Trends in Gas Chromatographic Science: 1997

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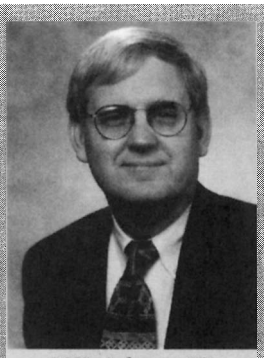
W.M. Coleman III

After receiving his B.S. in chemistry from the University of South Carolina in 1969, W.M. Coleman, III entered Virginia Tech on an NSF fellowship and received his master's degree in chemistry in 1970 under the supervision of Professor Larry T. Taylor. He then entered military service with the U.S. Navy and served at the Naval Dental Research Institute as a research scientist and at the Navy Environmental Health Center as Director of Laboratory Services. In 1975 he returned to Virginia Tech on a Navy fellowship to obtain his doctorate in chemistry under the supervision of Professor Taylor. In 1977, while serving as a naval officer, Coleman received his Ph.D. in transition metal chemistry. Upon completion of his degree, he was assigned to the Office of Naval Research Naval Biosciences Laboratory in Oakland, California, where he conducted research into organotin antifouling formulations, synthetic fuels, and synthetic oxygen carriers. Dr. Coleman completed active duty in 1981 and assumed a position with Dow Chemical Texas Operations in Freeport, Texas, where he conducted and managed research into novel Zieglar-Natta high-temperature catalytic complexes and processes. In 1986 he assumed a position with R.J. Reynolds Tobacco Company where he currently conducts research into natural product chemistries. His present research interests include the chemistries surrounding sugar–nitrogen reactions and hyphenated chromatographic techniques. Dr. Coleman is the author of 80 publications, holds 15 U.S. patents, and has contributed to several monographs on transition metal polymerizations and hyphenated chromatographic techniques.

Abstract

By combining the results of a review of the 1996 literature with that from a review of the 1994–1995 literature, it is possible to establish trends in the science of gas chromatography (GC). GC is found to embrace a diverse array of chemical interests from thermodynamic property calculations to the speciation of metal ion complexes in marine environments. Advances in speed, sensitivity, automation, computer modeling, detector design, and sample preparation are presented, indicating clearly that GC is a well-established, very healthy, expanding science finding influence in an ever-growing pattern of scientific endeavors.

Introduction

Webster defines *trend* as a general course or prevailing tendency, a current style or vogue. Obviously, to gain one perspective of the prevailing tendencies in gas chromatography (GC), it is necessary to survey the current peer-reviewed literature appearing from groups that are developing, using, modifying, and implementing the technology. A second perspective can be obtained from a survey of the industrial literature, that is, the newest instruments, columns, and accessories available on the market. This second perspective yields a glimpse into the future for applications of the technology but does not furnish an effective panorama as to what is being practiced of late and implemented at the bench level.

This review centers on the peer-reviewed literature published in 1996 as a barometer for the current course in GC.

Trends in GC Science

A review of the literature on fundamental developments in GC as reflected in publications appearing from 1994–1995 has recently appeared (1). The

contents of the exhaustive review included topics such as supports, phases, theory, columns, hardware, data processing, and detectors. In a very similar fashion, two reviews (2,3) appeared recently covering the developments in GC instruments, autosamplers, injection accessories, detectors, software, and columns as displayed by manufacturers at the 1996 Pittsburgh Conference. This review will present an account of the trend in GC science as disclosed in selected representative open peer-reviewed literature of 1996. This article is not constructed to cover every reference to GC that appeared in the 1996 literature but rather selected references that capture the essence of the trends in the science. When completed, an assessment of the trend as revealed in selected representative 1996 literature references will be collated with that of references appearing from 1994 to 1995 so as to more clearly establish any developing tendencies.

An overview of the 1996 literature strongly suggests activities in the broad areas of (*a*) sample preparation and collection, (*b*) sample injection, (*c*) sample separation, and (*d*) analyte detection. Thus, these domains are discussed individually below. Selections of references to appear in these broad areas were to some degree arbitrary in that many of the references could arguably disclose information on more than one of the selected divisions.

Sample preparation and collection

A diverse number of sample preparation, sample collection devices, and approaches prior to actual GC analysis appeared in the 1996 literature. Among these were: (*a*) microwave extraction and distillation, (*b*) solid-phase microextraction (SPME), (*c*) supercritical fluid extraction, (*d*) laser-induced desorption, (*e*) pyrolysis, (*f*) fiber-trapping, (*g*) solid-phase extraction (SPE), (*h*) gel permeation chromatography (GPC), (*i*) purge and trap, and (*j*) supersonic molecular beams.

The microwave approaches were directed at: (*a*) extraction of polynuclear aromatic hydrocarbons, organochlorine pesticides, and polychlorinated biphenyls in soil and sediments (4); and (*b*) extraction of organotin compounds in sediments and biomaterials (5). Also, microwave distillation in combination with solid-phase adsorption proved to be an excellent approach for the determination of off-flavor compounds in fish tissue (6).

Approaches using SPME included the extraction of volatiles from water (7–9) by insertion of the fiber into the headspace above the water or into the water itself. Likewise, quantitative analysis by headspace SPME was possible for soils containing chlorobenzenes and nitrobenzenes by exposing the fiber to the headspace above the soils (10). Using an automated approach, the presence of key compounds in flavor and aroma formulations were detected when SPME fibers were equilibrated in the headspace of vials containing the formulations (11). The behavior of a polydimethylsiloxane SPME fiber toward the extraction of Maillard reaction products from aqueous solutions has been described (12) employing GC with selected ion monitoring mass spectrometry (MS). In a similar approach employing SPME, quantitative analysis of phenols in tobacco smoke were reported (13). Headspace SPME combined with GC has been used for isolating and analyzing pyrazines formed in a model reaction system (14).

Selective collection of analytes via SPE, which were subsequently analyzed using GC, were depicted. In one case, an SPE procedure for the simultaneous determination of selected analytes in postmortem human whole blood was described using GC–MS (15). The detection limit for the selected analytes was approximately 1 ng/mL of whole blood. Phenols were extracted from water samples by SPE and subsequently converted into pentafluorobenzoylates. These derivatives were then determined by GC with electron-capture detection (ECD) and by GC with ion-trap MS (16); the detection limit for the phenols was 3–60 ng/L. An optimized automated at-line SPE–GC analysis for micropollutants in water has been described. The system demonstrated a detection limit of approximately 0.6 µg/L for triazines and organophosphorous pesticides in river water (17).

Supercritical and subcritical extraction procedures were described for sample preparation and collection prior to GC analysis. Desalted and lyophilized urine samples were extracted with supercritical carbon dioxide, derivatized, and separated by GC with identification of selected metabolites by negative chemical ionization MS (18). Full mass spectra were obtained at a level of 1 ng/mL. Subcritical (hot/liquid) water extractions of polycyclic aromatic hydrocarbons (PAHs) from soil and air followed by collection on a nonpolar SPME fiber and subsequent analysis by GC with selected ion monitoring MS were reported (19). Quantitative determinations were possible for a wide range of PAHs as well as alkylbenzenes and aromatic amines.

Pyrolysis of high molecular weight polymeric materials as a method of sample preparation was employed in assessing the nature of the starting materials. Acrylamide polymerized into a polymer backbone was qualitatively identified by using a method combining pyrolysis, trapping, and GC analysis with three detectors: a flame-ionization detector (FID), a mass selective detector (MSD), and an atomic emission detector (AED) (20). A pyrolysis GC method was developed to study the composition and microstructure of styrene–methylmethacrylate copolymers. Monomer peak intensity was employed to determine the composition of the copolymer. This method was a new approach for the investigation of copolymers that do not produce dimer and trimer peaks upon pyrolysis (21). A number of hyphenated techniques for characterizing coal wastewaters and associated sediments have been described (22). Upon pyrolysis, the released products included many low molecular weight compounds that were of limited value for characterizing the coal polymeric network.

Several different sample preparation and collection approaches were employed for the analysis of volatile organic compounds (VOCs) from a wide variety of sources. In one case, results of analyses employing purge and trap GC indicated that an Environmental Protection Agency-approved method using purge and trap for sample preparation measurement of VOCs in aged soils was very inefficient when compared with a hot solvent extraction (23). VOCs were continuously monitored on-line employing fast micro-GC with thermal conductivity detection (TCD). Nine different VOCs, methane, and carbon dioxide were separated and quantitated every 2 min (24). A thermo-desorbable silicone-coated glass fiber filter was

developed for sampling polychlorinated biphenyls in air. The air pollutants were analyzed after capture on the fiber in the field by GC–MS; the total analysis time was approximately 10 min (25). An improved method for the determination of perfluorocarbon tracers in the atmosphere based on adsorbent-collected ambient air samples coupled to a modified GC with ECD was described. The achieved increases in tracer sensitivities realized by the approach significantly reduced the cost of using the selected tracer, improved the definition of the plume, and extended the identification of the tracer plume dispersion limits (26). A variant of headspace analysis, full evaporation technique (FET), was combined with GC and ion-trap detection to quantitate VOCs in the blood of victims who had inhaled smoke during an arson or accidental fire. The quantitation limit was in the range of 0.4–1.0 nmol for the polar VOCs in blood and 0.03–0.1 nmol for the nonpolar VOCs in brain tissue (27).

Two rather unique sample preparation techniques that were coupled to GC analytical approaches were disclosed. In one case, a carbon dioxide laser was used to thermally decarbonize carbonates in naturally occurring materials, and the liberated carbon dioxide was quantitated by GC with isotope ratio MS. The method was employed to determine isotope ratios in samples such as calcite, dolomite, and magnestite (28). In a second case, supersonic molecular beams were used to create volatile molecules that were subsequently analyzed by GC–MS (29).

Injectors and injection systems

Reports focusing primarily on work with injection systems were dominated by results on large volume injection and temperature-programmable injections. Mol et al. have reviewed the use of programmed temperature vaporizing for large volume injection in capillary GC (30). Grob discussed new ways in which previous volume constraints in capillary GC could be overcome with novel large-volume injection hardware. Application to the trace analysis in biomedical contexts were discussed (31). In another account, Grob described a vaporizing chamber–precolumn solvent split–gas discharge system for large volume injection with on-line transfer of water-containing solvent mixtures. Permanently hot chambers were offered as the best method for removing the maximum amount of solvent (32). A temperature-programmable large-volume injection system has been applied to the analysis of pesticides in river water extracts with MS and electrochemical detection. Calibration results indicated that the large-volume injector allowed for a linear calibration range of 50–500 pg/mL pesticides (33). A large-volume temperature-programmable injector has been used in the on-column and solvent-vent mode for the analysis of alkanes and polar and thermolabile components. The device permitted the injection of 100 µL on-column with a deactivated retention gap (34). A system for sample injection of up to 100 µL of liquid and 800 mL of gas has been devised for capillary GC. A pretrap, heater cartridge, and cold-trap concentrator were configured together, interfaced with the capillary column, and used with light-pipe Fourier transform infrared (FTIR) and MS. Hydrocarbons and Grob test mixtures were used to qualify the system (35).

Several applications of temperature-programmable injection appeared in 1996. Among them was a comparison of two different injectors: a split–splitless and temperature-programmed vaporizer. These injectors were investigated as the interface in on-line supercritical fluid extraction–capillary GC. The parameters affecting peak shapes as well as the quantitative performance of the systems were described. Experiments were performed on polyaromatic hydrocarbons in sand and polymeric materials (36). Thermally labile pesticides have been determined by using GC–MS and GC–tandem MS with a temperature-programmed injector. With a cooled temperature-programmable injector, it was possible to analyze a series of thermolabile carbamate and phenylurea pesticides (37). GC–MS with a cooled temperature-programmable injector was used to analyze picogram amounts of explosives in water. Thermal decomposition, even in the thermolabile explosives, was minimized through the use of the cooled temperature-programmable injector. Traces of explosives in water in the range of 5–100 ppb could be detected as well as identified (38). A mixture of 10 ppb relatively low molecular weight halogenated species was trapped on fused-silica loops in liquid nitrogen followed by warming and injection of the cooled microloop onto a 4-m × 100-µm-i.d. GC column. The resolution of the system was shown to be a function of the sample loop size; resolution improved with the smaller loop (39). Using a similar system, the performance of two cryofocusing injectors for fast GC has been studied. The two systems, one consisting of bare metal tubes and the second consisting of a microloop injector coupled to narrow-bore fused-silica tubing were capable of trapping butane at –90°C. Comparison of the two injectors showed similar chromatographic resolution. Freezing of both injectors could be eliminated by an in-line Nafion drying system. Highly unstable compounds such as ethyldiazoacetate were injected without breakdown in the microloop system (40).

A device that allows the whole headspace to be sampled from a vial and the volatile components to be brought into a microtrap has been described. The contents of the microtrap are then transferred to a GC–MS system (41). In a departure from Curie-point pyrolysis injection at 700°C, a so-called "modified closeable sampling column" has been used as a batch reactor in thermal desorption experiments. To illustrate the approach, thermal desorptions at about 260°C were performed on waste wood samples in connection with GC–MS for identification and GC–FID for quantitation. The desorbed vapors were analyzed, and individual PAHs were determined in waste wood samples such as railway sleepers (42). In a cryotrap–thermodesorption inlet system, 10 different metal tubings were investigated for thermal decomposition of analytes. Six of the metal tubings demonstrated no noticeable decomposition for hydrocarbons and chlorinated hydrocarbons when hydrogen was used as a carrier gas. Deactivation of the metal surfaces was advanced as an explanation for the observations. Cryotraps using carbon dioxide and nitrogen were evaluated, and compounds with a boiling point of 80°C were effectively trapped (43).

Separation

This discussion on separation will center not only on disclosures in column technologies but also reports on hardware modifications such as multidimensional GC (MDGC) and the linking of diverse types of chromatography into one hardware

system. A discussion of approaches to work in MDGC appeared outlining that the highest chromatographic resolution is gained when there is no correlation between the separations. The maximum orthogonality between the separations can be obtained by hyphenating pairs of techniques such as LC and GC as well as chromatographies such as GPC and reversed-phase LC (44). Separation orthogonality was also demonstrated for mixtures of *n*-alkanes, *n*-alcohols, and polar compounds when retention times in two-dimensional optimized GC were independent of each other. This was possible because the retention of substances was different due to widely divergent column phases (45).

As a practical approach to environmental monitoring, multiplex GC techniques were disclosed. The multiplex GC technique allowed for multiple sample introductions to the column at high frequency in a random manner. The advantages of the system, simplicity, low cost, time efficiency, and automation, were discussed in terms of VOC analysis (46).

Oxidation reaction products of *n*-butane have been analyzed using MDGC. To monitor the automated process for the synthesis of maleic anhydride, a 0.53-mm-i.d. column and a multidimensional sequence of packed columns provided the required resolution of all components. FID and TCD were used to monitor the effluents of the columns. The system was shown to be very reliable over a period of several years with more than 50,000 injections (47). A multidimensional approach involving two LCs and one GC has been employed in the analysis of mineral oils in linseed oil. In the first LC separation, the column effluent is evaporated automatically, then injected onto the second LC column. The effluent from the second LC is transferred to the GC through an in-line vaporizer. The system is designed for the injection of large amounts of food extract (48). Ion chromatography has effectively been interfaced with GC–MS in the analysis of trace levels of alkaloids in cocoa. The structure of selected tropones as well as two additional previously unreported tropones were disclosed (49). High-performance liquid chromatography–high resolution GC–MS (HPLC–HRGC–MS) for the analysis of natural products has appeared in two reports (50,51). A fully automated system is used for the analysis of hydrocarbons and oxygenated fractions of natural products such as bitter orange, sweet orange, lemon, and mandarin leaf oils. Qualitative and quantitative analyses of most of the compounds present in the oils were possible.

Reports on chiral liquid crystals and metal ion modified phases appeared in 1996. A novel chiral phase with a tripodal selector was described for the separation of derivatized amino acids and hydroxyacids. Intermolecular and intramolecular hydrogen bonding networks were advanced to explain the selectivity (52). The interaction mechanisms of permethylated cyclodextrans using molecular modeling were studied with GC. Host–guest interactions were investigated as the fundamental mechanisms for separation, and computational methods were employed. The size of the cavities of permethylated cyclodextrans was found to be optimum for selected compounds (53). By varying the size of the 6-*O* substituents of cyclodextran-based GC stationary phases, a systematic modification of the separation selectivity could be demonstrated. The substituents on the cyclodextran influenced the chiral selectivity of the phases; the best results came from the *t*-butyldimethylsilyl group. The size of the substituent also precipitated some influences on the separations, particularly in the area of operating temperatures. A very widely diverse group of compounds were suitable for separation on the modified cyclodextrans (54). The most important chiral acids in wine were effectively separated by enantioselective capillary GC using a cyclodextran stationary phase. Simultaneous analysis of lactic, malic, and tartaric acids was possible (55). The influence of polysiloxanes with different polarities as diluting phases on the separation capacity of selected cyclodextran derivatives has been investigated. Minimum operating temperatures and separation capacities of the new columns were discussed and arose from only selected combinations of diluants and cyclodextrans (56). The relative polarities of modified cyclodextran GC column phases were evaluated. The evaluation involved a study of the apparent polarities of the cyclodextran columns at 100°C using eight standard McReynolds probe solutes. Similar columns coated with silicones and polyethyleneglycol were studied alongside the cyclodextrans. Some anomalous properties were observed and discussed (57). GC columns coated with a chiral polysiloxane have demonstrated enantioselectivity and thermal stability. By anchoring a chiral selector to a polysiloxane, through displacement of a leaving group, a phase capable of analyzing mixtures of pharmaceutical products' enantiomers was possible (58).

Interesting analytical performances were obtained in the isomeric separation of alkanes, aromatics, polyaromatics, and *cis*- and *trans*-isomers when selected liquid crystals of azobenzene were employed as stationary phases. The liquid crystals were efficient after solid–solid or solid–nematic transitions, and higher plate counts were found in the nematic state (59). Metal ion modification of GC column stationary phases have yielded some unique separations. Copper II (Cu II) complexes of cyano- and mercaptopropyl-bonded phases have been effectively used for the separation of low molecular weight hydrocarbons on micropacked systems. Unsaturated hydrocarbons can be effectively separated from saturated hydrocarbons using these phases presumably through the interaction of the olefins with the Cu II metal ions (60). Cobalt II and nickel II complexes were used to prepare a selection of GC column stationary phases. By covalently bonding the acetyl acetonates and hexafluoroacetyl acetonates of the two metal ions to silica, good chromatographic properties and high selectivities toward compounds containing π electrons were discovered (61). Alkali and alkali earth metal ions have been used to modify the behavior of alumina in the separation of mine air containing low molecular weight alkenes and alkanes. The effects of anions and cations were investigated as well as the effects of postcolumn heating. The optimum separation of the components in the mine air was obtained when the alumina was modified with 2% NaCl (62).

Two types of stationary phases, silica and molecular sieve (carboxen), were evaluated in PLOT columns for fast GC of light hydrocarbons. The carboxen column demonstrated excellent selectivity for permanent gases, whereas the silica PLOT column showed good separations of light hydrocarbons, all within 30 s with high speed injections of 40 ms (63). The per-

formance of an aluminum oxide PLOT column was compared to that of a new stationary phase, GasPro. The GasPro column was not adversely affected by water, carbon dioxide, or sulfur gases. Also, no decomposition of the most reactive gases was noted in the GasPro evaluations. Both columns effectively separated light hydrocarbons and inorganic gases (64).

Detectors

Obviously, all of the aforementioned references have in and of themselves included various types of detectors to accomplish the desired analyses. Thus, this section will contain information on new articles not previously mentioned in the sections above and will present a representative set of references that primarily emphasize detector technology.

The continued use of GC–MS was very evident in the 1996 literature. GC–MS has become such an accepted part of GC application that it was featured in its own section of a publication dedicated to chromatography fundamentals (65).

An SPE procedure has been described for beta-agonists in human whole blood using GC with electron-impact MS. The limit of quantitation in 1 mL of whole blood was 1 ng/mL for all analytes (66). When negative ion chemical ionization MS was used after chemical derivatization, novel metabolites of diclofenac were detected in small amounts of human urine. The lyophilized urine was extracted with supercritical fluid carbon dioxide and separated by GC, and full mass spectra were obtained at a concentration of 1 ng/mL (67). Three detectors, FID, MSD, and AED, were compared for the detection of acrylamide in an emulsion polymer. Prior to evaluating the detection systems, the sample was prepared by combining pyrolysis (PY) and solvent trapping. The advantages of each detection system were evaluated (68). Coal waste waters and associated sediments have been characterized using PY–GC–MS and PY–GC–AED. The products released upon PY included many low molecular weight compounds that were of limited value in characterizing the polymeric structure of the pollutants in the contaminated waste waters (69).

In addition to the use of MS alone, several reports appeared in which MS was used in conjunction with other information-rich systems. The use of inductively coupled plasma (ICP) with MS and GC has been described as a very powerful combination of information-rich detectors. The linking of these systems via a special transfer line allowed the speciation of organometals in complex environmental samples. The specific and multi-element capability of the ICP–MS system was addressed (70) in terms of sensitivity and specificity. Another GC–ICP–MS interface for the determination of organometals has been described. Organometallics in methylene chloride were first separated and transferred to the ICP–MS via a temperature-controlled stainless steel tube. The system was used to determine the nature of butyltin compounds in sediments (71).

GC–tandem MS (GC–MS–MS) for the analysis of anabolics in biological material was also described. The possibilities of using ion trap GC–MS, GC–MS (quadrapole), and GC–MS–MS for the multiresidue analysis of complex biological samples were discussed (72). GC–MS–MS was also reported for use in reducing the detection limit of thyreostatic drug residues in urine (73). GC–MS–MS has been proposed as a new method for the determination of chlorophenols in water below parts per billion levels. Preconcentrating the samples through the use of carbon cartridges after acetylation and the selection of proper parent ions and fragmentation conditions yielded positive identification of every species considered (74).

GC in combination with FTIR has been reported to assist computational chemistry in the identification of tetrachlorobutadiene isomers. When standard spectra and pure standards were unavailable, this approach indicated a potential means to confirm analytes of environmental concern (75). Simultaneous GC–MS and GC with nitrogen phosphorous detection (GC–NPD) have been used in the analysis of pesticides. The advantages of using both methods for the detection and determination of nitrogenous herbicides in drinking water and phosphorylated pesticides in agricultural products at low levels were discussed (76).

The use of pulsed discharge detectors of various types has been studied. Responses of a wide series of compounds as detected by pulsed discharge photoionization detectors containing helium and krypton have been reported. Self-consistent field–molecular orbital (SCF–MO) calculations were employed to understand the relative responses obtained from the detectors (77–78). The characteristics of a pulsed discharged ECD has been described. The absolute electron-capture coefficient was determined for a number of compounds that undergo different electron-capture mechanisms (79). The pulsed discharge ECD was modified by changing the detector geometry, the insulation materials, and the dopant gas. These changes produced a detector that could operate at 400°C and had improved sensitivity, linearity, and response time when compared with a ^{63}Ni ECD (80). A schematic drawing of the pulsed flame photometric detector (FPD) principle and gas chromatogram of a series of alkyl tin compounds has been presented. This detector can be used for determining trace amounts of elements in environmental samples (81). Organotin compounds have also been determined using GC–FPD. A derivatization procedure was used to drastically reduce the number of analytical steps, thereby improving both analysis time and reliability. Analysis of certified reference material demonstrated the method's accuracy (82). Organotin compounds have also been determined in biological fluids using a GC–FPD approach (83). Time-integrated spectra in the range of 400–700 nm from an FPD has been made possible through modification of an existing dual-channel FPD. The new device can monitor 100 data points in the given region at the rate of 10 times per second (84).

The effluent from GC columns has successfully transferred to an atomic absorption spectrometer (AAS) for the selected determination of elements of environmental interest. For example, tin speciation in selected environmental samples has been possible with a newly developed GC–AAS. Naturally methylated organotin compounds were detected in the environment using this procedure (85). AAS in a wavelength-modulated diode laser microwave-induced plasma has been used as an element-selective detector for chlorine. The detection limits for chlorine-containing compounds separated in a GC column that is interfaced to the detector were in the range of nanograms per milliliter (86).

Dual-channel photometry has been successfully demon-

strated as a viable approach for compound-specific detection. Perfectly coeluting peaks could be quantitated from a subtraction chromatogram using this approach. Also, the dual-channel system produced a detection limit of 0.2 pg/s for phosphorous at 526 nm (87–89).

The characteristics of a new GC detector based on hyperthermal positive surface ionization has been described. The detector operates at 900°C with a +200 V charge versus a collector electrode. Responses to methane, benzene, and toluene were linear over 4 orders of magnitude (90). The minimal detectable amount of toluene was approximately 10 pg/s. Applications were demonstrated using mixtures of terpenes, PAHs, and alkyl alcohols (91). An additional new GC detector based on the measurement of the frequency of acoustic transients generated at a flame has been disclosed. The acoustic flame detector (AFD) uses signals from a partly premixed hydrogen–air flame. The response of the AFD for dodecane was found to be linear over 3 orders of magnitude, and the sensitivity of the AFD to certain organometallics was roughly correlated to the carbon content of the organometallics (92). A detector based on ultraviolet–visible (UV–vis) molecular absorption has been described as a new approach to reach new peaks. In one case, a gas flow cell is incorporated into a micro GC, and applications in environmental and clinical chemistries are described (93). Packed-column technology was also shown to be compatible with UV–vis molecular absorption detection. Detection limits of approximately 1 µg/mL were delineated for benzene and its methyl derivatives (94). Because the detector is nondestructive, it can be used in conjunction with other detection methods (95).

Detectors based on FTIR molecular absorption continue to find applications as GC detectors. In one case, trimethylsilyl esters of disaccharides were positively identified using GC–FTIR. The degree of silation was shown to be critical to the effective use of the approach (96). In a method based on direct deposit FTIR, quantitation of two dichlorophenols was possible. Even though the two isomers were not resolved by the GC column, quantitation was possible using a multivariate calibration model. Detection limits in the range of nanograms per milliliter were possible in water (97).

Capillary columns

Steps for the proper care of capillary columns including tips to avoid column breaking, stationary phase damage, and column contamination were published (98). A primer on how to fix some unavoidable problems was presented. All of these tips were related to improved reproducibility, accuracy, and precision in GC analysis.

In a system of two GC capillary columns coupled in series, one gas–liquid chromatography (GLC) and the other gas–solid chromatography (GSC), the separation number (TZ) and height equivalent to a theoretical plate (HETP) have been studied (99). A homologous series of alkanes under temperature-programmed and isobaric conditions was employed in the study. The TZ and HETP were shown to be strongly dependent upon the midpoint pressure and the temperature, respectively. TZ and HETP were shown to be inversely related to the overall column length of the system.

Two new designs for the use of extremely fast temperature programming of GC columns have appeared (100). Resistive heating and temperature-sensing elements along the column were controlled via software. Linear increases in temperature rates of 10°C/s were demonstrated. Volatile and semivolatile hydrocarbons were employed to evaluate the performance of the two systems. The results compared favorably with commercially available instrumentation. Meaningful increases in peak width occurred for hydrocarbons beyond 13 carbons (i.e., tridecane). The new columns were very lightweight and consumed little power.

Computer programming and theoretical data analyses

Several novel approaches involving the use of computer simulations, programs, and software as well as other mathematical treatments in the analysis and prediction of chromatographic behavior were published in 1996. A pivot table approach was shown to be a very powerful way to summarize chromatographic data in a spreadsheet list from external databases (101). The chromatographic results could be placed in spreadsheets or retrieved from databases and used with a variety of data analysis tools, the pivot table being one such tool.

The values for some fundamental molecular thermodynamic parameters were obtained from molecules based on their chromatographic behavior. The separation characteristics of a homologous series of organic alkanes and alcohols in terms of their retention data at various temperatures as well as in polar, nonpolar, and carbon layer open tubular columns were employed to estimate the selected thermodynamic parameters (102). By simply finding the retention times of the compounds of interest and those of two standards, it is now possible to determine quickly and precisely the vapor pressure of selected compounds (103). To improve the reproducibility of the results between different instruments, a "cocktail" containing two standards was employed.

Theories and research on translations between isothermal and temperature-programmed chromatographic behavior were published in 1996. In one case (104), it was shown that a step-by-step calculation of retention time leads to an accurate description of the compound's trajectory in the column under nonisothermal conditions. The correlation between calculated and observed retention times was excellent. In another report, it was possible to calculate temperature-programmed GC data from isothermal retention indices. It was possible to avoid the need for retention times for a series of *n*-alkanes using this approach (105).

Computer programming and selective detection were used in attempts to resolve overlapped or completely unresolved components. The ratio of standard chromatographic peak profiles was employed in the quantitation of unresolved chromatographic peaks (106). The new method for extracting the desired information from overlapping peaks comes from the profile of a standard substance. Several cases of two- and three-component chromatograms were investigated. A multilayered perception network has been used for quantitatively correlating a set of parameters with the percentage area of an individual peak in the case of overlapping retention (107). Less computing time and high accuracy characterize this approach in compar-

ison with conventional methods.

The use of computer software for the simulation of GC analysis has been outlined (108). Thermodynamic retention indices (TRI) from enthalpy and entropy values were used to calibrate the software. Retention data from two separate temperature programs with correction for dead time were used in a special algorithm to calculate the TRI. Data for a range of organochlorine compounds were used to illustrate the concept. Good correlations between predicted and measured retention times were observed for PAHs, polychlorinated biphenyls (PCBs), and triazine herbicides. Through the use of a special algorithm, a new fast method for field-screening PCBs has been developed (109). Total analysis time in the field was approximately 10 min using a mobile GC–MS system. The special algorithm eliminated the superposition of ion fragments in the low-resolution GC run.

A Fourier analysis approach has been described for the evaluation of HRGC separations of multicomponent mixtures (110). It is based on obtaining an autocovariance function from the digitized chromatograms. The method is illustrated by application to hydrocarbons and Aroclor mixtures.

Trends in GC Over the Past Few Years

Having completed a review of selected articles appearing in 1996 and coupling this information with reviews in GC covering 1994 and 1995, it seems possible to establish trends in the science. Obviously, the science of GC is very healthy, finding applications across an increasing diversity of interests encompassing fundamental thermodynamic properties and metal ion analyses. The appearance of two books on the modern practice of GC in part substantiates this observation (111,112). The coupling of GC with highly sensitive and selective detectors continues to appear. Sensitivities in the range of picograms per liter for metals, organics, and inorganics are now possible. Fast separations of very complex mixtures with miniature gas chromatographs can now be performed in the field. Fast separations on the order of seconds that are capable of monitoring processes in a real-time mode have appeared. The increased power of computers and software continue to revolutionize the science. Simple and relatively complex detectors continue to appear with substantial reductions in cost. Front-end sample preparations have erupted to include, for example, procedures wherein the sample is effectively trapped on a syringe-shaped SPME fiber that is inserted directly into the GC injection port. Large volume injectors and temperature-programmable injection ports ultimately result in enhanced levels of detection. Multidimensional chromatography combining GC with other chromatographies has appeared, resulting in dramatic synergistic increases in the information available from the sample of interest. Further work will appear on the multidimensional front as it becomes easier to combine the technologies. Liquid crystals and stereoselective supports continue to appear and mature as viable for the separation of complex mixtures.

From a general overview perspective, some GC analytical techniques seem to have gained increased acceptance and expanded use during the period of 1994–1996. One such technique is sample preparation using SPME. The wide variety of SPME fiber characteristics coupled with automated sampling has made this approach very attractive across a broad array of applications. Another technique involves separation of optically active components in complex mixtures using stable capillary column chiral phases. Prior laborious and meticulous sample preparation procedures have been reduced to separation and identification via chiral GC coupled with detectors such as MS. The separation of very complex mixtures using MDGC is another method. Time-intensive chemical separations of complex mixtures are now essentially performed on a precolumn followed by further separation on an analytical column based on a different separation mechanism. Simulations of separations based on software programs and theoretical calculations are also gaining acceptance. Based on theory and a minimum number of actual separations, reasonably accurate predictions of chromatographic behavior can be made. Thus, the overall trend in GC science appears to be headed in the direction of faster, more sensitive, more specific, less labor-intensive, automated approaches to sample preparation and analysis.

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Manuscript accepted April 29, 1997.