

AD-A162 660 MULTIDIMENSIONAL HIGH-RESOLUTION GAS CHROMATOGRAPHIC
INVESTIGATIONS OF HY. (U) DAYTON UNIV OH RESEARCH INST
W A RUBEY AUG 85 UDR-TR-84-132 AFMIL-TR-85-2033
UNCLASSIFIED F33615-83-C-2359 F/O 21/4

MULTIDIMENSIONAL HIGH-RESOLUTION GAS CHROMATOGRAPHIC
INVESTIGATIONS OF HV. (U) DAYTON UNIV OH RESEARCH INST
W A RUBEY AUG 85 UDR-TR-84-132 AFMIL-TR-85-2033
F33615-83-C-2359 F/G 21/4

1/1

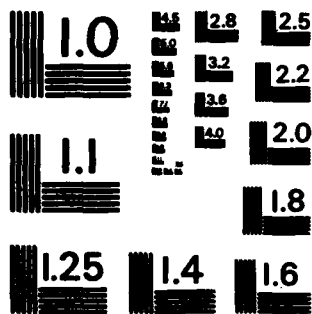
UNCLASSIFIED

F/G 21/4

NL

ENI

THE MFC



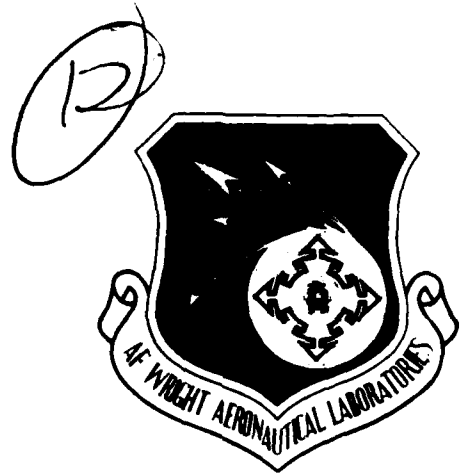
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

AD-A162 660

AFWAL-TR-85-2033

MULTIDIMENSIONAL HIGH-RESOLUTION GAS
CHROMATOGRAPHIC INVESTIGATIONS OF HYDROCARBON
FUELS AND VARIOUS TURBINE ENGINE FUEL
PRECURSORS

Wayne A. Rubey
University of Dayton
Research Institute
300 College Park
Dayton, Ohio 45469



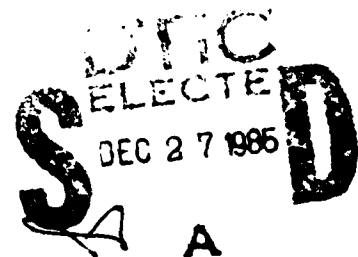
August 1985

Final Report for Period April 1984 - September 1984

DTIC FILE COPY

Approved for public release; distribution unlimited.

AERO PROPULSION LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433



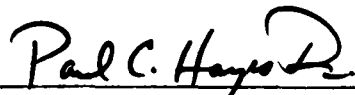
85 12 27 04 4

NOTICE

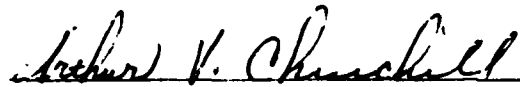
When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

This report has been reviewed by the Office of Public Affairs (ASD/PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

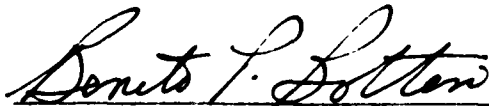


PAUL C. HAYES, JR.
Fuels Branch
Fuels and Lubrication Division
Aero Propulsion Laboratory



ARTHUR V. CHURCHILL, Chief
Fuels Branch
Fuels and Lubrication Division
Aero Propulsion Laboratory

FOR THE COMMANDER



BENITO P. BOTTERI, Assistant Chief
Fuels and Lubrication Division
Aero Propulsion Laboratory

"If your address has changed, if you wish to be removed from our mailing list, or if the addressee is not longer employed by your organization, please notify AFWAL/POSF, Wright-Patterson AFB, Ohio 45433-6563 to help us maintain a current mailing list."

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

UNCLASSIFIED

ADA 162 660

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS N/A	
2a. SECURITY CLASSIFICATION AUTHORITY N/A			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE N/A				
4. PERFORMING ORGANIZATION REPORT NUMBER(S) UDR-TR-84-132			5. MONITORING ORGANIZATION REPORT NUMBER(S) AFWAL-TR-85-2033	
6a. NAME OF PERFORMING ORGANIZATION University of Dayton Research Institute		6b. OFFICE SYMBOL (If applicable) N/A	7a. NAME OF MONITORING ORGANIZATION Fuels Branch, Aero Propulsion Laboratory (AFWAL/POSF)	
6c. ADDRESS (City, State and ZIP Code) Environmental Sciences Group 300 College Park Dayton, OH 45469			7b. ADDRESS (City, State and ZIP Code) Air Force Wright Aeronautical Labs. (AFSC) Wright-Patterson Air Force Base, Ohio 45433-6563	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Fuels and Lubrication Branch/APL		8b. OFFICE SYMBOL (If applicable) AFWAL/POSF	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER F-33615-83-C-2359	
8c. ADDRESS (City, State and ZIP Code) Air Force Wright Aeronautical Labs (AFSC) Wright-Patterson Air Force Base, Ohio 45433-6563			10. SOURCE OF FUNDING NOS.	
			PROGRAM ELEMENT NO.	PROJECT NO.
			63215F	2480
			TASK NO.	WORK UNIT NO.
			13	01
11. TITLE (Include Security Classification) Multidimensional High-Resolution (Con't on R)				
12. PERSONAL AUTHOR(S) Wayne A. Rubey				
13a. TYPE OF REPORT Final		13b. TIME COVERED FROM 4/84 TO 9/84		14. DATE OF REPORT (Yr., Mo., Day) August 1985
15. PAGE COUNT 80				
16. SUPPLEMENTARY NOTATION Report prepared under contract to Computer Software Analysts, Inc., via the AFWAL/POSF Scholarly Research Program (cont'd p. ii) Use single quotes				
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB. GR.		
07	01	03	multidimensional gas chromatography; "valveless" switching;	
21	04	05	negative thermal gradient device; shale oil; pyrolysis oil;	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) The instrumental chemical analysis of complex organic mixtures requires efficient chromatographic techniques for the separation and analysis of the mixture constituents. Highly complicated mixtures, such as petroleum crudes, turbine engine fuels, shale oil, composited industrial organic liquid wastes, etc., require the use of high-resolution gas chromatographic (HRGC) techniques. The recent introduction of multidimensional gas chromatographic (MDGC) procedures shows promise of advancing HRGC techniques even further. The literature pertaining to multicolumn and multidimensional procedures has been surveyed, and an MDGC system was assembled which used a previously optimized open tubular column gas chromatographic system. Special features were incorporated into this MDGC system which contained a two-column arrangement within a single temperature programmable chamber. The performance of the assembled MDGC system was evaluated and it was determined that for maximum performance to be obtained from such coupled-column assemblies, considerable attention must be given to the design and behavior of each of the many				
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS ☐			21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED	
22a. NAME OF RESPONSIBLE INDIVIDUAL P.C. Hayes, Jr.			22b. TELEPHONE NUMBER (Include Area Code) (513) 255-3190	22c. OFFICE SYMBOL AFWAL/POSF

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

#11 Gas Chromatographic Investigations of Hydrocarbon Fuels and Various Turbine Engine Fuel Precursors

#19 cont

different components within the entire chromatographic flow path.

It was concluded ~~from this study~~ that MDGC represents a valuable additional approach for obtaining high-quality analyses of complex organic mixtures. *Keywords: (t, i)*

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

FOREWORD

This report details the results of a study entitled "Multidimensional High-Resolution Gas Chromatographic Investigations of Hydrocarbon Fuels and Various Turbine Engine Fuel Precursors," which examined certain instrumental analysis and separation aspects associated with complex organic mixtures.

The effort was sponsored under the U.S. Air Force Contract F33615-84-C-2359, MOD P0001, Task #1, and Project 24801200, with Computer Software Analysts, Inc., Dayton, Ohio. The research was administered through the Scholarly Research Program of the Fuels and Lubrication Division, Aero Propulsion Laboratory (AFWAL/POSF), Air Force Wright Aeronautical Laboratories, Wright Patterson Air Force Base, Ohio. Ms. Eva M. Conley was the Air Force Contract Manager and Mr. Paul C. Hayes, Jr., was the Air Force Task Project Engineer.

This work reported herein was conducted in the Analytical Instrumentation Research Laboratory of the Environmental Sciences Group within the Research Institute at the University of Dayton, Ohio; under the direction of research chromatographer Mr. Wayne A. Rubey. The research was performed during the period of April 1984 through September 1984, and the report was released in August 1985.

The author is indebted to Mr. Paul C. Hayes, Jr., and Mr. Timothy L. Dues (AFWAL/POSF) for their help during the initiation of the experimental work, and Mr. Don Wright of Scientific Glass Engineering for his valuable consultations during the course of this work. Within the Research Institute, the assistance of several colleagues was especially helpful. The cooperation and continual encouragement of Douglas Hall, Barry Dellinger, and Dennis Gerdeman are appreciated. Mathematical portions of the appendices were reviewed by Jerry Strange and the typing and preparation of this report was performed by Margaret Bertke.

The program manager at Computer Software Analysts, Inc., wishes to express his appreciation to Ms. Eva M. Conley for her help and assistance in overcoming administrative problems associated with this Task 1 of Contract F33615-84-C-2359.

CONTENTS

I. INTRODUCTION	1
II. OBJECTIVES	3
III. REVIEW OF LITERATURE PERTAINING TO VARIOUS MULTIDIMENSIONAL GAS CHROMATOGRAPHIC ASSEMBLIES	4
IV. DESCRIPTION OF MULTIDIMENSIONAL GAS CHROMATOGRAPHIC SYSTEM	9
V. SPECIAL FEATURES INCORPORATED INTO CHROMATOGRAPHIC SYSTEMS	14
1. Electrometer Amplifier Response Time	14
2. Flowpath Junctions and Filtration of Gases	14
3. Instrument Modifications for Enhanced Performance	18
VI. PERFORMANCE EVALUATION OF THE MULTIDIMENSIONAL GAS CHROMATOGRAPHIC SYSTEM	23
VII. CONCLUSIONS AND RECOMMENDATIONS	31
Appendix A Chromatograms of Complex Organic Mixtures . .	33
Appendix B Theoretical Aspects of a Declining Thermal Gradient Gas Chromatographic Member	44
Appendix C Design of Components for Producing Precise and Controllable Negative Thermal Gradients in Tubular Assemblies	58
Appendix D The Influence of the Partition Ratio Upon the Location and Axial Motion of a Solute Zone	69
References	71

v

Available For	
CR&I	☒
IAB	☐
Unprocessed	☐
Distribution	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	



FIGURES

<u>Number</u>		<u>Page</u>
1	Photograph of assembled MDGC system	12
2	Detailed view of column chamber interior . . .	13
3	Electrometer circuit schematic	15
4	Damping circuits of electrometer amplifier . .	16
5	Simple diagram of four-path connector	17
6	Modified detector assembly	20
7	MDGC flowpaths	24
8	Multidimensional Gas Chromatograms	28
9	Chromatogram of a series of normal paraffins (n-C ₈ through n-C ₂₂)	35
10	Chromatogram of Alaskan crude oil (North Shore)	36
11	Chromatogram of refined cresote oil (Sunnyside)	37
12	Chromatogram of light pyrolysis fuel oil (83-POSF-0994, 95% Aromatics)	38
13	Chromatogram of light pyrolysis fuel oil (83-POSF-0162, 2% Aromatics)	39
14	Chromatogram of light pyrolysis fuel oil (83-POSF-0801, 30% Aromatics)	40
15	Chromatogram of Occidental shale crude (82-POSF-0195)	41
16	Chromatogram of HCL 68 PASS I, distillation cut - Initial boiling to 500°F	42
17	Chromatogram of HCL 68 PASS I, distillation cut - 500°F to 800°F	43
18	Graphs of solute zone behavior	52
19	Simultaneous programming of ambient and gradient	54
20	Velocity versus distance relationship	57
21	Basic thermal conductor for an OTC	59
22	Modified versions of basic conductor	61
23	Variation of inner radius with conductor length	64
24	Heat exchanger thermal gradient device	68

SECTION I

INTRODUCTION

The chemical analysis of volatile and semi-volatile organic mixtures is typically conducted by gas chromatography (GC). For mixtures that contain more than 20 different organic compounds, it is usually necessary to invoke some form of high-resolution gas chromatography (HRGC) to separate the constituents. A single-column HRGC system can be assembled which possesses a very broad operating temperature range (e.g., -75°C to +350°C) and such a system could produce between 10^5 and 10^6 theoretical plates.

The information content that a typical HRGC system can generate is very large [1]. Even with a single-column HRGC system, its ability to resolve highly complex mixtures is considerable. Nevertheless, it was recently theorized [2] that although a single-column chromatographic arrangement may possess a very large number of theoretical plates, numerous solute zones will still be fused or only partially resolved upon their emergence from such a high-efficiency system.

A recent study of HRGC as applied to the analysis of turbine engine fuels and other complex organic mixtures [3] showed that attention must be given to every aspect of the chromatographic system to obtain high performance, well shaped elution profiles, good quantitative data, and long useful life from the chromatographic system. From a theoretical standpoint, if two different solutes have a measurable difference in their partition ratios, they can be separated with an adequately efficient column. However, for some solute pairs, this chromatographic column would have to be extremely lengthy, and although a separation is theoretically possible, it would not be practical. For example, to separate isothermally two solutes that exhibit a relative retention ratio of 1.001 would require a very expensive column, tremendous inlet pressures, and a very long time to achieve the chromatographic separation.

Some of the earliest work in gas chromatography demonstrated that by merely changing the stationary phase of the column, one could readily modify the relative retention of two adjacent emerging solute zones. Consequently, it was common knowledge that if two solutes were difficult to separate on one particular stationary phase column, this difficulty might be overcome by obtaining a column with a different stationary phase which would disengage this difficult pair of solutes. From these early observations by chromatographers, there emerged many chromatographic column assemblies that used coupled columns. Specifically, part of the total chromatographic column may be of one stationary phase while another segment of the column contains a different stationary phase. In short, the total coupled column arrangement would be ideally suited for one particular difficult mixture of chemical constituents. In the latter 1960s, tandem packed column arrangements were common, and some analyses were conducted using column assemblies where a packed column inlet member was connected to a downstream open tubular column (OTC) member [4].

The theoretical foundations for multicolumn, multimember, multicomponent, multidimensional instrumental analysis systems have recently been advanced. Of equal importance, the analytical power [5] of such two-dimensional systems has been brought to light. Multidimensional chemical analysis instrumentation and associated techniques possess the ability to obtain high degrees of analytical information content [6] in relatively short amounts of time. Also, by having simultaneous data, the level of total information content concerning a complex sample is increased enormously. With respect to complex organic mixtures, e.g., hydrocarbon feedstocks, organic pollutant concentrates from air and water, turbine engine fuels, industrial organic wastes, etc., multidimensional gas chromatographic (MDGC) techniques have much to offer in obtaining highly descriptive data in a relatively short analysis time.

SECTION II

OBJECTIVES

The objectives of this study were to review, assess, and evaluate the current technology associated with multidimensional gas chromatography (MDGC) as applied to the analysis of complex organic mixtures. To perform this assessment, a high-resolution gas chromatographic system was modified, redesigned, and assembled for conducting a variety of separations and MDGC analyses using a single thermally controlled chromatographic chamber. The assembled high-resolution MDGC system was evaluated with respect to its performance in addressing the analysis of highly complex organic mixtures such as crude oil, shale oil, tar sands, coal liquids, and various biomass samples. Various turbine engine fuel samples were also examined using this system.

The primary objective of this research was to determine the merits of MDGC for the analysis of present and advanced turbine engine fuels along with possible hydrocarbon fuel precursors. Part of this assessment addressed system components and the refinement of instrumental practices. An evaluation of the possible use of MDGC in conjunction with other analytical instrumentation was included in this study.

SECTION III

REVIEW OF LITERATURE PERTAINING TO VARIOUS MULTIDIMENSIONAL GAS CHROMATOGRAPHIC ASSEMBLIES

Multidimensional gas chromatography (MDGC) is receiving increased attention in the analysis of complex organic mixtures. In addition, the body of literature pertaining to MDGC is growing rapidly.* Although very few instruments are specifically designed for MDGC operation, many of the more recently designed gas chromatographic systems can be modified for some form of multidimensional operation.

The early work by Schomburg and his colleagues [7] constituted the first major activity in MDGC. They employed different stationary phase glass capillary columns along with backflushing, intermediate trapping, and various other modes of operation. Since that early work [7], the potential for MDGC has advanced to the point where certain sophisticated MDGC systems [8,9] are considered to be the most powerful combination of analytical instrumentation ever devised for separation and identification of individual components in complex mixtures. A few of these sophisticated MDGC systems [9] are even capable of performing assessments for biological activity. Other researchers claim [10] that the development of MDGC is comparable in importance to the introduction of the flexible fused silica open tubular column.

The theoretical aspects of MDGC [11-13] have recently been examined. Also, the use of tandem dissimilar columns, column systems which incorporate various switching mechanisms, and the information content of this mode of gas chromatography have been investigated. Several studies [14-19] have investigated two-dimensional GC which involved dissimilar stationary phases, various forms of column switching, and backflushing to obtain

*A shorter and earlier review of MDGC with respect to GC system design was presented in reference [3], pages 101 through 106.

enhanced separations. In these studies, considerable attention has been given to the chromatographic flowpaths and switching components which enable the enhanced separations.

The use of highly selective stationary phases for the disengagement of troublesome compounds has recently been examined [20,21], and some MDGC work has been conducted where one of the stationary phases was of the liquid crystal variety. Such column systems should produce dramatic changes in chromatographic retention behavior by simply changing the temperature versus time profile. Again, only recently have liquid crystal stationary phases been available which could withstand the elevated temperatures necessary for eluting some of the higher molecular weight constituents. Studies have been conducted that [22,23] employed a sequential series of columns where individual members were held at different isothermal temperatures. Also, systems have been assembled which use dissimilar stationary phase columns in parallel and in series/parallel arrangements [24,25].

In MDGC, heart cutting has been one of the more popular techniques as it can provide valuable information on unresolved fractions that emerge from the inlet column [26,27]. Heart cutting has also been especially valuable in pulling out selected fractions eluted from a packed column and then reinserting them into a downstream capillary column [28]. These types of trapping procedures, and various versions thereof, permit trace-level analyses to be conducted with MDGC systems [29,30]. However, to obtain accurate trace analyses using MDGC procedures, special attention has to be given to the connection devices, switching mechanisms, and essentially every portion of the gas transport path.

With respect to the various hardware components used in MDGC systems, much thought has gone into the design of these components. Likewise, considerable attention needs to be addressed to the operation of each of these various precise components and the MDGC system as a whole entity. Examinations

of the band-spreading and the extra-column effects in MDGC systems have been conducted [31], and guidelines [32] have been given for the regions within the entire system that require special attention with respect to quantitative transport of solutes. Special interfaces have been designed for joining two chromatographic columns [33], and a newly designed coupling piece for incorporation into the column system has recently been introduced [34]. Two-dimensional gas chromatography has also been conducted which did not involve an intermediate trapping step [35]. Many of the small components such as connectors, junctions, tees, splitting devices, unions, takeoffs, diverters, etc., [36], are precisely machined and specially designed for MDGC applications. In many cases, these special components are key to the successful operation of the MDGC system.

Column and flowpath switching are very important in tandem assemblies of GC columns. Dean's valveless switching technique has permitted these tandem arrangements to function well, and there are now several versions of such closed-path switching arrangements [37,38] in use today. There are also several types of push-pull switching valves, rotary valves, and various solenoid actuated devices used with MDGC systems [39,40]. Switching the direction of gas flow through the primary column, such as in the backflush mode, requires care so that there are no retention hysteresis effects appearing within the column system [41].

To optimize the eventual resolution obtained with different column systems, studies have been conducted on the influence of internal pressure and column temperature in series-coupled GC columns [42]. Window diagram optimization techniques have recently been applied for enhancing chromatographic resolution [43]. Some work has also been done where a conventional capillary GC column was placed in parallel with a microbore OTC [44]. For these types of columns, which produce very narrow elution profiles, attention must be given to the phenomenon of thermal peak splitting, and the chromatographic system must be configured so that this adverse behavior does not occur. A high-performance MDGC system cannot tolerate distorted emerging solute zone profiles [3,45].

There has been some confusion with respect to the term multidimensional chromatography. For example, two-dimensional chromatography has been applied in both paper and thin-layer chromatography for several years [46], and recently there has been some reluctance to use the term "multidimensional" for a process consisting of selective re-chromatographing with an additional elution column which contains a different stationary phase. However, as this is the kernel of the selectivity dimension in chromatography, "multidimensional" persists.

Several attempts have been made to couple liquid chromatography and gas chromatography into a combined system [47-50]. Multidimensional arrangements have been assembled using liquid chromatographic components [51,52], and hydrocarbon group-type analyses, conducted on-line, have used a multidimensional LC-GC system [47,53,54].

Some of the more recent application areas of MDGC have been the analysis of volatile mixtures [55] and volatile organic compounds in ambient air [56]. It has seen extensive use in analyzing gasoline and particularly alcohols in gasoline blends [57]. MDGC has been used for analyzing additives in motor gasolines [58] and for measuring the trace-level heavier organics contained in natural gas [59]. This technique has been used in the analysis of complex hydrocarbons using packed and capillary columns in the same system [60].

Combining MDGC with other hyphenated instrumentation techniques can produce an enormous amount of analytical information. For example, the coupling of an MDGC with a mass spectrometer [60-63] can provide valuable information of both a quantitative and a qualitative nature. The use of MDGC with other special detection devices has also seen considerable application [64].

With the advent of fused silica OTCs, it has recently been possible to prepare an MDGC system which can be obtained within one chromatographic column chamber. Such a system has recently

been introduced [65] and is intended for use in high-performance gas chromatographs. MDGC technology has progressed to the point that a special instrumentation assembly was recently introduced for conducting analyses using a two-chamber system [66].

SECTION IV

DESCRIPTION OF MULTIDIMENSIONAL GAS CHROMATOGRAPHIC SYSTEM

The assembly of a multidimensional gas chromatographic (MDGC) system requires that attention be given to each component within the various gas flowpaths. For example, attention needs to be given to the pneumatics portion of the instrument as this controls the gas flow in the column, the injector, the detectors, etc. The details concerning the mode of admitting sample are also important, whether it be a sampling valve or some syringe-type injection.

The selection of the stationary phases for the columns that are used in MDGC assemblies requires considerable forethought. And, in modern HRGC, it is always desirable to be able to obtain Kovats Indices for the various eluted solutes. The different types of effluent splitting devices continue to warrant attention, and with the availability of an ever increasing arsenal of GC detectors, planning is necessary with respect to the detection devices that are to be used in a particular MDGC system.

With the increased versatility provided by multidimensional separations, other interesting capabilities present themselves, e.g., passing the effluent from the system into cells for testing the biological activities of certain fractions is becoming common. In addition, many new techniques can be applied with MDGC systems. A few examples are: purge and trap procedures, intermediate trapping of solutes, and special trace analyses for select components.

Before describing in detail the system that was assembled during the course of this study, it is beneficial to examine some of the recent chromatographic investigations and advances which have influenced certain aspects of this particular MDGC assembly. There have been some recent advances associated with controlling the gas flow in chromatographic inlet systems [67-70], and some of these flow controllers can be relatively simple [71]. The use of switching valves for admitting sample in arrangements using fused

silica capillary columns continues to be popular [71,72]. Also, there is increased interest in high-speed gas stream switching devices, such as the special fluidic switches [74].

Certainly one of the most active areas in OTC technology is the continuing development, fabrication, and testing of high-performance GC columns which possess moderately polar to polar stationary phases [75,76]. One special area that is receiving considerable attention is the development of liquid crystal stationary phase OTCs [77,78]. In these particular OTC development efforts, an objective is to obtain wide operating temperature range columns, e.g., sub-ambient to greater than 300°C. Also as there is continuing interest in reporting chromatographic retention data in terms of Kovats Indices [79], the output data from the various columns that make up a MDGC system should have features for reporting this qualitative information.

When assembling multicolumn chromatographic arrangements, the detailed aspects and performance of connectors and splitters are of key importance. Work is continuing in the development of polyimide and special metallic effluent splitter arrangements [80,81]. With these devices, and the various butt-end connectors, there is continuing concern about quantitative transport of higher molecular weight materials, e.g., C₃₀ and higher. It is difficult to quantitatively transport trace levels of these heavier substances through some of the present commercially available connectors and tee junctions.

Work is continuing in the area of optimizing certain chromatographic detectors [82], and increased MDGC applications are seen for the newly developed special purpose GC detectors [83] and other highly sensitive detection devices, such as, photoionization detectors (PID), flame photometric detectors (FPD), and the newly emerging mass selective detection (MSD) devices. With the recent interest in evaluating certain bioactive compounds, there are increasing examples whereby the effluents from MDGC systems are subjected to Ames testing [84] for isolating bioactive constituents in hydrocarbon mixtures.

Several recent innovations will have an impact on MDGC technology. For example, the use of whole column cryogenic trapping of volatiles for purge and trap work seems to have considerable promise [85]. Intermediate trapping with modified temperature vaporizers would appear to be of value in MDGC applications [86]. The coupling of packed columns and open tubular GC columns dates back almost two decades [4,87,88], and recently, this particular coupled column arrangement has been seen to have considerable practical value in MDGC applications [89].

The basic gas chromatographic system that is the foundation instrument for this MDGC work is a modified Varian 3700 Gas Chromatograph. This particular research grade instrument has been extensively modified [3] to perform state-of-the-technology high resolution chromatographic separations. The assembly of the MDGC instrumentation was performed in the Analytical Instrumentation Research Laboratory which is located within the Research Institute at the University of Dayton. Additional chromatographic modifications were conducted on this assembly which basically employed two OTCs, one of intermediate polarity and the other a non-polar stationary phase column.

The special capillary pressure switching system module is a product of Scientific Glass Engineering Inc., (SGE) and was adapted to the modified 3700 GC.

MDGC can be conducted in a single chromatographic chamber [65] and early and encouraging work [65,90] conducted by staff members of SGE prompted us to pursue this route for the initial MDGC investigation with the complex hydrocarbon mixtures that were of interest in this study

Figure 1 is a photograph of the assembled MDGC system (note that the oven door has been removed from the chromatograph). Figure 2 is a more detailed view of the interior of the column chamber and shows the many connections that are involved in a typical MDGC installation. This MDGC system incorporates numerous HRGC refinements, several of which are discussed in the next section of this report.

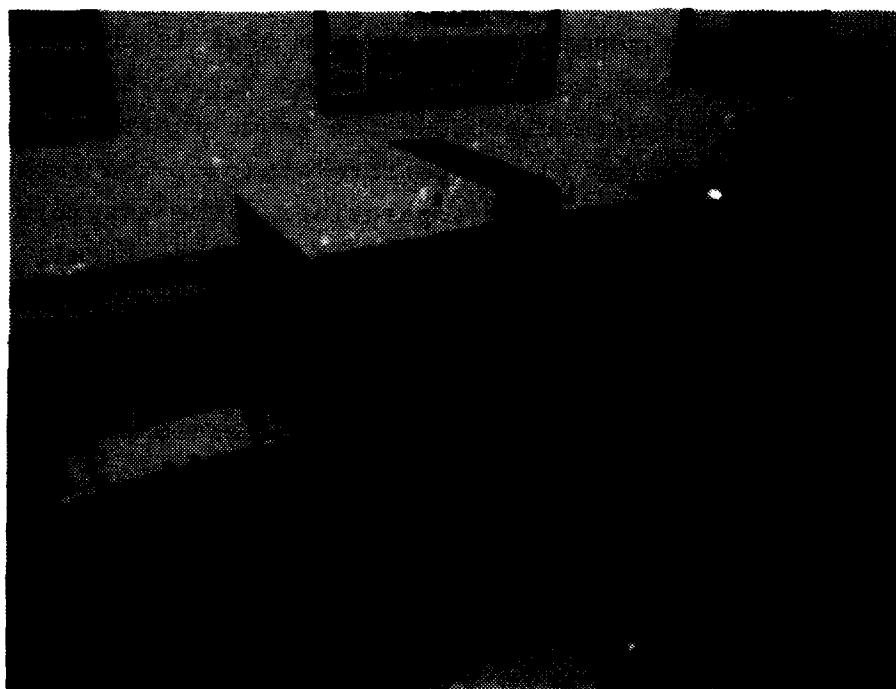


Figure 1. Photograph of Assembled MDGC System.

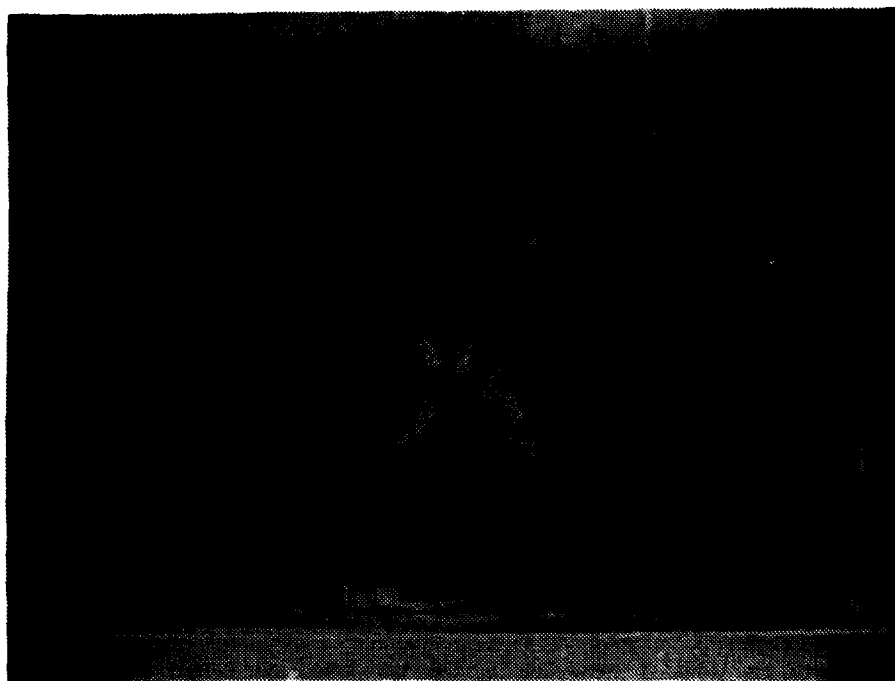


Figure 2. Detailed View of Column Chamber Interior.

SECTION V

SPECIAL FEATURES INCORPORATED INTO CHROMATOGRAPHIC SYSTEMS

With the advent of rapid separation gas chromatography (RSGC), and the recent introduction of microbore OTCs, increased demands have been placed upon certain components in a HRGC system.

1. Electrometer Amplifier Response Time

It is important that the solute zones that emerge from a GC system be faithfully amplified and measured. For rapidly emerging zones from a high-efficiency column, it is necessary that the electrometer response be fast enough to accurately follow the solute concentration profile. Most commercial GC instruments use amplifiers which have a time constant of about 0.25 seconds. For rapidly emerging narrow profiles this is not fast enough.

The intended flexibility of the MDGC system required that there be a ready adjustment of the time constant of the electrometer amplifiers that are used with the hydrogen flame ionization detectors (HFID). Figure 3 shows the complete circuit schematic for each electrometer that is used in this system, and an enlarged view of the important portion of this schematic is presented in Figure 4. With the removal of certain capacitors from the RC damping circuits (see Figure 4), it was possible to lower the time constant to a value of approximately 40 milliseconds. Hence, the electrometers would now be able to follow even the narrowest of emerging profiles from the MDGC system.

2. Flowpath Junctions and Filtration of Gases

In some coupled column chromatographic arrangements (and most especially in MDGC) the connection devices between tandem columns are of key importance. In many cases, it is desirable to be able to monitor eluting constituents at these junctions. Thus, a specially designed connector is needed to adequately accomplish this function. Figure 5 is a simple diagram of the

See Figure 4

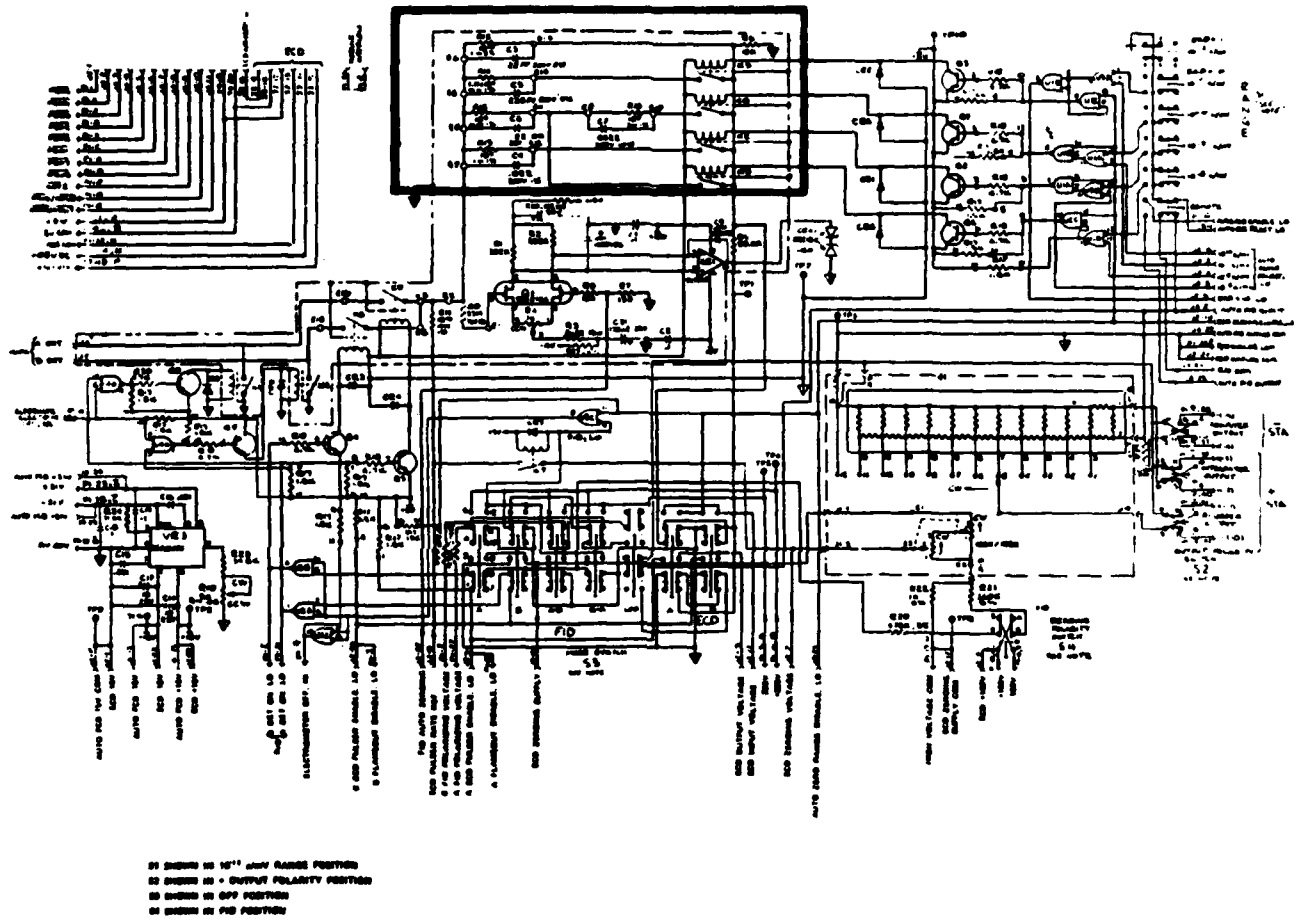
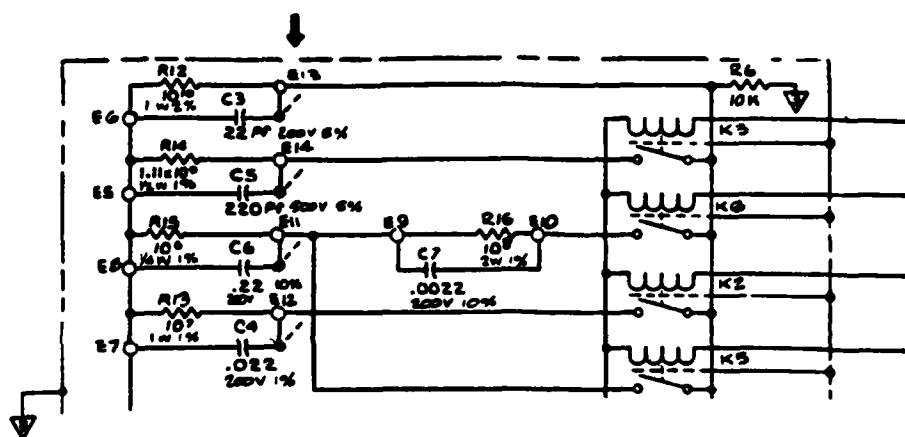


Figure 3. Electrometer Circuit Schematic.

CAPACITOR SWITCHES



Removal of parallel capacitors from 10-11 and 10-12 AFS electrometer circuits produced time constants of approximately 40 milliseconds

Figure 4. Damping Circuits of Electrometer Amplifier.

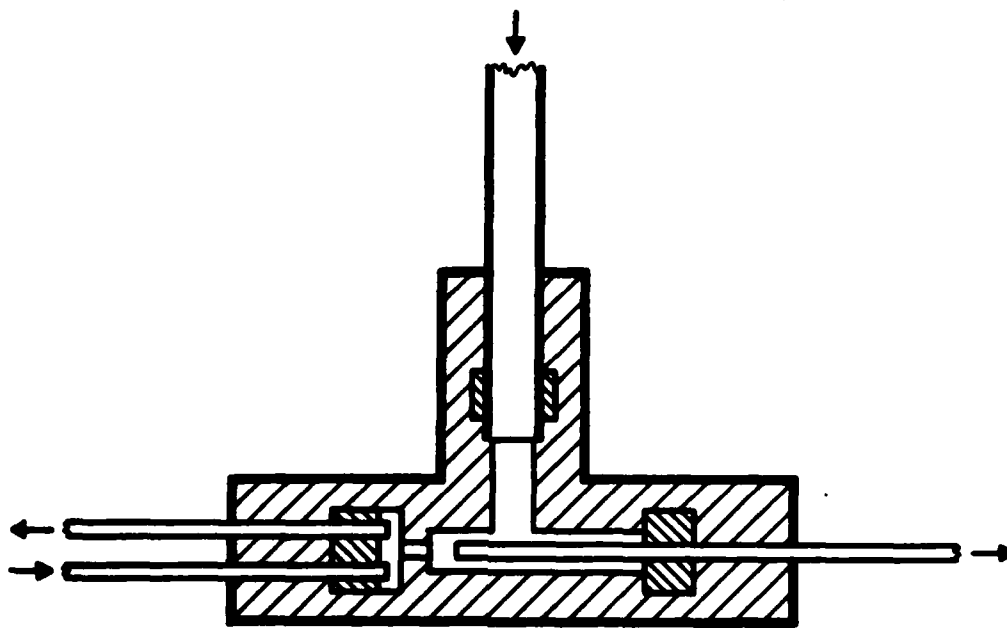


Figure 5. Simple Diagram of Four-Path Connector.

four-path connector that is used in the present MDGC system. It utilizes a fine-bore fused silica tube which eventually terminates in one of the HFIDs. This fine-bore flowpath transports the solutes from the exit of the primary column through a specially actuated on-off valve, and then into the inlet of the detector.

Numerous modifications had been performed previously [3] on the basic chromatograph that houses this MDGC system. The gases that enter the injector and the detection devices are extensively filtered to remove water, oil, and organic impurities. The system also contains special filters to remove minute dust particles. The chromatographic carrier gases have in-line filtration to remove even trace levels of oxygen. Rigorous attention was given to gas purification for the reduction of output signal noise, elimination of spurious transients, and for obtaining long-life column performance.

3. Instrument Modifications for Enhanced Performance

In previous work with high-quality fused silica OTCs, it was found desirable to place the entire column within a special aluminum chamber which was then in turn placed within the chromatographic oven. This feature was also available for the MDGC system, only now individual enclosures would be required for the two chromatographic columns. This chamber-within-a-chamber procedure had previously demonstrated its ability to remove even miniscule distortions in emerging solute profiles.

The chromatographic arrangement was further modified to eliminate unions and junctions in the various inlet and transfer tubes. Helium and hydrogen were premixed and then sent to the base of the HFIDs without the use of unions within the high-temperature chromatographic oven compartment. The mixture of helium and hydrogen was preselected so that optimum and stable chromatographic response would be obtained from the HFIDs. Also, elimination of unions would avert any possible thermal cyclic

leakage of gas. Union-less gas flowpaths in HRGC are desirable. However, there are some situations where special configured junctions are necessary, and in these cases, considerable attention to design details and performance is necessary [91]. Also, of key importance in complicated tandem column arrangements is the elimination of temperature fluctuations and gradients throughout the uniform column environment [92]. Within this MDGC assembly the detectors are continually kept at temperatures 20°C greater than the maximum experienced during the column's programmed temperature sequence.

The modified detector assembly shown in Figure 6, was used for both of the HFIDs that were employed in this MDGC system. Both detector assemblies contained inserts which place the exit of the fused silica column as near the active region of the detector as possible. These special adaptors used an alignment device and a very thin metal conductor partition between the column exit and the actual flame of the detector. In previous laboratory work, this detector assembly adaptation demonstrated especially responsive and stable sensing of emerging solute profiles.

Components and procedures for the cryofocusing of injected samples or solutes represents an area that is receiving considerable attention [93-95]. Although different coolants are used for conducting cryofocusing, the present MDGC system uses a liquid CO₂ coolant for localized cooling of the capillary column that is just downstream of the mid-point connector. Maximum performance in high-resolution MDGC depends to some extent upon the efficiency of thermal focusing at the sample insertion location, and more importantly, at various intermediate locations throughout the entire chromatographic system. Both the cryofocusing and the release of concentrated solutes are important.

At the University of Dayton, there has been interest in cryofocusing for many years [96], and it is the opinion of many that considerable progress remains to be made in this important area, particularly with respect to the very high-efficiency GC

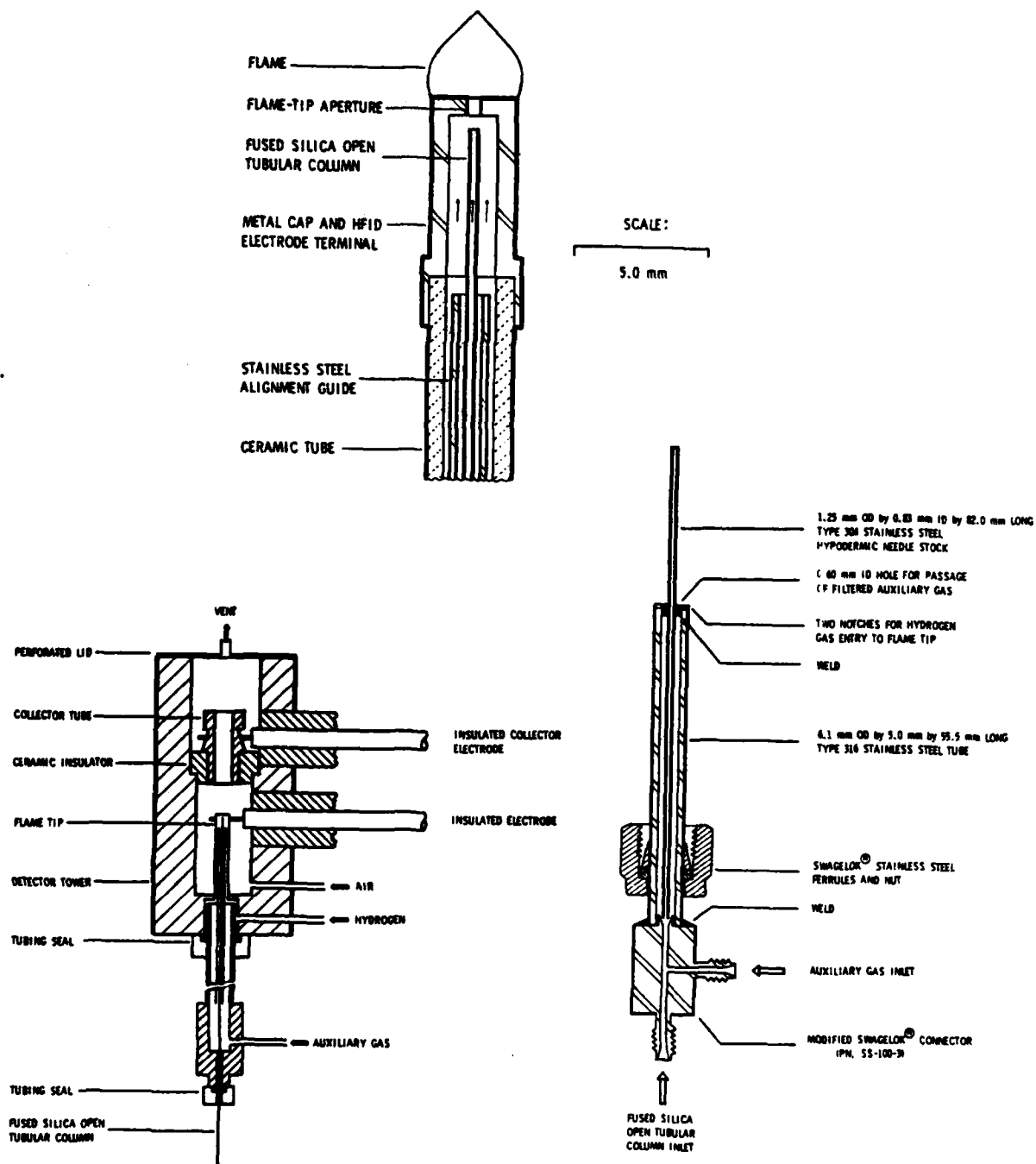


Figure 6. Modified Detector Assembly.

systems. Appendix B of this report contains a theoretical description of a thermal gradient-open tubular chromatographic concept that also has application to focusing and releasing solutes.

Appendix C of this report addresses some of the design considerations and concepts for producing well-controlled axial thermal gradients in chromatographic columns or open tubular trapping members. Appendix D is a description of the important influence of the partition ratio with respect to low-temperature gas-liquid chromatographic trapping of different solutes.

Microbore OTC gas chromatographic columns are receiving [97-99] increased attention as they are very efficient and can perform rapid separations of complex mixtures. In this MDGC assembly, a high-performance microbore open tubular GC column has been included as an optional secondary column for performing specific separations with very high efficiency. Some of the emerging peaks from this high-efficiency column can be on the order of 0.5 second width at half height. The only current method for injecting samples onto microbore fused silica OTCs is the split-mode of injection, however, when such OTCs are used as the secondary column in a column system, some form of tee splitter may serve quite well for admitting the sample.

For fast chromatographic separations with OTCs, hydrogen is the preferred carrier gas [100]. In fact, for suitable chromatographic systems, hydrogen carrier is superior to both helium and nitrogen in practically every aspect [101-103]. This is especially the case when long OTCs are operated in the programmed-temperature GC mode. The modified Varian 3700 gas chromatograph had been used in the past with hydrogen as a carrier gas and safety problems were minimal as the small-bore gas inlet tubing served as a flow restrictor. However, the use of a hydrogen carrier with the presently configured MDGC assembly could present some difficulties. For example, some of the devices within the control console, i.e., solenoids and switches, are not explosion proof, and although the interior of the enclosure can be purged

with nitrogen or argon, it was decided not to use a hydrogen carrier gas in the MDGC system.

The on-column injection of samples for chromatographic systems which use OTCs has received considerable attention and acceptance [104,105]. Although the MDGC system has been equipped with an on-column injector, most of the work performed thus far has been conducted using the split-mode of sample injection. With the present multidimensional flowpath configuration, it is not possible to operate in the backflush mode when an on-column injector is used for inserting samples.

It has been known for many years that increased sensitivity can be obtained with an HFID if nitrogen gas is used as the auxiliary or make-up gas. Initially, it was our intention to equip this MDGC system so that an optimized flow of nitrogen gas could be admitted with the hydrogen prior to entry into the HFID. After extensive discussions with Professor Cramers of Eindhoven University in Holland, we decided not to employ nitrogen as a supplementary gas for the HFID. Specifically, from studies conducted in Holland, it was found that although a nitrogen supplemental flow would produce approximately 40% greater response from the HFID, an equal or greater contribution to the signal noise was produced. Consequently, it was Professor Cramers' opinion that helium was the best make-up gas particularly when both the hydrogen and helium gases had been highly purified.

In the early days of OTC gas chromatography, flow programming [106] was considered an adjunct technique that could be conducted in conjunction with programmed-temperature gas chromatography. More recently, flow programming has found application in the analysis of simple mixtures using short capillary columns under isothermal conditions [107]. However, in view of the recent introduction of microbore OTCs, and their innate ability to separate complex solute mixtures rapidly, the appeal of flow programming is diminished. Even so, flow programming in a MDGC may still be of value particularly with respect to thermally labile solutes.

SECTION VI

PERFORMANCE EVALUATION OF THE MULTIDIMENSIONAL GAS CHROMATOGRAPHIC SYSTEM

The initial work conducted with the assembled MDGC instrumentation involved the use of several different OTCs. After trying a few different combinations, it was decided to use a moderately polar phase OTC as the primary column, i.e., the OTC that would receive the injected sample. The secondary column contained a non-polar stationary phase. Specifically, the majority of the work with the MDGC assembly was conducted with the primary column being a 15 m by 0.25 mm ID fused silica column containing a 0.25 micron film thickness of chemically bonded DB-1701 stationary phase, while the secondary column was of the same dimensions and contained a 0.25 micron layer of SE-30 silicone phase. A drawing of the MDGC column flowpaths is presented in Figure 7.

Earlier work had been conducted using wider bore OTCs such as a 0.31 mm ID column and one of the new megabore OTCs which had an inside diameter of 530 microns. Work was also conducted with a microbore OTC having an inside diameter of 100 microns.

The carrier gases and detector auxiliary gas used with this system were cleansed and filtered using a Hydropurge* near the gas cylinder regulator. Downstream close to the inlet of the chromatograph was located a large capacity Oxy-trap which was followed by an indicating Oxy-trap* for the removal of trace levels of oxygen from these gas streams. The hydrogen gas was also passed through similar Oxy-trap filters. Accordingly, throughout this study, very clean chromatographic signals were obtained, and after the columns had been efficiently conditioned, baseline elevations and phase bleed signals were extremely small. At no time were spurious transits observed during the recording of the chromatographic output data.

*Packaged gas purification filters supplied by Alltech Associates.

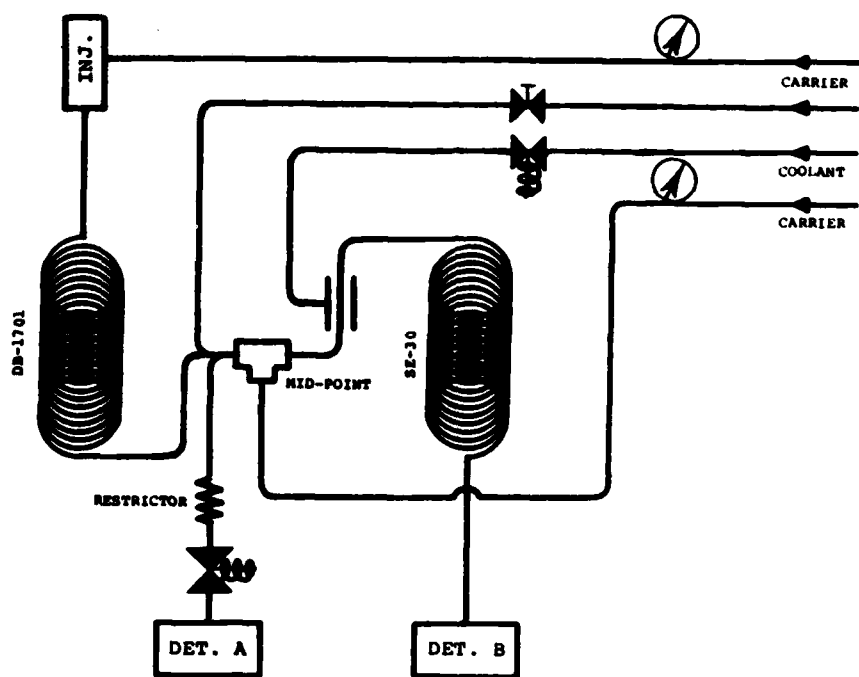


Figure 7. MDGC Flowpaths.

The installation of SGE's Multidimensional Capillary Switching System in the modified Varian 3700 instrument was time consuming. However, by following the detailed instructions provided by the manufacturer, and also having access to one of their video tapes covering the installation of the various components, this assembly was completed without undue difficulties. The most troublesome part of the installation was when OTCs of markedly different diameters (megabore/microbore) had to be installed in the assembly. This was tedious work and it required precise drilling of special two-hole ferrules (VG-2 blanks from Alltech) that were needed for these unusual installations. When the column diameters were small and of comparable size, the assembly attachments at the MDGC junctions presented few difficulties. It was only when a small-bore capillary was to be joined to one of the large-bore OTCs that problems were encountered, and, on many occasions, there was column-end breakage at these junctions and several attempts were necessary before attachments could be made.

One of the electrometer amplifiers had been modified for rapid response (time constant of that particular amplifier was approximately 40 milliseconds). GC output recorded using this electrometer channel was well behaved, although there did appear to be an increased noise level when monitoring the signal using a one millivolt full-scale recording potentiometer. The recorded output contained considerably reduced distortion when the signal was sent to a recording system that incorporated digital filtration.

After assembly of the column arrangement shown in Figure 7, (DB-1701 primary column and SE-30 secondary OTC), it was desirable to see if the assembled system was vulnerable to gas leaks as a result of thermal cycling of the various tubing components contained within the gas chromatographic oven. Many of the components used in this assembly were attached using the graphite/Vespel ferrules as supplied by SGE, however, some replacement ferrules (VG-2 blanks) were drilled out in our electronics shop using a special drill press that is routinely employed for precise

drilling of printed circuit boards. Once the entire MDGC system had experienced sufficient time at a temperature of 275°C, the assembly was returned to room temperature and each of the connections was retightened slightly. Subsequent testing that occurred over a period of many weeks revealed no detectable leaks occurring at these junctions. Thus, the MDGC system remained gas tight with respect to broad range thermal cycling.

After the initial leak checking of the system, helium gas pressures were applied to the column arrangement as shown in Table 1. The performance of this MDGC arrangement was then evaluated using special organic compounds and mixtures to establish the efficiency, inertness, and general behavior of the entire system with respect to complex hydrocarbon mixture analysis. The performance obtained with the particular MDGC flowpath arrangement shown in Figure 7 was quite remarkable.

Figure 8 clearly shows the ability of the MDGC system to separate clusters of solute zones. The "A" region as originally eluted through the DB-1701 column consisted of three recognizable solute zones. However, through a subsequent sample injection and trapping of this same "A" region, it is seen there are six separate solutes emerging in this particular region. Also from Figure 8, the "B" cluster appeared to have approximately five (5) detectable solutes in the original chromatogram. However, with the subsequent re-chromatographing of the "B" fraction using the SE-30 secondary OTC, it is seen that there are at least 12 different solute zones in this particular fraction.

Both of these OTCs had similar dimensions and film thicknesses. In addition, the elution zone profiles were symmetric. This indicates that for this particular column assembly, the flow-path junctions and the entire MDGC function well. Also, in previous work with the larger bore OTCs, good peak shapes were obtained.

TABLE 1
PRESSURE SETTINGS FOR MDGC COLUMN ARRANGEMENT

CALIBRATION DATA
MDGC SYSTEM

DB-1701 Primary Column Inlet Pressure (PSIG)	SE-30 Secondary Column Inlet Pressure (PSIG)
27.5	14.8
30.0	16.0
25.0	13.2
20.0	10.6
15.0	8.1
10.0	5.5

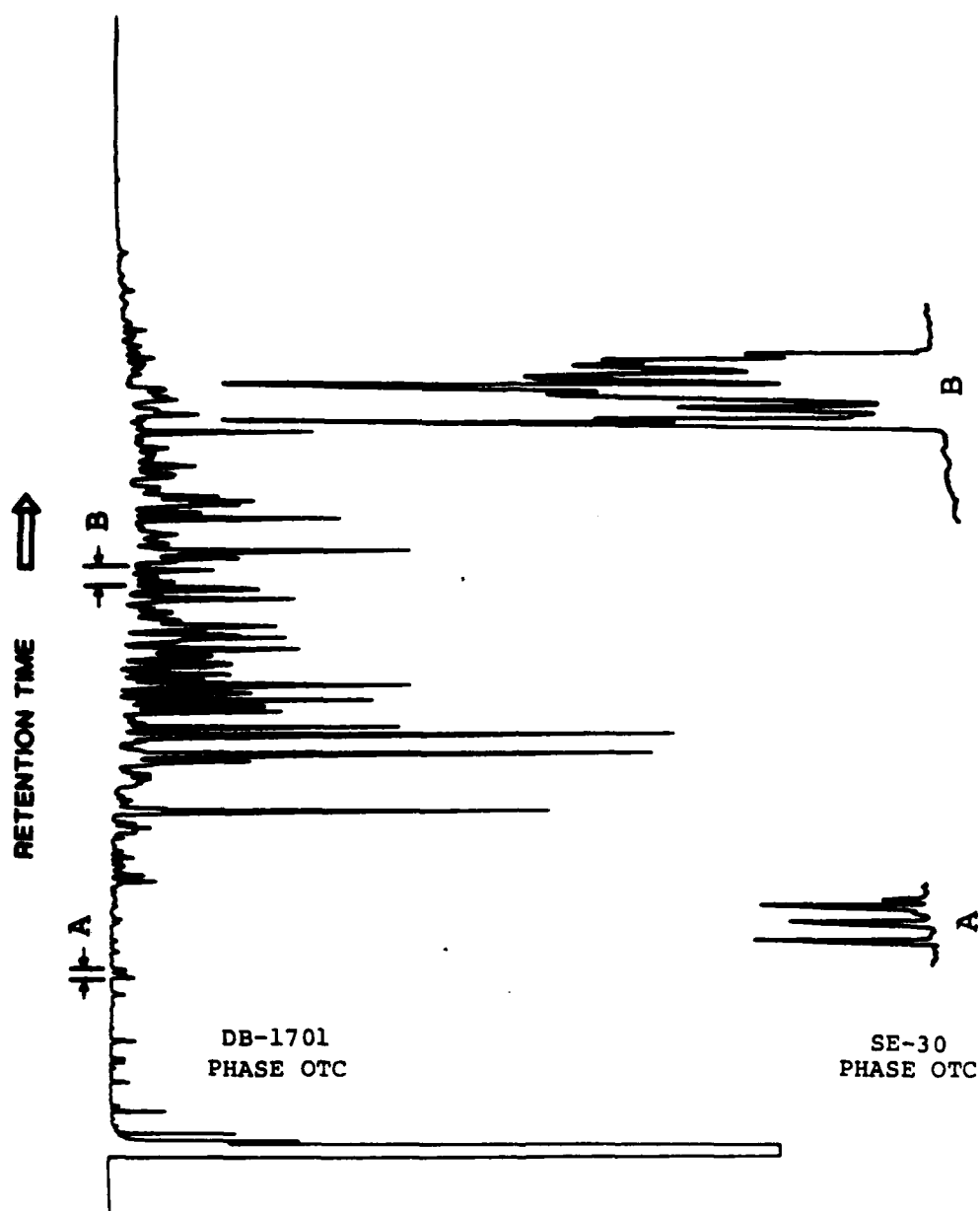


Figure 8. Multidimensional Gas Chromatograms.

The initial examinations with a microbore capillary column (25 m by 0.100 mm ID of bonded phenylmethyl silicone phase) exhibited superb chromatographic separations and practically ideal zone profiles. These initial examinations were performed using the modified HRGC instrument [3], and the output signal (chromatogram) was recorded using a Varian 4270 Recording Integrator. However, when the microbore OTC was connected into the MDGC system, considerable tailing of emerging solute zones was evident. It is anticipated that the slow rate of sweeping and the residual internal volume associated with the mid-point junction were responsible for the tailing of these otherwise sharp elution profiles. Such adverse behavior can be corrected downstream through appropriate solute cryofocusing, trapping, and controlled releasing procedures such as described by the methods presented in Appendix B of this report.

The multidimensional chromatographing of polar solutes and organic compounds that tend to adsorb would seem to require specially designed connection devices to optimize solute transfer into the small inside diameter microbore OTCs which exhibit very low gas-volume flow rates. High-molecular-weight solutes that are polar in nature and which contain certain troublesome functional groups are difficult to transport quantitatively in some chromatographic systems. Theoretically, transport difficulties would increase as solute concentrations diminish, and in many cases, this is the area (trace analysis) in which quantitative transport is most important [108]. Wide-bore OTCs that have a thick layer of bonded stationary phase do not have the same difficulty in transporting trace level concentrations as that experienced by a microbore OTC which possesses an extremely thin film of bonded phase.

The MDGC assembly as depicted in Figure 7 behaved quite well with a variety of different test compounds. Indeed, the separations and performance were quite remarkable, particularly for a system that contained two relatively short OTCs (each

column was 15 m long). This MDGC arrangement was then used to separate and analyze a variety of samples that were of interest, e.g., crude oil, shale oil, tar sands fractions, biomass liquified samples, coal oil fractions, and various other hydrocarbon mixtures that originated from petroleum or shale oil. Examples of work with these samples are presented in Appendix A of this report.

SECTION VII

CONCLUSIONS AND RECOMMENDATIONS

During the course of this study, it became increasingly clear that high-resolution MDGC provides a powerful mechanism for disengaging the numerous overlapping and fused solute zones as encountered in the chromatography of complicated mixtures. The applications for MDGC are going to be numerous as this is a valuable specialized technique for separating and analyzing organic mixtures that contain hundreds of organic compounds, such as turbine engine fuels, their associated feedstocks, and various other types of complex organic mixtures.

MDGC is definitely recommended for a laboratory that is involved with many analyses of complex volatile or semi-volatile organic mixtures. This technique not only provides increased resolution of mixture of constituents, but can also generate valuable analytical information in a much shorter period of time. Although MDGC operationally is more complex than single column chromatographic installations, its benefits far outweigh the increased level of complexity. In many HRGC analyses, only very small portions of the complex sample would need to be analyzed [109], and in such cases, even faster acquisition of data can be obtained. It would seem that the development of analytical methods which involve MDGC is an area that is just now beginning to open up. With increased versatility and analytical capabilities being offered by selective detection devices, particularly the recently introduced mass selective detection instruments [110,111], MDGC is potentially an even more powerful technique. With respect to further recommendations in MDGC technology and implementation, it would seem that these separation procedures could benefit from further study in establishing additional operational mechanisms for disengaging solute zones, e.g., employing variable temperature programming rates and different carrier gas velocities [112] for further separation of difficult solute pairs.

The incorporation of hydrogen carrier gas into an MDGC system has definite advantages as separations can be made faster and with greater detectability. However, specific precautions must be taken to insure that this mode of operation is carried out safely.

OTCs that possess a broad operating temperature range (-75°C to $+350^{\circ}\text{C}$) are now available. Therefore, it would seem that enhanced thermal focusing techniques could now be pursued which provide simultaneously solute zone focusing and separation.

As with HRGC systems, each component in an MDGC system needs to be designed and optimized for maximum chromatographic performance. Attention needs to be given to the injection devices, the various specially designed tubing connections, the thermal fluctuations throughout the system, the dynamic response of GC system components, and the processing of chromatographic output signals.

Equipment is currently available for conducting MDGC in both single-chamber and double-chamber assemblies. Each of these instrumental approaches to conducting MDGC has its own advantages and disadvantages, e.g., cost, versatility, complexity, etc.

One area receiving current attention in MDGC is the coupling of a large capacity inlet member (a packed column) with a high-efficiency OTC secondary member. Sample injection into such an assembly would be simple, and it is anticipated that the splitting of migrating solutes onto the high-efficiency secondary member may be quite satisfactory and not wrought with the same type of nonlinearity and discrimination effects that are involved with the high-temperature split-mode injectors. Injection of samples into such an MDGC system would have both high capacity, and when needed, high-resolution capabilities for disengaging closely spaced solute zones.

APPENDIX A
CHROMATOGRAMS OF COMPLEX ORGANIC MIXTURES

The multidimensional gas chromatographic instrumentation assembly was used for examining a variety of complex fuels, feedstocks, and industrial organic mixtures. Table 2 identifies the various samples, which were selectively dissolved in a volatile solvent prior to insertion in the system.

The chromatogram and sample shown in Figure 9 represents the Kovats Indices standard mixture. This particular sample was used as a reference for peak shifting relative to the two different gas chromatographic stationary phases, specifically, the DB-1701 and the SE-30 dimethyl silicone.

Chromatograms 10 through 17 represent extremely complicated organic mixtures and in all cases, the MDGC approach was beneficial in obtaining enhanced separations of certain fused solute zones. The tar sands bitumen sample, designated as sample J, was not amenable to gas chromatographic analysis as this material could not be eluted through the particular gas chromatographic columns.

TABLE 2

SAMPLES SUBJECTED TO HRGC AND MDGC EXAMINATION

Sample Designation	Solvent	Concentration (% v/v)	Description of Sample
A	n-hexane	5	Series of normal paraffins (8 through 22)
B	n-hexane	5	Crude Oil Alaskan (north shore)
C	methylene chloride	5	Sunnyside Refined Creosote Oil
D	n-hexane	5	Light Pyrolysis Fuel Oil 83-POSF-0801, 30% Aromatics
E	n-hexane	5	Light Pyrolysis Fuel Oil 83-POSF-0994, 95% Aromatics
F	n-hexane	5	Light Pyrolysis Fuel Oil 83-POSF-0162, 2% Aromatics
G	n-hexane	2	Occidental Shale Crude 82-POSF-0195
H	methylene chloride	5	HCL68 Pass I Distillation Cut Initial Boiling Point to 500°F
I	methylene chloride	5	HCL68 Pass I Distillation Cut 500°F to 800°F
J	methylene chloride	2	Tar Sands Bitumen 84-POSF-1937

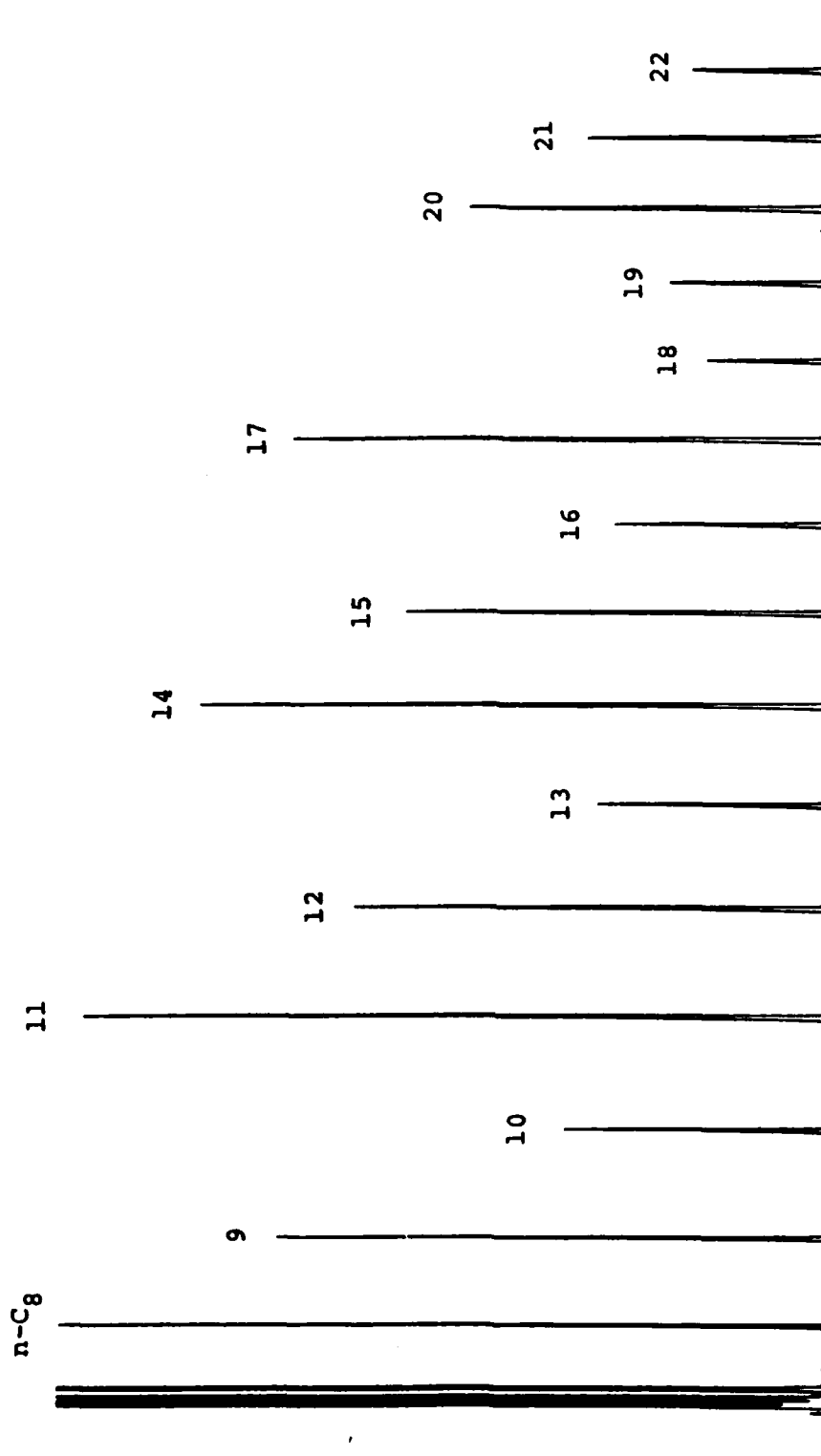


Figure 9. Chromatogram of a Series of Normal Paraffins (n-C₈ through n-C₂₂).

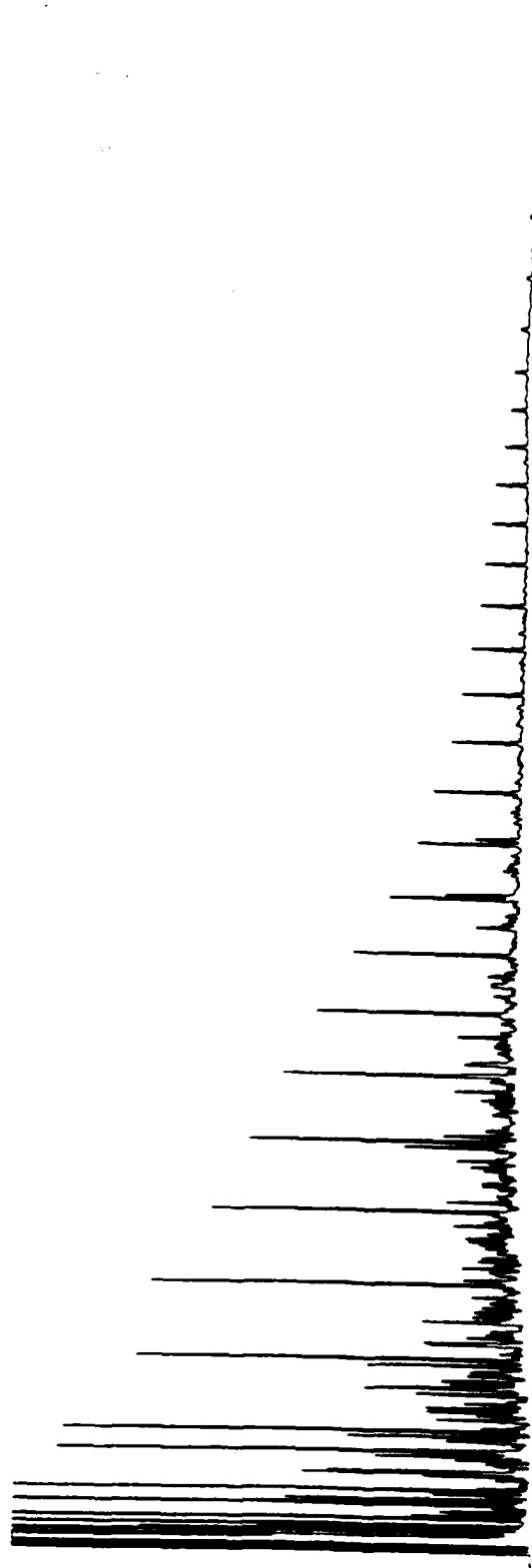


Figure 10. Chromatogram of Alaskan Crude Oil (North Shore).

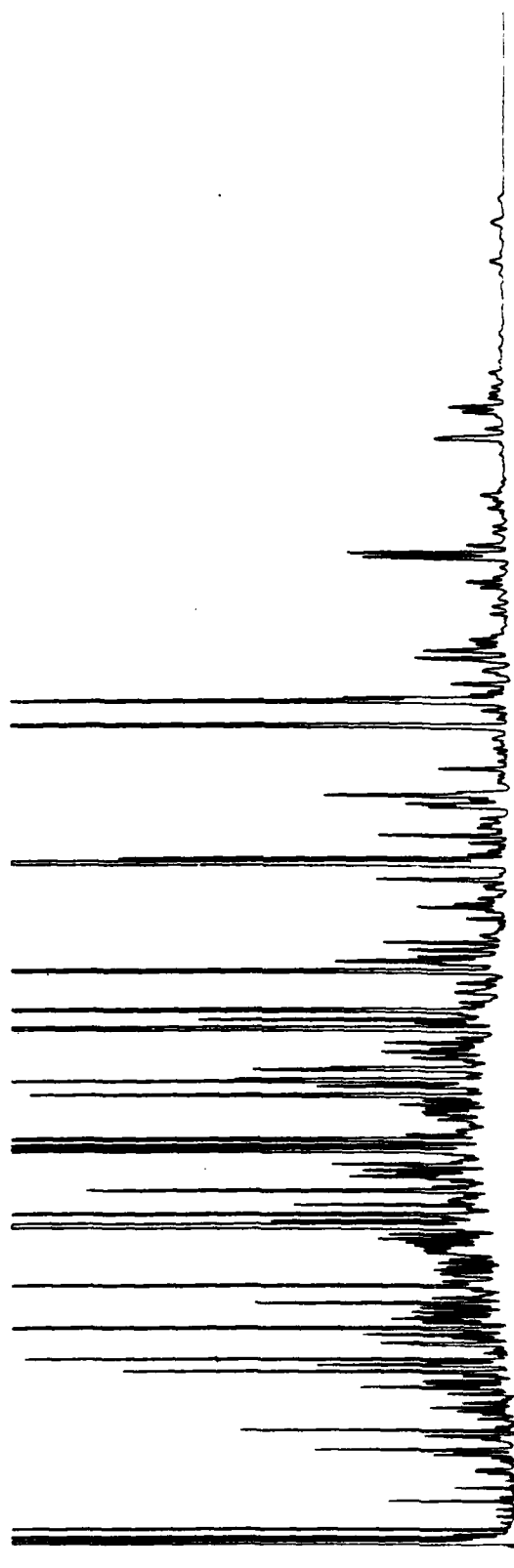


Figure 11. Chromatogram of Refined Creosote Oil (Sunnyside).

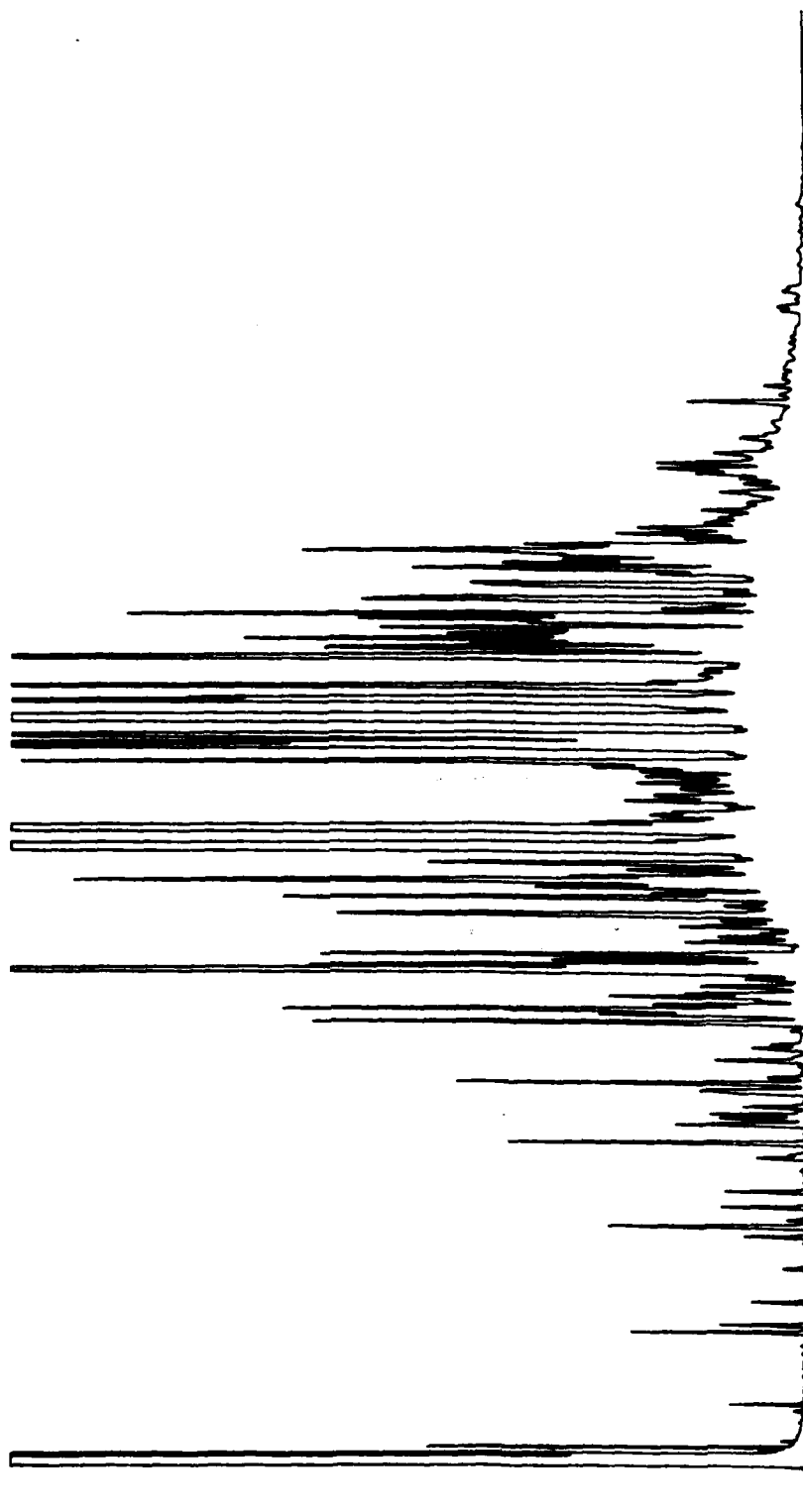


Figure 12. Chromatogram of Light Pyrolysis Fuel Oil (83-POSF-0994, 95% Aromatics).

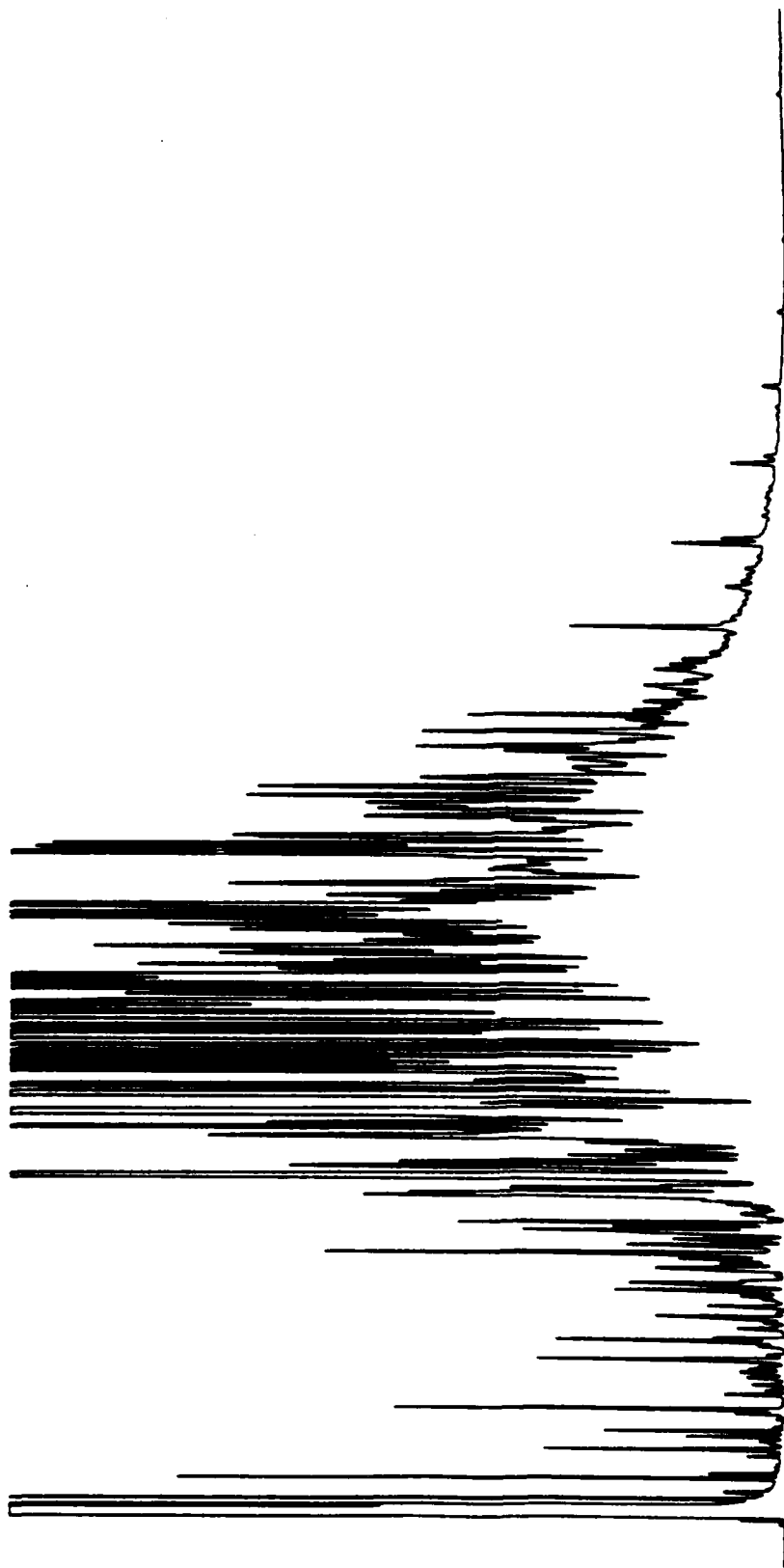


Figure 13. Chromatogram of Light Pyrolysis Fuel Oil (83-POSF-0162, 2% Aromatics).

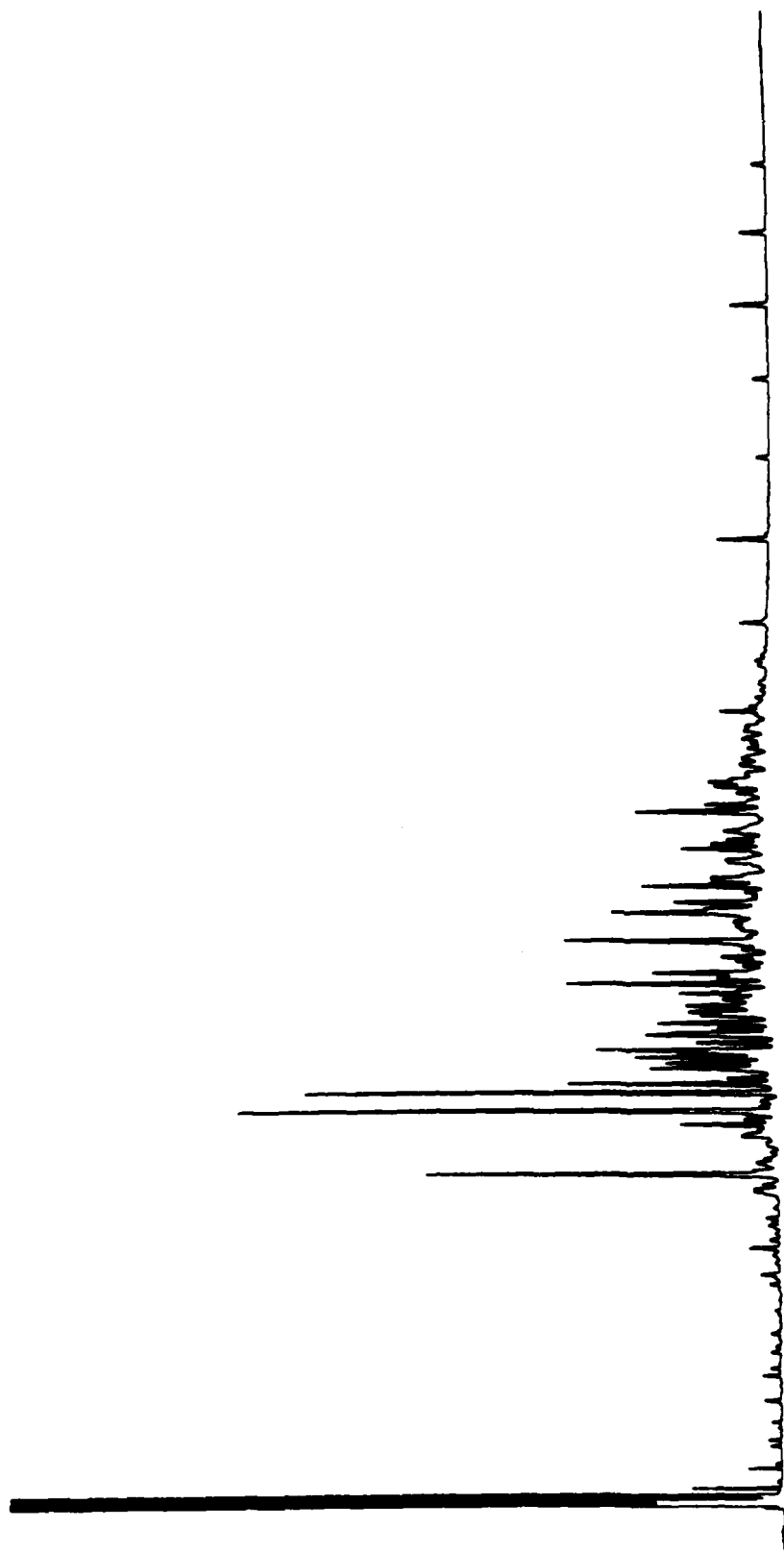


Figure 14. Chromatogram of Light Pyrolysis Fuel Oil (33-POSF-0801, 30% Aromatics).

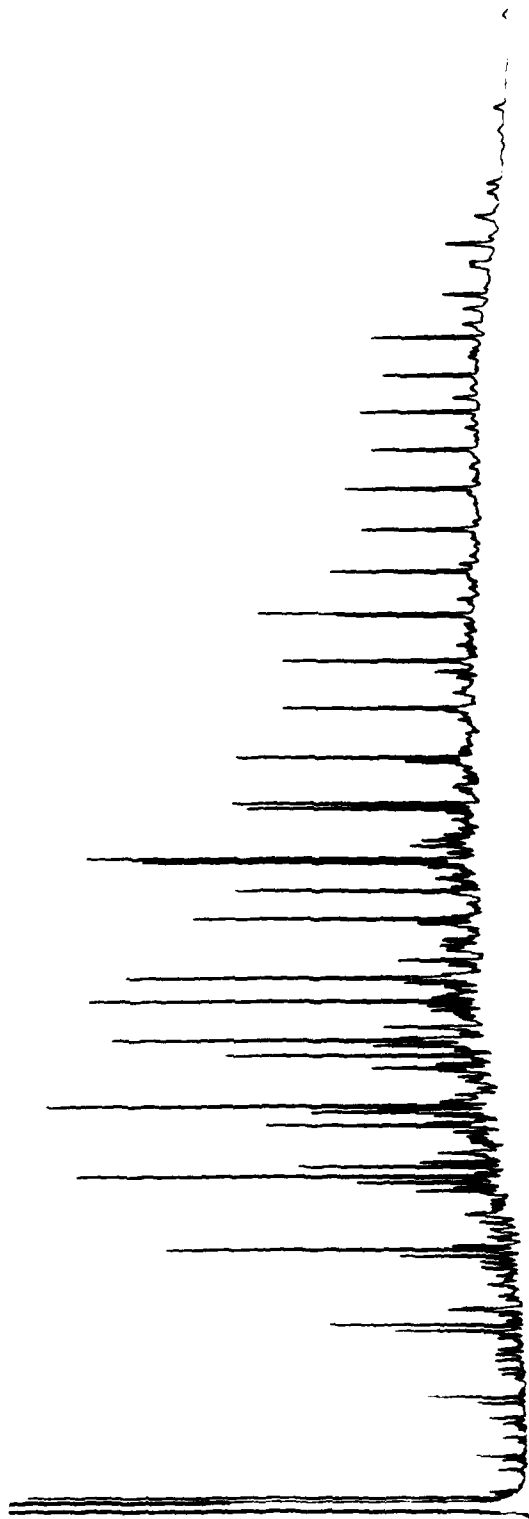


Figure 15. Chromatogram of Occidental Shale Crude (82-POSF-0195).

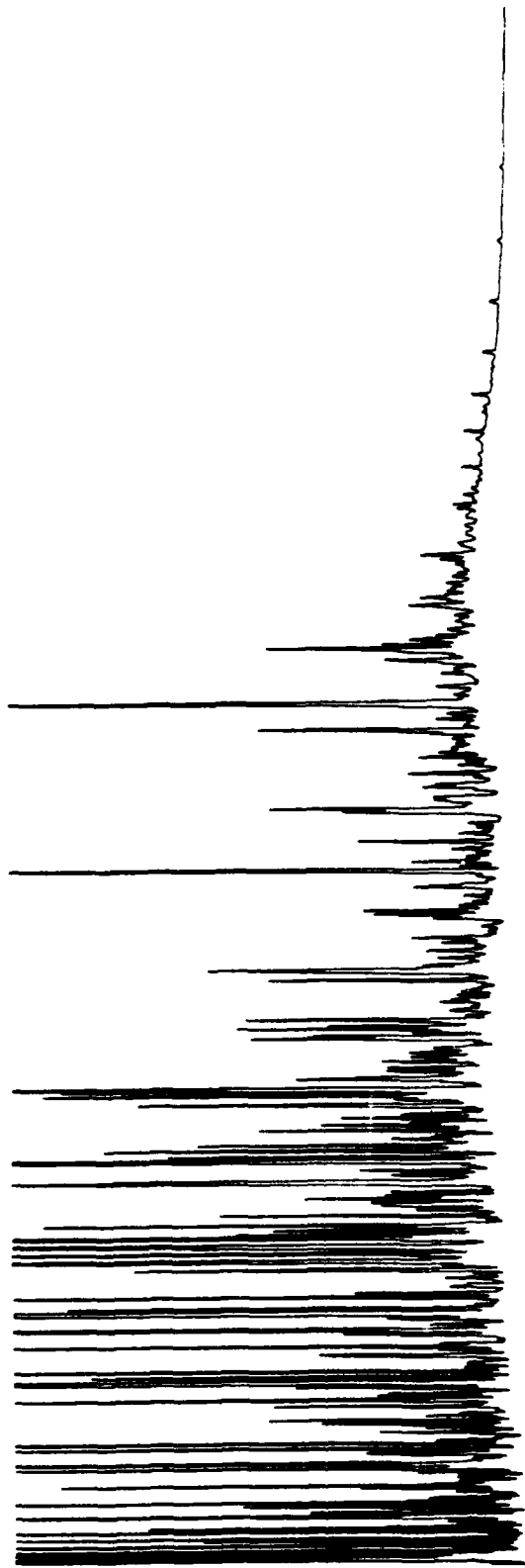


Figure 16. Chromatogram of HCL 68 PASS I (Distillation Cut--
Initial Boiling Point to 500°F).

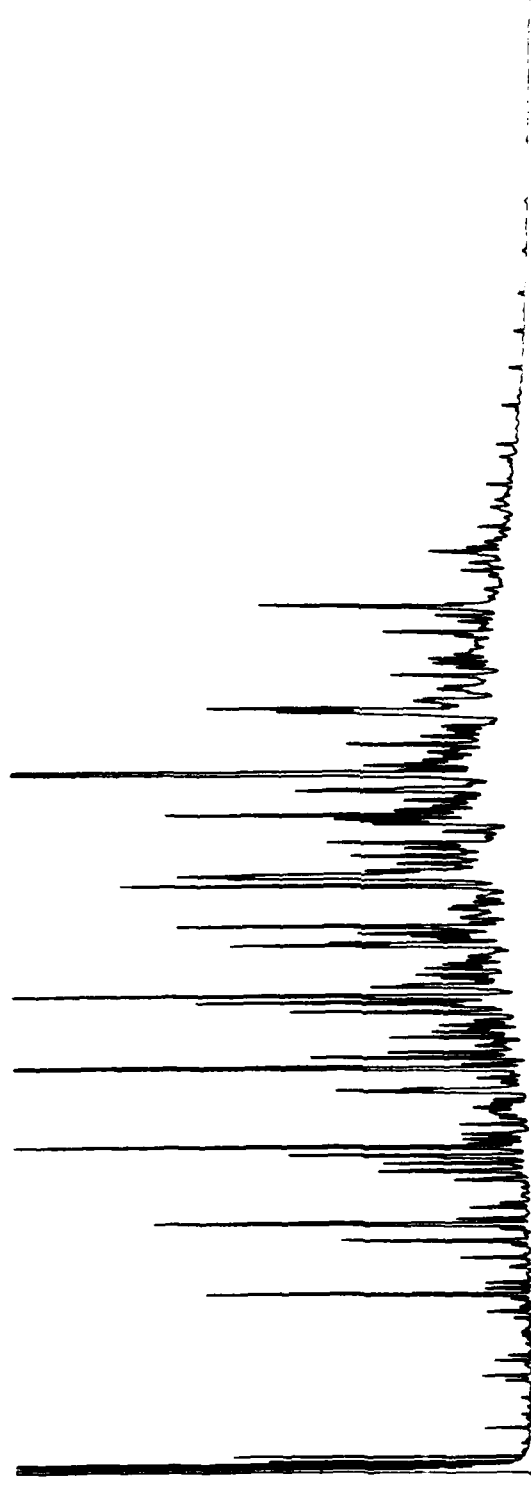


Figure 17. Chromatogram of HCL 68 PASS I (Distillation Cut-- 500°F to 800°F).

APPENDIX B

THEORETICAL ASPECTS OF A DECLINING THERMAL GRADIENT GAS CHROMATOGRAPHIC MEMBER

1. LOCATION AND MOTION OF A SOLUTE ZONE AS IT MIGRATES THROUGH A THERMAL GRADIENT COLUMN

The axial velocity of a retarded solute zone as it migrates through a gas chromatographic column can be described by

$$v_s = v R_f, \quad (1)$$

where v_s is the axial velocity of the solute zone centroid, v is the average linear velocity of the mobile phase, and R_f is the ratio of zone mean velocity to carrier gas mean velocity. When the column is maintained isothermal, R_f is a constant. However, when the temperature along the column axis varies, then both v and R_f vary according to the localized temperature.

We now examine the migration behavior of a solute zone as it moves through a gas-liquid chromatographic column which is located in a declining thermal field. It is assumed that the column is highly permeable with a negligible pressure drop and that the temperature decreases linearly from a value of T_b at the column inlet to an exit value of T_f .

According to Giddings [113] the R_f value for a particular solute zone can be written as

$$R_f = \frac{\left(\frac{A_m}{A_s}\right) \exp\left(-\frac{\Delta H}{RT}\right) \exp\left(\frac{\Delta S}{R}\right)}{1 + \left(\frac{A_m}{A_s}\right) \exp\left(-\frac{\Delta H}{RT}\right) \exp\left(\frac{\Delta S}{R}\right)}, \quad (2)$$

where A_m and A_s are the respective cross-sectional areas of the mobile and stationary phases, ΔH and ΔS are molar heat and entropy, respectively, of solute vaporization, R is the gas constant, and T is absolute temperature. If we let

$$c_1 = \left(\frac{A_m}{A_s}\right) \exp\left(\frac{\Delta S}{R}\right), \quad (3)$$

and

$$c_2 = \frac{\Delta H}{R} , \quad (4)$$

then Equation 2 can be rewritten as

$$R_f = \frac{c_1 \exp\left(-\frac{c_2}{T}\right)}{1 + c_1 \exp\left(-\frac{c_2}{T}\right)} , \quad (5)$$

and

$$v_s = \frac{vc_1}{c_1 + \exp\left(\frac{c_2}{T}\right)} . \quad (6)$$

Now for a thermal gradient column of negligible pressure drop, there will still be a variation in v with distance. Specifically, if the temperature of the mobile phase at the column inlet is T_b , then the temperature along the linearly declining thermal gradient column will be

$$T = f_1(z) = T_b + \left(\frac{dT}{dz}\right) z , \quad (7)$$

where z , in this case, is the distance from the column inlet. Likewise, in view of Charles' law, as applied to a uniform cross-section column and an ideal carrier gas

$$v = f_2(z) = v_b + \left(\frac{dv}{dz}\right) z , \quad (8)$$

where v_b is the mean velocity of the mobile phase at the column inlet. Hence, upon substituting Equations 7 and 8 back into Equation 6,

$$v_s = \frac{c_1 \left[v_b + \left(\frac{dv}{dz} \right) z \right]}{c_1 + \exp \left[\frac{c_2}{T_b + \left(\frac{dT}{dz} \right) z} \right]}, \quad (9)$$

and, for a linear thermal gradient column of negligible pressure drop,

$$\frac{dv}{dz} = c_3, \quad (10)$$

and

$$\frac{dT}{dz} = c_4, \quad (11)$$

where c_3 and c_4 for a particular linear thermal gradient column are constants. The solute zone velocity can now be expressed as

$$v_s = \frac{c_1 (v_b + c_3 z)}{c_1 + \exp \left(\frac{c_2}{T_b + c_4 z} \right)}. \quad (12)$$

Using Equation 12, we can determine the solute zone deceleration, or velocity change, as it moves through the column. Specifically,

$$\frac{dv_s}{dz} = \frac{c_1 c_3 \left[c_1 + \exp \left(\frac{c_2}{T_b + c_4 z} \right) \right] + c_1 (v_b + c_3 z) \frac{c_2 c_4}{(T_b + c_4 z)^2} \exp \left(\frac{c_2}{T_b + c_4 z} \right)}{\left[c_1 + \exp \left(\frac{c_2}{T_b + c_4 z} \right) \right]^2}. \quad (13)$$

This term will be of value later during the characterization of a zone's dispersion as it migrates through the thermal gradient column. However, before examining zone spreading, it should be pointed out that since

$$z = \int_{t=0}^t v_s dt , \quad (14)$$

where t is time, we can also use Equation 12 to determine the location of a migrating zone's centroid as a function of elapsed time.

2. ZONE SPREADING IN A THERMAL GRADIENT COLUMN

As a solute zone approaches the exit of a chromatographic column, its distance-based variance can be expressed as

$$\sigma_f^2 = \sigma_o^2 + \sum_{i=1}^n H_i (\Delta z)_i , \quad (15)$$

where σ_f^2 is the final variance value, σ_o^2 is the original variance of the deposited solute zone, while H_i and $(\Delta z)_i$ are the plate height and incremental length, respectively, of the column's n increments. The additive property of independent plate height terms permits individual contributions to be summed. Therefore, for a declining thermal gradient column which has both zone expanding and zone compressing features, we can write

$$H = H_e + H_c , \quad (16)$$

where H is the resultant plate height, while H_e and H_c represent the expanding and compressing contributions, respectively. From the accepted definition of plate height in gas chromatography, that is,

$$H = \frac{d(\sigma^2)}{dz} , \quad (17)$$

where σ^2 is the distance-based variance of the zone, Equation 16 can be re-stated as

$$\frac{d(\sigma^2)}{dz} = \left[\frac{d(\sigma^2)}{dz} \right]_e + \left[\frac{d(\sigma^2)}{dz} \right]_c \quad (18)$$

Now for a highly permeable uniform column that is functioning under a given set of conditions, it is permissible to consider the zone expanding contributions as a lumped constant. However, such a simplifying assumption can not be made for the zone compressing term.

A description of zone compression was set forth by Ohline [114] in his studies of chromathermography. In the case of a linear decline in temperature with distance, the distance-based zone compression, relative to time, can be written as

$$\frac{d\sigma}{dt} = \sigma \frac{dv_s}{dz} \quad (19)$$

which can also be expressed relative to distance as

$$\frac{d\sigma}{dz} = \frac{d\sigma}{dt} \cdot \frac{dt}{dz} = \left(\frac{\sigma}{v_s} \right) \frac{dv_s}{dz} \quad (20)$$

Integrating and evaluating Equation 20 between an initial value, designated as σ_i , and σ

$$\int_{\sigma_i}^{\sigma} \frac{d\sigma}{\sigma} = \int_{v_{s,i}}^{v_s} \frac{dv_s}{v_s} \quad (21)$$

we find

$$\sigma = \left(\frac{\sigma_i}{v_{s,i}} \right) v_s \quad (22)$$

or

$$\sigma^2 = \left(\frac{\sigma_i}{v_{s,i}} \right)^2 v_s^2 . \quad (23)$$

Thus, the zone compressing action term can be expressed as

$$\left[\frac{d(\sigma^2)}{dz} \right]_c = 2v_s \left(\frac{\sigma_i}{v_{s,i}} \right)^2 \frac{dv_s}{dz} . \quad (24)$$

Then from Equations 16, 18, and 24, we can write

$$\frac{d(\sigma^2)}{dz} = H_e + 2v_s \left(\frac{\sigma_i}{v_{s,i}} \right)^2 \frac{dv_s}{dz} . \quad (25)$$

Equation 25 can also be written in differential form as

$$d(\sigma^2) = H_e dz + \left[2v_s \left(\frac{\sigma_i}{v_{s,i}} \right)^2 \frac{dv_s}{dz} \right] dz , \quad (26)$$

or

$$d(\sigma^2) = H_e dz + 2 \left(\frac{\sigma_i}{v_{s,i}} \right)^2 v_s dv_s . \quad (27)$$

Upon integrating between respective limits

$$\int_{\sigma_i^2}^{\sigma^2} d(\sigma^2) = H_e \int_{z_i}^z dz + 2 \left(\frac{\sigma_i}{v_{s,i}} \right)^2 \int_{v_{s,i}}^{v_s} v_s dv_s , \quad (28)$$

we have

$$(\sigma^2 - \sigma_i^2) = H_e (z - z_i) + \left(\frac{\sigma_i}{v_{s,i}} \right)^2 (v_s^2 - v_{s,i}^2) , \quad (29)$$

and upon changing subscripts

$$\left(\sigma_i^2 - \sigma_{i-1}^2\right) = H_e \left(z_i - z_{i-1}\right) + \left(\frac{\sigma_{i-1}}{v_{s,i-1}}\right)^2 \left(v_{s,i}^2 - v_{s,i-1}^2\right). \quad (30)$$

By including the original variance, σ_o^2 , which represents the axial spread of the deposited solute, and then summing the variance increments, we finally arrive at

$$\sigma_f^2 = \sigma_o^2 + \sum_{i=1}^n \left(\sigma_i^2 - \sigma_{i-1}^2\right), \quad (31)$$

where σ_f^2 is the distance-based variance of the solute zone at the column outlet.

3. SAMPLE INSERTION IN A THERMAL GRADIENT COLUMN AND SUBSEQUENT PROGRAMMED TEMPERATURE OPERATION

The sample reception process in a declining thermal gradient column is distinctly different from that experienced in the usual gas-liquid chromatographic column. Even so, the mechanics associated with injecting a sample are essentially the same as those used in isothermal (ITGC) and programmed temperature gas chromatography (PTGC). The sample is still injected into the injection port* of the chromatograph. Likewise, the instant of sample injection remains as the starting time, t_o , for recording the analytical signal from the chromatograph. The main procedural difference between sample insertion in conventional PTGC and that employed in thermal gradient operation is that an extended initial hold of oven temperature is required with the latter technique.

In the thermal gradient mode of operation, temperature programming of the column oven is eventually required to elute the various components. However, before the programmed increase of oven temperature, an extended holding time, t_h , is needed for the different compounds of the multicomponent sample to be efficiently distributed along the thermal gradient column axis.

*An injection port specifically designed for programmed thermal gradient operation would differ slightly from that normally encountered in ITGC or PTGC. Additional information on the requirements of such an injection port are contained in the design information for thermal gradient devices.

The temperature of the thermal gradient column inlet is held constant throughout a given chromatographic program. This constant inlet temperature is namely the wall temperature, T_w^* . Likewise, throughout the extended hold interval during which the sample is being longitudinally distributed along the declining gradient, the instrument oven temperature, T_a , is maintained at a significantly lower constant value. Consequently, for this initial hold period, the temperature distribution along the column can be described.

After the extended initial hold period, the column oven is temperature programmed; thus, T_a will increase with time while T_w remains time invariant. Therefore, this increasing of the instrument oven temperature will gradually decrease the magnitude of the thermal gradient along the column.

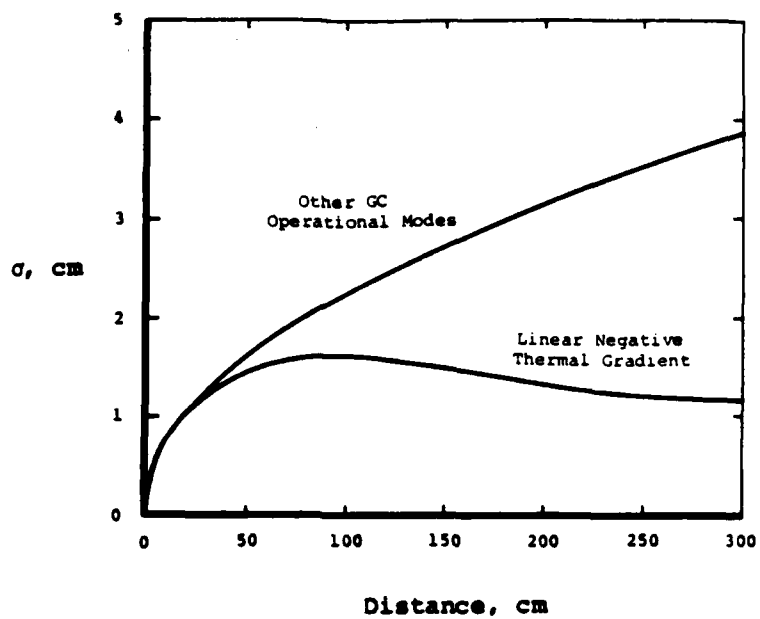
The value of the arbitrarily selected holding time t_h is primarily dependent upon the length of the thermal gradient portion of the total column system. The selected temperatures T_w and T_a are essentially governed by the volatility and molecular weight range of the anticipated sample mixture.

4. SIGNIFICANCE OF THE DECLINING THERMAL GRADIENT COLUMN CONCEPT

A thermal gradient GC column possesses several unique performance properties. Solute zone migration in such a column is in sharp contrast to that occurring in a conventional GC column whether it be operated in the isothermal, temperature programming, or pressure programming modes. Based upon the results of this theoretical study, it is seen that in the linear decline thermal gradient mode, the width of a migrating solute zone will initially expand and then later be axially compressed. This is entirely different behavior from that of other GC operational modes where zone width continually increases as the zone migrates. Figure 18a shows these contrasting zone migration behaviors.

* T_w is defined and discussed in the design information for producing controlled thermal gradients.

(a)



(b)

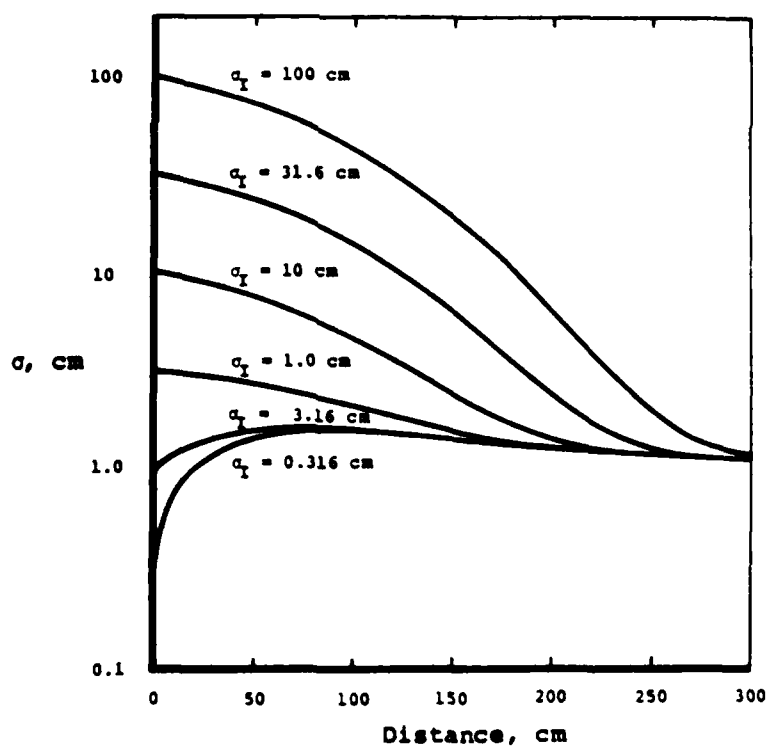


Figure 18. Graphs of Solute Zone Behavior.

The second behavioral property that is particularly interesting with respect to a thermal gradient column, is that very broad injection zones can be applied to the column inlet. Furthermore, broad input profiles have almost no effect on the width of individual solute zones at the column exit. This particular behavior is depicted graphically in Figure 18b with a series of increasingly broad input zones. The significance of this behavioral property is that multicomponent samples can be injected into such a column without saturating the stationary phase at the inlet region. This particular sample injection property has special appeal if the thermal gradient column can be subsequently (or simultaneously) operated in a superimposed temperature programming mode. (see Figure 19).

Lastly, it seems highly probable that the thermal gradient GC concept would be capable of admitting practically any sample to a variety of extremely high-resolution open tubular column systems. It is this potential which is most intriguing and promising.

5. ERROR INVOLVED IN NONLINEAR VARIATION OF SOLUTE VELOCITY WITH MIGRATION DISTANCE

As a solute zone migrates through a thermal gradient gas chromatographic column, it will continually experience a change in axial velocity. Specifically, for a highly permeable column that has a negative thermal gradient, the average value of the axial velocity will continually decline as the zone migrates. During migration, regions will be encountered where the solute velocity v_s will decline essentially in a linear manner with distance z . However, there are also regions where this v_s versus z relationship possesses curvature, that is, exhibits nonlinear behavior. The adverse effect of this nonlinearity is that a measure of error is introduced into the basic zone compression description.

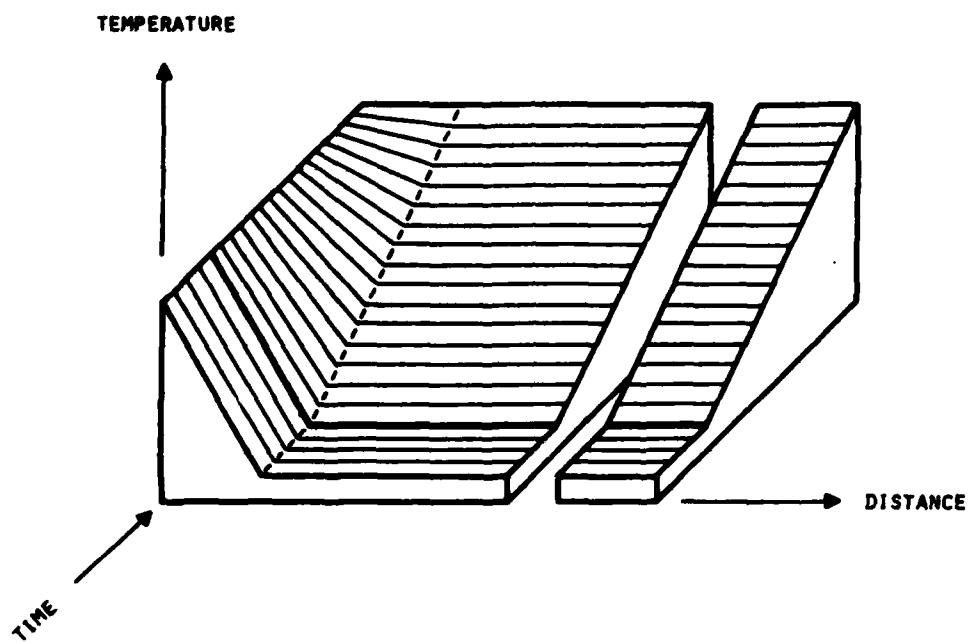


Figure 19. Simultaneous Programming of Ambient and Gradient.

As an explanation, it is recalled that in the derivation of the zone compression equation, that is,

$$\left[\frac{d\sigma}{dz} \right]_c = \left(\frac{\sigma}{v_s} \right) \frac{dv_s}{dz} , \quad (32)$$

the assumption was made that the velocity changed linearly with distance over the σ value of the migrating zone. Therefore, with the reality that different extents of curvature occur in certain regions of the v_s relationship, i.e.,

$$v_s = f(z, v_b, T_b, c_1, c_2, c_3, c_4) = \frac{c_1 (v_b + c_3 z)}{c_1 + \exp \left(\frac{c_2}{T_b + c_4 z} \right)} , \quad (33)$$

then, a corresponding error of departure is introduced in the above assumption.

Theoretically, the curvature of the v_s versus z relationship can be expressed as

$$K = \frac{\frac{d^2 v_s}{dz^2}}{\left[1 + \left(\frac{dv_s}{dz} \right)^2 \right]^{\frac{3}{2}}} . \quad (34)$$

Hence from the viewpoint of a strict interpretation, a $|K|$ maxima will occur at a point where the following equality has been established:

$$\left[1 + \left(\frac{dv_s}{dz} \right)^2 \right] \frac{d^3 v_s}{dz^3} = 3 \left(\frac{dv_s}{dz} \right) \left(\frac{d^2 v_s}{dz^2} \right)^2 . \quad (35)$$

However, from a practical point of view, an axial location of maximum absolute curvature can be approximated by the occurrence of a second derivative maximization.

Upon further examination of the basic v_s versus z relationship for a linear-negative thermal gradient, it is found that maximum curvature occurs at the lower migration velocities for the typical retarded solute zone. Therefore, such a solute zone will have encountered an extended region of linear velocity decline before reaching the nonlinear region (see Figure 20). Thus, as described earlier by Equation 30, the solute zone will have already experienced considerable axial compression before migrating into the curvature region. Furthermore, upon re-examination of Equation 32, it seems that the descriptive error resulting from nonlinearity will be substantially reduced if the σ value of the migrating zone is diminished beforehand by the compressive action of the thermal gradient.

In summary, it is seen that for a given migrating solute zone, a linear velocity decline region will produce a predictable zone compression effect. This will in turn diminish the σ value of the migrating zone. Consequently, if σ is small before the migrating zone encounters the region of nonlinearity the error associated with the description of zone compression in this region will be correspondingly small.

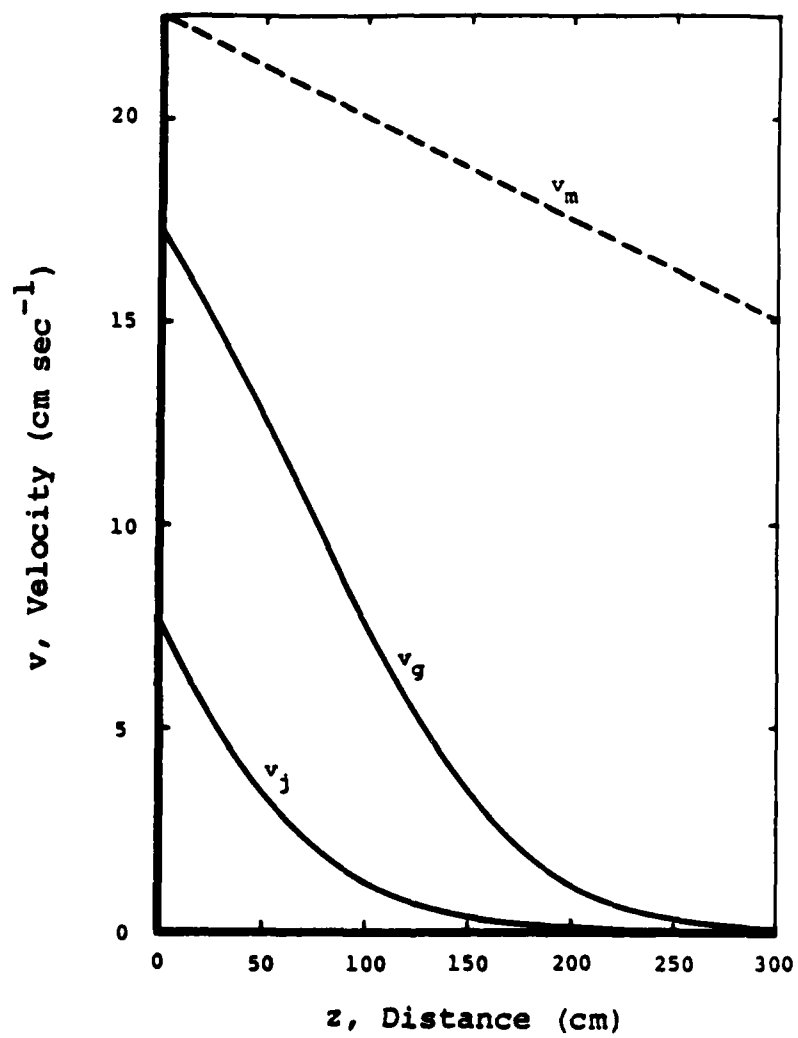


Figure 20. Velocity Versus Distance Relationship.

APPENDIX C

DESIGN OF COMPONENTS FOR PRODUCING PRECISE AND CONTROLLABLE NEGATIVE THERMAL GRADIENTS IN TUBULAR ASSEMBLIES

In earlier investigations with thermal gradient GC columns [115-117], axial heat exchangers and electrical spiral wraps were used to produce a temperature gradient along packed columns. These GC columns were relatively short in length, and therefore, the magnitude of the negative thermal gradients were substantial, approximately $-2^{\circ}\text{C cm}^{-1}$.

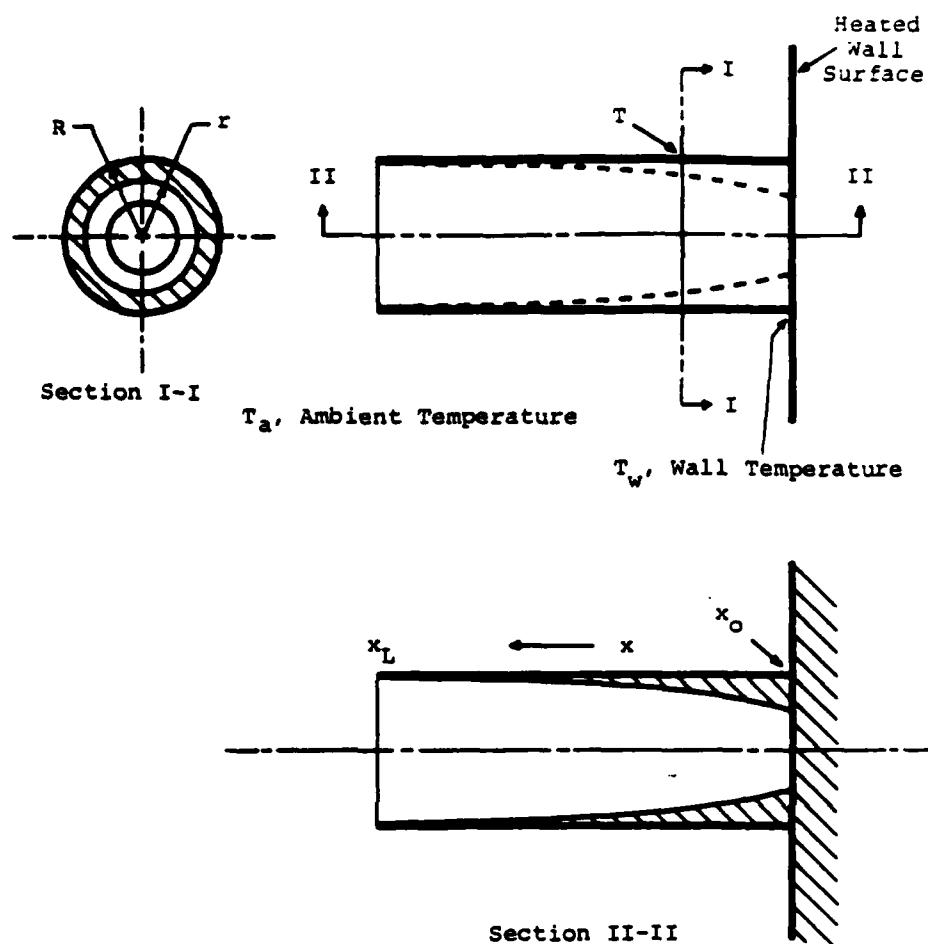
1. A METALLIC CONDUCTOR THERMAL GRADIENT DEVICE

To apply a uniform temperature gradient to a long open tubular column (OTC) requires the use of a well controlled and gradually declining thermal field. One approach is to mount an OTC on a metallic thermal conductor. This assembly could then be installed in a gas chromatograph equipped for temperature programming.

The basic design of such a metallic thermal conductor is illustrated in Figure 21. This concentric device extends from a uniformly heated wall surface and into a chamber which circulates thermally controlled air. According to fundamental heat conduction theory [118], a simplified one-dimensional heat balance description for this concentric conductor can be written as

$$\frac{d^2E}{dx^2} + \frac{1}{A} \left(\frac{dA}{dx} \right) \frac{dE}{dx} - \left(\frac{\bar{h}P}{kA} \right) E = 0, \quad (36)$$

where E is the excess temperature defined as the difference between the surface temperature T and the controlled ambient T_a , x is the perpendicular distance from the heated wall, A is the cross-sectional area of the metallic conductor parallel to the wall surface, $\bar{h}$ is the effective heat transfer coefficient, P is the perimeter of the exposed surface parallel to the wall surface, and k is the thermal conductivity of the metal.



SYMBOL	DESCRIPTION
R	-- Outer radius
r	-- Inner radius
T	-- Temperature
T_a	-- Ambient Temperature
T_w	-- Wall Temperature
x_o	-- Origin of x axis
x_L	-- Conductor length

Figure 21. Basic Thermal Conductor for an OTC.

Two variations of this basic thermal conductor are depicted in Figure 22. For the design shown in part (a) of this figure, heat is transferred away from the outer diameter by either free or forced convection. For the conductor shown in part (b), the outer diameter is insulated and heat is carried away through the inner surface or cavity of the conductor.

Returning now to the basic thermal conductor shown in Figure 21, it is necessary to employ certain simplifying assumptions in order to obtain a workable design. First, as stated earlier, Equation 36 describes only unidirectional heat flow. Thus, in this description there is no radial thermal gradient across the metal conductor. Next, it is assumed that $\bar{h}$ and k remain constant. These simplifications appear to be tolerant assumptions. The small thickness of the metal conductor would not permit a large temperature difference to exist across the metal conductor. Similarly, as the conductor would be mounted in an instrument oven which would be continuously circulating thermally controlled air, the average heat transfer coefficient, $\bar{h}$, would experience negligible change. Also, as the exposed temperature range is not large, e.g., from -50°C to 300°C , the change in thermal conductivity will accordingly be small (approximately 5% variation for most metals). If these same assumptions are granted for the insulated conductors shown in Figure 22, then Equation 36 is also descriptive for these modified devices. However, P is dependent upon which surface of the conductor is exposed to the thermally controlled ambient. Specifically, for the design shown in Figure 22a,

$$P = P_a = 2\pi R, \quad (37)$$

while for cooling with air moving through the cavity of the conductor, as in Figure 22b,

$$P = P_b = 2\pi r. \quad (38)$$

It is this latter design which is of special interest.

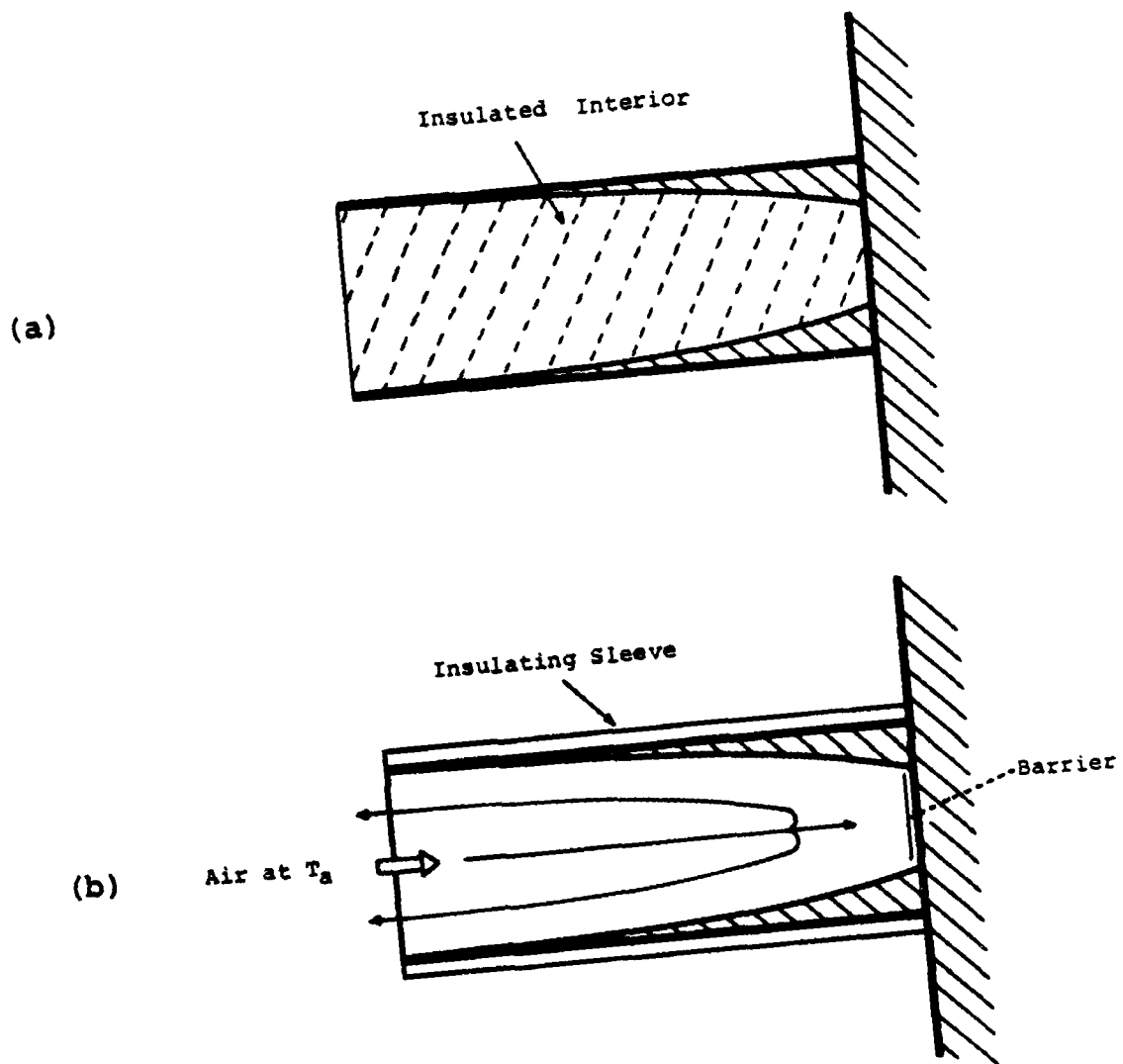


Figure 22. Modified Versions of Basic Conductor.

For the inlet portion of a lengthy OTC system, one particular type of thermal conductor has definite appeal. Special merit is seen in a device which produces a negative thermal gradient that remains linear along the conductor axis. Therefore, by applying such a design criteria to the device shown in Figure 21, it is found that

$$\frac{dE}{dx} = c = - \left(\frac{T_w - T_a}{x_L} \right), \quad (39)$$

and

$$\frac{d^2E}{dx^2} = 0. \quad (40)$$

Previously, it was stated that

$$E = T - T_a, \quad (41)$$

however, for the situation where there is a linear decrease in surface temperature with distance from the wall, E can also be written as

$$E = \left(1 - \frac{x}{x_L} \right) (T_w - T_a). \quad (42)$$

Consequently, when the relationships expressed by Equations 39, 40, and 42 are substituted back into Equation 36, it is seen that this heat balance equation reduces to simply

$$\frac{dA}{dx} = - \frac{\bar{h}P}{k} (x_L - x). \quad (43)$$

Remembering now that

$$A = \pi (R^2 - r^2), \quad (44)$$

then

$$\frac{dA}{dx} = -2\pi r \frac{dr}{dx} . \quad (45)$$

Combining Equations 38, 43, and 45, and integrating according to

$$\int dr = \frac{\bar{h}}{k} \int (x_L - x) dx, \quad (46)$$

it is seen that

$$r = x \left(x_L - \frac{x}{2} \right) \frac{\bar{h}}{k} + c_k, \quad (47)$$

and since when x is zero, c_k equals r_o , then

$$r = r_o + x \left(x_L - \frac{x}{2} \right) \frac{\bar{h}}{k} . \quad (48)$$

By rearranging Equation 48 and then multiplying through by x_L^{-2} , we find

$$\frac{2k}{\bar{h}x_L^2} (r - r_o) = \frac{x}{x_L} \left(2 - \frac{x}{x_L} \right) . \quad (49)$$

Thus, Equation 49 relates implicitly the inner radius r and the relative length of the conductor. This relationship is shown in the graph of Figure 23.

Referring now to the thermal conductor depicted in Figure 22b, the outer diameter of the metal portion of this conductor represents a right circular cylinder. Therefore, with the use of a rapid advance lathe, a precise groove could be readily machined into this surface, thus forming a cylindrical helix along the axis of the conductor. The depth and diameter of this finished groove would be sufficient to accommodate a length of fine bore tubing. Hence, an OTC could be fitted into this rigid form, thereby producing a column with a configuration of an accurately

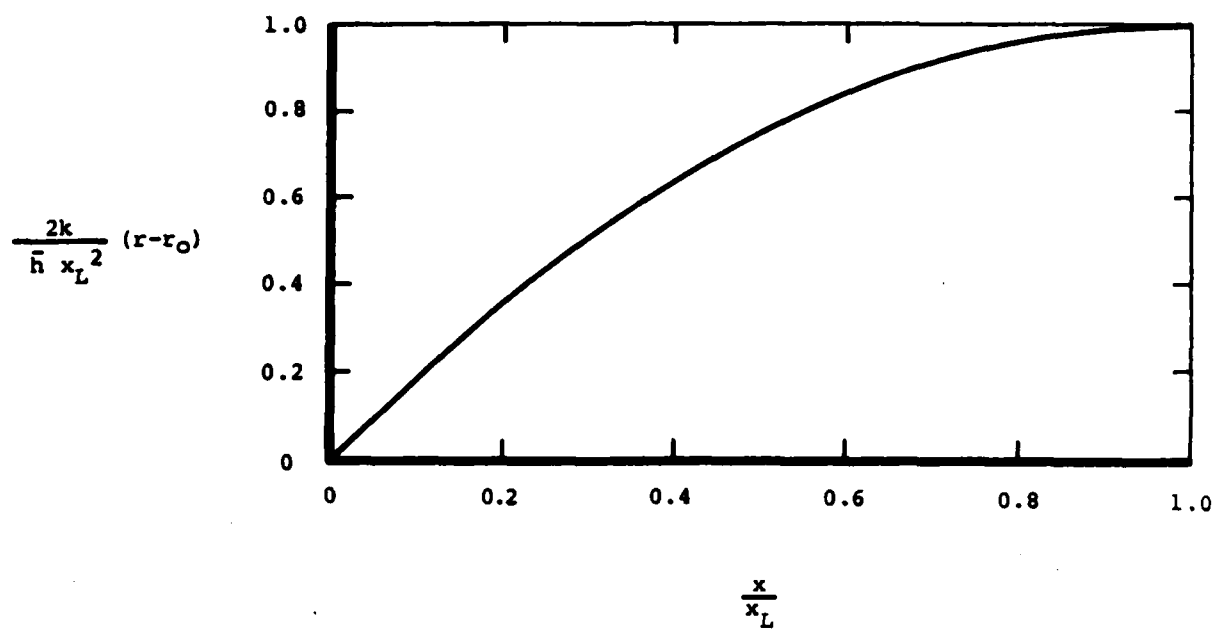


Figure 23. Variation of Inner Radius with Conductor Length.

defined helical coil. Such a mounting arrangement should produce in the OTC a thermal profile approaching that described by

$$T - T_a = \left(1 - \frac{z}{z_L}\right) (T_w - T_a), \quad (50)$$

where z_L represents the length of the gradient column, and z is the distance along the column axis. This latter term, z , is related to the conductor length according to

$$z = \sqrt{(2\pi R_h)^2 + x^2}, \quad (51)$$

where R_h represents the radius of the tubular helix.

With careful attention given to the design details, along with the fabrication, assembly, and installation of this inlet thermal gradient device, one would expect a uniform temperature decline and an absence of thermal inflections along the column axis.

Earlier, while developing this particular thermal conductor design, it was stipulated that

$$\frac{dT}{dx} = c, \quad (39b)$$

where c represented some negative constant. This linear decrease of temperature along the conductor axis applied only for the steady-state condition. However, an unsteady-state thermal condition is encountered upon the initiation of the programming of the instrument oven temperature. At the same time, a gradual decline is experienced in the electrical energy required to heat the inlet portion of this thermal conductor (recall that T_w is maintained at a constant temperature throughout the entire chromatographic process). Therefore, the temperature distribution along the thermal conductor is dependent upon the variable T_a , and the rate at which T_a varies with time.

In the temperature programming of OTCs, low rates of increase are generally used. Most separations with these columns are customarily accomplished with programming rates ranging from 0.5°C to $4.0^{\circ}\text{C min}^{-1}$. Now for such low rates of changing T_a , and with a controlled thermal input (constant T_w), it is safe to assume that the thermal gradient remains linear. Granted this assumption, the conductor thermal gradient is thus seen to vary with time t according to:

$$\frac{d}{dt} \left(\frac{dE}{dx} \right) = \left(\frac{1}{x_L} \right) \frac{dT_a}{dt}, \quad (52)$$

while the variation in the thermal gradient along the OTC is

$$\frac{d}{dt} \left(\frac{dE}{dx} \right) = \left(\frac{1}{z_L} \right) \frac{dT_a}{dt}. \quad (53)$$

Also, in the linear temperature programming mode,

$$\frac{dT_a}{dt} = P_r, \quad (54)$$

where P_r is the constant programming rate in units of $^{\circ}\text{C min}^{-1}$. Hence, in this programming mode, T_a can be expressed as

$$T_a = T_i + P_r t, \quad (55)$$

where T_i is the initial temperature, that is, the oven ambient temperature at the start of the programming.

Therefore, during the linear temperature programming of the GC column oven, the gradient along the mounted OTC can be described by

$$\frac{dE}{dz} = - \left[\frac{T_w - (T_i + P_r t)}{z_L} \right]. \quad (56)$$

Consequently, in view of the previous assumptions, the gradient is seen to change with time at a constant rate; specifically,

$$\frac{d}{dt} \left(\frac{dE}{dz} \right) = \frac{P_r}{z_L} , \quad (57)$$

when a low rate of linear temperature programming is applied to a linear thermal gradient inlet column.

2. COUNTERFLOW HEAT EXCHANGER FOR PRODUCING PRECISE THERMAL GRADIENTS

Another approach to producing a well controlled and gradually declining thermal field is to mount a precisely coiled OTC in a counterflow heat exchanger. This assembly could then be installed in a gas chromatograph equipped for temperature programming.

The basic design of a counterflow heat exchanger thermal gradient device is illustrated in Figure 24. This design produces a negative gradient which remains essentially linear along the axis of the heat exchanger. Also, this design allows for mounting in a GC oven and facilitates control of the inlet and outlet temperatures of the heat exchanger.

For the simplified device shown in Figure 24, it is seen that Equations 50 through 57 would also apply for a tubular member mounted in this heat exchanger device.

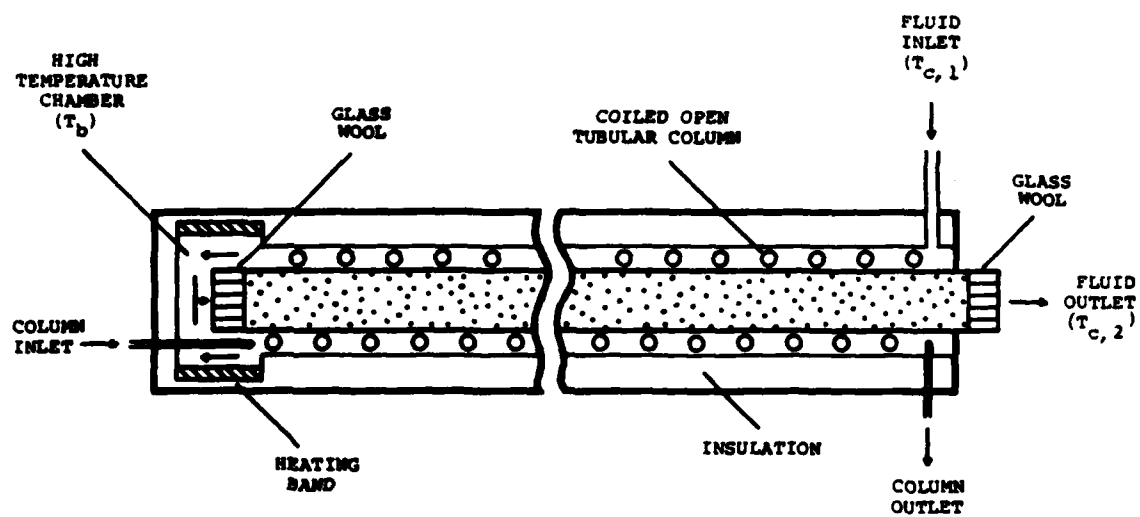


Figure 24. Heat Exchanger Thermal Gradient Device

APPENDIX D

THE INFLUENCE OF THE PARTITION RATIO UPON THE LOCATION AND AXIAL MOTION OF A SOLUTE ZONE

In gas-liquid chromatography (GLC) migrating solute molecules spend time in the inert mobile phase and in the liquid stationary phase. If it is assumed that migrating molecules are retarded only by partitioning or residency in a liquid substrate and are not influenced by any adsorptive behavior, then axial motion of a migrating zone can be characterized in terms of the localized mobile phase velocity and the solute's partition ratio.

In the selection of a stationary phase for a GLC column, whether it be a packed column, a conventional OTC, or a recently introduced OTC with a chemically bonded phase, it is important to choose a substrate that has a very wide temperature range.

The maximum usable temperature of a liquid phase is determined by the thermal degradation properties of the substrate or its vapor pressure (phase bleed). The minimum working temperature of a liquid substrate is established by the solidification temperature, or more commonly in the case of the polymeric stationary phases by the glass transition temperature, T_g . At temperatures below the T_g value of a substrate, solute retention may be governed by mechanisms other than pure gas-liquid partitioning.

Once it has been established that molecular migration is occurring only by gas-liquid chromatographic processes, then the axial motion can be described in meaningful terms.

Chromatography is basically a dynamic process that uses the concept of differential migration to obtain separation of dissimilar solutes. Specifically, the axial location of the centroid of a zone of like molecules that is passing through a GLC column can be expressed as

$$z = \int_0^t v_m \left(\frac{1}{1+k} \right) dt , \quad (58)$$

where z is the distance along the column axis, t is time, v_m is mobile phase mean velocity, and k is the partition ratio. The localized mean velocity of the migrating solute zone can then be written as

$$v_s = \frac{dz}{dt} = v_m \left(\frac{1}{1+k} \right) . \quad (59)$$

Even if k remains constant through the column length, it has been determined that the solute zone velocity experiences a very gradual increase as the zone migrates through the column. This small increase is due to the decompression of the carrier gas as

$$v_m = f(p) = \frac{p_o v_e}{p} = - \left(\frac{K}{\eta} \right) \frac{dp}{dz} , \quad (60)$$

where p is internal pressure, p_o is outlet pressure, v_e is mobile phase outlet velocity, K is column permeability, and η is the carrier gas viscosity. However, in usual practice where p_o is atmospheric pressure, v_m does not change by more than a factor of two or three over the length of the column.

Now if k is initially very large and then diminishes with time, as in programmed temperature gas chromatography where it can eventually approach zero, it is seen from Equation 59 that v_s experiences an orders of magnitude increase with the passage of time. Therefore, if the given solute can be deposited in the column while having a corresponding initial k or k_i such that

$$k_i \gg \bar{k}_e , \quad (61)$$

where $\bar{k}_e$ is the average partition ratio upon elution, it is evident that the initial v_s is very small indeed. Thus the time period over which the solute zone is deposited is of small consequence. If k_i is sufficiently large, the sample depositing time can be tens of minutes.

REFERENCES

1. K. Eckschlager and V. Stepanek, Information Theory in Analytical Chemistry, Anal. Chem., 54:1115A, 1982.
2. J. M. Davis and J. C. Giddings, Statistical Theory of Component Overlap in Multicomponent Chromatograms, Anal. Chem., 55:418, 1983.
3. W. A. Rubey, Aspects of High-Resolution Gas Chromatography as Applied to the Analysis of Hydrocarbon Fuels and Other Complex Organic Mixtures: Vol. I. Chromatographic System Details, University of Dayton Report UDR-TR-82-156, For Air Force Aero Propulsion Laboratory, Wright-Patterson Air Force Base, Ohio, September, 1983.
4. P. W. Centers and W. A. Rubey, An Experimental Approach to High-Resolution Gas-Liquid Chromatography for High Molecular Weight Compounds, Report AFAPL-TR-68-137, Air Force Aero Propulsion Laboratory, Wright-Patterson Air Force Base, Ohio, November, 1968.
5. J. C. Giddings, Two-Dimensional Separations: Concept and Promise, Anal. Chem., 56:1258A, 1984.
6. T. Hirschfeld, The Hy-phen-ated Methods, Anal. Chem., 52:297A, 1980.
7. G. Schomburg, H. Husmann, and F. Weeke, Aspects of Double-Column Gas Chromatography with Glass Capillaries Involving Intermediate Trapping, J. Chromatog., 112:205, 1975.
8. S. R. Lipsky and W. J. McMurray, Recent Developments in the Field of Glass Capillary Column Gas Chromatography, Paper presented at 1981 American Chemical Society Meeting held in Atlanta, GA, March, 1981.
9. S. R. Lipsky, The Development of New Methods for the Isolation and Identification of Certain Components Found in Complex Mixtures Derived from Energy Sources and the Determination of Their Biological Activity Via Bioassay Systems, Report for U.S. Department of Energy, DOE/EV/02958-7, November, 1983.
10. S. Sonchik, S. Spencer, and J. Walker, The Advantages of Dual Gas Chromatographic Column Ovens for Packed and Capillary Column Separations, Paper Presented at National ACS Meeting held in St. Louis, MO, April, 1984.
11. G. Guiochon, L. A. Beaver, M. F. Gonnord, A. M. Siouffi, and M. Zakaria, Theoretical Investigation of the Potentialities of the Use of Multidimensional Columns in Chromatography, J. Chromatog., 255:415, 1983.

12. W. Blass, K. Riegner, and H. Hulpke, Double-Column Gas Chromatography Using Packed Precolumns and Glass Capillary Main Columns, J. Chromatog., 172:67, 1979.
13. J. Sevcik, Information Content of Multidimensional Switching Systems in Gas Chromatography, In: Advances in Chromatography 1979, A. Zlatkis, ed., University of Houston, Houston, TX, 1979.
14. B. Welton, M. Goedert, and T. Lyons, Multidimensional Gas Chromatography, Paper presented at 1981 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.
15. B. Welton, Column Switching and Backflush Techniques with Open Tubular and Packed Columns in Gas Chromatography, Paper presented at 1978 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.
16. R. Miller, Multidimensional Gas Chromatography, In: High Resolution Gas Chromatography, 2nd edition, R. R. Freeman, ed., Hewlett-Packard, 1981.
17. W. Bertsch, Methods in High Resolution Gas Chromatography: Two-Dimensional Techniques, HRC & CC, 1:85, 1978.
18. A. Ducass, M. F. Gonnord, P. Arpino, and G. Guiochon, Simple Techniques for Two-Dimensional Gas Chromatography, J. Chromatog., 148:321, 1978.
19. E. L. Anderson, M. M. Thomason, H. T. Mayfield, and W. Bertsch, Advances in Two-Dimensional GC with Glass Capillary Columns, HRC & CC, 2:335, 1979.
20. R. E. Kaiser and R. I. Rieder, Polarity Change in Capillary GC by Serial-Column Temperature Optimization (SECAT mode in Capillary GC), HRC & CC, 2:416, 1979.
21. G. Schomburg, H. Husmann, E. Hubinger, and W. A. Konig, Multidimensional Capillary Gas Chromatography - Enantiomeric Separations of Selected Cuts Using a Chiral Second Column, HRC & CC, 7:404, 1984.
22. W. A. Spencer and L. B. Rogers, Multitemperature Gas Chromatography Using Isothermal Columns in Series, Chem. Biomed. and Environ. Instrumentation, 11(1) 1, 1981.
23. L. B. Rogers, Fundamental Studies of Separation Processes, Report for U.S. Department of Energy, DOE/ER/00854-34, January, 1982.
24. C. W. Wright, Simultaneous Quantitation Analysis Using Dual Capillary Columns of Different Polarities, HRC & CC, 7:83, 1984.

25. T. W. Smuts, K. de Clerk, T. G. du Toit, and T. S. Buys, Retention Time and Effective Separation Factor in Series-Coupled Columns with Different Stationary Phases, HRC & CC, 3:124, 1980.
26. D. R. Deans, Use of Heart Cutting in Gas Chromatography: A Review, J. Chromatog., 203:19, 1981.
27. K. Herkner and W. Swoboda, The Application of Multicolumn Capillary Gas Chromatography ("Heart-Cutting") to Shorten Analysis Time, Paper presented at Fourth International Capillary Chromatography Symposium, Hindelang, Germany, May, 1981.
28. R. J. Phillips, K. A. Knauss, and R. R. Freeman, Applications of Heart Cutting from Packed to Capillary Columns, HRC & CC, 5:546, 1982.
29. J. F. K. Huber, E. Kenndler, W. Nyiry, and M. Oreans, Evaluation of Multi-Stage Gas Chromatography in Quantitative Chemical Analysis, J. Chromatog., 247:211, 1982.
30. M. Oreans, F. Muller, and D. Leonhardt, Trace Analysis in Coupled Systems: Total Transfer of Traces from Packed to Capillary Columns, J. Chromatog., 279:357, 1983.
31. J. Sevcik and T. A. Gerner, Extra-Column Effects in Multidimensional Switching Systems (MDSS)-GC, HRC & CC, 2:436, 1979.
32. G. Schomburg, H. Husmann, and F. Weeke, Aspects of Contemporary Capillary Gas Chromatography with Emphasis on Coupled Systems, Paper presented at 1982 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.
33. J. F. Pankow and L. M. Isabelle, Interface of the Direct Coupling of a Second Gas Chromatograph to a Gas Chromatograph/Mass Spectrometer for Use with a Fused Silica Capillary Column, Anal. Chem., 56:2997, 1984.
34. G. Schomburg, F. Weeke, F. Muller, and M. Oreans, Multidimensional Gas Chromatography (MDC) in Capillary Columns Using Double Oven Instruments and a Newly Designed Coupling Piece for Monitoring Detection After Pre-Separation, Chromatographia, 16:87, 1982.
35. H. Brotell, G. Rietz, S. Sandqvist, M. Berg, and H. Ehrsson, Two-Dimensional Capillary Gas Chromatography Without Intermediate Trapping: Electron Capture Detector Quantitation of an Amino Alcohol (KABI 2128) in Serum after Trifluoroacetylation, HRC & CC, 5:596, 1982.

36. W. Dosch, Unit Construction System for Coupling Operations in High Resolution Gas Chromatography, In: Proceedings of Fourth International Symposium on Capillary Chromatography, Hindelang, Germany, May, 1981.
37. F. Mueller, Column Switching in Capillary Gas Chromatography, Amer. Lab., October, 1983.
38. D. J. Abbott, Valveless Flow Switching Using Constant Flow Controllers, HRC & CC., 7:577, 1984.
39. J. C. M. Wessels and R. P. M. Dooper, Switching Valve for Glass Capillary Gas Chromatography, J. Chromatog., 279:349, 1983.
40. R. J. Miller, S. D. Stearns, and R. R. Freeman, The Application of Flow Switching Rotary Valves in Two-Dimensional High Resolution Gas Chromatography, HRC & CC, 2:55, 1979.
41. G. H. Stewart, Retention Hysteresis in Backflush, J. Chromatog. Sci., 19:216, 1981.
42. T. S. Buys and T. W. Smuts, A Study of the Effects of Temperature and Pressure on the Retention Time in Series - Coupled Columns under Conditions of Constant Mass Flow Rate, HRC & CC, 4:102, 1981.
43. J. H. Purnell and P. S. Williams, Relative Retention in Serially Connected Binary Gas Chromatographic Capillary Column Systems and the Implications for Window Diagram Optimization of Such Systems, J. Chromatog., 292:197, 1984.
44. F. Poy and L. Cobelli, Quantitative Aspects of the Programmed - Temperature Vaporization Technique of Sample Introduction in Parallel Capillary Column and Microbore Capillary Column Gas Chromatography, J. Chromatog., 279:689, 1983.
45. F. Munari and S. Trestianu, Thermal Peak Splitting in Capillary Gas Chromatography, J. Chromatog., 279:457, 1983.
46. I. M. Hais, Two-Dimensional, J. Chromatog., 187:466, 1980.
47. J. A. Apffel and H. McNair, Hydrocarbon Group-Type Analyses by On-Line Multi-Dimensional Chromatography: II. Liquid Chromatography - Gas Chromatography, J. Chromatog., 279:139, 1983.
48. K. Grob, Jr., D. Frohlich, B. Schilling, H. P. Neukon, and P. Nageli, Coupling of High-Performance Liquid Chromatography with Capillary Gas Chromatography, J. Chromatog., 295:55, 1984.

49. R. E. Majors, E. L. Johnson, S. P. Cram, A. C. Brown, III, and E. Freitas, A Coupled HPLC/GC System: Applications, Paper presented at 1979 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.
50. S. P. Cram, A. C. Brown, III, E. Freitas, R. E. Majors, and E. L. Johnson, A Coupled HPLC/GC System: Instrumentation and Automation, Paper presented at the 1979 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.
51. R. E. Majors, Multidimensional High Performance Liquid Chromatography, J. Chromatog. Sci., 18:571, 1980.
52. K. Ogan and E. Katz, Analysis of Complex Samples by Coupled - Column Chromatography, Anal. Chem., 54:169, 1982.
53. E. L. Anderson and W. Bertsch, Heartcutting with Glass Capillary Columns and Selective Detectors, Paper presented at American Chemical Society Meeting, Chicago, August, 1977.
54. V. G. Berezkin, L. N. Kolomiets, A. A. Korolev, Y. B. Shmidel, and V. P. Chizhkov, Compound Chromatography, J. Chromatog., 191:95, 1980.
55. J. Sevcik, Application of Multidimensional Switching to the Analysis of Volatiles, HRC & CC, 4:86, 1981.
56. S. Berg and A. Jonsson, Two-Dimensional Gas Chromatography for Determination of Volatile Compounds in Ambient Air, HRC & CC, 3:166, 1980.
57. J. Sevcik, Determination of Alcohols in Gasoline Blends Using A Multidimensional Switching System, HRC & CC, 3:166, 1980.
58. N. G. Johansen, The Analysis of C₁ - C₄ Alcohols, MTBE, and DIPE in Motor Gasolines by Multi-Dimensional Capillary Column Gas Chromatography, HRC & CC, 7:487, 1984.
59. E. H. Osjord and D. Malthe-Sorensen, Quantitative Analysis of Natural Gas in Single Run by the Use of Packed and Capillary Columns, J. Chromatog., 297:219, 1983.
60. L. Huber and H. Obbens, Gas Chromatographic Analysis of Hydrocarbons up to C₁₆ and of Inert Gases in Natural Gas with a Combination of Packed and Capillary Columns, J. Chromatog., 297:167, 1983.
61. W. V. Ligon, Jr., and R. J. May, Quantity Optimized Two-Dimensional Gas Chromatography for Mass Spectrometry, Anal. Chem., 52:901, 1980.

62. W. V. Ligon, Jr., and R. J. May, Target Compound Analysis by Two-Dimensional Chromatography - Mass Spectrometry, J. Chromatog., 294:77, 1984.
63. W. V. Ligon, Jr., and R. J. May, Isomer Specific Analysis of Selected Chlorodibenzofurans, J. Chromatog., 294:87, 1984.
64. H. J. Stan and D. Mrowetz, Residue Analysis of Organophosphorous Pesticides in Food with Two-Dimensional Gas Chromatography Using Capillary Columns and Flame Photometric Detection, HRC & CC, 6:255, 1983.
65. D. W. Wright, K. O. Mahler, T. G. M. Weaver, and E. F. Dawes, A Multidimensional GC Conversion System for Vitreous Silica Capillaries, Paper presented at 1983 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.
66. U. Goekeler, Multidimensional, Double-Oven GC for Jet Fuel Analysis, Amer. Lab., p. 66, October, 1984.
67. S. Wicar, Mass Flow Control and Temperature Programming in Gas Chromatography: I. Precise Digital Mass Flow Controller, J. Chromatog., 295:395, 1984.
68. S. Wicar, Mass Flow Control Temperature Programming in Gas Chromatography: II. Flow Continuity Equation and its Consequences in Programmed - Temperature Gas Chromatography, J. Chromatog., 298:373, 1984.
69. N. W. Davies, Determination and Optimization of Flow Rates in Vacuum Capillary Gas Chromatography, Anal. Chem., 56:2618, 1984.
70. N. W. Davies, Temperature Programming and Flow Rates in Capillary Gas Chromatography, Anal. Chem., 56:2600, 1984.
71. Y. Takayama, Simple Carrier Gas Flow Controller Unit for Capillary GC with On-Column Injection, HRC & CC, 7:48, 1984.
72. M. L. Hopper, Capillary Fused-Silica On-Column Injection of Chlorinated Pesticides with an Ultra-Low Volume Rotary Valve, J. Chromatog., 302:285, 1984.
73. J. C. M. Wessels and R. P. M. Dooper, Switching Valve for Glass Capillary Gas Chromatography, J. Chromatog., 279:349, 1983.
74. R. Annino and J. Leone, The Use of Coanda Wall Attachment Fluidic Switches as Gas Chromatographic Valves, J. Chromatog. Sci., 20:19, 1982.

75. K. Grob and G. Grob, Practical Aspects of the Dependence of Polarity on Temperature, Chromatographia, 17:481, 1983.
76. T. Spitzer and W. Dannecker, Glass Capillary Gas Chromatography of Polynuclear Aromatic Hydrocarbons in Aircraft Turbine Particulate Emissions using Stationary Phases of Varying Polarity, J. Chromatog., 267:167, 1983.
77. H. Moser and H. Arm, Separation of 3- to 6-Ring Polycyclic Aromatic Hydrocarbons by Capillary Gas Chromatography with a Liquid Crystal as Stationary Phase, HRC & CC, 7:637, 1984.
78. F. Janssen, Glass Capillary Column with Nematogenic Liquid Crystals as Stationary Phases for Separating Polycyclic Aromatic Hydrocarbons, Chromatographia, 17:477, 1983.
79. P. C. Hayes, Jr., and E. W. Pitzer, Kovats Indices as a Tool in Characterizing Hydrocarbon Fuels in Temperature Programmed Glass Capillary Gas Chromatography: Part 1, Quantitative Identification, Report AFWAL-TR-81-2102, Air Force Aero Propulsion Laboratory, Wright-Patterson Air Force Base, Ohio, November, 1981.
80. P. Sandra, M. Verzele, and E. Vanluchene, Construction of a Polyimide Effluent Splitter for Multiple Detection in Capillary Gas Chromatography, HRC & CC, 6:504, 1983.
81. E. L. Anderson and W. Bertsch, Practical Aspects of Pt/Ir Effluent Splitters for Multidetector GC and Pneumatic Solute Switching, HRC & CC, 1:13, 1978.
82. G. Wells, Comparison of Optimized Gas Chromatography Detectors for Packed and Capillary Columns, J. Chromatog., 270:135, 1983.
83. J. S. Warner and R. P. Kenan, Analytical Techniques for Aromatic Components in Aircraft Fuels, Report AFAPL-TR-79-2093, Air Force Aero Propulsion Laboratory, Wright-Patterson Air Force Base, Ohio, October, 1979.
84. I. T. Salmeen, A. M. Pero, R. Zator, D. Schuetzle, and T. L. Riley, Ames Assay Chromatograms and the Identification of Mutagens in Diesel Particle Extracts, Environ. Sci. Technol., 18:375, 1984.
85. J. F. Pankow and M. E. Rosen, The Analysis of Volatile Compounds by Purge and Trap with Whole Column Cryotrapping (WCC) on a Fused Silica Capillary Column, HRC & CC, 7:504, 1984.
86. S. Nitz, F. Drawert, and E. Julich, Trace Analysis by Intermediate Trapping with a Modified Programmable Temperature Vaporizer, Chromatographia, 18:313, 1984.

87. P. W. Centers and W. A. Rubey, A Packed and Open Tubular Series Column System, Unpublished report of University of Dayton, October, 1968.
88. D. J. McEwen, Backflushing and Two-State Operation of Capillary Columns in Gas Chromatography, Anal. Chem., 36:279, 1964.
89. Literature from Siemens Instruments, 1983.
90. A Multi-Dimensional GC Conversion System for Vitreous Silica Capillaries, Literature from Scientific Glass Engineering, Inc., 1983.
91. F. R. Guenther, S. N. Chesler, and R. M. Parris, The Quantitative Analysis of Some n-Heterocyclics in Shale Oil by Two-Dimensional GC², Paper presented at 1981 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.
92. M. Goedert and G. Guiochon, Investigations of the Effects of Temperature Gradients and Fluctuations on Gas Chromatographic Retention Data, Anal. Chem., 45:1180, 1973.
93. H. U. Buser, R. Soder, and H. M. Widmer, Influence of a Sophisticated Cold Trap on the Shape of Capillary Chromatography Peaks, HRC & CC, 5:156, 1982.
94. R. Rothchild and P. R. DeForest, Simple Device for On-Column Cryofocusing in Capillary Column Gas Chromatography, HRC & CC, 5:321, 1982.
95. S. Adam, Efficiency of Cryogenic On-Column and Pre-Column Focusing of Volatile Compounds for High-Resolution GC, HRC & CC, 6:36, 1983.
96. W. A. Rubey, Theoretical Behavior of Declining Thermal Gradient Gas Chromatographic Column, University of Dayton Report, October, 1976.
97. M. F. Gonnard, G. Guiochon, and F. I. Onuska, Narrow Bore Open Tubular Columns for Improvement of Gas Chromatographic Analysis Time, Anal. Chem., 55:2115, 1983.
98. C. P. M. Schutjes, E. A. Vermeer, J. A. Rijks, and C. A. Cramers, High Speed Profiling of Complex Mixtures by Means of Gas Chromatography in Narrow Bore Capillary Columns, In: Proceedings of Fourth International Symposium on Capillary Chromatography, Hindelang, Germany, May, 1981.
99. C. P. M. Schutjes, E. A. Vermeer, G. J. Scherpenzeel, R. W. Bally, and C. A. Cramers, Practical Aspects of Fast Gas Chromatography on 50 μ m I.D. Capillary Columns: Combination with Electron-Capture Detection, J. Chromatog., 289:157, 1984.

100. A. Nohl, Fast GC with WCOT Columns, Chromatography Review (Spectra Physics), 11(1)13, 1984.
101. C. A. Cramers, F. A. Wijnheymer, and J. A. Rijks, Optimum Gas Chromatographic Conditions in Wall-Coated Capillary Columns: Extended and Simplified Forms of the Golay-Equation, HRC & CC, 2:329, 1979.
102. W. Jennings, Gas Chromatography with Glass Capillary Columns, Academic Press, New York, 1980.
103. R. R. Freeman, High Resolution Gas Chromatography, Hewlett-Packard, 1981.
104. W. A. Rubey and W. E. Dirkes, Jr., Aspects of High-Resolution Gas Chromatography as Applied to the Analysis of Hydrocarbon Fuels and Other Complex Organic Mixtures, Vol. II: Survey of Sample Insertion Techniques, University of Dayton Report UDR-TR-83-97, For Air Force Aero Propulsion Laboratory, Wright-Patterson Air Force Base, Ohio, January, 1985.
105. W. G. Jennings and A. Rapp, Sample Preparation for Gas Chromatographic Analysis, Huthig, Heidelberg, 1983.
106. A. Zlatkis, D. C. Fenimore, L. S. Ettre, and J. E. Purcell, Flow Programming - A New Technique in Gas Chromatography, J. Gas Chromatog., 3:75, 1965.
107. A. Nohl, Flow Programming of Short Capillary Columns, Chromatography Review (Spectra Physics), 11(3)10, 1984.
108. J. Roeraade, Are High Resolution GC Techniques Fully Reliable for Ultra Trace Analysis?, HRC & CC, 1:135, 1978.
109. P. C. Hayes, Jr., and E. W. Pitzer, Rapid Monitoring of Hydrocarbon Blending Stocks in Modified Aviation Turbine Fuels, J. Chromatog. Sci., 22:456, 1984.
110. Chemical and Engineering News, August 2, 1982, p. 20.
111. G. C. Stafford, Jr., P. E. Kelley, and D. C. Bradford, Advanced Ion Trap Technology in an Economical Detector for GC, Amer. Lab., 15(6) 51, 1983.
112. P. C. Hayes, Jr., and E. W. Pitzer, Disengaging Solutes in Shale- and Petroleum-Derived Jet Fuels by Altering GC Programmed Temperature Rates, Paper presented at 1984 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.

113. J. C. Giddings, Retention Times in Programmed Temperature Gas Chromatography, J. Chromatog., 4:11, 1960.
114. R. W. Ohline, Chromothermography - The Application of Moving Thermal Gradients to Gas-Liquid Partition Chromatography, Ph.D. Dissertation, Northwestern University, 1960.
115. A. A. Zhukhovitsky, Some Developments in Gas Chromatography in the USSR. In: Gas Chromatography, 1960, R. P. W. Scott, ed., Butterworths, Washington, p.293, 1960.
116. V. G. Berezkin and V. S. Tatarinskii, Gas-Chromatographic Analysis of Trace Impurities, Consultants Bureau, New York, 1973.
117. M. Fatscher and J. M. Vergnaud, Graphical Determination of the Retention Time obtained by Gas Chromatography with Longitudinal Temperature Gradient, J. Chromatog., 47:297, 1970.
118. Fourier, J. B. J., The Analytical Theory of Heat, Paris, 1822, Eng. Trans. (Freeman, A.) Dover Publications, 1955.

ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

DET	-- detector
FPD	-- flame photometric detector
GC	-- gas chromatography
HFID	-- hydrogen flame ionization detector
HRGC	-- high resolution gas chromatography
ID	-- inside diameter
ITGC	-- isothermal gas chromatography
LC	-- liquid chromatography
MDGC	-- multidimensional gas chromatography
MSD	-- mass selective detector
OD	-- outside diameter
OTC	-- open tubular column
PID	-- photoionization detector
PN	-- part number
PSIG	-- pounds per square inch gauge
PTGC	-- programmed temperature gas chromatography
RC	-- resistance capacitance
RSGC	-- rapid separation gas chromatography
cm	-- centimeters
m	-- meters
min	-- minutes
mm	-- millimeters
sec	-- seconds

SYMBOLS

A	-- cross-sectional area
A _m	-- mobile phase cross-sectional area
A _s	-- stationary phase cross-sectional area
°C	-- degree Celsius
E	-- excess temperature
H	-- height equivalent to a theoretical plate
H _c	-- plate height, compressing
H _e	-- plate height, expanding
H _i	-- incremental plate height
ΔH	-- molar heat of vaporization
K	-- curvature; permeability
L	-- column length
P	-- parameter of exposed surface
P _a	-- external perimeter
P _b	-- internal perimeter
P _r	-- constant programming rate
R	-- gas constant
R	-- radius
R _h	-- radius of the tubular helix
R _f	-- velocity ratio, of zone to carrier
ΔS	-- entropy, solute vaporization
T	-- temperature; absolute temperature
T _a	-- ambient temperature
T _o	-- initial temperature
T _b	-- inlet temperature
T _w	-- wall temperature

$T_{c,1}$ -- inlet temperature
 $T_{c,2}$ -- outlet temperature
 T_h -- chamber temperature
 T_i -- initial temperature
 c -- a constant
 c_1 -- a constant
 c_2 -- a constant
 c_3 -- a constant
 c_4 -- a constant
 c_k -- a constant of integration
 $f_1(z)$ -- time function of distance
 $f_2(z)$ -- velocity function of distance
 $f(p)$ -- velocity as a function of pressure
 $\bar{h}$ -- effective heat transfer coefficient
 k -- partition ratio; thermal conductivity
 k_i -- initial partition ratio
 $\bar{k}_e$ -- average partition ratio upon elution
 p -- pressure
 p_o -- outlet pressure
 r -- radius
 r_o -- radius at origin
 t -- time
 t_h -- extended holding time
 t_m -- time of mobile phase displacement
 t_o -- time zero

v -- average linear velocity of the mobile phase
 v -- volume
 v_b -- inlet velocity
 v_g -- axial velocity of g solute
 v_j -- axial velocity of j solute
 v_m -- mobile phase linear velocity
 v_s -- axial velocity of solute zone
 x -- a Cartesian axis
 x_o -- origin of x axis
 x_L -- conductor length
 z -- distance axis along the column
 z_i -- initial distance
 η -- fluid viscosity
 π -- usual geometrical constant
 σ -- solute zone standard deviation
 σ_i -- initial zone standard deviation, increment i
 σ_I -- distance - based standard deviation of inlet band
 σ^2 -- variance
 σ_o^2 -- original variance of deposited zone
 σ_f^2 -- final variance value

END

FILMED

1-86

DTIC