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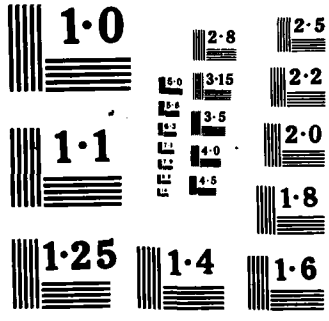
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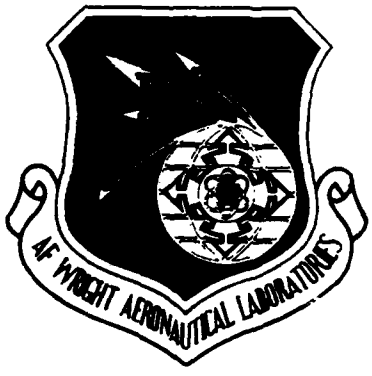

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Volume II

ASPECTS OF HIGH-RESOLUTION GAS CHROMATOGRAPHY AS APPLIED TO THE ANALYSIS OF HYDROCARBON FUELS AND OTHER COMPLEX ORGANIC MIXTURES

Volume II - Survey of Sample Insertion Techniques

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Special attention needs to be given to the sample injection process in high-resolution gas chromatography (HRGC). For the analysis of highly complex organic mixtures, such as turbine engine fuels and various hydrocarbon feed stocks, the sample insertion process is especially important. Presently, it is this admitting of sample to an HRGC system which most seriously limits the chromatographic analysis.

Many different procedures have been used for injecting samples into an open tubular column gas chromatograph with the use of microliter syringes. These many procedures can be grouped into four classifications known as: the split, the direct, the splitless, and the on-column injection procedure, respectively. These four types of injection procedures have been surveyed and evaluated with respect to idealized injection practice, solute overloading, use of injector inserts and precolumns, fast injection procedures, and various methods for focusing inserted solute zones.

In view of the importance of sample insertion in HRGC, improved sample insertion

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19. (Abstract continued) procedures are under development. Also, recommendations are presented for obtaining adequate insertion of highly complex and undiluted hydrocarbon mixtures with HRGC systems.

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FOREWORD

This report was prepared by the Environmental Sciences Group within the Research Institute of the University of Dayton, Dayton, Ohio 45469. The work reported herein was conducted under Task 40 of the Senior Investigator Program on Contract F33615-77-C-2004, which was funded by the Aero Propulsion Laboratory, Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio 45433-6563. The Project Officer for this effort was Major Donald D. Potter (AFWAL/POSF). This present document is Volume II of the two volume report and the experimental portion of this work was conducted between January and September of 1980.

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The authors wish to acknowledge the support and encouragement of the Air Force Project Officer, Major Donald D. Potter, of the Aero Propulsion Laboratory (APL). The authors are also indebted to several other APL personnel for their help during the course of this investigation. The chromatography consultations with Paul C. Hayes, Jr., and Edward W. Pitzer were of continual value with respect to assessing the operation of the in-house laboratory analytical instrumentation. The sample insertion experiments performed by Charlotte R. Eigel clarified many of the variables and other aspects associated with the split sample injection process. Also, the exchanges with Ronald D. Butler relative to high-resolution gas chromatography theory and applications were of considerable help during the course of this investigation.

Within the Research Institute at the University of Dayton, several of our colleagues were especially helpful. Anita Cochran has been especially helpful in improving the readability of the report. In the early part of this work, Don S. Duvall encouraged the undertaking of this research and it was completed under the administrative leadership of our present Group Leader, Barry Dellinger. Also, the authors are especially grateful to our secretary, Margaret Bertke, for the diligent typing of the various text drafts.

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SECTION I

INTRODUCTION

High-resolution gas chromatography (HRGC) is the major instrumental analysis technique for separating and quantitating constituents in complex organic mixtures. The extreme complexity of turbine engine fuels and associated organic feedstocks challenges even the most advanced chromatographic techniques. In analyzing these mixtures, increased resolution is sometimes needed for certain organic constituents. Accordingly, there are continuing efforts to expand the resolving power and quantitation capabilities of HRGC.

Through a systems approach, the important components of a dedicated HRGC system have been studied [1] and evaluated with a view to optimizing performance. One conclusion reached was that the sample admitting process is especially crucial to ultimate analytical performance.

Sample handling and insertion are troublesome problem areas [2] not only in gas chromatography (GC), but in many instrumental analysis techniques. For example, sample introduction is still a major limitation in atomic spectroscopy [3,4] and in other instrumental chemical analysis procedures.

In view of these sample handling difficulties in HRGC, an assessment was desired of the different methods for admitting samples using microliter syringes. By studying and summarizing the different procedures, it should be possible to make recommendations concerning future sample insertion processes for the analysis of highly complex hydrocarbon mixtures.

This report presents a survey of the sample insertion methodologies currently being used in HRGC. In addition, because of the special problems in conducting complete analyses with samples as complex as advanced turbine engine fuels and their various precursors, certain aspects of the split-mode of sample introduction were investigated.

SECTION II

BACKGROUND AND DISCUSSION OF SAMPLE INSERTION TECHNIQUES FOR OPEN TUBULAR GAS CHROMATOGRAPHIC COLUMNS

The many sample insertion techniques for admitting samples to an open tubular column (OTC) gas chromatographic system can be grouped into four classifications. From the early days of capillary column GC, sample insertion techniques have received considerable attention. Even so, there is still no universally accepted method. In many cases the sample insertion process is the major source of quantitative error in HRGC technology. In the following discussion, the basic types of sample insertion are summarized and comparisons are made.

1. SPLIT-TYPE INJECTORS

The first capillary or OTCs used in gas chromatography possessed a bore diameter of approximately 0.25 mm. The stationary-phase film thickness was approximately 0.4 microns. Consequently, these GC columns could accept only very small quantities of individual solutes (i.e., relative to the massive injections that could be made into packed columns). To solve this sample injection problem, split-type sample introduction procedures [5,6] were developed.

Most of the early work with OTCs involved volatile liquids, and the initial splitter designs permitted analyses with these types of organic samples. However, almost immediately, non-linearity and discriminating effects from inlet splitters were noted. As OTC gas chromatography progressed into analyzing gaseous samples and substances of higher molecular weight, the need for improved inlet splitters was apparent. The special inlet splitters that were developed [7] employed inserts and features intended to homogenize the gas-phase sample prior to entry into the column. As HRGC technology progressed further with the use of glass tubing and then fused silica OTCs, there were increased demands for adequate sample insertion techniques.

Since the basic split-type sample injection technique has many desirable features, and is a very practical method for introducing samples, considerable study has been given to this sample insertion process. Recent studies [8] have identified many of the variables in this insertion process, such as: evaporation rate of different molecules, internal pressure variations, gas viscosity differences, condensation behavior, time alloted for evaporation, mixing difficulties, diffusion limitations, formation of droplets and aerosols, adsorptive behavior, gas expansion into unswept recesses, etc. In view of these variables, special stopped-flow gas insertion techniques were also used with splitters.

Once the extreme complexity of the split insertion process had been realized, several new inlet splitter devices [9-11] were introduced. Some of these splitters were relatively simple in that they could be used with gas chromatographs employing either OTCs or packed columns. However, the more recent inlet splitters have been designed exclusively for use with fused silica OTCs. In addition to lingering fractionization problems with the typically high-temperature inlet splitters, they can also cause thermal degradation of some of the more thermally labile constituents in a complex sample.

2. DIRECT INJECTION AND SPLITLESS INJECTORS

In the middle 1960's, two other sample insertion processes were introduced. The syringe injection of sample into a single exit insert, or chamber, upstream of the OTC inlet essentially depicts the process known as direct injection. The earliest versions of the direct injection technique [12-14] were performed using both metal and glass OTCs, and care had to be taken that the total admitted sample (including solvent) was not excessive. At that time, the direct injection of sample still required that a relatively small quantity of total sample be admitted to the OTC system. Syringes and delivery devices capable of slowly admitting 5.0 microliters, or less, of total sample had to be used with the early direct injection techniques.

Splitless injection, introduced in the latter 1960's [15,16], permitted the venting of the solvent for some fixed time interval after admitting the total sample. In essence, the solutes of interest are passed into the OTC entrance while the massive gaseous solvent is vented. Clearly the term "splitless" is somewhat misleading, for indeed part of the admitted sample is split to the vent.

Of these two techniques, the splitless injection procedure has thus far been more highly developed. It has also been widely accepted, particularly for conducting trace-level analyses of complex organic samples where the solutes of primary interest are of moderate molecular weight. That is, the solutes cannot be gaseous species, nor can they be of extremely high molecular weight, e.g., greater than 500 MW.

In their early development stages, both of these techniques experienced difficulties with contamination from materials such as the injector septa, the special ferrule that is used for attaching the column to the injector body, and even upstream components, e.g., organics liberated from pressure regulator diaphragms, seals on in-line filters, etc. The more recent versions of the splitless injection technique have features [17,18] which essentially eliminate the systematic errors, the ghost peaks, and the various sources of organic artifacts.

3. ON-COLUMN INJECTION

Excellent quantitative results were not achieved in packed-column GC until acceptable on-column injection techniques were developed. If the admitted sample contained material that encompassed a relatively narrow molecular weight range, good quantitative results could be obtained with flash vaporization devices, etc. However, for samples with wide molecular weight distributions, or samples of a multiphase nature, success in quantitation came [19] only after the advent of on-column injection methods. To a lesser extent the same can probably be said for OTC gas chromatography.

Numerous researchers [20-24] have been instrumental in conceptualizing and developing the on-column injection techniques for OTCs. With the introduction of very small diameter fused silica syringe needles, it was possible to insert the delivery tube well into the interior of the capillary column's sample reception region. Most of the presently available on-column injectors are designed for subambient or room temperature insertion of the sample, thus largely eliminating the degradation of thermally labile solutes. By being able to program the entire column and insertion region to high temperatures, it is now possible to obtain adequate quantitations of heavy organics, such as C_{40} hydrocarbons and even higher molecular weight substances. This was not possible with the previous split-type sample insertion devices, which tended to selectively reduce the high-molecular-weight fraction during the column entry process. Again, the on-column procedure is well suited for those high-molecular-weight organic substances that are also thermally labile. Specifically, solutes do not have to experience the temperatures necessary to keep them in the gas phase prior to the entry into the inlet region of the OTC.

The on-column sample insertion process is also suited for multiphase samples as it can be adapted to handle gases, liquids, and dissolved solids. Indeed, one of the choice features of the on-column technique is that the heavier substances can be subjected to solute focusing at distinct inlet locations, and individual solute bands can initially be very narrow using this procedure.

With the recent introduction of bonded-phase OTCs, it is now a common practice to chemically flush a contaminated OTC. For many samples to be analyzed by HRGC, the admitted sample will often contain various types of organic residue (some of a polymeric nature) that could permanently contaminate the inlet region of an otherwise acceptable OTC. In short, with these bonded-phase columns it is possible to clean up the column after a series of unclean sample injections.

On-column injection procedures have been developed for admitting large quantities of sample [25], and thereby permitting

trace-level determinations to be made. Special valve-type sample admitting techniques [26] have also been developed for on-column injection. Another procedure [27] stops the flow of carrier gas during the sample admitting process.

Although the very early on-column insertion procedures were quite sophisticated and delicate with respect to admitting a sample, many simpler and more practical versions of the on-column injection technique [28,29] have recently appeared. In addition, progress has been made in automating the sample insertion procedures for on-column injection as autosamplers are coming from various instrument manufacturers.

4. COMPARISONS OF INJECTION TECHNIQUES

Currently four basic types of sample insertion procedures can be used with high-resolution open tubular gas chromatographic columns: the split, the direct, the splitless, and the on-column injection procedure. Each procedure has areas where it is applicable, yet each has certain limitations. Certainly it is fair to say that at present, no universally accepted OTC sample insertion procedure is best for all situations.

The split injection technique has, until recently, been the most widely used for introducing samples onto an OTC. Of the various techniques this particular admitting process can place solutes into an OTC in the shortest time. Thus, the splitter can be used for very rapid insertion of samples, and some of the best elution profiles (narrow and symmetrical) are obtained with the split injection technique, which can be readily adapted for autosampler control and designed to have minimal adsorptive effects in the sample insertion region. Well designed splitter assemblies can eliminate artifact solutes and ghost peaks. Split injection is relatively easy to operate and it can be accomplished with a wide variety of different types of organic samples along with a broad range of solute concentrations in the solvent. This technique can also be used with neat samples i.e., solutes in the absence of a solvent. In addition, the split mode can readily be used for making injections into microbore OTCs.

With the conventional split mode of injection, high temperatures are needed for homogeneous vaporization of solutes prior to column entry. Also, for good quantitation to be accomplished, it is vital that the sample contain an internal standard. The interior surfaces of most splitter assemblies possess a high surface area and must therefore be as inert as possible. The split mode can be used with relatively large sample sizes, provided large split ratios are used, and it is most adaptable to programmed temperature GC analysis. Here the time duration over which the sample is placed within the OTC interior is negligible. Split-type injections are not highly conducive to trace-level analyses, and since high temperatures (flash vaporization) are needed, there is a distinct possibility of sample degradation in the insertion port. The major drawback to the split-type injection technique is the discrimination that occurs prior to sample entry onto the OTC. This is further accentuated by uneven and unpredictable needle delivery contributions.

Direct injection is probably the least used of the four basic sample injection procedures; its greatest use is in applications with wide-bore OTCs. An easy injection technique to install and perform, it is typically used with relatively large quantities of sample. Direct injections can be readily carried out with an autosampler; however, the entire sample must pass through the injection region and onto the OTC. It is primarily used for trace-level determinations, and in many cases this procedure is invoked in conjunction with cold trapping. Because of the wider-bore OTCs used with this technique, and the accompanying tendency for emerging solutes to tail, direct injection is not used where maximum chromatographic resolution is desired. The direct technique can best be performed with a slow injection procedure for it is vulnerable to flashback of solvent and solutes into the upstream recesses of the GC system. The direct injection method suffers from possible contaminants that have their origin within the septa and other organic sources, e.g., connecting ferrules, trapped residue from previous injections, etc.

Splitless injection has received emphatic acceptance by chromatographers interested in conducting trace-level determinations via HRGC. Splitless injection can be accomplished with an autosampler, and large injection volumes are common with this procedure. Also, samples can be injected at relatively low temperatures, thereby avoiding thermal degradation of certain solutes while in the injector region. With the use of the solvent effect, solutes of interest can be focused in the entrance region of the OTC. In view of the timed venting feature employed with this technique, the solvent tail is eliminated prior to the emergence of the solutes of interest. Solvent selection is crucial in splitless injection, and timing aspects of the required purge of the inlet region are of key importance. This technique usually requires frequent changing of the inserts or liners located in the sample injection port. If care is not exercised with splitless injection, spurious solutes can appear in the finished chromatogram, resulting from numerous sources, e.g., septa, septa thermolysis products, or possibly organics emitted upstream of the injector. Splitless injection can usually tolerate a slow rate of sample insertion.

Various on-column injection techniques have been the most recently developed and one of their major advantages is that they can permit trace-level analyses to be conducted for a broad molecular weight range of constituents. This procedure essentially avoids the thermal degradation of admitted solutes, and it currently provides the highest degree of quantitative accuracy and reproducibility. The ability to produce high-resolution separations with on-column injection is rivaled only by that of the conventional high-temperature split mode of sample injection. However, if properly designed and implemented, advanced versions of the on-column injection process should eventually demonstrate the maximum possible chromatographic resolution of solutes. With presently available on-column injection procedures, it is difficult to handle and analyze neat samples. Thus far, versatile autosamplers for this sample insertion process have not fully materialized. On-column

injection does require special attention to the many details associated with admitting sample, and if many samples are being processed, they must be free of substances which cannot be chromatographically migrated, e.g., polymers, inorganics, etc.

Because of the good quantitative behavior associated with the on-column injection technique, variations of this sample-admitting process exhibit the greatest long-term potential. Accordingly, this technique is receiving the most attention in terms of continued research and development. Although some of the processes associated with on-column injection are quite complicated, it is anticipated that eventually it will be quite routine, easily performed, and amenable to practically any type of organic sample that can be analyzed by gas chromatography.

SECTION III

REQUIREMENTS FOR ACCEPTABLE SAMPLE INJECTION

Gas chromatographic analyses performed with high-resolution OTCs can be classified into two separate types. Specifically, there are HRGC separations performed strictly in the isothermal mode (i.e., ITGC) where the OTC temperature is held constant throughout the entire chromatographic process, and there are analyses performed using some form of programmed temperature gas chromatography (PTGC). These two different modes of conducting GC analyses basically require different criteria with respect to sample injection.

In this report, attention is given to sample insertion processes used in PTGC, or variations thereof.

1. INJECTION THEORY AND SOLUTE OVERLOADING IN PROGRAMMED TEMPERATURE GAS CHROMATOGRAPHY WITH OPEN TUBULAR COLUMNS

The introduction of samples into an OTC system must be such [30,31] that the solutes of interest quantitatively enter the GC flowpath so that they can be representatively transported and sensed at the completion of the separation process by a suitable detection device. Whether the total sample enters the GC column or whether a fixed fraction of the uniform sample is passed into the GC column interior is not the major issue. The important criterion is that a representative ratio of the entire sample is processed. Thus, if a splitting device is used at the column entrance, the split ratio must be constant regardless of the chemical constituents that make up the sample.

The chromatographic process itself can not be destructive to admitted solutes. Nor can the chromatographic flowpath exhibit adsorptive behavior wherein it selectively retards some solutes in a nonlinear manner. In addition, the ideal chromatographic column cannot exhibit retentive behavior that is concentration dependent. What can be said of the chromatographic column can

also be stated for the sample insertion device. Specifically, the sample delivery device, i.e., syringe, sampling valve, collection trap, precolumn insert, etc., must not impart preferential treatment for certain chemical species.

The sample insertion portion of the GC system must be capable of delivering solutes to the column entrance in such a manner that the solute zones do not overload the OTC either with respect to volume overloading [31] or concentration overloading criteria. Overloading at this intitial portion of the chromatographic process is permissible for solutes that will not be subjected to strict retention characterizations. It is also permissible for solvents and the major solutes when trace-level analyses are being conducted for certain compounds while in the presence of a larger matrix of organic substances.

With respect to highly complex organic mixtures, e.g., crude oil, biological organic samples, volatile organic environmental contaminants, and multicomponent organic feedstocks, special demands [32] are placed upon the sample introduction process when it is desirable to have equal analytical capability for every constituent in the mixture. In PTGC, whether it be an OTC or a packed column used for the separation, it is necessary that the initial portion of the column have sufficient stationary phase to adequately receive the admitted solutes without overloading, saturating, or modifying the GC phase. Table 1 is a listing of some of the different types of gas-liquid chromatographic columns and the amount of liquid phase deposited per unit length of the column. To some extent the quantity of liquid phases limits the amount of sample that can be admitted to the GC column without overloading.

In HRGC where we have access to highly sensitive detection devices, overloading [33] is only a problem when using the very fine bore OTCs. Even then it seldom has serious consequences except when we want to perform trace-level analyses for certain solutes. In fact, for HRGC one major injection limitation is

TABLE 1

STATIONARY PHASE LOADINGS

Column Description	Liquid phase per unit column length (mg cm^{-1})
WCOT, 0.25 mm ID, film thickness = 0.4 μm	0.003
SCOT, 0.5 mm ID, phase ratio = 65	0.03
Small bore analytical packed column, with low liquid loading (2.0 mm ID, 4% liquid phase loading on diatomaceous earth*)	0.3
Medium bore analytical packed column, with moderate liquid loading (4.5 mm ID, 8% liquid phase loading on diatomaceous earth*)	3.0

*diatomaceous earth density $\cong$ 0.24 gm cm^{-3}

associated with the delivery device. Specifically, there is a tremendous need for syringes that can deliver 0.001 to 0.01 microliters of neat sample to the sample reception region of an OTC (without discrimination, adsorption, degradation, or other types of undesirable behavior).

2. INJECTOR INSERTS AND PRECOLUMNS

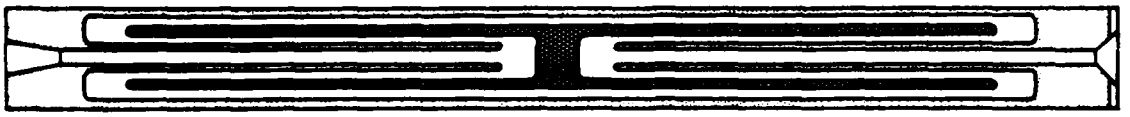
The use of interchangeable inserts within the injection chamber of a chromatograph dates back to some of the earliest activities with packed column GC. They were installed to permit the injection and analysis of relatively dirty samples. Then, after the insert or precolumn had been contaminated, it could be replaced and thereby avoid damage to the valuable downstream separation column.

In HRGC, injection inserts have been used primarily to obtain a more homogeneous gas-phase sample immediately before subjecting the gaseous environment to the split at the column entrance. Numerous different designs of inserts have been evaluated with respect to both fractionation of the input sample and transport efficiency observed with various solutes detected at the column exit.

Some of these inserts [34] are quite simple, e.g., a glass tube containing glass wool, and some are more exotic, such as cupped devices for inducing gas-phase mixing prior to the splitting operation. Figure 1 shows a drawing of a special insert developed during the course of this work to obtain adequate gas-phase mixing and homogeneity before subjecting the gaseous environment to the split at the GC column entrance. This particular splitter insert was fabricated in the Scientific Glass Shop at the University of Dayton and was evaluated for splitting behavior using hydrocarbon fuels.

Certain injector inserts have contained packed chromatographic media, e.g., stationary phases coated onto diatomaceous earth. This type of packed insert has evolved into what is referred to as a precolumn. There is little doubt that

CROSS-SECTIONAL VIEW OF INSERT



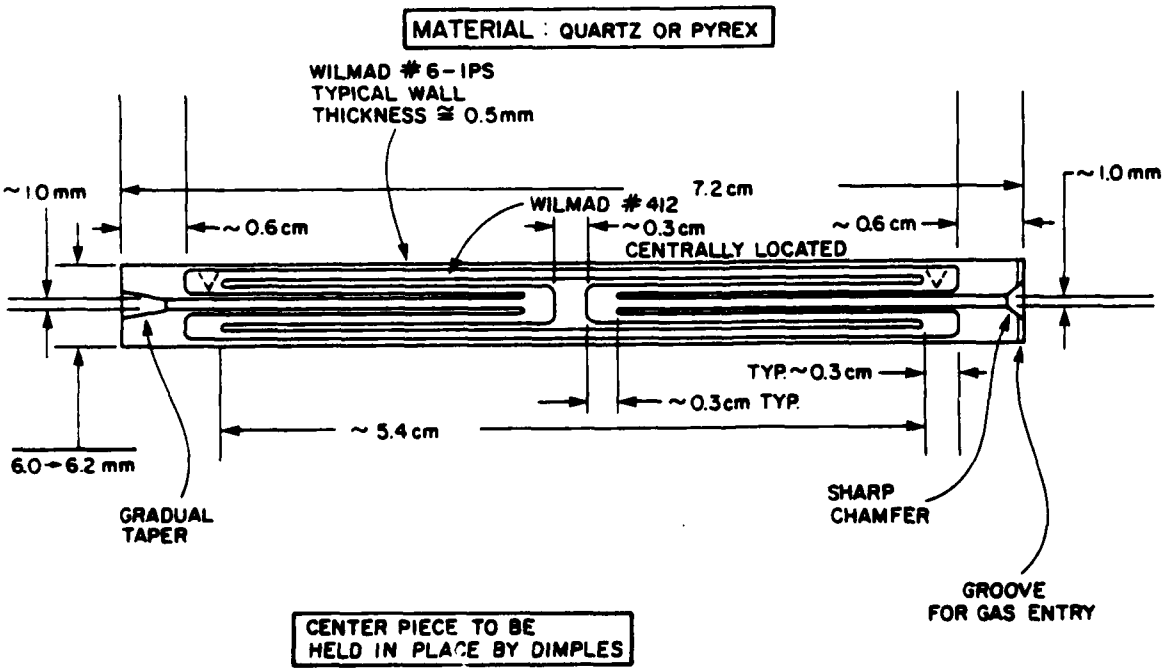


Figure 1. Special Insert for Split Injector.

appropriate and properly installed precolumns can preserve the integrity of a downstream chromatographic column. Various precolumns have demonstrated that they can prolong the life of certain separation columns.

Packed precolumns can also be used upstream of special splitters. For example, several investigators have used packed precolumns for receiving the admitted sample and then sending the effluent from the precolumn simultaneously into a downstream parallel arrangement involving a packed column and an OTC. Separate detectors are usually used for monitoring the effluents from precolumn/parallel column arrangements. In such installations special consideration must be given to minimize the solute zone spreading that occurs in the packed precolumn even before its entry into the downstream column(s). Excessive zone width at the column entrance will be reflected eventually in poorer chromatographic resolution.

Over the years, considerable effort [35-37] has been given to developing concentration techniques for organic substances, particularly for the environmental and biological sciences. As a result of these concentration techniques, many procedures have been introduced whereby a sample that has been concentrated onto a precolumn can be inserted into an appropriate injection port and subsequently desorbed into a PTGC arrangement, permitting trace-level analyses of important volatile organic compounds. Thus far, the trapping media used in these precolumns consists primarily of activated charcoal [37] and various polymeric adsorbents.

With respect to the thermal desorption or liberation of compounds from charcoal traps, several procedures have been developed including a microwave desorption process [38]. However, most of the thermal desorption work with charcoal has involved volatile organic substances. High-molecular-weight materials that would be contained within such charcoal precolumns would usually be degraded in the thermal desorption process,

as the temperatures required for liberation of such organic substances from charcoal are intense.

Thermal desorption procedures for porous polymer adsorbents are highly developed [39] and one particular packing material known as Tenax-GC has received considerable attention. This trapping media is not highly influenced by the presence of water. Also, organic substances of moderate molecular weight can be readily thermally desorbed from the surface of Tenax-GC. Several studies [40] have examined the effects of gas flow rate and temperature on the thermal desorbability of moderately high molecular weight organic substances from Tenax-GC traps.

The use of injector inserts and various precolumns in HRGC systems definitely has a place. However, it must be recognized that such upstream devices [41] must behave extremely well for nondiscriminating quantitative transfer to be accomplished onto the inlet region of HRGC columns without contributing to the chromatographic background and thereby possibly masking out important trace-level organic species.

3. RAPID OR PROGRAMMED HEATING OF INJECTORS

The programmed heating of the sample insertion region is a special procedure practiced [42] for over 20 years in gas-liquid chromatography. Only recently has this controlled heating procedure been accomplished rapidly.

Special heating circuits [43,44] have been designed and tested which can accomplish the controlled heating of appropriately designed GC inlets in time intervals down into the low millisecond range. With such rapid heating capabilities, several programmable temperature vaporizers have been recently introduced [45-48] for use in HRGC. Such vaporizers and sample insertion regions have been applied to splitter inlets, splitless injection, and various on-column injection techniques. These programmed temperature injectors can also be used with automated systems having auto-samplers, and basically they contribute an expanded capability

for use with a variety of different size OTCs. They can be used with several types of wide-bore capillaries and with the highly efficient microbore OTCs.

In theory, similar procedures for controlled rapid heating could be applied for solute trapping and liberation at intermediate locations throughout the chromatographic train. This type of controlled localized heating could also be applied at special solute reception regions, as in multidimensional HRGC, which can provide dramatically increased versatility with admitted solutes.

4. FAST SAMPLE INJECTION PROCEDURES

In isothermal gas chromatography with OTCs, the time-width of the injected sample band [49] is very important. If the total time for introducing sample is excessive (greater than one second) then the resultant chromatographic resolution can be diminished. In HRGC, there are instances when it is desirable to rapidly insert a sample into a chromatographic flowpath, and in a special operational mode known as rapid separation gas chromatography (RSGC), this fast insertion of sample is paramount.

One area in which fast injection is definitely needed is where dissimilar parallel GC columns are dedicated to handling different fractions of a complex sample. In situations where very rapid temperature programming is conducted, the fast insertion of sample is also needed.

Rapid switching of gas streams [50,51] in GC has been accomplished using either actuator-driven switching values or fluidic injection systems. For samples that do not contain a broad molecular weight distribution, these rapid insertion techniques can accomplish their task in less than 10 milliseconds.

Rapid sample insertion procedures would seem to be ideally suited for re-injection of fractionated or partially separated samples into microbore OTCs. Numerous applications for rapid insertion procedures can be found in various forms of multidimensional gas chromatography (MDGC).

SECTION IV

PROCEDURES FOR FOCUSING INSERTED SOLUTES

In PTGC it is necessary at some point in the chromatographic development to have the inserted solutes in the form of narrow bands near the inlet portion of the GC column. Chromatography is essentially a differential migration process which accomplishes a disengagement of dissimilar solute zones. Therefore, for this disengagement to be efficiently conducted, it is necessary that zone widths at the outset be as narrow as possible.

This section of the report discusses several mechanisms which can be invoked for concentrating, or even focusing, the solute zones prior to their chromatographic migration.

1. COLD TRAPPING AND SOLUTE COLLECTION

The use of in-line cold traps for capturing volatile solutes dates back to the early 1960s when Nylon capillary tubing [52] was placed upstream of a separation column, and this short length of tubing was immersed in coolant to capture the condensable admitted components. More recently, the same type of in-line trapping has been used with capillary columns. Many applications have been observed where the inlet portion of a fused silica OTC served as a trap [53] by placing it in a vessel containing liquid nitrogen. Several techniques have been developed using this procedure for trapping volatile organic compounds. Also, studies have examined the temperature-dependent collection efficiency [54] associated with cryogenic trapping of trace-level volatile organic constituents. Some of these studies [55] have focused upon the automation aspects of procedures which use reduced temperature in-line trapping.

Several methods have been developed for cooling the inlet section of a column. Some have employed sheathed-type assemblies [56], while others have used procedures that directed cold nitrogen gas onto a select segment of the OTC. The most popular procedure

is to merely place the entire GC column under a uniform low-temperature gaseous environment. Even at liquid nitrogen temperatures, some researchers [57] have observed incomplete trapping of some low-molecular-weight chlorocarbons and chlorinated hydrocarbons. Consequently, the time of trapping and the axial length of the cryogenic trap are important in applications that use cold trapping for concentrating volatile organic constituents. Fewer problems are associated with the cryogenic trapping of moderate and higher molecular weight organics, and these procedures can be extremely efficient, provided the stationary phase of the OTC is still permitted to function as a gas-liquid partitioning substrate and not as a gas-adsorption surface.

Several cryogenic fluids have been used for trapping solutes. The earliest work was conducted with liquid oxygen. Currently, carbon dioxide [58] is receiving consideration as a coolant fluid for inlet regions of OTCs. However, the major coolant for in-line cryogenic concentrating of solutes has been liquid nitrogen.

Several investigators [59] have conducted definitive experiments on the efficiency of cold on-column injection procedures for low temperature focusing of admitted solutes. Some of these studies [59] have addressed the influence of the low temperature upon peak splitting and profile distortion phenomena. Cryogenic focusing has been used in conjunction with the split and splitless modes [60,61] and experimentally examined. Low temperature focusing of solutes has also been employed for intermediate trapping [62,63] such as used in tandem arrangements of columns and MDGC systems. In addition, several devices have been introduced which can perform on-column cryofocusing at intermediate locations within a GC system.

Cold trapping and solute collection through the use of different coolants such as liquid nitrogen are valuable additions to HRGC, and they will be practically indispensible in future application areas involving highly complex organic mixtures.

2. SOLVENT EFFECT AND RETENTION GAP CONCEPT

The solvent effect for concentrating solute zones has been in use for over a decade [64] to create sharp concentration profiles near the chromatographic entrance region. Several investigators have recently studied the various solvent effects [65-70] and characterized numerous aspects of this behavior in the splitless mode of injection and various hybrid modes of sample insertion. Indeed, the solvent effect is presently receiving a considerable amount of study, both with respect to its behavior in the psuedo stationary phase where the solute is lagging, and in situations where similar solvent effects are being used in packed precolumns [71,72]. There have already been several theoretical studies [73-75] of the various types of "solvent effect" due to the many variations of this focusing phenomena.

For high-molecular-weight materials, the band broadening in space and the retention gap concept [76-82] have been used for admitting large samples to OTC systems. One drawback to the full use of the retention gap technique is that there are difficulties with the transition from the nonretentive retention gap section of the flowpath to the portion of the tubing interior that possesses a uniform film of stationary phase. If junctions* are used at this transition, there is always the possibility for loss of low concentration solutes, peak distortion, or decreased resolution. Currently, it is somewhat difficult to prepare a high-performance OTC which contains a retention gap. This is especially the case with the bonded-phase OTCs.

High-performance OTC systems of the future will probably incorporate several features using on-column injection techniques in conjunction with the various solute focusing procedures that utilize the solvent effect, the retention gap concept, and various forms of cryofocusing.

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* e.g., couplings, joining devices, unions, butt-end connectors, etc.

3. PHASE SOAKING

Another solute focusing procedure receiving considerable attention is termed phase soaking. This form of sample insertion and concentration is for analyzing solutes that are comparable in volatility to the solvent. Several studies [83-87] have examined the effects of injections made under phase soaking conditions, and these have been conducted with both non-polar and polar stationary phase columns. Phase soaking is basically one of the various solvent effects which permits the elution of more volatile species prior to the emergence of the massive quantity of solvent. It also influences the behavior of solutes that emerge after the sample solvent. The selection of solvent is important in this particular process.

Phase soaking in conjunction with other procedures for concentrating solute zones can provide increased performance, particularly for volatile species. However, it would seem that the other procedures would be far more desirable, particularly when interest is centered upon highly complex organic mixtures that cover a broad range of molecular weights. If the HRGC analyses can be performed without a solvent, this is undoubtedly the best situation. When the sample of interest is diluted in a solvent, one is always faced with the problem of distinguishing between solvent impurities and actual volatile constituents of the sample. Even with extremely high purity solvents, the time duration of solvent elution can mask valuable GC information.

4. ADVANCED CONCEPTS FOR ACCEPTING AND FOCUSING INTRODUCED SOLUTES

Highly complex organic mixtures require efficient chromatographic separation columns and equally efficient sample injection procedures. To obtain maximum information from a submitted chemical sample, the analyst would prefer not to subject the sample to a lengthy sequence of sample pretreatment processes.

Generally the more pretreatments, the more chance for data scatter and error in the final analysis. To minimize this quantitation loss, it is often necessary that real-world dirty samples [88] be subjected directly to the HRGC instrumentation. Therefore, the high-performance injection devices of the future will probably be designed to accept samples that are less than pristine. This would imply that these high-performance injectors will be able to handle dirty samples and can be readily serviced, maintained, and placed back into operation.

The intrinsic nature of PTGC and of various thermofocusing techniques [89-91], minimizes many procedural aspects that previously were crucial to sample insertion. Advanced injection procedures of the future will be designed for programmed temperature GC operations and will give little attention to the numerous dynamic physico-chemical aspects of admitting the sample to the HRGC system.

SECTION V

EXPERIMENTS WITH SPLIT-MODE AND SYRINGE INSERTION TECHNIQUES

In view of the very small cross-sectional area of a typical HRGC column, the carrier gas volume flow rates are relatively small and range from approximately 0.2 to 5.0 cm^3 min^{-1}. As the inner surface of an OTC is coated with very thin films of stationary phase, typically ranging from 0.1 to 5.0 microns, it is apparent that only small quantities of admitted sample can be accepted by an OTC.

The earliest practical mode of sample injection into an OTC system used a splitter arrangement. Specifically, the sample was drawn into a microliter syringe and then injected into a hot inlet port where the gas-phase species were quickly split into two dramatically different streams. The vast majority of gas-phase sample was passed through an orifice or flow restrictor and then vented. The much smaller fraction (approximately 1% of the gas-phase sample) was swept into the inlet region of the OTC. This type of split injection permitted small syringes (0.5 to 10.0 microliters volume) to be used for delivering the sample to the chromatograph and, by controlling the split ratio, the analyst could select the quantity of gas-phase sample to be subjected to chromatographic analysis.

Over the years, a wide variety of split-type injection devices have been used in OTC chromatography. Basically, one can say that most splitter injectors have functioned fairly well for samples that did not contain a wide molecular weight range of constituents. However, when wide boiling range samples are injected into a conventional heated splitter assembly, a certain amount of selective fractionation invariably occurs, and there are other difficulties such as thermal degradation of labile constituents, catalytic effects, etc. Most splitter injectors function at elevated temperatures, e.g., 300°C. Consequently, at these temperatures, some sensitive compounds would be thermally

decomposed. Therefore, several of the current splitter injectors contain special inert sleeve inserts to prevent possible catalytic reactions on hot metal surfaces. Even with these precautions, many sensitive compounds cannot be accommodated by a high-temperature gas-phase splitting injector.

1. VARIABLES AND OPERATIONAL DIFFICULTIES ASSOCIATED WITH SPLIT-TYPE INJECTORS

The injection of a highly complex and broad molecular weight range organic sample (e.g., a jet fuel) presents special problems in HRGC analysis. The chromatographic analysis of an unfractionated jet fuel sample should be conducted in its undiluted form. Specifically, this type of organic mixture should not be placed in a solvent and then subjected to analysis, as any solvent (and its impurities) would interfere and mask jet fuel constituents. The same analytical procedure is also advisable for similar type samples, e.g., collected environmental contaminants, edible oils, volatile fragrances, certain biological fluids, etc. In short, total analysis of the sample in its neat form is needed.

At the present state of HRGC technology, the largest sample that a typical 0.25 mm bore (0.2 micron film) OTC can accept without overloading is approximately 0.01 microliters of liquid, and this applies only for a very complex wide-boiling-range sample which contained no single prevailing constituents. There are at present no syringes that can repetitively deliver this small quantity of liquid to the head of the column with precision and without fractionation of the sample. Consequently, the split-type injection device seems to be the only current method by which diluted samples can be readily admitted to OTCs.

There have probably been dozens of inlet splitter designs used in gas chromatography and, especially for wide-boiling-range samples, many variables and nonlinearities are associated with these devices. The major problem in the injection and subsequent HRGC analysis of jet fuels is not related to quantitative delivery

of the entire sample, but is one of selective fractionation. Physically, it is very difficult to obtain a single high-temperature splitter assembly that will produce for a given complex sample the exact same degree of stream splitting for: (a) the low-molecular-weight constituents (b) the middle fraction, and (c) the high-molecular-weight materials, such as in crude oil or shale oil. Basically, with split-type injectors the high-molecular-weight substances are simply not delivered quantitatively to the column entrance. Even so, some splitter designs are better than others with respect to performing the intended functions.

2. EXPERIMENTS WITH INJECTING JET FUEL SAMPLES INTO A MODIFIED SPLITTER ASSEMBLY

In a series of experiments, different quantities of various jet fuels and a standard mixture of hydrocarbons were injected into a modified splitter assembly. Many injection conditions were examined during the course of these experiments which were conducted using a 60 m by 0.25 mm ID fused silica open tubular column that contained a 0.25 micron thick film of SE-30 dimethylsilicone phase. During these tests, the GC column was temperature programmed from 40°C to 250°C at 2°C/min.

Two different injector inserts were tested, one packed with silanized glass wool, and the other with a glass frit. Both of these inserts were tested using various combinations of four parameters:

a. injection size (either 0.1 µℓ or 0.3 µℓ)

b. purge flow: low; 6ml/min., at a 1 to 4 split ratio
medium; 16ml/min., at a 1 to 10 split ratio
high; 80ml/min., at a 1 to 50 split ratio

c. dilute or concentrated sample (concentrated sample had major compound equal to 10%; dilute sample was a 1.0 to 10 mix of the concentrated sample in n-heptane)

d. injection procedure (5 second hold or no hold)

All tests were performed using a Varian 3700 Gas Chromatograph with autosampler and a CDS-111 data recorder, and tests were

conducted in triplicate. The n-decane, n-tetradecane, and n-docosane emerging solute profile areas were used for statistical evaluation, which included the Student-t test to determine differences between the various parameters and an analysis of variance (ANOVA) to determine the repeatability of each of the experimental modes.

From the data obtained form the tests for the various sample sizes, split ratios, sample dilutions, and injection hold times while using the glass frit (WR 80-201) and the glass wool insert (WR 80-200), the three best analyses for each injector were selected. These experimental data were evaluated using the $n\text{-}C_{22}/n\text{-}C_{14}$ ratios and their respective standard deviations. For each injector the three best analyses were compared by the Student-t test and ANOVA. Then the data for each injector were compared, with the following observed results:

Glass Frit

With the glass frit injector, the 0.3 µℓ injection of a dilute solution with a medium split flow was the most advantageous and was not significantly different from the other test results.

Glass Wool

The three best analyses were not significantly different. Therefore, the glass wool injector can be used for a 0.3 µℓ dilute sample with a low split, a 0.3 µℓ dilute sample with a medium split, or a 0.3 µℓ concentrated sample with injection hold and a medium split.

Comparison

When comparing the best analysis with the glass frit versus the best analysis (actually any of the three is acceptable) of the glass wool, it was found that there was a statistical difference only in the t-test for the n-decane.

Other Observations

The glass frit insert seemed to handle n-decane better than the glass wool insert. Results were statistically similar in all other respects. This is in contrast to work performed previously which indicated that an injector packed with glass wool performed better than the glass frit using a 0.3 and a 0.1 µℓ injections.

The results of these tests indicated that under many conditions the glass wool insert and glass frit insert produced comparable and repeatable delivery of sample; however, there were some differences. The glass wool insert delivered the n-decane to the column better (less data scatter) than the glass frit when a 0.3 μℓ sample was used. This difference was seen regardless of whether the sample was concentrated or dilute. Another comparison showed that the glass frit delivered the n-decane to the column better when a 0.1 μℓ dilute solution with an injection hold was used than when the normal n-decane was delivered with a 0.3 μℓ dilute sample with no injection hold. Paradoxically, the n-docosane was delivered more consistently with a 0.3 μℓ dilute solution with no injection hold than when a 0.1 μℓ dilute injection with a hold was used. In all other cases, the silanized glass wool and the glass frit were found to be equal in sample delivery and repeatibility. Earlier tests showed that a very low septum purge flow gave irreproducible results. Therefore, the above tests were run with a septum purge flow of ∿5 ml/min.

This testing showed that the silanized glass wool inlet and glass frit inlet are essentially equal in performance in most routine GC uses. Because there are no discernible differences when an adequate septum purge flow is used, it would be advisable to use a moderate flow (3 to 10 ml/min) to conserve compressed gas. This septum purge also prevented "ghosting" from backflush of sample, which was often seen with low septum purge flows. Finally, because the fuels analyst is routinely concerned with "concentrated" samples and prefers a small sample size, it is advantageous that the silanized glass wool insert be used as it is significantly better under these conditions in delivering the n-decane and other light hydrocarbons to the GC column.

3. FACTORS ASSOCIATED WITH SAMPLE INSERTION USING MICROLITER SYRINGES

There are several methods for inserting a sample into an HRGC instrument without the use of a microliter syringe.

For example, capsule insertion techniques and micropipette sampling have been used, as have special techniques involving glass capillary sampling tubes. Special syringes using extended plungers have also been used for injecting samples into OTC injectors. One special-purpose injector for high-molecular-weight substances uses a movable extension rod for the eventual insertion of sample into the entrance region of an OTC. This particular all-glass-solids sampling device has seen considerable use in biological applications. However, even though there are other sample delivery devices, the microliter syringe is currently the most common method of inserting samples into an OTC gas chromatograph.

At the present time, the smallest of these liquid syringes has a full-scale capacity of 0.5 microliters. Consequently, 0.05 microliters is probably the smallest liquid quantity that can be delivered with relatively good precision. With various microliter syringes, there are several procedures for inserting samples into an injector. The solvent flush technique and the air flush procedure are relatively common methods for depositing samples in packed column technology. However, with automatic samplers, the conventional displacement delivery technique is the most common.

One method that has worked fairly well in the Analytical Instrumentation Development Laboratory at the University of Dayton (where only manual injection techniques are used) is described in the following procedure. Injected samples are always less than 0.3 microliters and are injected with the column at the initial temperature of a programmed temperature sequence. Usually this temperature will be somewhere between minus 20°C and plus 50°C. The procedure is as follows:

a. A #7000 Series Hamilton Syringe is loaded with sample and the needle is wiped thoroughly to remove sample from the outer diameter of the needle.

b. The needle is then inserted to full depth in the injection port. Immediately the plunger is rapidly depressed.

c. With the syringe needle held in this position, the plunger is withdrawn to its full-scale mark (approximately two-second withdrawal time) and then rapidly depressed again.

d. The syringe is then quickly retracted from the GC injector port.

This sample insertion procedure has worked well, particularly when used with a precolumn injector upstream of an OTC.

Recently, considerable data from various laboratories have indicated that fractionation can occur within the syringe needle itself, whether the syringe is of the open-needle variety or the plunger-within-the-barrel design. Specifically, there is a tendency for preferential delivery of volatile species and a corresponding loss of higher molecular weight substances. Heavier substances tend to stay within the needle interior for the former type of syringe and on the barrel and plunger surfaces with the latter type of syringe. This fractionation behavior persists, with either room temperature or hot injection techniques, although for ambient injection there is much less scatter and a far more quantitative delivery than with the hot needle injection procedure.

Syringe injection procedures that involve the piercing of a septum continue to present difficulties such as: (a) septum bleed, (b) particulate arising from the piercing of the septum, (c) thermal degradation products from the septa, and (d) septa that prematurely leak when high-inlet pressures are applied to the injector. If the injection port and the septum location are held at high temperatures, there will be a certain level of leaching of the plasticizer into the flowing gas region. Eventually, these bleed components will be passed downstream where a portion will enter the OTC. In several studies the septum region of the injector was intentionally held at lower temperatures than the body of the injector. In some cases this is advantageous, while in others it tends to contribute to a low delivery of the high-molecular-weight substances.

A procedure was recently recommended whereby a cylindrical opening was placed in the septum which was then sealed upon tightening the septum holder. The logic behind this particular septum installation was that it would eliminate the multiple piercing of the septum (a new hole is usually placed in the septum each time a sample is injected). This approach using a single-hole septum with a syringe alignment guide was intended to eliminate the small particles resulting from the puncture of the soft silicone rubber being deposited into the interior of the injector. This particular single-hole septum has not worked as well in our laboratory as conventional septa. We have experienced leak problems, and indeed this is a serious problem when working with high-inlet pressures such as those associated with long and narrow-bore OTCs.

For high-inlet pressures, septum life is much shorter as the multiple punctures of the septum tend to create leakage earlier than when the inlet pressure to the injector region is relatively low. Several new on-column injection techniques do not use a conventional septum, but instead use a type of ductbill valve for sealing after the syringe has deposited the sample. Several variations of this nonseptum sample entry technique are currently being used and are still going through stages of design evolution and evaluation. The nonseptum technique does present one approach to eliminating spurious solutes (commonly referred to as ghost peaks) that appear in the eventual chromatogram. These spurious solutes which have their origin in the septum, or polymeric materials upstream of the septum, can be considerably reduced by using septum purge flows and by maintaining moderate temperatures for the injector septum region. Several injectors have been designed specifically to reduce the so-called ghost peaks, with good success. However, for HRGC work that involves trace analysis, this is still somewhat of a problem since there are invariably trace levels of solutes in the eventual chromatogram that can be attributed to the injector and other organic emitter sources associated with the injection process.

Sample carry-over is also a problem in OTC technology. Specifically, solutes inserted into the GC system during a previous injection have been retained by some components of the chromatographic system and then appear in the chromatographic readout for a subsequently injected sample. The ferrule connections in an injector may be somewhat suspect in this area. One way of reducing sample carry-over is to maintain a continual purge of the injector and septum during solute migration, and to place a charcoal trap on the exit of the septum purge. A large-capacity, very low-pressure drop charcoal trap should also be installed on any splitter exit vents.

SECTION VI

RECOMMENDATIONS PERTAINING TO SAMPLE INJECTION

Successful analysis of highly complex organic mixtures which contain constituents covering a broad molecular weight distribution requires considerable attention to detail with respect to the sample injection process. Although sample injection in HRGC will remain a complicated multi-variant procedure, progress is being made in understanding this process and eventually it will be automated to the point that efficient injections can be made on a routine basis. This section presents several recommendations for improved insertion of complex samples.

1. GENERALIZED RECOMMENDATIONS FOR FUTURE HRGC ANALYSES

Although it would not be advisable to conduct extensive pretreatments with a complex sample, it would seem desirable to filter a quantity of the sample primarily to remove the non-chromatographable particulates. A small quantity of the filtered fluid can then be set aside for chromatographic analysis.

One of the important design improvements in an HRGC system can be the removal of the septum from the system, thus largely eliminating a major source of extraneous background solutes. Fortunately, many of the new on-column injection systems can operate in a septumless mode.

Another improvement would result if the system could be operated with hydrogen as the chromatographic carrier gas. As stated in Volume I of this report, there are several operational advantages in using hydrogen carrier gas in HRGC, not the least of which is that it can be obtained with extremely high purity.

The microliter syringe has been such a valuable delivery device in every facet of chromatography, and in the past very little criticism has been leveled at this device. As HRGC advances further in its development, more attention must be given to this delivery device. Specifically, the syringe needle

with its viscous flow of discharging fluid can produce deficient delivery of larger molecules, e.g., they will be forced near the needle surfaces. This phenomenon has been referred to as "capillary creep" and clearly some attention should be given to this problem when dealing with samples that exhibit a broad molecular weight range.

It is important that the inlet portion of the HRGC system be as inert as possible. Several researchers have found that replacing the glass insert used in various injectors with a quartz counterpart produced dramatic improvement in performance with respect to both adsorptivity and catalytic behavior. Even so, such quartz inserts should be frequently cleaned or replaced.

With each type of injection device, there are specific instructions concerning the operation of that particular injector. For the newly introduced on-column injectors such guidance must be followed very closely, for it is quite easy to obtain distorted input profiles and split solute zones if precautions are not taken.

Although the injection of samples is currently a major problem area in HRGC, it is anticipated that through research and special attention to matching the injection technique with the sample type, sample insertion problems can be significantly reduced.

Through the use of newly emerging intermediate trapping procedures (such as used in MDGC) and with special injection devices for the new microbore OTCs, there is considerable promise that the insertion of complex organic samples will not remain a major problem in HRGC. Again, to accomplish this it is important that the injection methods and the trapping techniques be matched to the type of sample.

Finally, the sample injection process has been recognized as a problem that must be addressed before HRGC can be advanced significantly further. Accordingly, this area is receiving attention and there is good probability that several acceptable sample injection techniques will soon be developed for admitting undiluted complex organic mixtures in HRGC.

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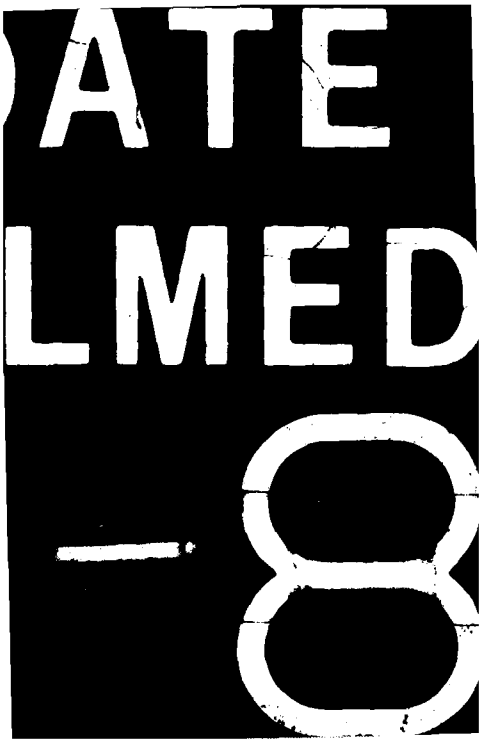
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