Gas Chromatography

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This review of the fundamental developments in gas chromatography (GC) includes articles published from 1996 and 1997 and an occasional citation prior to 1996. The literature was reviewed principally using CA Selects for Gas Chromatography from Chemical Abstracts Service, and some significant articles from late 1997 may be missing from the review. In addition, the online SciSearch Database (Institute for Scientific Information) capability was used to abstract review articles or books. As with the prior recent reviews, emphasis has been given to the identification and discussion of selected developments, rather than a presentation of a comprehensive literature search, now available widely through computer-based resources.

During the last two years, several themes emerged from a review of the literature. Multidimensional gas chromatography has undergone a transformation encompassing a broad range of activity, including attempts to establish methods using chromatographic principles rather than a totally empirical approach. Another trend noted was a comparatively large effort in chromatographic theory through modeling efforts; these presumably became resurgent with inexpensive and powerful computing tools. Finally, an impressive level of activity was noted through the themes highlighted in this review, and this was particularly true with detectors and field instruments.

**REVIEWS, BOOKS, AND GENERAL INTEREST**

Review articles appeared on subjects closely paralleling the previous format here, including highlights with multidimensional chromatography and extraction of information from chromatographic data among others. A noteworthy effort was a review of attempts toward creating unified chromatography, i.e., a single instrument supporting GC, LC, and SFC methods (A1). The long-standing interest in chromatography through specific retention principles was represented by a review of complexation gas chromatography and molecular recognition in separations (A2). Significant amounts of research from the former eastern bloc nations have become conveniently available as translations, typified by a review on physiochemical fundamentals of capillary gas chromatography (A3), where emphasis was given to retention mechanisms. A third area of advance, that of data extraction from chromatographic information, was reviewed for artificial intelligence tools (A4) and multivariate mathematical models for evaluation of retention data matrix (A5).

Multidimensional gas chromatography received substantial treatment, with reviews reflecting the growing interest in GC–GC or liquid chromatography (LC)–GC and the creation of a substantive body of experience and research. A broad argument for multidimensional separations focused on a comprehensive approach with theory (A6), and others presented reviews with specific applications to aromas (A7) and environmental samples (A8). A multiple detector alternative to multiple columns was presented and reviewed (A9).

Reviews on chromatography with emphasis on uses directed toward specific materials were published and are included here since the presentations may provide insights into limitations and basic challenges in GC. The articles were directed toward pheromones (A10), odorants in foods (A11), pesticides (A12), and anesthetic gases (A13).

Two books published during this review cycle included a discussion of the theory and practice of headspace sampling with GC (A14) and a GC/MS handbook with little fundamental and wholly pragmatic importance (A15). The presentation of data in this handbook reflects the need for continued work in artificial intelligence in data treatment per section below.
SOLID ADSORBENTS AND SUPPORTS

Several types of liquid phases have been reported during this review cycle and include synthetic organic phases, chiral and natural phases, inorganic salts, and metal-based phases. As in prior reviews, discussions in this section have been restricted to reports in which solid adsorbents are discussed or characterized with emphasis on new or modified materials. As in past reviews, inverse gas chromatography (IGC) was an important method for investigating surface structure and interactions between solid surfaces and probe solutes.

Natural Adsorbents. The effect of nanotexture on the adsorption and chromatographic properties of carbon adsorbents was evaluated (B1). In this study, the arrangement of hexagonal layers in the nanostucture of carbonaceous materials was determined to help their adsorption and GC properties. The intramolecular interactions in GC on carbon black coated with monolayers of hydrocarbons with different electronic structures was also explored (B2), and a series of novel GC graphite-coated capillary columns were evaluated by using polarity parameters (B3). A hexafluoropropylene epoxide-coated graphitized carbon black adsorbent was used to determine the retention characteristics of 13 heavier than ethane-based and eight ethene-based halocarbon fluids (B4). The relative retention data were fitted to linear models for the purpose of predicting retention behavior of these compounds to facilitate chromatographic analysis. Also, a similar hexafluoropropylene epoxide-modified graphitized carbon material was used to determine the Henry's law gas-solid second virial coefficients for hydrocarbons, chlorofluorocarbons, ethers, and sulfur hexafluoride with a microporous carbon adsorbent (B6). The thermodynamics of gas adsorption on coal was also studied (B7). Others attempted to alter or improve carbon black adsorptivity through surface modifications with a high-frequency plasma (B8).

Modified GC equations were studied with nonporous silica particles packed into fused silica capillary columns (B9), and the adsorption properties of silica gels with chemically bonded aminopropyl and guanidinoethanethiol groups were also investigated (B10). Column packing containing N-benzylthiourea copper(II) complexes chemically bonded to silica supports were used to study the specific interactions of this modified silica with electron-donor adsorbates such as ketones, ethers, and nitroalkanes (B11). More recently, the same investigators studied the adsorptive properties of silica chemically modified by Cu(II) complexes via amino groups (B12). The surface of silica was also modified using octadecyl (B13, B14), amino, and guanidino groups (B15). A review on molecular statistical modeling and gas chromatographic studies of hydrocarbons on modified layered silicates and silica in the Henry's law region was reported (B16). The results of this study can be used to develop new, efficient adsorbents and supports based on layered silicates and silica. A salt-modified silica gel adsorbent, coated with disodium hydrogen phosphate, was also studied (B17). The dispersive and specific adsorption energies of alkanes (B18) and benzene on silica gel were also studied (B19). Other types of silicas, amorphous silicas and crystalline silicic acid, were evaluated for their alkane adsorption energies (B20). The value of the surface energy of the crystalline silicic acid was found to be higher than that of the amorphous silicas, because of the possibility of a partial adsorption of alkane chains between the layers of this silica.

Reports on other natural adsorbents and supports, including alumina, quartz, various types of clays, and cellulose, were given during this review period. The diffusion of ethyl methyl ketone, methyl alcohol, and acetaldehyde vapors on alumina was studied (B21). Carbon-modified aluminum oxide columns were used to separate saturated hydrocarbons (B22). In this report, the investigators found that the adsorption capacity of adsorbents with respect to saturated hydrocarbons increases significantly with carbon content. A study on the adsorption of water vapor on activated alumina also appeared (B23). This report indicated that a molecule of water is bound to two adjacent hydroxyl groups. Others evaluated aluminum oxide-coated porous layer open tubular columns for the analyses of propylene and ethylene (B24). Others studied the adsorption of gaseous chlorides and oxochlorides on quartz chromatographic columns (B25).

The effect of thermal and chemical treatments on the variation of specific surface area of porous bentonite as a support in gas chromatography was studied (B26). These processes changed the surface structure of bare bentonite and contributed to a good separation of hydrocarbon mixtures. Others modified diatomaceous supports with phenol—formaldehyde, polyoxyalkylene—polyurethane, polymethacrylate, and epoxy resins to investigate the possible use of the obtained sorbents in gas chromatography (B27). A method for the deactivation of diatomaceous solid supports based on the adsorption of polyethyleneimine and cross-linking by a bidentate reagent was also reported (B28). The retention ability of different types of solid supports with respect to active agents was studied using NaX-type zeolites (B29). The relative contribution of the zeolite to the overall adsorption of certain hydrocarbons was determined. The kinetic parameters for the ring opening of cyclohexane over modified ZSM-5 zeolites were also studied (B30). The separation of aliphatic alcohols was successfully performed on a packed column with a support coated with cellulose tribenzoate, and GC temperature programming improved the separation (B31). A report showed the selectivity of a saltwater stationary phase for the separation of mono- and polyhydroxy isomers on a chromatographic column containing the stationary phase CaCl$_2$·H$_2$O (B32). In summary, the studies suggest a high level of sustained development and discovery of natural materials to be used for separations in GC methods.

Synthetic Adsorbents. Inverse gas chromatography was utilized to investigate properties of several materials. Reports that used IGC included the following: the structural characterization of the deactivation of silica surfaces with a silanol-terminated polysiloxane (B33); the examination of acid—base and some other properties of solid materials (B34, B35); the estimation of surface energy of modified TiO$_2$ pigments (B36); the surface characterization of cellulose fibers (B37); the determination of the properties of the films formed by organic substances on a silica gel surface (B38); the measurement of the surface energies of spherical cellulose beads (B39); the determination of the chemical and morphological characteristics of inorganic sorbents with respect to gas adsorption (B40); the characterization of the cork surface (B41); the determination of intermolecular interactions for hydrocarbons on Wyodak coal (B42); the assessment of the surface energies of theophylline and caffeine (B43); the estimation of the
thermodynamics of adsorption of n-alkanes on maleated wood fibers (B44); the investigation of surface properties of protective coatings of optical fibers (B45); the study of the physicochemical properties of polypyrrole–silica nanocomposites (B46); and the determination of the surface properties of illites and kaolinites (B47). In addition, surface adsorption isotherms, solubility parameters, thermodynamic interactions, and glass transitions were all characterized using IGC for several new polymeric materials (B48–B62). Other studies showed the adsorption and gas chromatographic properties of microspherical hyper-cross-linked polystyrene sorbents (B63). The highest retentions for various types of organic compounds were observed on polymer microspheres with the highest degrees of cross-linking. In another report (B64), the adsorption properties of the porous polymers Porapak R and Porapak T were studied. Others studied the adsorption of various organic compounds, including alkanes, aromatic hydrocarbons, aldehydes, ketones, and esters, on Porolas polymers (B65). The vinyl chloride adsorption properties of the polymer poly(vinyl chloride) were also studied (B66). Others reported the structure and gas chromatographic properties of new sorbents prepared by the radiation-stimulated polymerization of 2-butyne-1,4-diol, 2,4-hexadienoic acid, and 1,2,3-propenetricarboxylic acid on the surface of polysorb-1, a styrene–divinylbenzene copolymer (B67). The retention properties of 15 hydrocarbons on a new GC stationary phase, poly(perfluoroalkyl ether), were also reported (B68). The hydrocarbon–perfluoro compound interactions showed pronounced positive deviations from the ideal behavior and can be attributed to repulsions between the hydrocarbon and the perfluorocompound segment. In another work (B69), quantitative structure–retention relations in GSC were employed as a method to study the inclusion properties of the p-tert-butylcalix[4]arene phase in a micropacked column. Synthetic inorganic materials were the subject of one study that reported the use of thorium bis(monodecyl phosphate) as a GC adsorbent (B70).

**LIQUID PHASES**

**Synthetic Organic Phases.** The interaction capacity of 26 liquid GC stationary phases ranging from squalane (retention polarity = 0) to bis(cyanooxethyl)formamide (retention polarity = 144.6) was reported (C1). Several liquid crystals were studied as possible stationary phases in GC. The separation properties of hydrocarbons were examined with AVIK-85 (a tetrahydroxyquinone derivative) on Chromosob-W and Silochrom C-80 supports (C2). The same AVIK-85 liquid crystal was evaluated through various cycles of heating and cooling of a chromatographic column (C3). Other liquid crystal phases were evaluated for the separation of 2,3,7,8-substituted chlorinated dioxin isomers in capillary columns (C4), the separation of isomeric phthalic acids (C5), and selectivity for polycyclic and aromatic compounds (C6). Others compared two azobenzene liquid crystal stationary phases in open tubular column GC for the isomeric separation of various types of organic compounds (C7). The separation of positional isomers of aliphatic, aromatic, and polyaromatic hydrocarbons of three laterally substituted liquid crystal stationary phases was also reported (C8). A review with 101 references on the development of liquid crystals as stationary phases in GC was given (C9). This review includes the classification of liquid crystals for GC (e.g., nematic, smectic, cholesteric, low-molecular, high-molecular, crown ether, and macromolecular crown ether liquid crystals).

Several GC stationary phases containing crown ethers were reported (C10–C12). Two new chiral polysiloxanes containing crown ethers were prepared for capillary GC (C10). Others reported good separation of C1–C6 alcohols and of the ethyl esters of C1–C6 carboxylic acids when using benzo-15-crown-5 as stationary phase (C11). A new calixcrown polysiloxane GC stationary phase was synthesized (C12). This phase, in which the calixcrown monomers lie in the main chain of polysiloxane, showed good separation properties for nitro-, chloro-, and methyl-substituted benzene or phenol isomers. Other new developments with liquid phases were made with more traditional polymers, such as dicyanobiphenyl polysiloxane stationary phases (C13). Others evaluated chemically bonded squalene phases for the separation of hydrocarbons (C14, C15). Also, the effect of the dioxa[11]-paracyclophane group in polysiloxane stationary phases was examined (C16). The incorporation of n-alkyl groups on cyclic siloxane bonded phases was also studied (C17). The incorporation of octyl and octadecyl groups on the siloxane skeleton greatly improved the retention capacity for light hydrocarbons. This behavior was due to the high surface coverage of the packing material and, thus, to a better solute–stationary phase interaction. In addition, the effect of alkylbenzene groups (C18), N-alkylimidazole groups (C19), and phenyl groups (C20) in polysiloxane stationary phases was investigated. Others examined the possibility of using three polar-type liquids containing (methyl)oxyalkane, cyanalkane, and alkanethiol groups as GC stationary phases (C21). Chemically bonded cyclic organosiloxanes–silica gels were evaluated (C22) for possible use in microcolumn GC of light hydrocarbons. Two reports appeared on the use of dicumyl peroxide for the cross-linking of GC stationary phases (C23, C24). Two related studies (C25, C26) showed the variation of selectivity among many polysiloxane stationary phases for GC. The selectivity differences were explained in terms of differences in the cohesive energy of the solvents and their capacities for dispersion, dipole-type hydrogen bonding, and electron pair complexation interactions. These reports concluded by speculating on the needs for new phases to explore the full selectivity potential in GC. Others evaluated resorcarene derivatives for the separation of substituted benzenes (C27), and 1(R)-trans-N′-1,2-cyclohexylenebisbenzamide for the separation of l-2-hydroxyglutaric acid in urine (C28).

**Chiral Phases and Natural Phases.** As in the previous review, the most prevalent phases in this section were based on cyclodextrin and cyclodextrin derivatives (C29–C64). Cyclodextrin and modified cyclodextrin stationary phases were used for the separation of stereoisomers of 3,4-diphenylcyclopentene (C29), methyl 2-chloropropionate (C30), volatile compounds in oils (C31–C33), PCBs (C34), organophosphorus chemical warfare agents (C35), xylenes (C36), fatty acid methyl esters (C37), furanoids (C38), aromatic alcohols (C39), di- and trisubstituted benzene (C40, C41), methyl and phenols (C42), α-camphorone and fencholone derivatives (C43), amino alcohols (C44), and DDT (C45). The mechanisms of separation of cyclodextrin and modified cyclodextrin stationary phases are based on van der Waals forces (C46), hydrogen bonding (C47, C48), sizes of the inclusion cavity (C49–C51), polar interactions (C52–C54), and
steric interactions (C55). Others found a synergistic effect when cyclodextrin stationary phases were mixed with resorcarene (C56), and the necessity of an aromatic system for enantioselective separation of phenoxypropionates on β-cyclodextrin stationary phases was determined (C57). In addition, cyclodextrin and modified cyclodextrin stationary phases were examined to determine the contribution of thermodynamic parameters to chiral resolutions (C58–C60), the influence of diluting the phases on enantioselectivity (C61–C63), and the influence of structural characteristics on chiral selectivity (C64).

The adsorption properties of a GC glucose-modified silica surface were reported (C65). The additional glucose modification increased the adsorption potential for molecules with polar functional groups. The resolution of enantiomers of various compounds was evaluated using l-valine-tert-butylamide (C66, C67), chirasil-Val (C68, C69), l-tert-leucine-tert-butylamide (C70), and tripeptide derivatives (C71).

**Inorganic Salts and Metal-Based Phases.** The chromatographic properties of stearyl-1-α-naphthyl acetate were examined as a GC stationary phase (C72). This phase falls in the medium polar category and can be a versatile, easily available phase for GC. A GC stationary phase containing chiral chelates of europium was found to exhibit high selectivity for nucleophilic solutes (C73). Successful enantiomeric separation of selected alcohols and ketones was obtained. However, no separation of chiral compounds containing double bonds and chloro aliphatic compounds was observed. Others evaluated copper(II) chelates of tetradeionate β-ketomaines as GC stationary phases (C74). These phases showed a high potential for the separation of alcohols, ketones, and heteroaromatic compounds. The complexing GC stationary phases containing tris[3{[(trifluoromethyl)hydroxymethylene]camphorato}]-derivatives of lanthanides were also characterized (C75). In another report (C76), IGC was used to determine the solubility and polarity parameters for pyridinecarboxamides and their complexes with copper(II).

**CHROMATOGRAPHIC THEORY**

The major themes for this section are based on studies where chromatographic behavior is associated with the molecular structure of solute or stationary phase and the connections between thermodynamic parameters on efficiency, resolution, or retention.

**Structure–Retention Studies.** A high level of vitality was noted in this subject, with over 73 articles on a main premise: Can retention times be predicted from molecular structure? Three descriptors or guides for linking structure to retention have emerged: topologic, geometric, and electronic terms (D1–D4). In general, these tools are still in a semiempirical stage of development, where the models are being developed through correlations between retention indexes and molecular details. In other models, molar volume and solubility parameters have formed the basis of correlations (D5). Still others have used selected descriptors, including topologic (D6), electronic interactions (D7), conformations (D8), and van der Waals volumes (D9). In these, molar volumes appear to be an influential descriptor (D10, D11), except where gas solid chromatography was involved (D12).

### Table 1. Examples of Physicochemical Parameters for Solution Studies Using Gas Chromatography

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<td>Partition coefficients of benzenes and essential oils</td>
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<td>Activity coefficients and Flory–Huggins interaction parameter</td>
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<td>Partial molar enthalpies of mixing at infinite dilution</td>
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<td>Equilibrium vapor pressures of C40–C60 aldehydes</td>
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<td>Vapor pressure and heat of vaporization of tetrachlorobenzyltoluenes</td>
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| Other retention models were described and were useful in restricted models for prediction, such as the use of number of chlorines in predicting PCB retention (D13). Others have used carbon numbers in alkyl chains (D14), boiling points (D15), enthalpy (D16), and combinations of these (D17). On the whole, these attempts are directed at fairly narrow variations on structure and will be useful for targeted understandings. In contrast, the works referenced in the previous paragraph have universal significance. Predictions on the role of temperature on retention dates from before the inception of temperature programming, though oven programming has elevated the importance on linking retentions from isothermal and programmed temperature experiments. This has reached an advanced stage of refinement, and some have reported differences of below 1% between predicted and measured retention times (D18–D20). A flexible model, in which temperature plateaus are allowed, showed errors of 4% on retention and 10% on peak widths (D21). An attempt to minimize the number of experiments for such accomplishments was described (D22), and one model included a detailed consideration of column parameters (D23).

General retention within gas chromatography underwent significant advances during the last two years, with noteworthy advances in a unified retention concept (D24), in a universal database (D25), and in classification of stationary phases using Kovats coefficients (D26, D27). These works have a common aim, which is to free investigators from the inconvenience of empirical determinations of retention when various stationary phases are employed. While developments toward this goal seemed promising (D26), interfacial adsorption for polar phases was recognized as a variable which cannot be ignored (D25) and may defeat wishes for a highly refined and broadly applicable set of tools.

**Thermodynamic Parameters.** The subject of solute–solvent interactions has been a mainstay in gas chromatography for decades, and this area saw active development, even in 1996–1997. Since the studies are often very specific and only together comprise significant importance for GC, the results are summarized in Table 1. The listing demonstrates that GC has been maintained as a research tool for gleaning constants and physical terms for molecular events or properties.
COLUMNS AND COLUMN TECHNOLOGY

The major themes of this section are new developments and improvements in column designs as well as new attempts at creating columns for evaluation of chromatographic principles or for enhanced selectivity. A review with 11 references appeared on the use of metal capillary GC columns as an alternative to fused silica columns (E1). A new wall-coated open tubular metal column was developed for the separation of petroleum-derived waxes and high-molecular-mass linear alcohols and acids (E2). Others made new inert stainless steel capillary columns by a multigradient layer technology (E3). Also, a new deactivated metal capillary GC column was used for the determination of trace amounts of triazolam in serum (E4). This metal column exhibited excellent thermostability at high temperatures. Several new GC porous layer open tubular (PLOT) columns were also reported (E5–E10).

Some characteristics of these new PLOT columns included the in situ polymerization of the monomer (E5, E6), a new method of silica modification (E7), a less reactive column which is sufficiently inert to separate volatile chlorofluorocarbons (E8), a charcoal-based column capable of resolving light hydrocarbons (E9), and an ultrafine zeolite-based column with high speed and selectivity (E10). Others also reported the preparation of a zeolite membrane PLOT column by in situ synthesis (E11). A new type of SCOT column with ultrathin zeolite was also described (E12). The ultrathin zeolite had a fine and uniform particle size, large specific surface area, regular crystal structure, and similar chemical constitution to glass. Two new methods for the preparation of microcolumns were also evaluated (E13, E14). These columns contained cross-linked, bonded polysiloxane stationary phases of well-defined thickness (E13) and aminopropylsilyl dichloroamide bonded phases (E14). The use of a short microcapillary GC column (i.d. = 50 μm) for rapid triglyceride analysis in fats and oils was reported (E15). Open tubular GC columns were used to correlate GC equations with thermodynamic parameters (E16) and to determine the adsorption mechanism of n-alkane retention with various liquid stationary phases (E17). Also, a super long open tubular GC column (450 m long, 200 μm i.d.) was developed for the separation of gasoline (E18). The column had 1.3 million effective plates and was built up by connecting nine 50-m columns in series. This new column resolved up to 970 components in a standard gasoline. A dynamics study on a new GC two-dimensional packed-capillary column was reported (E19). In the two-dimensional system, the column efficiency was determined by the solute's retention time and the ratio of peak spreading in the precolumn and the main column. It was concluded that, in order to improve column efficiency, matching of the precolumn and main column conditions was necessary. Others reported (for the first time) the chemical modification of open tubular columns with a functionally selective immobilized stationary phase (E20). The column modification was performed by the oxidation of the polystyrene with nitric acid. The optimization of temperature-programmed GC separations using off-line simplex optimization and column selection was studied (E21). This study indicated that fully off-line simulation and optimization of single ramp and multiramp temperature-programmed GC separations as well as column selection was possible. A subambient GC temperature programming method using two isothermal gas chromatographs was also reported (E22). Another report in this area was the development of a thermal desorption modulator for GC (E23). In addition, automatic thermal desorption in GC was used for the analysis of volatile food components (E24, E25). A new GasPro GC PLOT column for the separation of gases and highly volatile compounds was reported (E26). A comparison was made between the GasPro column and a conventional doped aluminum oxide capillary column. The GasPro column was not adversely affected by water, carbon dioxide, and sulfur gases, and it appeared to be more inert than the aluminum oxide column, since it did not cause decomposition of most reactive analytes. Also, a new type of quartz-lined aluminum capillary GC column coated with graphitized carbon black was prepared (E27). This new column was resistant to drastic acid or alkaline treatments, and it was evaluated for the analysis of amines, VOCs, and oil products. Others reported a new type of high-performance submicroparticle packed column (E28). This column was found to have properties similar to those of capillary columns for the analysis of high-boiling-point compounds at relatively low column temperatures. A packed glass capillary column with multicores was also prepared and was shown to have a better permeability than conventional packed capillary columns (E29). In addition, a GC capillary column which can be directly heated by an internal chromium/nickel wire was developed (E30). The separation of C1–C4 hydrocarbons was demonstrated with this column, and it was compared to conventional column oven heating. High-temperature GC capillary columns, which can be used up to 360 °C, were prepared and characterized (E31). Others developed a new type of strongly polar organic polymer PLOT column by in situ copolymerization of acrylonitrile and divinylbenzene (E32). Also, a way of controlling the maximum allowable oven temperature during on-column injection by the column pressure drop was suggested (E33). In this report, an arrangement using a restrictor at the column outlet for adjustment of the column inlet pressure.
was evaluated. The polarity and adsorptivity of nondeactivated GC capillary surfaces were tested (E34). The effect of various leaching and etching procedures used for column preparation, as well as the stability of uncoated fused silica precolumns toward water and some organic solvents, was studied in this report.

**MULTIDIMENSIONAL GAS CHROMATOGRAPHY**

The growing trend in multidimensional gas chromatography was distinguished during this review cycle by advances in the subject of modeling and optimizing two-dimensional gas chromatography and by a dramatic increase in liquid chromatography (LC)–GC techniques. Applications continued to lead in all reports, as true throughout gas chromatography literature everywhere, though the foundations of a systematic methodology are being explored, fortunately. Automation and hardware were minor themes, in contrast to reports from the past decade.

Models and optimization constitute an encouraging development in multidimensional gas chromatography, since, without foundational tools for designing methods or interpreting results, the subject will remain in a highly empirical condition. The article that best represents this involved modeling retention and separations in three capillary columns (F1). In three other articles, a main theme was optimization of selectivity in two-dimensional GC (F2–F4). These articles are not directly available in English and are noted for their importance in the development of multidimensional gas chromatography. Elsewhere, attempts to maximize 2-D GC were made by exploiting thermal modulation for complete characterization of every peak eluting from the first column (F5, F6).

A remarkable activity in the coupling of LC with GC has occurred, despite a first impression of apparent incompatibility in strengths of LC for large nonvolatile molecules. However, in nearly all reports for LC–GC, the liquid chromatograph was used principally for prefractionation of a complex mixture to isolate a targeted GC-compatible substance. Examples include polycyclic aromatic hydrocarbons (F7, F8), alcohols and sterols (F9), morphine and analogues (F10), PCBs and pesticides (F11), β-blocker (F12), and thiols and other sulfur-containing compounds (F13). Though these are application-driven reports, they are noted here to document the activity in one future direction for multidimensional gas chromatography and the relevant basic research needs.

A persistent subject in multidimensional gas chromatography has been the hardware to combine multiple columns without degradation in peak shape and automation of instrumentation. This was a weakly active area in the last review cycle and is best typified by interest in valve connections or traps between columns in GC–GC (F14, F15) and LC–GC (F16). A noteworthy variation from linearly coupled columns is that of parallel columns, after a precolumn, with a single detector (F17). In this work, retention behavior was modeled and was 0.3–0.6% of predictions.

Enhancements in confidence or specificity of detection via resolution with two stationary phases was and remains a motivation for multidimensional gas chromatography. Consequently, the literature in this subject is weighted toward applications, as is true in all of gas chromatography. A few articles illustrate a mixture of application and critical evaluation, such as the comparison of LC–GC versus the official analytical method for steroideal hydrocarbons in edible oils (F18). In another article, the conditions of sampling the first column were explored relevant to recovery of reference standards in determination of polychlorinated biphenyls (F19). Finally, the linearity and precision for LC–GC were documented using phyrethroid insecticides in fruit extracts (F20). Recoveries were good, and reproducibility was high (0.6–6.6%).

**DATA PROCESSING AND QUANTITATIVE ASPECTS**

Previously, data processing was regarded as a means to provide insights into chromatographic events, and the efforts were limited in scope. During this last review cycle, a remarkable surge occurred in reports on data processing. This occurred in both the scope and the number of studies. The causes for this vitality and diversity are unknown but might be attributed to the availability of powerful and affordable computers.

**Optimization and Simulations.** Optimizations and simulations represented a significant portion of work in this section and included an examination of signal processing, such as the performance of digital processing for selected ion monitoring (G1). Computer modeling was used for optimizing column parameters via commercial software (G2) and through neural networks (G3). Selectivity in GC was optimized and verified experimentally through simplex methods, enhanced through the use of a polynomial gleaned from preliminary measurements (G4).

Advances in comparison of retentions were made using thermodynamic retention indexes (G5) and used with simulations to explore separations by GC (G6). Predictions of numbers of components were accomplished via a statistical model of overlap (G7). The high level of current capabilities in the overlap between computation and separations is illustrated by simulations of retention for highly complex mixtures (G8) and for simultaneous programming of temperature and column head pressure (G9).

**Pattern Recognition and Artificial Intelligence.** As in past activity within this section, multivariate data analysis has been used powerfully with complex mixtures, suggesting that tools exist for coping with the large information density presented by high-resolution chromatograms. Thus, data processing has become an element of foundational significance in handling chromatographic data, extending and expanding the meaning of chromatographic resolution. Also, as in the past, the best examples come from complex natural or environmental samples. These have included blueberries (G10), orange juice (G11), microbial defects in milk (G12, G13) and fresh cabbage (G14) for foods. Neural networks were found to correlate sensory evaluation with chromatographic headspace analysis with good success (G15). Complex processes of weathering for a complex sample, jet fuel, were successfully modeled and linked to discriminant functions, demonstrating the advanced role of artificial intelligence methods with chromatography (G16). Similar success was obtained with plastic-bonded explosives (G17). These routes to data processing are sufficiently mature to become common tools for ordinary GC studies.

An ancillary challenge to handling complex data sets for refined understanding of total composition or sources assignment is the extraction of specific information from simple or complex chromatographic data. Information theory and calibration standards were used to establish chromatographic performance (G18), and throughput increases were controlled with an expert system.
Chromatographic separation was also established using simplified Fourier analyses, with additional benefits of disclosing overloading effects (G20). Extraction of information from GC/MS screenings was accomplished automatically with low S/N levels (G21) and through differential results (G22). The automatic retention index comparison attracted some effort, including a merging of isothermal and programmed data sets (G23) and the use of diverse literature sources (G24). Such advances will be necessary for full exploitation of chromatographic data in chemical identifications, as typified by a new software program (G25).

Quantitative Aspects. The subject of quantitative determinations by GC received small but refined examinations during this review cycle. For example, the influence of matrices on pesticide determinations was addressed (G26). Matrices can reduce losses of pesticides on surfaces, and matrix standard calibration solutions were described. In another work, the signal associated with a chromatographic blank was obtained through use of background noise, suited to further statistical evaluation (G27). The determination of morphine in opium using complex pyrolysis chromatograms was advanced using principle component analysis and provided quantitative results (G28). Quantitative determinations with gas chromatography—mass spectrometry were also explored and characterized for variance from various steps of an entire method for cholesterol. Not surprisingly, sample collection and preparation contributed the bulk of variance, and the instrumental determination was less than 30% of the total (G29). Methods for testing scanning mass spectrometry for linearity of response were presented (G30), and minimum detection limits were approached using principal component analysis (G31).

HIGH-SPEED AND PORTABLE GAS CHROMATOGRAPHY

In recent years, the need for rapid and portable analytical measurements has led to the development of gas chromatographs with fast separation times and small instrumentation (H1). Several recent reviews examined the techniques for increasing analysis times in GC, such as using short narrow-bore columns (H2, H3) and optimizing the mobile phase parameters (H4). Theoretical expressions for typical high-speed gas chromatography (HS-GC) conditions have been derived and compared with the Van Deemter equation (H5). Differences were found due to the higher pressure drop across the column for HSGC. Conventional GC instruments have been reviewed for compatibility with HSGC conditions (H6), and one major problem discovered was due to slow data acquisition rates and large amplifier constants (H7).

New commercial HSGC systems have been presented which utilize smaller thermal ovens (H8) and innovative column heating arrangements (H9). Column heaters based on resistive heating were shown to be compact, utilize minimal power, and decrease sample analysis times (H10). Resistive-heating combined with temperature gradients along one column (H11) resolved 13 compounds with baseline separation in 3.5 s (H12) and was shown to be compatible with the addition of a second column (H13). Dual-column HSGC has been investigated for both the theoretical possibilities (H14) and its applications (H15). Two-column separations with high-resolution mass spectrometry (HRM S), improved sensitivity, short analysis times, and decreased costs of analysis were obtained for a series of pesticides (H16). Multidimensional HSGC showed low-capacity factor compound separations (H17) with many possible applications (H18). Two columns with opposite stationary phases (polar and nonpolar) were optimized by adjusting the midpoint pressure to attain maximum resolution for a critical pair (H19).

Injection techniques for HSGC must provide narrow bandwidths due to fast analysis time requirements without compromises in resolution (H20). Cryogenic inlets were the most popular method of introduction. Two cryofocusing inlets provided bandwidths between 5 and 10 ms (H21). A cryogenically controlled microloop gave bandwidths of <10 ms (H22) and was compared with a capacitance-heated metal cryotrap in a recent study (H23). A cryotrap/thermal desorption inlet with 10 different deactivated tubes was evaluated and found to provide minimal thermal decomposition in 6 of the 10 tubes (H24).

As with injectors, compatible detectors for HSGC must be fast enough to resolve narrow peaks, which requires minimal dead volume and fast electronics (H25). When a mass spectrometer is coupled to HSGC (H26), fast scanning rates are necessary, and scanning rate limits of ~25 000 amu/s have been shown when a quadrupole mass filter was implemented (H27). Utilizing a fast double-focusing mass spectrometer showed improvements in both detection limits and interferences (H28).

One tradeoff for HSGC is the loss of capacity due to the smaller diameter and shorter columns. Application of packed capillary columns in HSGC has been shown to improve capacity and selectivity (H29) while obtaining high-speed separation for light hydrocarbons (H30). By implementing supercritical fluid/gas chromatography conditions along the column, less volatile compounds can also be separated by using packed capillary columns (H31). A multicapillary column improved capacity while maintaining the efficiency obtained with small internal diameter columns (H32).

Many portable HSGC instruments are being used for on-site analysis (H33). A micro-GC coupled with a thermal conductivity detector (TCD) was shown to separate C02 and C1–C6 alkanes within 30 s. Petroleum industry application included detection of H2S and COS impurities (H34) and rapid screening for gasoline to diesel range organic compounds (H35). Environmental problems are a major application for portable GC systems due to the complexity of the samples (H36). Recent separations in this area include separation of multiple pesticide residues in agricultural products (H36), air analysis (H37), and the detection of polychlorinated biphenyls (PCBs) (H38). Other applications which have recently been tested with HSGC involve leak verification (H39), identification of pesticides in plasma samples (H40), and separation of thermally labile steroids, carbamates, and drugs (H41).

Because gas chromatographic instruments can be made light and energy efficient, considerable emphasis over the past two years has been placed on developing portable gas chromatographs for the separation and detection of target compounds in the field (H42). Gas chromatographs have been developed which are truly portable, with approximately 100 W of power at peak-to-peak power consumption (H43). More importantly, small GCs are not limited to operation in the field. In the laboratory, they have the advantages of operation with minimal consumption of utilities such as compressed gases, electricity, space, and so forth.
The primary focus of research and development in field gas chromatography (FGC) during the past two years has been instrument miniaturization. The ultimate miniature FGC system was designed and developed using Si micromachining and integrated circuit processing techniques (H44). The chromatograph consisted of a 10-μm-long sampling loop, a 0.9-m rectangular-shaped column, and an injection loop and column each with a width of 300 μm and height of 10 μm. The column was coated with a 0.2-μm thickness of Cu phthalocyanine as the stationary phase. Detection was based on a dual detection scheme using a coated chemiresistor and thermal conductivity detection. The complete FGC system was packaged in less than 23 cm² and was 2.5 mm high. Although limited in scope to the detection of ammonia and nitrogen dioxide, this miniature chromatograph offers exciting possibilities for future field instruments.

One of the more novel approaches reported for FGC during the review period was the miniaturization of a tandem GC instrument (H45). This potential field-portable GC–GC method of separation involved dynamic coupling between two short capillary columns. Each column could be independently optimized with regard to temperature and flow rate. Dynamic coupling was accomplished by automated vapor sampling (AVS) techniques. Thus, a slowly eluting GC peak from the first column can be rapidly sampled into the second column, providing a two-dimensional separation of complex samples. The feasibility of this tandem GC approach was demonstrated by two-dimensional separation of C5−C6 ketones. Other miniature FGC systems have also been reported (H46, H47). A detachable column cartridge was developed which permitted the substitution of columns in the field (H48).

The most common uses for field gas chromatography (FGC) have been in the determination of volatile and semivolatile organic compounds in the atmosphere. Target compounds for on-site screening by FGC include benzene in complex environments at the ppm level (H49), dimethyl sulfide (DMS) and carbon disulfide (CS2) (H50), and polychlorinated biphenyl (H51). Indoor air pollutant such toluene, α-pinene, and 1,4-dichlorobenzene were determined, with detection limits in the low microgram per cubic meter level (H52), and long-lived species were identified in the upper troposphere and lower stratosphere (H53). Methylphosphonic acid esters were detected at the 5 ppb level in air (H54). Other volatile organics compounds (VOCs) in the atmosphere (H55) were targeted, as well as soil gases containing BTEX and chlorinated solvents (H56). Chemicals for chemical weapons convention treaty verification (H57) and explosives in air from a walk-through sampling module which provides automatic screening of humans at rates of 10/min (H58) have been screened by FGC. These chemicals encompass a wide range of vapor pressure and chemical properties.

Problems associated with FGC have included the fluctuation of retention times and the nonreproducibility of injections. Humidity may also affect the results of analyses (H59). In general, however, understanding the difference between field screening and field analysis can reduce the problems associated with field measurement (H60). By adjusting the data quality requirements with the time requirements, optimal parametric conditions can be selected in which reliable on-site data can be obtained. In efforts to minimize problems associated with field GCs, several instrumental control methods have been developed for more precise control of the operating temperatures and gas flow rates (H61, H62). One approach for improved injection technologies is called thermal modulation (H63). Thermal modulation was produced from the rotation of a heater element over a capillary column. This rotation accumulated the analyte and then focused it into a sharp concentrated pulse, injecting the pulse onto the GC column. Because the modulation was produced from a controlled rotation of the heater module, repetitive and reproducible sample injections were possible.

One major problem of FGC when compared to laboratory-based instrumentation is the reduced resolution that most field instruments exhibit. This reduced resolution is compensated for, in part, by the use of selective detectors. Detectors such as the electron capture detector (H48), the photoionization detector (H47, H64), and a miniature dual flame photometric detector for phosphorus and sulfur compounds (H57) have all been interfaced to field gas chromatographs.

The most versatile selective detector for GC is the ion mobility spectrometer or detector; recently, it, too, has been coupled to gas chromatographs for field analysis (H65, H66). A new hand-portable GC/ion mobility spectrometer has been constructed and named the EVM II (environmental vapor monitor). The unique feature of this instrument was the GC column-to-source interface, in which a transfer line was used as the chromatographic column. The concept has led to the term transfer line gas chromatography (TLGC). The utility of this hand-held GC ion mobility detector was demonstrated by the separation and detection of chemical warfare agents such as DMMP within 20 s (H67). One interesting application of GC/ion mobility spectrometry was for the determination of fish freshness (H68, H69). The presence of 1,5-diaminopentane (cadaverine) was detected after 4 days, indicating the on-set of fish decay. Coupling an automated vapor sampler with a transfer line gas chromatograph (AVS-TLGC) and an extremely small ion mobility spectrometry detection device (15 in.²), an attempt was made to construct a personal chemical hazard detector (H70).

Mass spectrometry is a mature technology and, perhaps, the ultimate GC detector, but due to size, vacuum, and energy requirements, it has been limited as a field method. Nonetheless, considerable attention has been paid to the development of this technique due to the tremendous benefits that field portable gas chromatography/ mass spectrometry would provide. One portable GC/mass spectrometer was contained in a standard size suitcase, weighed about 70 lbs, and required about 600 W of energy for operation under peak load conditions (H71). Such a portable GC/MS system can be transported to a clandestine laboratory for the on-site identification of illicit drugs and other related compounds (H72). A “roving” GC/MS, mounted on a golf cart, was capable of analyzing up to 1000 samples/h while traveling at a speed of 20 mi/h (H73). Portable GC/MS instruments were also used for industrial hygiene applications (H74). The primary advantage of portable GC/MS instruments is the large number of applications for with this method is useful. As the need for field measurements increases and mass spectrometry becomes miniaturized, the number of field portable GC/MS systems can be expected to dramatically increase.
GAS CHROMATOGRAPHIC DETECTORS

In addition to high resolution and speed, gas chromatography offers the considerable advantage of interfacing with a wide variety of detection methods. The myriad of detectors available for gas chromatography can be separated into two primary categories: ionization detectors and optical detectors.

Ambient Pressure Ionization Detectors. Ionization detectors remain the most common devices used to measure analytes separated by gas chromatography. Although these methods are reaching a mature state of development, considerable research activity still exists. Research and development on the following ionization detectors have been reported in the literature during the past two years (listed in order of presentation): the flame ionization detector (FID), the helium ionization detector (HID), the nitrogen–phosphorus detector (NPD), the electron capture detector (ECD), the surface ionization detector (SID), the photoionization detector (PID), the ion mobility detector (IMD), and the glow discharge detector (GDD).

(a) Flame Ionization Detector (FID). The detector workhorse for gas chromatography remains the carbon-selective flame ionization detector. Several new applications for this detector were reported. They included the determination of castor oil fatty acid composition (I1), an Empore disk elution method coupled with injection port derivatization for the quantitative determination of linear alkyl benzenesulfonates (I2), the determination of paracetamol and dicyclopamine hydrochloride (I3), and dual-column hydrocarbon analysis (I4). Related to these routine applications was a simple and efficient method for the determination of retention parameters using a methane marker device (I5).

Developmental advances in FID included several modifications in design. A compact and low-fuel FID was developed for portable GCs (I6). Fuel flow rates were as low as 12–15 mL/min, and oxidant flow rates were as high as 120–150 mL/min. Another improvement to FIDs was reportedly made by the incorporation of a precombustion chamber to mix the fuel and sample gas (I7). Similarly, a premixed FID was developed by adding hydrogen and air at the same flow rate to the outlet of the capillary column (I8, I9). Both hydrogen and oxygen were produced by an electrolyzer that was incorporated into an FID design (I10). This electrolyzer flame ionization detector (EFID) was similar to a standard FID, except that the flame tip had a narrower bore to prevent flame flashback, and the entire detector structure needed to be maintained at a temperature greater than 100 °C in order to prevent water condensation. Sensitivity of the EFID was similar to that of the FID, but detectivity was improved by a factor of 2.

Other developments included a dual-channel detector in which the effluent from a reactive flow luminescence detector (RFD) was burned to form a tandem, stable, air-rich flame ionization detector, providing dual response of compounds from a single separation (I11). Fundamental research on the FID has included a mechanistic study of the effect of relative molar response (RMR). RMR did not change when deuterium was substituted for hydrogen in most hydrocarbons (I12). The fast response time of a flame ionization detector was modeled (I13).

(b) Helium Ionization Detector (HID). The helium ionization detector (HID) was most often used for the detection of inert gases (I14). In one example, traces of Ar and N₂ were determined in water (I15). A new type of HID based on dc plasma ionization was reported for use with GC (I16, I17) and applied to the determination of flammable gases in coal gas (I18).

(c) Nitrogen–Phosphorus Detector (NPD). The most common GC detector based on the ionization of the analyte in the presence of a heated alkali source is the nitrogen–phosphorus detector. Developed to maturity, this detector was used in a number of novel applications. Quantification of the metabolite dichloroethylcyclophosphamide was preformed after direct capillary gas chromatography without prior derivatization, with a detection limit of 1 ng/mL (I19). Other applications to biological matrices included determination of yohimbine in commercial yohimbe products, study of a dietary supplement alternative to anabolic steroids (I20), nitrate analysis in biological fluids, in which nitrobenzene was produced from the dissolved nitrate (I21), cyclophosphamide metabolites (I22), simultaneous quantification of two antidepressant drugs, fluoxetine and desipramine (I23), and quantification of clozapine (I24) and zolpidem and zopiclone (I25) in human plasma or serum. The NPD was also applied to food analysis for the determination of fungicide residues in cucumbers (I26), herbicides in drinking water (I27), and imazalil residues in lemons (I28). An important environmental application of the NPD was the determination of underivatized nitrophenols in groundwater (I29). Simultaneous determination of 15 organonitrogen pesticides was accomplished with a flame thermionic detector (I30). Also, online determination of organophosphorus pesticides in water by solid-phase microextraction techniques was reported (I31). One approach was investigated for the selective detection of oxygenated volatile organic compounds (I32).

In one, more fundamental study, severe tailing of phosphorus pesticides was found to be associated with the thermionic ionization source and not the column (I33). A novel type of alkali source was reported in which the alkali salt was continuously introduced into the detector as a solution in water by means of a liquid chromatographic pump (I34). This design had the advantage of continuous freshening of the source. Also, an alkali flame ionization detector (AFID) was reported in which an alkali chip was mounted on top of the collecting electrode (I35) or the temperature of the alkali source could be varied (I36). Flame-free ionization detectors were reported which used a heated ionization tube of high-purity alumina (I37, I38).

(d) Electron Capture Detector (ECD). Sensitive and selective for halogenated and other electronegative compounds, the electron capture detector (ECD) remains one of the most widely used GC detectors. Novel applications reported during the past two years include the following: the shipboard analysis of halocarbons in seawater and air for oceanographic tracer studies (I39), the determination of chlorobutanol in mouse serum, urine, and embryos (I40), the measurement of organochlorine compounds in milk products (I41), the identification of pesticides and other organochlorides in water (I42), organochlorine pesticides in edible oils and fats (I43), metabolites from permethrin, and cypermethrin in foods (I44), and the determination of phenols from aqueous solutions as bromo derivatives (I45). A brominated internal standard was found to be useful for the determination of organochlorine pesticides (I46).

In more fundamental studies, a nonradioactive ionization source was compared with a radioactive source. Initially, the
nonradioactive source was found to be 20 times more sensitive than the radioactive source, but after 9 months of use the sensitivity of the nonradioactive source decayed to levels equivalent to the radioactive source (147). In a similar study, it was found that a pulsed discharge electron capture detector, a nonradioactive source, was more sensitive than the radioactive source for most compounds, covered a wide dynamic response range similar to the radioactive source, and demonstrated a temperature dependence similar to that of the radioactive source. A kinetic description of the detector response was provided (148). Amine response in a radioactive source demonstrated that the relative molar sensitivity factor, $T_M$, was correlated with the $pK_BH_1$ of the individual amine (149). Finally, it was noted that the addition of ammonia to the nitrogen makeup gas in amounts as large as 20% increased the response for various chlorinated compounds (150).

(e) Surface Ionization Detector (SID). Over the past few years, surface ionization detectors have been given considerable attention for the determination of organic compounds with low ionization potentials. Recently, however, a novel design for surface ionization detection was reported based on hyperthermal positive surface ionization (151–154). The primary requirement for the operation of this detector was the use of a supersonic free jet nozzle to introduce the sample to a high-work-function surface of rhenium oxide. The primary advantage of this new SID is that it produced a higher sensitivity for all organic compounds, providing a universal GC response. Detection limits of $10^{-13}$ g/s for pyrene and $10^{-12}$ g/s for toluene were reported, with a linear dynamic range of $10^6$. A second surface ionization detector provided a unique sensitivity for tertiary amines, with detection limits down to $10^{-14}$ g/s (155, 156). Finally, a GC/SID system was reported for the detection of underivatized codeine and dihydrocodeine (157), strychnine (158), and various benzamides (159) in body fluids.

(f) Photoionization Detector (PID). Although some method development using PID was reported, such as the monitoring of volatile contaminants in wastewaters (160), much of the research revolved around the development of novel photoionization detectors. One study incorporated the use of selective photoionization detectors with nonselective detectors to provide both quantitative and qualitative information about the sample (161). Another used a variety of rare gases to identify and quantify unknown compounds (162), while a pulsed discharge in He was demonstrated as a He photoionization detector with a selective photoionization mode of operation (163). The measuring chamber arrangement of a photoionization detector was modified by dividing the main chamber into several smaller volumes, permitting these smaller volumes to share a common anode and cathode (164). Benzene relative response factors for the PID were reported in which energy models were developed using HyperChem and compared to experimental data (165).

(g) Ion Mobility Detector (IMD). The number of applications of ion mobility spectrometry as a detector for gas chromatography continues to grow. Over the past two years, much of the emphasis on ion mobility detection after gas chromatography as been in the area of portable analytical instruments. Many of the IMS references are discussed in that section of this review. One major thrust in the development of GC/IMS has been as a personal chemical warfare detector (166). In addition, IMS has been used as a detection method after pyrolysis GC. With this system, bacillus spore detection was achieved through the characteristic pyrolysis decomposition products of the spores, which were identified as dipicolinic and picolinic acid. The detection limit was found to be on the order of 100 ng of bacillus spores (167). Other IMS investigations have included the development of an IMS with an internal gas chromatographic column (168) and IMS detectors using tritium ionization and photoionization sources (169).

(h) Glow Discharge Detector (GDD). A novel detection method investigated for GC was glow discharge ionization (170). The effect of discharge gas on the GC response was reported (171), along with analytical characteristics for organic compounds (172). Glow discharge detectors have also been used as ionization sources for gas chromatography/mass spectrometry (173).

Mass Spectrometric Detectors. Is gas chromatography an inlet for mass spectrometry, or is mass spectrometry a detector for gas chromatography? In past gas chromatography reviews, the former concept prevailed, and the review of GC/MS methods was covered only in the mass spectrometry section. Today, however, given the growth in number of applications for which GC/MS instruments are well suited, the decrease in size and required operator expertise, and the increase in reliability and ruggedness, mass spectrometry has become a simple but powerful detector for gas chromatography. Thus, for the first time, mass spectrometers are reviewed in this section along with other standard, routine gas chromatographic detectors. While all mass spectrometric detectors fall into the category of ionization detectors, they have been split into a separate category in this review due to the breadth of ionization mechanisms and GC applications reported in the literature during the past two years. These mass spectrometric detectors (MSDs) have been separated according to their ionization mechanisms for this review.

(a) Electron Impact Ionization. Electron impact ionization is, of course, the oldest of the ionization methods currently used. Its mechanism is well understood, and the fragmentation patterns produce valuable information for the identification of organic compounds. GC/MS applications using this ionization source have been developed for environmental (174–182), agricultural (183–185), food science (186–188), biological (189–1100), forensic (1101), petroleum (1102, 1103) and industrial (1104, 1105) samples. On a more fundamental level, a novel ionizer was reported (1106), and region II of the a/q stability diagram was used for fast scanning of a linear quadrupole mass spectrometer. The purpose of this experiment was to evaluate this method as a means of detection for high-speed gas chromatography. Scan rates of 1000 scans/s were obtained, with mass spectral peaks resolved over an 80-u range (1107).

Using ion trap mass spectrometry (ITMS) with GC/MS, airborne carbonyl compounds were separated and detected as their pfbha oximes (1108), residues of chlorinated pesticides in eggs of the gray heron were identified (1109), and pesticides in the marine environment at the low nanograms per liter level were determined (1110). Novel developments in ion trap mass spectrometers included a three-dimensional quadrupole ion trap coupled to a capillary GC (1111) and the addition of a sample inlet with a pressure working range from 1 to 1000 mbar (1112).
Isotope ratio mass spectrometry was used with GC for the high-precision D/H measurement from organic mixtures ([113]) and the determination of 15N of N2 and N2O in soil atmosphere ([114]). In general, gas chromatography was coupled to isotope ratio mass spectrometry via a combustion furnace ([115], [116]).

(b) Chemical Ionization. Chemical ionization, a less energetic ionization method than EI, is often used with EI to aid in identifying the molecular ion and to increase the sensitivity of a method. As with the EI source, fundamental investigations of the ionization mechanism have been extensive, but novel GC/MS applications are still being developed. 4-(Carbethoxy)hexafluorobutyl chloride was used for the derivatization of ethylene glycol from human serum. This derivatization product produced a distinct protonated molecular ion peak at m/z of 563, providing an unambiguous confirmation of ethylene glycol ([117]). When ammonia was used as a reagent gas, direct and rapid characterization of paraformaldehydes after pyrolysis gas chromatography was possible ([118]). Solid-phase extraction and positive chemical ionization mass spectrometry were used for the analysis of cocaine and its metabolites ([119]). Other positive chemical ionization methods included identification of higher alcohols in cosmetics ([120]) and the characterization of low-molecular-weight polyethyleneimines ([121]). Negative ion chemical ionization was used to analyze α- and β-endosulfan in biological samples by selectively monitoring the product ions at m/z 35 and 37. The selectivity and sensitivity of negative ion chemical ionization were demonstrated by the direct measurement of endosulfan in mouse brain without purification of samples ([122]). Electron capture negative ion chemical ionization was used for the analysis of 5-methoxytryptamine ([123]).

For improved selectivity and sensitivity, GC was coupled to MS/MS instruments. The primary advantage is that a sharp, well-resolved GC peak is produced for quantitative analysis, and a simple, unambiguous spectrum is available for qualitative confirmation ([124]). With this method, as low as 10 pg of an isotope-labeled amino acid was detected in 20 ng of the endogenous compound ([125]). In another example, phosphate esters in diesel exhaust were detected and confirmed ([126]).

(c) Inductively Coupled Plasma Ionization. A powerful technique for the separation and speciation of volatile organometallic compounds is capillary gas chromatography coupled to inductively coupled plasma mass spectrometry (ICPMS) ([127]). The primary advantage of GC–ICPMS is that the total analyte was transferred into the ICPMS without loss due to nebulization ([128]). Several methods for coupling a GC to an ICPMS have been reported. In one case, the interface did not require any changes in the ICP and could be completed in less than a minute ([129]). For alkyltin compounds, coupling was accomplished with a heated stainless steel transfer line ([130]). A heated transfer line made from quartz was also reported ([131]). Applications of GC–ICPMS have included organometallics from river and harbor sediments ([132]) and the speciation of organolead compounds from environmental waters ([133]). One interesting application was the detection of dimethylselenide in human breath in the range of 80–98 ng/m3 ([134]).

(d) Laser Ionization. Normally, laser ionization methods are used for large nonvolatile compounds. However, the combination of gas chromatography, supersonic beam UV spectroscopy, and time-of-flight mass spectrometry was reported with isomeric-selective multiphoton ionization ([135], [136]).

Optical Detectors. As with ionization detectors, optical detectors fall into a wide range of categories. Atomic and molecular absorption and emission provide multiple approaches for both qualitative and quantitative information from samples separated by gas chromatography.

(a) Atomic Absorption Detectors. Coupling gas chromatography to atomic absorption spectrometry (AAS) provided selective detection for many compounds. Tetramethylene and tetraethylene were used as test analytes in the evaluation of a quartz tube atomizer ([137]). A comparison of GC/AAS with differential anodic stripping voltammetry for organolead was reported ([138]). A simple and reliable method for the detection of organolead compounds in a water sample was developed ([139]). GC/AAS proved to be especially useful for the speciation of organomercury compounds. Mercury speciation in natural water samples ([140]) and in human body fluids ([141]) was reported. GC/AAS was also applied to the analysis of organotin species ([142]). A novel atomic absorption technique after gas chromatography was reported using a microwave-induced plasma for the determination of chlorinated hydrocarbons ([143]). In addition, element-selective diode laser plasma detection for chlorinated compounds was reported ([144]).

(b) Atomic Emission Detector (AED). The most utilized GC detector based on optical mechanisms was the atomic emission detector (AED) ([145]–[148]). It was especially useful as a complementary analytical technique to GC/MS for environmental screening ([149]) and for the separation and detection of organometallic compounds ([150], [151]). With respect to organo-metallic compounds, a number of analytical methods were reported for the determination of organomercury ([152]–[157]) and organotins ([158], [159]). Other applications included the determination of chlorophenols in tap water ([160]), measurement polychlorinated and polybrominated biphenyls in the environment ([161], [162]), and herbicide analysis in soils ([163]).

Fundamental studies of the AED were also reported ([164]). Parametric investigations included temperature effects on quantification ([165]) and makeup gas flow on emission ([166]). A round-robin study demonstrated that intralaboratory procedures ranged from 1.3 to 22% RSD and that interlaboratory results ranged from 11 to 40% RSD ([158]). Elemental C/Cl and C/Br ratios deviated by less than 20% from calculated values ([167]). Development and evaluation of several novel analytical systems were reported. A direct-current AED was described for use with gas chromatography ([168]). Pyrolysis/GC/AED was demonstrated by the determination of silicones in air down to the 0.1 ng/L level ([169]). Also, an LC/GC/AED system provided high-efficiency separation for analytes in a complex sample matrix ([170]).

(c) Molecular Absorption Detectors. The use of molecular absorption detectors in gas chromatography is less common than other optical detection methods. The primary approach is IR detection. Analysis of cis- and transfatty acid isomers after separation by capillary GC was reported to be simple and fast, but its lower detection limit of 5% limited its use ([171]). In some cases, sensitivity limitations could be overcome by the use of large
injection volumes (1172). Fourier transform methods can also improve detection limits (1173, 1174). The most sensitive approach is matrix-isolation IR spectrometry, but the instrument is more complicated, and chromatographic resolution may be reduced (1175). In a unique approach, diffuse reflectance Fourier transform infrared spectrometry was coupled with GC (DRIFT-GC) for catalyst characterization (1176).

Another molecular adsorption technique coupled a packed column with a UV-visible molecular absorption spectrophotometer for the detection of benzene, toluene, 1,4-xylene, 1,2-xylene, and mesitylene (1177, 1178). In addition, the determination of isoprene in human breath was reported by thermal desorption gas chromatography with UV detection (1179).

(d) Molecular Emission Detectors. The flame photometric detector (FPD) is, by far, the most common molecular emission detector. Routinely used for the determination of tin- (1180–1185), lead- (1186), germanium- (1187–1189), nitrogen- (1190), sulfur- (1191), and phosphorus- (1192) containing compounds, it has the option of multichannel response (1193, 1194). An improved performance of the detector was demonstrated using a pulsed mode of operation and optimal operating conditions (1195).

Miscellaneous chemiluminescence detectors were reported as well. The determination of trace amounts of organic explosives, in which 0.2 ng of HM X was detected, was accomplished using a thermal energy analyzer (TEA) (1196). One detector, called the sulfur chemiluminescence detector, was based on the principle of the formation of sulfur dioxide in a reducing flame. The sulfur dioxide is then detected by its chemiluminescence reaction with ozone (1197). Mechanisms were also discussed in the literature (1198). Application of the detector was reported for volatile sulfur compounds in water, with a linear response from 10 to 100 μg/L (1199). A selective chemiluminescence detector after GC was also applied to the detection of nitrogen compounds in crude and refined petroleum fractions. This detector was based on initial pyrolysis combustion at 1100 °C in the presence of oxygen, followed by a luminescence reaction of the product NO with ozone. Its lower detection limit was approximately 200 ppb (1200).

Miscellaneous and Multiple Detectors. Miscellaneous GC detectors not conveniently included in categories discussed above are covered in this section. An acoustic flame detector (AFD) for gas chromatography monitored the frequency of the sonic bursts from a flame. Shifts in the frequency were indications of analyte presence in the flame (1201). Olfactometry (OD) is one of the oldest detection methods for GC, and still, novel methods were reported (1202, 1203). Electrolytic conductivity detection (EICoD) coupled with solid-phase extraction was used for the trace analysis of vinclozolone (1204). Radiochemical detectors were used for special applications (1205–1207) and, in a few specific cases, GCs were interfaced to a nuclear magnetic resonance spectrometer to provide molecular structural information on the analyte (1208, 1209). Semiconductor detectors were investigated to replace the FID (1210) and for breathalyzers (1211). Finally, improvements in thermal conductivity detectors (TCD), for years the primary detection method for gas chromatography, were reported for sensitivity (1212) and for interfacing with capillary columns (1213, 1214). The ability to combine GC detectors in a single analysis is a powerful approach for the investigation of complex mixtures and the identification of unknown compounds. The combinations of detectors shown in Table 3 were used in novel ways to solve analytical problems during the past two years.

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