (G13) studies were reported. Novak and Cermak (G14) reported the use of high-speed crups for transferring substances from trapping columns into a gas chromatograph without affecting the conditions for injecting sample standards through the common septum port. Other novel transfer techniques have been reported as well. Goldsmith (G15) reported the use of microwave desorption and Pavlisyn and Liu (G16) described a sample introduction method using laser desorption. Of particular interest was the introduction of volatile samples into very small diameter columns. Phillips et al. developed a method for thermal desorption modulation (G17) while Van Es et al. (G18) evaluated input bandwidths as a function of column diameter. There was interest in the area of high molecular weight and polar compounds. Standard techniques such as pyrolysis continued to be investigated (G19, G20) but more emphasis was placed on the introduction of high molecular weight compounds without thermal degradation. Bayona et al. (G21) discussed the advantages and disadvantages of standard vaporizing injectors for high molecular weight introduction and Lawrence (G22) reported a method for transferring high-boiling compounds from sample adsorption tubes. Considerable interest, however, was shown for programable-temperature injection (PTI) techniques. With initial investigations primarily focused on the determination of triglycerides (G23, G24), the use of PTI proved promising. Reglero et al. (G25) have reported on the optimization of the technique.

One driving force behind investigations into PTI was the difficulties encountered when injection ports are maintained...
continuously at elevated temperatures. Complications from septum decomposition are especially troublesome. Although Skornyakov and Poshemanski (G26) reported the development of a septumless injection device, supercritical fluid injections were also investigated to minimize high-temperature problems (G27, G28). Typically, a supercritical fluid such as CO₂ was used to extract the sample from a solid matrix and quantitatively transfer the extract through a decompression chamber directly to the inlet of a gas chromatograph. Injection via supercritical fluids was also accomplished after preliminary separation of the sample by supercritical fluid chromatography. Levy et al. (G29) reported the development of this new multidimensional separation technique with heartcut examples. Of course, if supercritical fluid chromatography is to be used as an injection method for gas chromatography, injection methodologies for the supercritical fluid chromatography must also be considered (G30).

Liquid chromatography was also investigated as a method for introducing compounds into a gas chromatograph. Of primary concern in this interface was solvent elimination and evaporation. Grob et al. (G31–G33) developed a method for concurrent solvent evaporation in which they use the retention gap approach. Raglione and Hartwick (G34) used a bundled capillary stream splitter for solvent volume reduction. In a related injection method, Rogelqvist et al. (G35) directly coupled a liquid–liquid extractor to a gas chromatograph by using magnetic coupling.

Two reviews were published that provided an excellent overview of modern inlets for capillary gas chromatography (G36, G37).

**Detectors**

As always, a number of excellent reviews on gas chromatographic detectors were published. Dressler (H1) has written a comprehensive book covering selective detectors and Patterson (H2) compared the various methods of ionizing GC effluents. Brinkman and Maris (H3) reviewed GC detectors that use liquid chromatography and other general review papers were also published (H4, H5).

Although investigations were reported that used catalytic cracking (H6), electrochemistry (H7, H8), and thermal conductivity (H9), the majority of research on GC detectors was focused in three areas: ionization, light absorption, and light emission.

**Ionization Detectors**

For routine analytical quantification of components separated by gas chromatography, ambient pressure ionization detectors remain the primary detector of choice to most analysts. This category of detectors includes the flame ionization detector (FID), the electron capture detector (ECD), the photonionization detector (PID), the thermionic ionization detector (TID), and He ionization detector (HeID), and the ion mobility detector (IMD) plus several miscellaneous ionization methods.

The FID continues to receive considerable attention. Recent research on the detector has been focused on efforts to improve its sensitivity. Cool and Goldsmith (I1) have reported ionization enhancement of the FID with laser excitation of CH. Using stilbene 420 in a dye laser that was pumped with an argon-ion laser, they were able to achieve a 5% enhancement of the ionization response of methane in hydrogen. In another study, Axner et al. (I2) investigated laser-enhanced ionization for 23 different elements in aqueous solutions with ionization in an acetylene/air flame. Other methods to enhance performance of the FID have also been investigated. Gonnord et al. (I3) compared various electronic methods to improve signal-to-noise ratio and Colson (I4) has suggested methods to improve the high-end linearity of the detector. Flame ionization for the selective detection of Si-containing compounds was also reported (I5, I6).

Mechanistic investigations of the ECD continue to produce surprising and useful analytical results. Arguments for the space-charge mechanism of electron-capture response were presented in several papers by Aue and co-workers. Using ac polarization of two commercial detectors and two lab-built detectors as a probe for the mechanism, they achieved two response maxima as they scanned the polarization frequency from 10 to 10⁶ Hz (I7). The low-frequency maximum was attributed to cation–electron recombination within the plasmas while the high-frequency maximum was attributed to a migrating negative space charge. Analytically, ac electron-capture detection behaved similarly to unipolar detectors but it was suggested that ac operation may have benefits for the detection of weak electron-capturing molecules. Confirmation of the space-charge mechanism was provided by the development of an electron-capture detector which provided a current increase in response to electron-capturing molecules (I8). Supporting information for the heterogeneity of charge distribution in the electron capture detector was provided by a study of ²¹²Ni β range and backscattering in confined geometries (I9). In these studies, it was found that the majority of gas-phase ionization occurs within 4 mm of the foil. No evidence was found for the very large range estimates reported in the literature. In other ac potential experiments, Baumbach et al. (I12) found that superimposing a high-frequency ac potential over the dc potential of an ECD can provide orders of magnitude response specificity for some compounds. The response of low electronics-density compounds was also investigated by Valkenburg, Knighton, and Grimsrud (I13). Improved response for aromatic hydrocarbons using positive ion stabilization and alkyl chloride sensitization was reported and a kinetic model developed to explain this response enhancement. Chen et al. (I14) reported the importance of kinetics and low ion mobility for the kinetic model for the electron-capture response. Simmonds (I15) investigated photoemission from thin metallic films as a source for thermal electrons. Wise et al. (I16) reported the development of a multimode ionization cell that provides tunable selectivity. By varying the internal pressure of an electron-capture-type cell from ambient to less than 1 Torr, they could operate the detector as a conventional electron capture detector, a low-pressure Ar ionization detector, and a cross-section ionization electron emission detector. A new derivatization reagent for the ECD, pentfluorobenzyl p-toluenesulfonate, was reported which enables the determination of bromide, iodide, thiocyanate, and nitrite by GC/ECD (I17). Other derivatizing reagents used with ECD were reviewed for trace analysis (I18). ECD detection was applied for the determination of total and free thyroxin in serum (I19), mitotane in plasma (I20), and propafenone in biological fluids (I21).

Investigations of the FID included high sensitivity studies and optimization of the detector for gas capillary chromatography. Driacoll (I22) reported the operation and performance characteristics of a PID with a cell volume less than 50 μL for use with capillary chromatography. The use of the PID for the trace determination of volatile polar compounds was investigated by Sung et al. (I23) and Norlander and Carlson reported the detection of 70 μg of methadone (I24). Aue et al. (I25) also reported the use of a photoionization detector with high sensitivity. Its uses for the detection of purgeable halocarbons (I26) and in recycle GC systems (I27) were investigated.

The TID, also known as the NPD, is thought to respond to nitrogen- and phosphorus-containing compounds by surface ionization on heated solid surfaces. In a study of the nitrogen mode of the TID using 36 compounds, Jones and Grimsrud (I28) report that thermal decomposition of the analyte on the hot emitter surface followed by electron transfer from the surface to one of the decomposition products was the mechanistic mode which best fit all the results of their experiments. Patterson et al. (I29) reported that changes in their analyte implied variations of each of three key parameters (the work function of the thermionic emission surface, the temperature of the thermionic surface, and the gas phase environment), thermionic detection can be expanded to a variety of operational modes. Fujii and co-workers (I30–I33) have investigated the ionization response of a high electron density low workfunction for the detection of compounds eluting from a GC. While much of the initial investigations of high work function surfaces such as Pt and Re have been conducted with trimethylamine, response for non-nitrogen-containing compounds such as the polycyclic aromatic hydrocarbons have also been reported. Aue and co-workers (I34) have investigated the reduction of disaccharides (I34), chlorinated phenolic compounds (I35), nitrogen-containing hazardous pollutants (I36), nitrogen-containing drugs (I37), opium alkaloids (I38), and the classification of Bacillus stearother-
mophillus after pyrolysis GC (J39). Klyos et al. (J40) have compared the usefulness of thermionic detectors for toxico-
logically active analytes. The HeID operates on the principle of Penning ionization and has been useful for the determination of volatile inorganic gases which do not respond well in the FID, although it can be used to detect organic compounds as well. A major development in the HeID during the past two years has been the introduction of a pulsed-mode option that allows the detection of dynamic range. Bowers et al. (J42) constructed a Penning ionization detector from Teflon and glass which was extremely inert and had a detector cell volume of less than 5 L. Useful after capillary gas chromatography, the detector can be operated with both Ar and He. General theory of operation of the HeID was reviewed by Fehl and Mayer. The pulse-mode offered greater stability and the constant-
current mode obviated the need to adjust the detector current. Two approaches were reported: the focusing method of identifying GC peaks and by Rotin et al. (J44).

The IMD is an atmospheric pressure time-of-flight ion separation device developed as a capillary GC detector by Hili and co-workers. Its multimode capabilities permit FID-like, ECD-like, and molecular selective operation. Using a Fourier transform method, they were able to obtain ion mobility spectra from ions produced on columns eluting from a capillary column. Mobility data collected in this manner can be used to predict ion separation (J46) and detector selectivity from literature data which have been compiled into a single table (J47).

Another detector investigated was based on quenchless ionization in a microwave plasma (J42). For most organic species detection limits were in the range of 10⁻⁸ to 10⁻⁵ g/s with a linear dynamic range of 4-6 orders of magnitude.

Absorption Detectors

Atomic absorption spectrometers were interfaced to gas chromatographs to provide specific detection of volatile metal-containing compounds. A general review of the technique was presented by Ebdon et al. (J1) but the primary focus for research was on the determination of organolead compounds. Forsyth (J2) described a low-volume quartz T-tube furnace for the atomization and AA detection of alkyllead species separating by capillary gas chromatography. Key design features of this furnace were extension of the heating elements to the edge of the detector casing, the addition of an in situ hydride generator, and the transfer of the analytes as hydrides from the GC to the furnace. Propylation of ionic alkyllead species with PrMgCl was found to offer better recovery than butylation (J5). Mobility data collected in this manner can be used to predict ion separation (J46) and detector selectivity from literature data which have been compiled into a single table (J47).

Next to GC/MS (covered elsewhere in this review), GC/IR provided the most detailed information for compound identification. With Fourier-transform operation "on-the-fly" IR spectra could be obtained and new algorithms were developed for interpretation and selective detection. Several reviews on GC/FT-IR provided current information on this rapidly advancing method of identifying GC peaks (J5-J8). FT-IR was successfully employed for the identification of compounds in complex samples and is particularly advantageous for low molecular weight compounds (J9). An advantage of FT-IR over MS identification methods was demonstrated by the determination of various isomers encountered in the determination of flavors (J10) and dioxins (J11). Because of the nondestructive nature of FT-IR, identification of peaks after GC was possible. Another approach to direct coupled GC/FT-IR/MS systems (J14-J17). Sensitivity of the technique was reported to be improved down to the low nanogram and picogram range (J18). Sensitivity improvements were largely due to continued development of the optical configuration. Two approaches were reported: the light pipe and matrix isolation/isolation detectors. Ghijsen et al. (J20) compared these two approaches. Ghijsen et al. (J20) studied the effects of increasing the diameter of the light pipe while Henry et al. (J21) investigated methods to discriminate against emission from the end of a hot light pipe. Rossiter et al. (J22) reported that gold light pipes provided exceptional inertness and excellent high-temperature performance. Fuoco et al. (J23) investigated the matrix isolation method by trapping the GC elute on the surface of an IR window cooled to temperatures of -40°C. Ebel and Marns (J24) reported the problem of FT-IR sensitivity by applying a preconcentration step utilizing an injector/trap procedure. The tremendous quantity of data generated by FT-IR has prompted the development of a variety of algorithms for data reduction. Anderegg and Pyo (J25) reported a library search routine to retrieve spectra of compounds of interest. Bowater et al. (J26) developed a new algorithm for the generation of chromatograms from FT-IR data based on maximum absorbance. This method was found to be more sensitive than the integrated absorbance method and offered an alternative to the Gram-Schmidt method. Wang and Isembox (J27) introduced the use of a time-warping algorithm which eliminated the time axis of a chromatogram so that chromatograms can be adjusted to match peaks. Other absorption methods that were investigated included optoacoustic detection (J28) and photothermal detection (J29, J30). By use of a Helmholtz resonator as the opto-
acoustic detection cell, detection limits as low as 18 fmol were reported for SF₆. With photothermal methods, detection limits of 0.7 ng for Freon and 1 pg/s for SF₆ were reported.

Emission Detectors

The category of gas chromatographic detectors that operate on the principles of light emission encompasses a wide variety of design, modes of operation, and analyte response. In general, the diversity of this category can be attributed to the means by which the analyte, or its products, is excited. Because of the specificity of excitation energy and emission energy, these detectors generally provide selective or specific responses. Detectors in this category include the flame photometric detector (FPD), chemiluminescence detectors, plasma emission detectors, laser-based fluorescence detectors, and radioactive detectors.

The FPD was characterized in the sulfur mode for compounds in petroleum (K1) and in the phosphorus mode for organophosphorus pesticides (K2). Lee and Siebert (K3) reported a new procedure for calibration. A number of improvements to the FPD were reported as well. Baringa and Farwell (K4) constructed a system that reduced the dead volume in a commercial FPD by 5- to 20-fold and Wakahayama et al. (K5) developed a background correction method in which they quenched the P response with a modulated magnetic field. Chlorine and bromine compounds were selectively detected in the FPD by doping with Cu (K6). Detection limits of 0.5 ng/s for 1,4-dichlorobutane and 0.07 ng/s for bromoform were reported. Infrared emissions from flames as the basis for gas chromatographic detection and an ion species detection-specific detector was invented by Hudson and Busch (K7). Using an optical filter to isolate the asymmetric stretch of carbon dioxide at 4.3 μm, they calculated a detection limit of about 300 μg for ethanol.

Plasma excitation methods include inductively coupled and microwave induced systems. The inductively coupled method was investigated by Duselbeis et al. (K8) for the detection of volatile organometallics but microwave induced plasmas were investigated more extensively. Goode and Kimbrough (K9) studied the signal-to-noise ratio of the microwave-induced plasma detector (MIPD) and determined that the dominant noise was the load and performed the improvement. Although the MIPD has potential as a versatile element-specific detector in gas chromatography (K10), there was special interest in its operation as an oxygen (K11), fluorine (K12), and deuterium (K13) selective detector. Panaro et al. (K14) used an optical detector to accept the signal and improve the detection limit of mercurymethyl in fish samples. Detection limits were lower than those obtained with ECD but the cleanup procedure was more extensive.

Laser based emission detectors offer both atomic and molecular fluorescence detection. D'Ulivo et al. (K15) interfaced a multichannel atomic and ionic laser detector to a capillary chromatograph by using a miniature flame for atomization. The system was evaluated for alkyleneenides, alkylacids, and alkyltin and detection limits of 10 pg of Se, 30 pg of Pb, and 50 pg of Sn were reported. Atomic fluorescence detection of a variety of his(trifluoroethyl)dithiocarbamate complexes was also reported after GC separa-
ration (K16). Molecular fluorescence was typically accomplished at subambient pressures after supersonic jet expansion. Most of the development efforts have been focused on the jet. Imasaka et al. (K17) used a high-temperature pulsed nozzle, Pipich and co-workers (K18, K19) employed a pulsed jet expansion system in which they achieved detection limits from 2 to 6 ng for monomethylanthracenes, and Stiller and Johnston (K20) were able to achieve a very low detection limit of 0.03 nmol by using a jet nozzle based upon sheath flow gas dynamic focusing.

Excitation from chemical reactions form a subgroup of GC detectors known as chemiluminescence detectors. In general, the excitation energy is supplied by reactions with ozone. A review of the development of chemiluminescence detection strategies that can be used with SFC while Later et al. (K26) discussed spectroscopic detection methods for capillary SFC.

While the FID remained the GC-type detection method most commonly used in SFC, other detectors, traditionally employed with gas chromatographs were interfaced to supercritical fluid chromatographs. Novotny (K21) reviewed detection strategies that can be used with SFC while Later et al. (L5) discussed spectroscopic detection methods for capillary SFC. The unique gaslike and liquidlike properties of supercritical fluids continue to encourage investigations in which gas and liquid chromatographic detectors were interfaced to supercritical fluid chromatographs. Novotny (K21) reviewed detection strategies that can be used with SFC while Later et al. (L5) discussed spectroscopic detection methods for capillary SFC.

Beam and co-workers (L9) evaluated a thermomolecular detector for nitroated polycyclic aromatic compounds found that the nitro-selective mode of operation produced a 20-pg detection limit for p-nitrophenol although linearity was confined to a narrow range. Two other modes of operation were found to be either unstable during density programming or too low in sensitivity. Nevertheless, with the nitro-selective mode of operation, they successfully detected a variety of nitro-containing compounds that could not be separated by gas chromatography. Sulfur- and phosphorus-selective detection modes of a dual-flame photometric detector were found to be less sensitive after SFC than after GC (L4). Another unsuccessful attempt to adapt a GC technique for SFC was the construction of a high-pressure photoionization detector. When CO₂ was used as the mobile phase, the quenching effect of the gas reduced the sensitivity of the detector to an unacceptable level (L5). Perhaps the most successful of the GC-type detectors to be investigated in the past two years was the ion mobility detector (IMD). Rokushika et al. (L6) constructed a capillary SFC system in which an IMD was placed after an on-column UV detector. With CO₂ as both the chromatographic mobile phase and the ion mobility drift gas, this investigation demonstrated the advantage of IMD for the detection of compounds that do not contain chromophoric groups. Eatherton et al. (L7), using a unidirectional flow ion mobility detector, were able to efficiently eliminate COP mobile phase from the detector so that the ion mobility spectrometer could be operated in the conventional manner with N₂ as the ion mobility drift gas. Using the Fourier transform capabilities of this instrument, they were able to capture complete ion mobility spectra of individual oligomers separated by SFC and, using the selective monitoring mode, they were able to detect specific oligomers in polymeric material.

The UV absorption detector has been the LC-type detection method most widely used in SFC. Jinno et al. (L8, L9) employed a multichannel ultraviolet detector with computer-enhanced spectroscopic separation to identify EPA priority pollutants and a variety of PAHs after SFC separation. Light scattering after nebulization of CO₂ supercritical fluid was found to be more sensitive as an SFC detector than as an HPLC detector (L10). Separation and detection of triglycerides, poly(ethylene glycol), poly(oxyethylene), polysaccharides, and phospholipids were demonstrated with this technique (L11).

Light scattering from an Ar ion laser beam was also used to probe the presence of aerosol after supersonic jet expansion of supercritical CO₂, N₂O, SF₆, n-pentane, and benzene (L12). The most active area of SFC detector research during the past two years has been in the development and investigation of quadrupole mass spectrometry. For infrared spectrometry, two types of interfacing approaches have been investigated: direct flow cell and solvent elimination. The direct flow cell method has the advantage of in-line, real-time detection but offers some limitations as well. One problem with a direct flow cell is that the CO₂ transparency varies in the Fermi resonance band region as a function of pressure (L13) and the addition of polar modifiers degrades the overall quality of the spectra (L14). Solvation effects of supercritical CO₂ were also monitored as a function of density (L15). Nevertheless, CO₂ offers large transparency regions where many functional groups can be detected (L16). For example, free fatty acids were detected by FT-IR after SFC from butter, soap, soybean oil, and coconut oil samples (L17). The extent of dimerization and the degree of unsaturation of each component could be determined by FT-IR spectra obtained for individual chromatographic peaks. In addition to CO₂ and modified CO₂, Freon was investigated as a mobile phase for SFC/FT-IR (L18). Although the instrumentation required was somewhat more complex, enhanced sensitivity, more extensive spectra, and a greater selection of mobile phases were possible when FT-IR was interfaced to SFC via the solvent elimination method. With components aspirated from a capillary SFC column directly onto a ZnSe window through a restrictor, FT-IR spectra were obtained without interference from the mobile phase (L19). Complete identification spectra were obtained at the 50-ng level (L20). In a similar approach, diffuse reflectance FT-IR spectra were obtained after capillary SFC (L21). A comprehensive review discussing both direct flow cell and solvent elimination methods for infrared detection was reported by Jinno (L22).

Mass spectrometry coupled with supercritical fluid chromatography received considerable attention over the last two years for the identification of high molecular weight and thermally labile compounds. The fundamentals and practice of supercritical fluid chromatography/mass spectrometry were reviewed in which supercritical fluid properties, various methods of SFC/MS interfacing, and a variety of SFC/MS applications were discussed (L23–L25). The majority of investigations of SFC/MS involved chemical ionization mass spectrometry (CI-MS) after capillary SFC. By use of a capillary restrictor, CI-MS data were reported for polynuclear aromatic hydrocarbons in various lipid detector oils (L26). Lee and Henion used a benchtop mass spectrometer with CH₃Cl for the detection of dcafluorotriphenylphosphine but found tailing at the low nanogram levels for caffeine and fatty acids (L27). They attributed this tailing to the capillary restrictor interface and suggested that improvements in the interface were required. For example, when additional structural data, other CI reagents were investigated including ammonia for the determination of carbamate and acid pesticides (L28, L29). Improved methods for interfacing microbore and capillary SFC using a high flow rate interface were described by Smith and Udseth (L30). In this design, a vacuum-actuated pump system was constructed in which the chemical ionization repeller electrode to allow higher gas flow rates. Matsumoto et al. (L31) reported the use of a self-spouting, vacuum nebulizing assisted interface for the determination of styrene oligomers, triglycerides, and poly(ethylene glycol) derivatives. Direct introduction of CO₂ into Fourier transform mass spectrometers provided higher resolution than quadrupole systems (L32, L33). Electron-impact ionization was also reported in which chemical ionization contributions and clusters from the solvent were not observed (L34).

**GAS CHROMATOGRAPHY**

Few fundamental developments in the area of GC/MS were reported during the previous two years. A review discussed the limitations and guidelines for the qualitative and quanti-
that survived prepyrolysis to be identified by pyrolysis GC/MS. Hagman demonstrated the advantages of this technique for the determination of volatile organic compounds in polymers by dynamic headspace multidimensional GC/MS (M6). Capillary-to-capillary column heartcutting provides superior selectivity for selected components resulting in purer mass spectra and improved identification by computer library searching (M6).

Developments in GC/MS data evaluation were reported. Smoothing of GC/MS selected ion monitoring data was found to achieve only a minor improvement in precision while introducing bias in the peak height ratio calculation (M7). It was found by Pettit that at least five selected ion monitoring scans need to be taken over the top half of the peak to achieve an error less than 3% in the estimate of a GC peak height (M8). A method was described to estimate GC/MS response factors when standards are not available (M9). It was shown that the relative standard deviation method for determining the working range of a GC/MS may have greater probabilities of large errors than previously suspected, and a new method based on the $\chi^2$ distribution was proposed (M10). Scott presented a new method of classifying and identifying air pollutants based on pattern recognition of mass spectral data (M11).

Work continues to be performed on the combination of GC/MS with the FT-IR technique. Wilkins described the automated correlation of FT-IR and GC/MS reconstructed ion chromatograms (M12). A mass analyzer was interfaced to the light pipe of an FT-IR in a serially interfaced GC/FT-IR/MS system (M13). Negative chemical ionization and accurate mass measurements were used to find the improvements in both IR and MS search results in a GC/FT-IR/MS system (M14). Laude described the use of a pulsed valve that provides momentary gas pressure in GC/FT-IR chemical ionization operation (M15). Use of this valve overcome problems in source pressures that restrict the mass resolution and accuracy obtainable. Laser ionization GC/MS of nitro and nitroso-containing compounds was found to produce substantial quantities of NO$^+$, in contrast with electron impact ionization operation (M16). Lasers were also used for a multidimensional instrument applied to the characterization of environmental samples for polycyclic aromatic hydrocarbons in another investigation (M17). The laser-analyte products (cations, electrons, and photons) were simultaneously monitored. The time-of-flight mass spectrometer used allowed an entire photoionization mass spectrum to be obtained for each laser pulse. Time-of-flight mass spectrometers are ideal for use in GC/MS applications because they can produce up to 10,000 mass spectral transitions to the system so allowing processing of such large number of spectra are needed (M18).

**METHODOLOGY**

**Pyrolysis**

Recent developments in improving the reproducibility in solids analysis by pyrolysis GC have been reviewed (N1). Reviews of pyrolysis GC for characterizing polymers have also appeared (N2, N3). The combined use of pyrolysis GC with other techniques such as infrared spectroscopy (N4), FT-IR (N5), and mass spectrometry (N6) is increasing in importance. Such techniques have been used for characterization of polymeric materials (N6), machine copier toners (N4), and other macromolecules such as epoxy and phenolic resins (N5). The techniques of pyrolysis MS, pyrolysis GC, and infrared spectroscopy to analyze paint resins were found to be complementary, and the use of a combination of these techniques was recommended (N7). Prepyrolysis was used for the identification of many polymers in paper by pyrolysis GC (N8). Sufficient polymers were present in the paper tested that survived prepyrolysis to be identified by pyrolysis GC at a higher temperature. Pyrolysis GC/MS was successful in distinguishing the pyrolysates resulting from the presence of a single chemical marker appearing only in the pyrograms of group B organisms (N9). The potential exists for further correlations between the chemical structure of microorganisms and pyrolysis products.

**Multicolumn Chromatography**

Multidimensional GC is becoming less a topic of research and more a method of routine analysis. It is surprising that few commercial systems are yet available. Definitions and characteristics of multidimensional GC/MS have been described by Schomburg (O1). A new type of packed column was used in two-dimensional systems without need of cold-trapping (O2). Combined SFC-multidimensional GC was found to be very useful for selective heartcutting (O3, O4).

Many new studies were reported concerning the development and use of serially coupled columns. The theory and practice of coupled columns were described by Purnell (O5), who also presented experimental verification of the theory (O6). Their general theoretical treatment of the coupled columns was shown to be valid and free of assumptions other than that of carrier gas ideality. Jiansing developed a multidimensional window diagram method to select optimum column temperature and gas flow velocities in the series-coupled systems (O7). Fundamental relationships in multicolumn GC used for tuning selectivity were discussed (O8). Methods of preparing hybrid fused-silica columns were described (O9). An equation to predict plate height on serially coupled WCOT columns has been developed and was found to have good agreement with experimental data (O10). Methods for optimizing separations in serially coupled columns (O11) and for columns composed of packed stationary phases (O12) have been reviewed. Dramatic selectivity changes in serially coupled columns of differing polarity were shown to occur with even slight carrier gas flow changes in one part of the column series (O13). Serial micropacked fused-silica capillary columns were studied by Malik (O14). He explained theoretically the advantages of locating the segment containing the finer sorbent fraction near the column outlet on the basis of better efficiency and mass transfer coefficient.

A review of multidimensional LC/LC and LC/GC separations has been presented (O15). The state-of-the-art and future outlook of HPLC/GC have been reviewed by Grob (O16). Introduction of HPLC fractions directly to capillary GC columns is performed either by a direct injection technique or by fully concurrent solvent evaporation (O17, O18). A loop-type interface for concurrent solvent evaporation has been described (O17). Experimental background for facilitating column temperature selection with concurrent HPLC eluent evaporation in coupled HPLC/HRGC systems was discussed (O19) and the minimum column temperatures required for eluent transfer were experimentally determined for solvents used as HPLC eluents (O20). The use of HPLC/ HRGC was demonstrated for residue analysis (O21) and as a replacement for GC/MS in the determination of diethyl-stibestrol in bovine urine (O22).

**Headspace Gas Chromatography**

Reviews on the use of headspace GC (HGC) in the flavor and fragrance industry (P1) and for systems not in thermodynamic equilibrium (P2) have been presented. Techniques for cryofocusing and cryogenic trapping have also been reviewed (P3). A collaborative study for ethanol in canned salmon showed that repeatability and reproducibility of HGC can be better than 5% (P4). Most new work in HGC was to study cryogenic focusing (P5-P9). By simple cooling of the GC oven, headspace vapors were cryofocused at the head of a cold-silica WCOT columns coupled to the injection port (P5). A multiple headspace injection technique was used to increase analytical sensitivity. The theoretical background and instrumentation of cryogenic trapping for HGC have been presented (P6). Profiling mid-to-high boiling compounds in the headspace of foods was performed by off-line sorbent trapping followed by adsorption-desorption and splitless injection into a cryogenically cooled WCOT column (P7). Principles of purge-and-trap (P&T) onto Tenax TA followed by thermal desorption onto a WCOT column retention gap with cryofocusing were discussed as an alternative. Their theoretical treatment of the effects of sampling and desorption parameters on recovery for this system were reported (P9). Effects of trapping temperature and WCOT column film thickness in P&T GC were studied (P10). Quantitative recoveries and good chromatography can be obtained by careful control of conditions. GC analysis of...
trapped headspace volatiles has also been performed by microwave desorption from graphite (P11) and by on-column injection of solvents used to recover volatiles from activated carbon traps (P12).

Chemometrics

A theoretical model of peak overlapping was presented where sample components are randomly distributed along the retention axis (Q1). It allows for a prediction of the probability distribution of the number of sample components when the number of resolved peaks is known. Deconvolution of overlapping GC peaks was studied by using Jansson’s method (Q5) and by extension of the Fourier spectrum (Q6). Partially overlapping chromatographic peaks can be deconvoluted without any assumptions about chromatographic peak shape or prior knowledge of the spectra of the individual compounds by using multichannel detectors that produce spectra characteristic of the eluents (Q6). SIMCA pattern recognition was applied to the grouping of bacteria (Q6) and the homologue-specific analysis of PCBs (Q7). The effects of sludge treatment on soil samples were determined by pattern recognition without prior knowledge of chromatogram peak identity or compound class type (Q8). For the principal component modeling of crude oil fractions using GC profiles, prior normalization to percentages was unnecessary when logarithmic data were used (Q9).

A method for the generation of GC/FT-IR chromatograms using maximum absorbances was reported (Q10). Because it can create both universal and selective reconstructions with good sensitivity, this method is an alternative to the Gram-Scatter method which should result in improved integrated absorbance method. Howery predicted retention indices for 42 solutes and 24 stationary phases to better than 1% by using target factor and multiple regression analysis (Q11). New numerical methods were also reported for the scaling of analytical data (Q12) and for selecting exponential flow programs in WCOT GC (Q13). An integration method for modeling GC line shapes (Q14) and a fast multiparameter least-squares adjustment of GC data by using Wentworth’s method (Q15) were also presented.

MISCELLANEOUS

Several recent reviews are of interest. Grob published a book describing on-column injection techniques (R1) and reviewed the use of retention gaps (R2). Recent developments in inverse GC are reviewed in a book on polymer standards (R3) and for the determination of the polarity of nonionic surfactants (R4) have also been reviewed. Bereznik reviewed the main applications of temperature gradients as used in GC (R5). Miller used recycle GC to obtain improved separations for nonpolar analytes (R6). Adsorptive polarity is additive, and therefore a serious limitation for the use of recycle GC for polar analytes. An improved method for determining dead times in inverse GC (R7) and the use of reversed-flow GC to determine mass transfer and partition coefficients across gas–liquid boundaries (R8) were discussed. Schurig presented a method for separation of isomers of undervatized aliphatic alcohols and ketones by complexation GC on optically active metal chelates (R9). Thermodynamic and kinetic parameters relating to the sorption-diffusion of aromatic hydrocarbons in zeolites at high temperature (613–713 K) were evaluated by the GC pulse method (R10). Ha and co-workers studied the operational characteristics of a moving-feed injection system for the GC separation of diethyl ether and dichloromethane (R11).

Bartu presented heuristic methods to minimize retention times of the most difficult to separate component pairs in mixtures (R12). Thermal desorption modulation was discussed as a replacement for conventional sample injection in very small diameter WCOT GC columns (R13). Multiple pulses of the same solvent were studied by using temperature and precisely controlled output in a multiplexed detector output signal from which chromatograms can be computed. Methods were presented for precise detection of void zones in packed GC columns (R14) and for the determination of intraparticle distributions of in-pore particles in packed columns (R15). A new means of quick and safe optimization to achieve maximum efficiency, termed “peak number 10”, was developed by Kaiser (R16). A mathematical procedure to predict the optimum composition of mixed stationary phases for complex mixtures was presented (R17). By measuring retention on SE50 and OV-555 columns, Kuchar was able to simulate the octanol-water system for estimating the lipophilicity of selected esters of aromatic and aliphatic acids (R18).

LITERATURE CITED

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GAS CHROMATOGRAPHY
Mass Spectrometry

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A. OVERVIEW

The frontiers of mass spectrometry have shifted dramatically from small molecules to macromolecules, their biologically mediated covariant interactions with small molecules, and the topological nature of their specific molecular recognition of other macromolecules. Biological substances may be "trampolined" from the surface of their solutions as intact stable molecular ionic species, virtually irrespective of whether they contain previously unobserved or uncharacterized structural modifications or new moieties. This sole fact, coupled with potentially unsurpassed sensitivity even at higher mass, procures for mass spectrometry a vital new role in deciphering the molecular language of life. Biological mass spectrometry will eliminate many of the experimental stum-

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