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CHROMATOGRAPHY 1990: REVIEW

by

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MANAGEMENT PERSPECTIVE

The manuscript is prepared in response to a standing request for Dr. Francis I. Onuska to make a bi-yearly contribution on the subject of open tubular column and porous layer open tubular column technology and advances in supercritical fluid extraction and chromatography for a review published by the Journal of Analytical Chemistry. This review covers the period between 1988-1990. Co-authors of the review with their contributions are Dr. R.E. Clement from Ontario Ministry of the Environment, Prof. G.A. Eiceman, New Mexico State University, and Prof. H.H. Hill, Jr. from Washington State University.

This review is a useful compendium of international achievements in the field of gas chromatography. It should be of interest to scientists and researchers in Canada and all over the world and should help to avoid duplication in research areas covered in separation sciences during the review period.

Dr. J. Lawrence
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PERSPECTIVES DE GESTION

Le document a été préparé en réponse à une demande de contribution bisannuelle par F.I. Onuska à une étude publiée par le Journal of Analytical Chemistry et portant sur les sujets suivants : technologie sur colonnes et techniques de chromatographie en phase gazeuse, chromatographie gazeuse avec colonne tubulaire ouverte, chromatographie sous pressions hypercritiques. L'étude couvre la période de 1988 à 1990. Cette contribution avec d'autres faites par R.E. Clement du ministère ontarien de l'environnement, G.A. Eiceman, qui enseigne à l'université du Nouveau-Mexique, et H.H. Hill, Jr., professeur à l'université de l'État de Washington, couvrent tous les progrès fondamentaux accomplis dans le domaine de la chromatographie gazeuse.

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

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RÉSUMÉ

Compte rendu des techniques et méthodologies chromatographiques basées sur une recherche approfondie de la documentation portant sur les principales méthodes de séparation comme la chromatographie gazeuse sur colonne tubulaire ouverte, l'extraction par fluide supercritique et la chromatographie par fluide supercritique. Ce compte rendu est mis à jour tous les deux ans pour le compte rendu biennal.

ABSTRACT

A review of chromatographic techniques and methodologies based on an extensive literature search covering principle separation methods such as open tubular column gas chromatography, supercritical fluid extraction and supercritical fluid chromatography. This review is updated every two years for the biennial review.

WALL-COATED OPEN TUBULAR COLUMNS

Advances in wall-coated open tubular columns (WCOT) and porous layer open tubular columns (PLOT) technology in 1980s were focused on improvements of bonding procedures, especially in more polar phase reproducibility and the development of selective bonded phases for specific applications. There has been more interest in the optimization of columns, with decreased length and/or internal diameters and further studies on wide-bore open tubular columns. New inert column deactivation procedure as well as new designs in column hardware continue to be developed.

The last two years have produced important progress towards unified capillary chromatography as described by Ishii (1F). Different separations could be carried out by changing the column temperature and the pressure by using a single system. Liao (2F) derived equations without k' values that allow calculation of plate numbers, resolving power and minimum time for analysis. Using these equations it is possible to select and optimize column operating conditions. New developments of high speed GC have resulted in the complete redesign of microchip GC instrumentation. The dual channel GC package is compact and consumes minimal amounts of carrier gas and electricity. The system has an analog as well as digital output for optimal output flexibility. A user friendly software automation package has been specifically developed for this system (3F).

The effect of open tubular column (OTC) characteristics on the minimum analyte concentration and the minimum detectable amount versus the stationary phase film thickness was studied by Noy and Cramers (4F). As a general guideline for OTC gas chromatography with respect to values of minimum analyte concentration and the minimum detectable amount the use of thin film OTCs is to be preferred. Ettre and Hinshaw (5F) disputed a number of inaccuracies in the

paper of J. Zhang as related to van Deemter equation and the equation that relates the gas phase diffusion coefficients with temperature and pressure. Van Es (6F) discussed existing theoretical models for axial turbulent dispersion in OTCs. Comparison with theoretical models shows that the plate height increased greatly with increasing solute capacity factor. This effect is due mainly to mobile phase mass transfer. Therefore, the gain in analytical speed is limited to low capacity factors. Repka (7F) developed a method for optimization of selectivity for coupled in series OTCs in a twin-oven GC system. The method is based upon computer-aided calculations of Kovats retention indices of the coupled columns by means of second and third order polynomial functions of the temperatures of the individual OTCs. Noy (8F) proposed a method for the determination of trace components in air and water. Dynamic headspace sampling is found to be a suitable technique for the trace analyses of volatile organics in water. Purging at high temperature drastically improves the recovery. Schilling (9F) described a technique for widening glass capillary butt connectors. Pouwelse (10F) recommended the use of retention gaps coated with a very thin polar film of CP Wax 52 for the introduction of large volumes of polar solvents in on-column injection mode. Gao and Zhang described deactivation of OTCs using methylhydrosiloxane and dynamic coating (11F). Nawrocki (12F) studied the structure of an organic layer bonded to the silica surface after treatment with hexamethylcyclotrisilazane, hexamethyldisilazane and their mixtures. Vecchi and Walther (13F) described a simple and versatile method for connecting fused silica and glass OTCs using a modified polyimide prepolymer. Kobus and Maehly (14F) developed an adsorption sampling method combined with HRGC and cryogenic focusing for trace analysis of volatile organic compounds which is suitable for forensic sampling. Similarly, Hagman and Jacobsson (15F) evaluated the traps that were either capillary tubes packed with glass beads or open tubular capillary cold traps. The trapping efficiency was expressed as a function of the amount of alkane and the temperature gradient of the trap. The trapping efficiency of the OTC-traps is dependent on both these factors but the packed cold trap retained the alkanes quantitatively. Etzwiler (16F) described a computerized system for micropreparative enrichment of analytes from a mixture being separated on an OTC. The enrichment procedure is based on a

repetitive absorption of eluting analytes after separation from an OTC, by sucking them through an absorption tube mounted at the outlet splitter. This technique can be applied for sample recovery after analysis by non-destructive elucidation methods or by chemical micro-reactions without loss.

A large share of the literature has been focused on preparation of crosslinked stationary phases in fused silica capillaries (17F-27F). While many of the included articles might be considered as improvements, we felt that either the novelty of the approach or the empirical observations reported may provide some insights into fundamental processes for those researchers with a primary interest in their preparation. Mathes (18F) described preparation of OTCs containing the polyaryl ether sulfone PZ-179 which is thermostable up to 380 C. Arrendale and Martin (22F) showed that moderately polar OV-1701-vinyl siloxane can be used as a surface deactivation agent. Schmid and Mueller (25F) described preparation and evaluation of OV-240-OH coated glass OTCs for isomer specific

determination of polychlorinated dibenzo-p-dioxins and dibenzofurans. The OTCs were persilylated with 1,3-bis- (3-cyanopropyl) tetramethyldisiloxane and coated with OV-240-OH. Column performance is shown to be superior to cyanopropyl columns such as SP-2330. The high temperature limit of these columns opens the way for the analysis of high boiling compounds. Blum and Damasceno (26F) confirmed previous findings using hydroxyl terminated polysiloxane stationary phases for high temperature GC separations up to 420 C. David (27F) prepared hydroxy-terminated cyanopropyl silicones containing a high cyanopropyl content. Blomberg and Roeraade (27F) developed a technique for coating OTCs with a very thick film (up to 100 um) of crosslinked stationary phase. These columns can be employed as enrichment traps in air pollution studies.

Use of small diameter OTCs for ultrahigh resolution HRGC have been studied by Hyver (28F) and by Cartoni (30F). In spite of some instrumental difficulties, improved sensitivity and a considerable decrease in the time of analysis is achieved over that obtained with the large diameter columns in spite of some instrumental difficulties.

Various aspects of the use of wide-bore OTC columns were discussed (29F, 31F, 32F). The discussion includes the evaluation of the catalytic activity, resolution, selectivity analysis time, and efficiency of the columns. Bemgaard (33F) described siloxane-silarene copolymers as stationary phases for OTC HRGC.

Discussion of porous layer open tubular columns (PLOT) received only light attention in the literature. Recently their revival is evident from number of articles (34F, 36F-40F). Reviews (34F, 37F) describe PLOT columns as OTCs which are coated with a porous layer of a solid adsorbent instead of a stationary liquid phase. Preparation of PLOT columns with carbon molecular sieve as the stationary phase has been described (36F). The column can be used to separate permanent gases at subambient temperature. Russo (38F) investigated the nature of solid supports used as precoating in the preparation of PLOT columns. A higher efficiency was obtained with the caolin precoating. De Zeeuw (39F) coated his PLOT columns with 10 to 30 μ m layer of a porous polymer based on styrene-divinylbenzene. The inertness of the porous polymer allows the elution of a range of apolar and polar compounds and tolerates even water injections. Lagesson and Newman employed packed microbore columns using 10 μ m HPLC packing materials as supports for various liquid phases. This type of column is characterized by a very short gas hold-up time leading to possibilities for relatively fast separations.

Two papers describing methods for preparing OTCs with crosslinked chiral stationary phases were published (41F, 42F). The silanes may be selected from vinyl-, epoxy-, amino- and methylacryl-modified trimethoxysilanes. They are used in enantiomer separations.

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SUPERCRITICAL FLUID CHROMATOGRAPHY AND SUPERCRITICAL FLUID EXTRACTIONS

As supercritical fluid chromatography becomes a more mature technique, it is being used more frequently for the analyses of more difficult sample matrices. The improvements in modern supercritical fluid extraction and chromatographic instrumentation and commercially available valving systems make it easier to automate and design the hyphenated systems into an integral unit. The current status of supercritical fluid chromatography has been reviewed by several authors (1G-6G). The advances in SFC emphasizing instrumentation, the use of mobile and stationary phases, applications of gradient techniques, the usefulness of packed and open tubular columns (OTC), and the effect of column pressure drop are covered. Martre (7G) presented a unified theory of adsorption chromatography with heterogeneous surfaces. The primary results confirm that the natural mobile state variables are its reduced temperature and reduced density. Studies of retention characteristics, resolution and gradient methods have been performed (8G-13G). It was found that the dependence of retention and resolution on temperature, pressure, density, linear velocity and mobile phase composition are of particular relevance. Packed and OTC columns were used in these studies. For the polar solutes the adsorption of modifier molecules on residual silanol groups plays an important role. Roth and Ansorgova (14G) derived relationships describing the pressure profile along a OTC in supercritical fluid chromatography in terms of experimental parameters. The calculated results for CO_2 as mobile phase suggest that under normal operating conditions in capillary SFC, the pressure profile is nearly linear. Strubinger and Selim (15G) obtained data showing that mobile fluid uptake by the stationary phase decreases with increasing temperature and pressure, which indicates that the stationary phase swelling in SFC could be largely due to stationary phase thermal expansion or relaxation. Yonker (16G) studied stationary phase solvation in capillary SFC. Results demonstrated that the amount of 2-propanol as a modifier, sorbed in the bonded polymer decreased with increasing fluid

density. Heats of sorption of 2-propanol for transfer from the fluid phase into the stationary phase were determined.

Modelling linear and tapered restrictors using two mathematical models that accurately predict mass flow through fixed restrictors was evaluated (17G). These models indicate that the same restrictor used under different chromatographic conditions can produce either laminar or nearly turbulent flow that can result in both major changes in mobile phase linear velocity and pressure. Berger and Toney (18G) studied linear velocity control in capillary SFC by restrictor temperature programming. Restrictor temperature programming offers the potential for independent control of column efficiency while pump pressure at constant oven temperature controls fluid density. Back-pressure regulated restrictor for flow control and the flow characteristics of supercritical CO₂ through an integrally restricted capillary have been described (19G, 20G).

Since the last review, there has been a great deal of interest in instrumentation design. Bruno (21G) described an SF-chromatograph to make physico-chemical measurements. The instrument is used to the measurement of diffusion coefficients. Bally (22G) described sample introduction techniques for SFC. Implications of the use of mass flow restrictors in capillary SFC are discussed, also factors determining separation and speed of analysis are outlined. Because of the importance of instrumental considerations on obtaining the full utility of microbore and capillary columns, improvements in technology have been made (23G-25G). Hirata (26G) described direct injection in SFC. His method allowed solutions, neat liquids and even solids to be introduced onto the column. Bruno (27G) developed a solvent free injection using sintered glass deposition.

Recent developments in detectors have been focused on increasing sensitivity (28G-30G). Many of the detectors commonly used in gas chromatography and liquid chromatography have been interfaced to SFC. David and Novotny (31G) characterized selective responses of the thermionic detector in the nitrogen and

phosphorus modes with respect to detector gas flow rates, thermionic source composition, and supercritical fluid composition. Pekay (32G) studied the sensitivity of SFC-flame photometric detection for organosulfur compounds. The detection limit was greater than that of SFC-FID and increased slightly with increasing molecular weight of the sample. The useful combination of capillary SFC with UV-multichannel detection was demonstrated by France and Voorhees (33G). A pseudo on-column detection approach was used. Detection limits are at the low nanogram levels. Chemiluminescence sulfur detector was successfully interfaced to a capillary SFC (34G,35G). Detector response is linear over three orders of magnitude. Morrissey and Hill (37G) compared ion mobility constants of selected drugs after HRGC and SFC. There were no differences in the mobilities of the reactant ions caused by CO₂ contamination which indicates that the identities of the reactant ions were not affected by CO₂ flow. A radio-frequency plasma was evaluated as an element-selective detector for sulfur and chlorine after SFC. Minimal spectral interferences were found for the CO₂ and N₂O doped plasma. Detection limits depended on the mass flow of CO₂ into the detector. The detection limits and sensitivities ranged from 50 to 300 pg/s (39G). Similarly, a microwave-induced plasma sustained in helium was evaluated as an element sensitive detector for SFC (40G). A review describing the types of interfaces available for SFC/Fourier-transform infra red spectroscopy (FT-IR), including modifications, and the sensitivity studies that have appeared in the literature were discussed by Taylor (38G and 41G).

A review on SFC as a separation technique intermediate to GC and LC discussed the advantages and disadvantages of the three methods (42G). The proper choice of the column type for a given application was treated. Different column configurations and column packings were evaluated for packed column SFC under pressure programmed conditions (43G). The best performance was observed for columns of about 15 to 25 cm in length packed to a moderate density with small diameter particles of low surface area. Porous glass beads as stationary phase in SFC were evaluated in microcolumns for separating oligomers of styrene (44G). A crosslinked cyanopropyl polysiloxane bonded silica phase has been prepared (45G). The bonded phase impeded access to uncapped silanol sites,

thereby giving rise to better peak shapes and more rapid elution without the necessity of a polar modifier. Chromatographic properties of three highly fluorinated stationary phases were compared with those of conventional phases (46G). Schoenmakers (47G) discussed some aspects of OTC vs. packed columns. Attention was paid to the stationary phase film thickness, the speed of analysis, and to the maximum number of theoretical plates. A computer-controlled splitting device was used to study splitting ratios from 1:3 to 1:500 in SFC. At low to medium-high splitting ratios, a solvent effect dependent upon the solvent density was observed (48G).

The influence of operational variables on the various properties of supercritical fluid has been studied by several laboratories. The capabilities of sulfur hexafluoride as a mobile phase were investigated by Hellgeth (49G). An evaluation of its overall utility on the basis of separations of standard aromatic hydrocarbon mixtures performed on a variety of bonded phases with UV-detection was presented. The SF₆ exhibits low solvating power. No adverse effects on the stationary phase or column deactivation was observed (50G). Use of xenon as a mobile phase (51G) indicated the total transparency in the IR region. The discrepancy in reported results with helium head-pressure CO₂ as a pump-filling technique were examined to determine if they were related to instruments hardware, such as the type of injection system or pumping system used, or to an inherent property of the technology itself (52G).

Modifier effects on packed, microbore and capillary columns were investigated (53G-57G). The chromatographic effects of various concentrations of an additive requires detailed studies of the parameters governing retention parameters.

An attractive technique emerging from utilization of a suitable supercritical fluid separation is supercritical fluid extraction. Wright (58G) discussed off-line supercritical fluid extraction, ultrasonic-SFE, and on-line SFE-HRGC methodologies that have been developed specifically for analytical sample preparation and analyses. These methods offer the potential for

extraction rate increases of over an order of magnitude. They are particularly useful for small sample sizes or trace levels of analytes. Combined ultrasonic SFE can further enhance extraction rates from macroporous materials by inducing convection through internal pores. The apparatus and instrumentation are described in detail and several examples are presented, illustrating the applicability of these methodologies. Yamauchi(59G) reviewed applications of SFE-SFC. Similarly, on-line extraction and separation by SFC using packed columns and flame ionization detection was applied to drug and food characterization by (60G). Extraction of caffeine and quinine from various plant materials and morphine from serum was accomplished (61G). The advantages of using combined SFE-SFC for analyzing of complex mixtures and natural products was discussed in detail by Kumar (62G). The system was equipped with a FID and multiwavelength UV-detector. Standard samples of wood, tar residue, engine oil and organometallic compounds have been tested using direct on-line coupling of small SF-extractors with packed columns (63G). A SFE-SFC fraction collection system was constructed to provide extraction, separation and fraction collection of biologically active compounds on an analytical scale (64G). The SF-extractor was decompressed through a small i.d. linear restrictor and analytes were deposited in a deactivated capillary concentrator within a cryogenic trap. The trap was directly connected to the SFC column. After a prescribed period of time, SFE was discontinued and SFC was started with density-programmed mobile phase. Fractions were collected from a frit restrictor at the column outlet in vials that contained a solvent. Liebman (65G) described the combined sample processing, on-line analyzer and data manipulation system using applied artificial intelligence in the integrated instrumentation. Nair (66G) evaluated on-line SFE-accessory interfaced to a HPLC system. The simple and inexpensive method can be used to obtain rapid qualitative information about complex matrices by extraction in sub- or supercritical conditions with a concurrent separation by capillary SFC (67G). Davies (68G) reviewed coupled column chromatographic techniques such as HPLC-GC, SFC-GC and SFE-SFC and their use for the analysis of complex matrices. The development and evaluation of online SFE-GC instrumentation and methodology for the analysis of volatile organic compounds (VOC) from adsorbent sampling devices were reported

by Wright (69G). The results of the methodology validation studies were also presented. These studies included recovery of model VOCs spiked on three different types of Tenax sampling devices, including authentic actively pumped and passive devices. Hawthorne (70G) described rapid extraction and analysis of organic compounds from solid samples using coupled SFE-HRGC. Class-selective extractions can be achieved by performing multiple SFE-HRGC analyses with different extraction pressures. A simple microscale SFE system and its application to GC-mass spectrometry (MS) of lemon peel oil was presented by Sugiyama et al. (71G). Wheeler and McNally performed SFE-optimization experiments with a capillary SFC system using static extraction technique for diuron and linuron pesticides from soil, which resulted in more than 95 percent extraction efficiency. Extraction solvent additives, i.e. polar modifiers, were required to obtain those high recoveries. Carbon dioxide alone was not an effective solvent. Increased extraction efficiencies were obtained at higher densities and extraction temperatures. A correlation between chromatographic retention and extraction efficiency parameters have been established. This suggests using chromatography for optimizing extraction parameters.

Schwartz (73G) compared packed columns and capillary columns for practical SFC separations. Relatively polar compounds were eluted from a microbore column with good peak shape using a mobile fluid consisting of CO₂ modified with formic acid and water. This combination is an effective modifier suitable for use with pressure programming and flame ionization detection. Industrial applications of SFC, their advantages to the separation and analysis of polymers, surfactants, pesticides, industrial pharmaceuticals and isocyanates were discussed (74G, 75G). A review of SFC from the bioanalytical perspective was published by Niessen (76G). Special attention is also given to the various detection techniques applicable to biological materials. Environmental applications of SFC were presented by Borra (77G). A large spectrum of nonvolatile trace organics from various water samples was preconcentrated for subsequent high resolution separations involving microcolumn liquid chromatography with UV detection at 230 nm and capillary SFC with flame

ionization detection. A methylpolysiloxane stationary phase substituted by chiral moieties of the Pirkle type was immobilized on surfaces of fused silica capillary columns for SFC. SFC-separations of enantiomeric amino acids with this chiral polymer stationary phases can be achieved (78G).

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