QUANTITATIVE ANALYSIS OF ROCKET PROPELLANT BY CAPILLARY GAS CHROMATOGRAPHY

by

Gregg S. Sotack

Thesis submitted to the Faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for
the degree of

MASTER OF SCIENCE

in

Analytical Chemistry

APPROVED:

Harold M. McNair, Chairman

Gary L. Long

James F. Wolfe

December, 1988

Blacksburg, Virginia

c.2

LD
5655
V855
1988
S667
c.2

QUANTITATIVE ANALYSIS OF ROCKET PROPELLANT BY CAPILLARY GAS CHROMATOGRAPHY

by

Gregg S. Sotack

Committee Chairman: Harold M. McNair

Department of Chemistry, VPI & SU

December 28, 1988

(ABSTRACT)

The analysis of nitrate-ester propellants and explosives has been performed extensively by gas chromatography for the past decade. As capillary GC technology has advanced, new opportunities for the improvement of existing methods have developed. This investigation probes several of these possibilities.

The effect on quantitation of: the solvent, the analysis time, and the use of splitless injection were investigated. Precision was shown to be improved by:

1. using a non-volatile solvent (toluene) rather than CH_2Cl_2,
2. using the most time-efficient method that will allow adequate resolution of the components,
3. using splitless injection (0.80 min. splitless time).

After these potential improvements of method were investigated, the mechanism employed in splitless injection was investigated. This mechanism is known as the SOLVENT EFFECT. The investigation showed that:

1. non-volatile components required less splitless time to achieve 100% sample transfer to the column;
2. using splitless injection improved precision over split injection;
3. injector liner design had no effect on precision;
4. column overload did not hurt precision, as long as all peaks remain baseline-resolved;
5. the initial column temperature must be below the boiling point of the solvent (how far below did not appear to be very significant);
6. quantitation is improved by using a solvent that is as non-volatile as possible;
7. varying the split ratio after the split vent has re-opened (within the range of 20:1 to 500:1) has no effect on resolving peaks that occur extremely close to the solvent peak.

ACKNOWLEDGEMENTS

The author would like to express his heartfelt gratitude to the following for their assistance and encouragement during his graduate studies:

Dr. Harold M. McNair first and foremost, for not only being an advisor and financier, but for being a mentor and friend;

Drs. James Wolfe and Gary Long for serving on this committee and for both being exceptional professors in the coursework taken by the author;

Pat Smith, whose labor on behalf of the research group was greatly appreciated, if not recognized as often as was deserving;

James O. Frazier, for his always-patient advice and willingness to share his expertise;

Nicholas Snow, for allowing free access to his computer and to his computer expertise;

Dr. Tomas Hudlicky, who, early in the author's career, hired him as an organic synthesis technician, under whose tutelage the author learned practical organic chemistry;

Dr. Abbas Kamalizad, for his advice, patience, and willingness to work with the author in coursework and in the laboratory;

The fellow graduate students in the research group: Laura Cerruti, Victoria Johnson, Lee Polite, George Reiner, Henrik Rasmussen, Vicente Sanchez, Greg Slack, William Wilson for their moral support, team mentality, and professionalism;

The chromatographic research group for funding the author's work;

George Nauflett and Bernie Alley of JANNAF, for their financial, moral, and logistical support, and for providing samples;

Lastly, but most significantly, Harry and Gloria Bezold, the author's parents without whose moral (and financial) support and nine years of patience, this work would not has been possible.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION

The principle for separation by Gas Chromatography (GC) is the partitioning of a vaporized analyte mixture between the mobile (gas) phase and the stationary (liquid) phase. If the components of an analyte mixture have different solubilities in the stationary phase, separation is accomplished (in theory, anyway). Packed column GC involves using, as a stationary phase, a packed bed where the liquid phase is deposited on the inert particles of the bed. Packed column GC is theoretically described by the (simplified) Van Deemter [12] equation, which states:

$$\mathbf{HETP} = \mathbf{A} + \mathbf{B}/\underline{\mathbf{u}} + \mathbf{C} \times \underline{\mathbf{u}}$$

The variables are defined in Reference 12.

In capillary column GC, the stationary phase is deposited on the inner wall of an open tube. Capillary column GC (CGC) is theoretically described by an equation which is similar, known as the (simplified) Golay equation [11]:

$$\mathbf{HETP} = \mathbf{B}/\underline{\mathbf{u}} + \mathbf{C_g} \times \underline{\mathbf{u}} + \mathbf{C_s} \times \underline{\mathbf{u}}$$

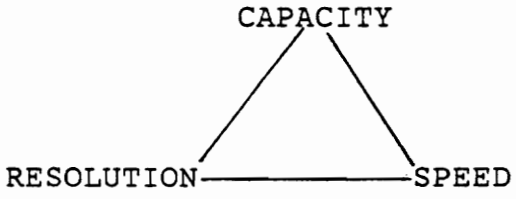
Note that there is no "A" (eddy diffusion) term in the Golay equation. This is because, in an open tube, all sample travels the same path length. This is a major contributor to a capillary column's efficiency advantage over packed columns. Indeed, the term "capillary" is not strictly correct. A more accurate term would be "open-tubular", since it is the column's open state, not it's small diameter which generates the great increase in

efficiency observed with capillary columns.

The C-term (resistance to mass transfer of the solute in the stationary phase) in the Van Deemter equation has also been split into two terms: Cg and Cs, which are the terms for resistance to mass transfer of solute in the gas phase and liquid (or stationary) phase, respectively.

Two plots of the Van Deemter (or Golay: they look very similar) equation are shown in Figures 1 and 2. Figure 1 illustrates how three different carrier gasses affect the plot. Figure 2 shows how the three terms each contribute to the Van Deemter plot.

A critical concept in column selection for development of a chromatographic method is that of the trade-off between capacity, speed, and resolution as illustrated by the triangle below:



One can maximize a system's resolution, but at great loss of speed and capacity, or one can maximize both resolution and capacity but the analysis time will be very long.

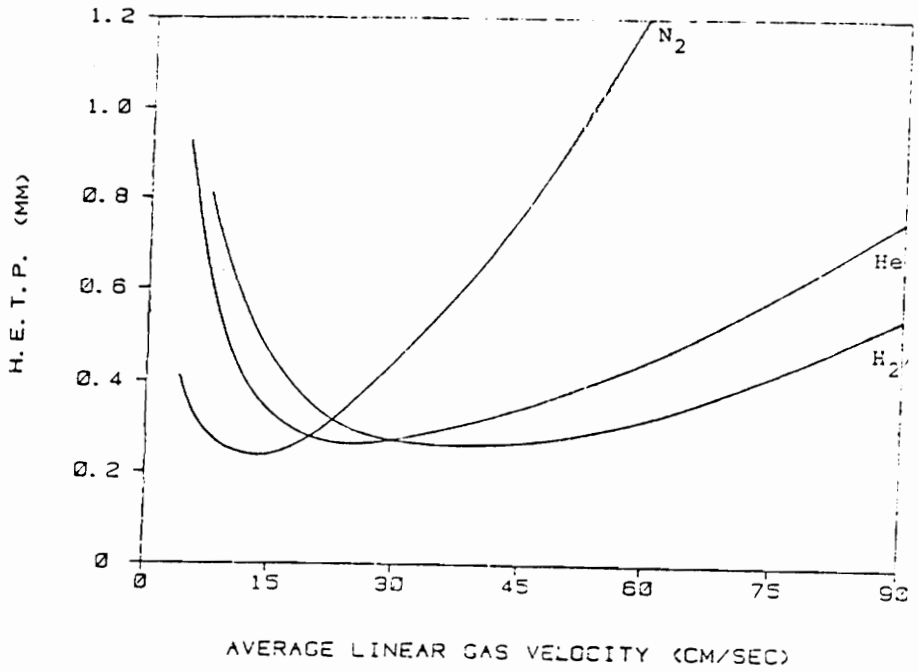


FIGURE 1. The Van Deemter Equation Plotted for Hydrogen, Helium, and Nitrogen [14].

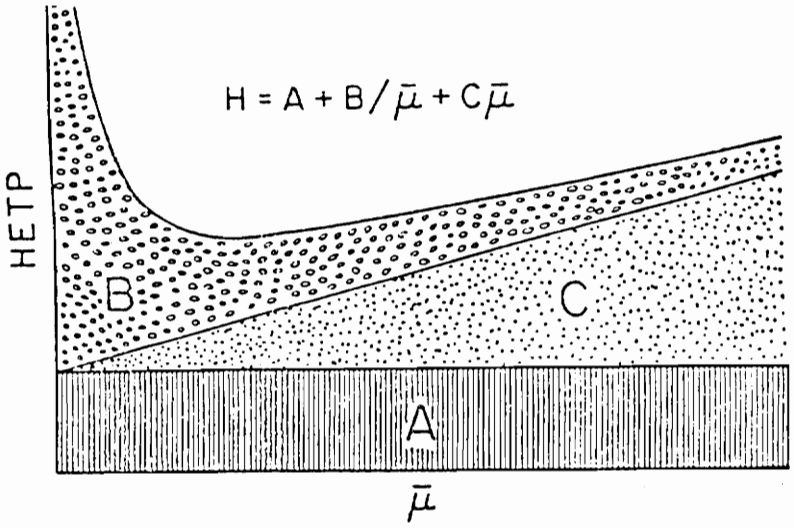
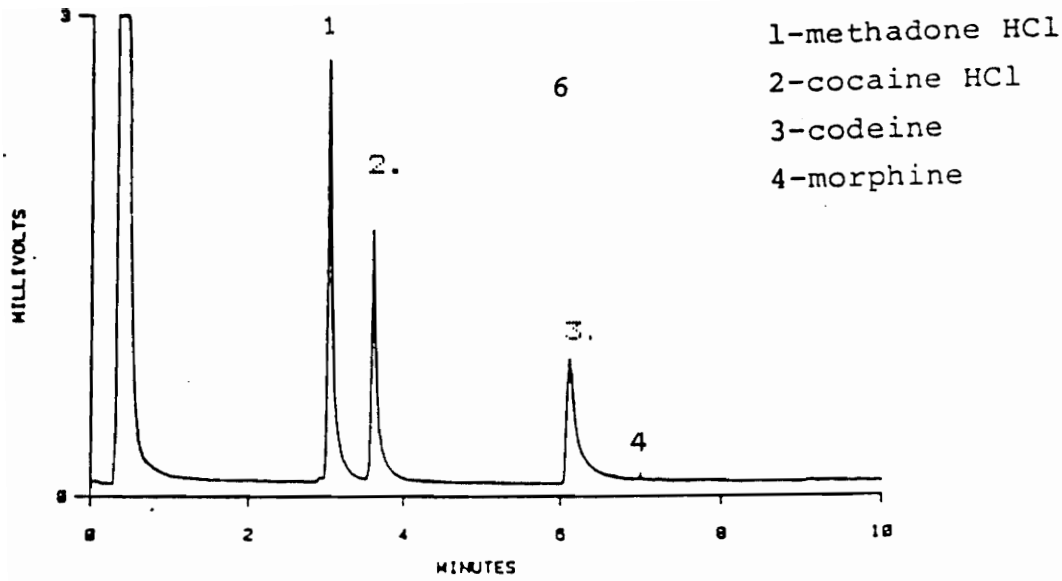


FIGURE 2. Individual Contributions of the Three Terms in the Van Deemter Equation [13].

The only exception to the trade-off concept is in the use of thick-film megabore (0.53 mm I.D. or greater) capillary columns which, for many applications, can replace packed columns. A thick-film megabore column has the high efficiency and reduced analysis time of a capillary column while retaining the capacity of a packed column. Yet for many real (nonideal) samples in complex matrices, with time constraints on the analyst (who may not be trained to do methods-development) such an improvement can be a godsend.

An advantage of CGC that is not reflected on the triangle is inertness. First, fused silica is far more inert than solid supports. Second, capillary columns have 50 to 1000 times less internal surface area than packed columns, and the surface area that is exposed to analyte can be deactivated far more efficiently by silylation. The advantage of inertness can be graphically illustrated by a chromatogram of alkaloids and cocaine at low ppm levels, as shown by McNair and Ogden [7], see Figure 3. The peaks approach the ideal Gaussian shape, with only slight tailing. Thus, inertness allows one to quantitate samples by CGC which cannot be quantitated by packed GC, e.g. trace levels of free acids, free bases, other highly polar compounds, or compounds that are thermally or catalytically (i.e. by Lewis-active sites) labile.

Quantitative trace analysis has always been difficult, and although CGC solved many problems it created some of it's



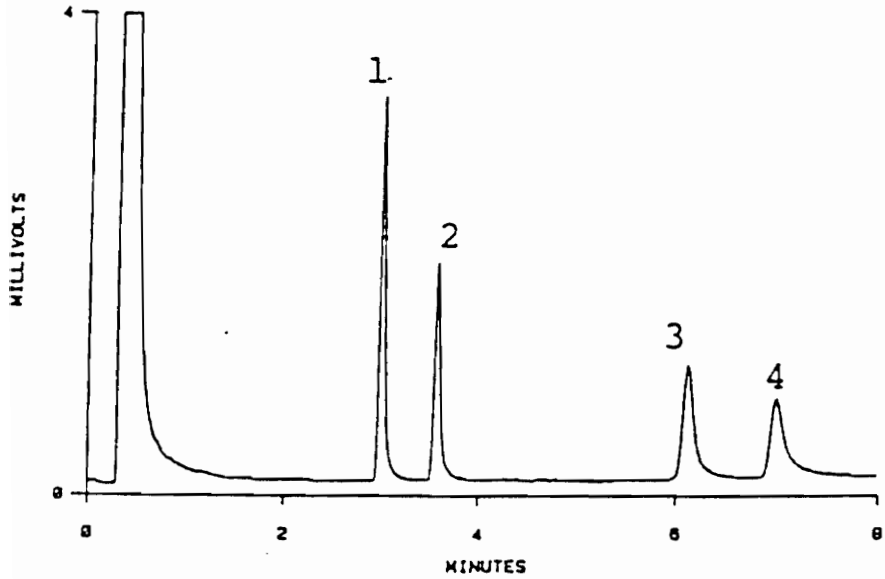


FIGURE 3. Low-Level Analysis of Alkaloids:

A) Non-Deactivated vs.

B) High Temperature Silylated Capillary Columns [7].

own. For example, if one splits a sample 50:1, sensitivity is reduced 50 times, yet if one doesn't split the sample, the column (due to it's low capacity) gets swamped with solvent. The logic in overcoming this paradoxical situation is to pre-concentrate the solute without increasing the amount of solvent passing through the column. This has been shown to be possible, and it can actually occur **in** the column. This is known as the SOLVENT EFFECT, and will be referred to repeatedly. The solvent effect is accurately called solvent-condensation trapping since analytes that have been vaporized in the injector are recondensed in a bead of solvent that has, itself, recondensed. The solvent effect occurs as described below.

With the column temperature set well below the boiling point of the solvent, and with a sample containing analyte that is less volatile than the solvent, a fixed volume of sample is injected onto the column (**without** splitting) and is vaporized in the injector. The resultant band of vapor cloud has a finite width. The vapor cloud encounters the cold column and recondenses to a narrower liquid band (with essentially a Gaussian shape and distribution of analyte). Under the influence of the carrier gas flow and solvent revaporization, the solvent peak radically departs from it's Gaussian shape and develops a long, gently sloping tail and a very sharp vertical front. As revaporization of the solvent occurs, the less volatile components are then

blocked on the steep vertical front wall, as if a parade leader led his entire highly obedient entourage into a wall (see Figure 4). When the temperature of the column reaches the requisite temperature, each component selectively revaporizes very rapidly (relative to the rate of revaporization of the solvent) from a nearly infinitely narrow liquid band. Then after a pre-set time, the split vent reopens, allowing the remaining still-unvaporized solvent (but not analytes, which have long since revaporized and are travelling down the column) to exit via the split vent and not enter the column. Thus, the solvent peak exhibits exponential tailing, then an almost instantaneous and precipitous drop to the baseline, as shown in Figure 5.

Many very subtle factors influence precision, such as the presence and location of glass wool in the injector, the shape of the injector liner, the stability of detector fuel gas regulators, syringe needle length, the activity of the column, the solvent in which the sample is dissolved, and especially, injection technique. The analysis of difficult samples in industrial applications should yield less ideal results, since they create their own special problems. In this investigation, several of these factors will be probed using an actual rocket propellant sample. Furthermore, there exists some ambiguity in (hence opportunity to fine tune) the procedure and mechanism of the solvent effect. Thus, there is room to optimize the chromatographic condi-

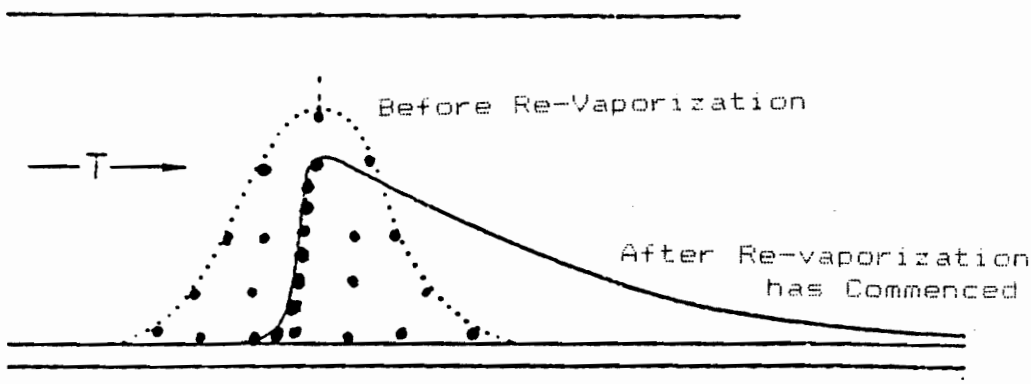


FIGURE 4. The Condensed Solvent Peak and Solute Before and During Solvent Revaporization [8].

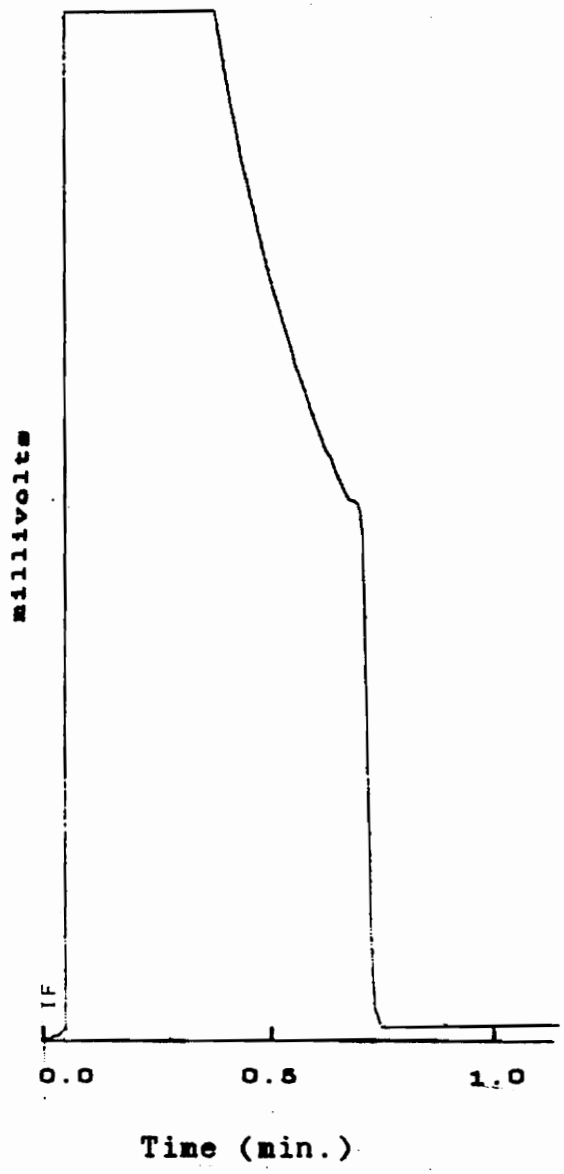


FIGURE 5. Effect of Splitless Injection (0.35 min. Splitless Time) On the Solvent (THF) Peak Shape.

tions to make the splitless technique more useful. This investigation also will probe the solvent effect and it's ambiguities and limitations.

This investigation has several objectives. One objective is to analyse a rocket propellent and it's stabilizers, using a standard method as required by the U.S. Navy [17], then try to improve the method by by making it faster and more reproducible. This will be done by:

a. increasing the speed of analysis by optimizing the column's initial temperature, carrier gas flow rate, and column temperature program,

b. using solvents that are less volatile than methylene chloride (e.g. toluene and THF),

c. using splitless injection.

The propellant sample used in this investigation consists of propylene glycol dinitrate (PGDN: a volatile nitrate ester that acts as a plasticizer and is used as a rocket propellant), diethyl phthalate (DEP) internal standard (not a very good choice due to it's omnipresence, but dictated by the Navy's standard method), 2-nitrodiphenylamine (2-NDPA: a fairly non-volatile free amine used as a stabilizer for PGDN), and dibutyl sebacate (DBS: a desensitizer for PGDN). When the sample is diluted tenfold, PGDN, DEP, and DBS are present in 100 to 450ppm levels (not difficult for a packed column system), but 2-NDPA is at around 5 ppm: not easily quantitated by packed column GC. A chromatogram of this

sample is shown in Figure 9 (1.0 uL, split ratio = 50:1).

Another objective of this investigation is to examine how splitless injection affects reproducibility, and how several parameters influence the solvent effect, hence affect quantitation by splitless injection. These parameters are:

a. concentration of the solute (300 vs. 30 and 3 ppm),

b. boiling point of solvent (hexane vs.iso-octane),

c. initial column temperature,

d. amount of splitless time,

e. carrier gas flow rate,

f. split ratio after the split vent has reopened.

The sample used was a solution of C-9, C-14, C-15, and C-16 normal hydrocarbons in iso-octane or hexane.

This investigation also seeks to show that:

a. peak sharpness contributes to better precision in peak identification

b. employment of the solvent effect by use of splitless injection sharpens trace peaks as well as concentrating them, thus improving quantitation for many applications.

Though a capillary system is somewhat more complex than a packed system (with split ratios, detector make-up gas, different injector types and modes, linear carrier gas velocity, etc.) most of these adaptations can be easily mastered by properly trained personnel.

HISTORICAL

Gas chromatography is a technique used for the separation of mixtures into their individual compounds by vaporizing all components in the mixture then, via a gaseous transport medium (or mobile phase) separating them on the basis of:

a. differential solubilities in a liquid stationary phase or,

b. differential energies of desorption from a solid surface.

GC can be further divided into two distinct techniques: Packed Column (the mobile phase passes through a bed packed with particles on which the stationary phase is coated), and Capillary Column, or CGC (the mobile phase flows through an open tube which is coated with a thin film of the stationary phase on its inner surface).

GC was introduced by James and Martin in 1952. Their project involved the analysis of free amines and free fatty acids partitioning between the nitrogen carrier gas and 10% silicone oil on kieselguhr packing, using an auto-titrator as the detector [1,2]. Modern CGC was introduced by Marcel Golay in 1956. He observed that an air peak eluting from a teflon tube was significantly narrower than the peak having the same retention time on a packed column. Therefore, he coated the inner wall of the tube with a stationary phase and created the first capillary column. This created consi-

derable interest in academia, but for the next two decades, CGC was slow to develop commercial useage, particularly in the USA. This was due to several factors. First, packed GC gained rapid acceptance in industry due to the simplicity of the technique and the instrumentation, hence it created it's own inertia. Second, difficulty in producing stable, inert, reproducible, strong columns hindered commercial acceptance of CGC. Third, and most significantly, Marcel Golay's employer, Perkin-Elmer, held most of the patents for basic CGC application, thus strictly limiting development by other (especially American) producers. CGC instrumentation has several requirements:

a. reproducible splitting of the sample at variable ratios (necessary since capillary columns have 50 to 1000 times less sample capacity than a packed column),
b. low volumetric gas flow rates (0.10 to 5.0 ml/min.) that are stable and reproducible,
c. detectors that can detect small amounts (nanogram to picogram level) of sample, and
d. hardware to interface the column to the injector and detector with a leakproof seal and minimal dead volume.

These hindrances were mostly overcome once researchers stopped trying to convert packed column systems and started designing capillary-specific instrumentation.

The first stream splitters were T's and coaxial tubes placed into packed injectors (which are inherently on-column). More useful splitters were designed by Condon in 1959 [3], Ettre & Averill in 1961 [4], and Clarke in 1963. Splitters were needed that allowed flash vaporization with minimal dead volume, precise (NOT necessarily accurate) splitting, constant column head pressure as the split ratio is changed, and equal carrier gas viscosity in the column's head and outside the column head (i.e. inside the injector but around the exterior of the column). Current designs yield precisions of 2% to 5% relative standard deviation (RSD) using manual injection.

Other significant developments in CGC were:

a. detectors with small volumes and a capacity for auxiliary (or make-up) gas to prevent sample diffusion in the detector's dead volume,
b. sample-selective stationary phases,
c. selective detectors,
d. stationary phases could that withstand temperatures up to 350°C,
e. column deactivation by high temperature silylation,
f. the GC/MS interface, and
g. the production of thin, flexible, inert fused silica tubing with a uniform internal diameter.

The development of high quality, flexible fused silica was the single most important factor in CGC's acceptance (espe-

cially in the USA). This is due to fused silica's inertness (much greater than glass since it contains virtually no metal oxides) and its strength and flexibility (due to its polyimide coating). A fused silica process was designed by Desty in 1960 [5], but the product showed poor consistentcy even within the same batch, thus was not of much practical use to chromatographers.

Dandeneau, in 1979 [6], introduced a much better process for the manufacture of fused silica. The inertness of fused silica, combined with deactivation using high temperature silylation allowed chemists to quantitatively analyse samples that were hitherto not doable, such as trace analysis (less than 100ppm) of free acids and amines, as illustrated by McNair and Ogden [7], see Figure 6.

The use of megabore columns with thick coatings (1.0 um or greater) also greatly aided the acceptance of CGC for routine industrial applications. These columns do not need sample splitting due to their large sample capacities (which are comparable to packed columns), and they allow one to inject a sample directly onto the column with a conventional syringe. Thus, one is able to achieve the improved resolution and shortened analysis time made possible by the open-tubular column without radically altering the instrumentation of a packed column system.

More recent advances in CGC have focused on overcoming limitations that had been considered inherent to gas

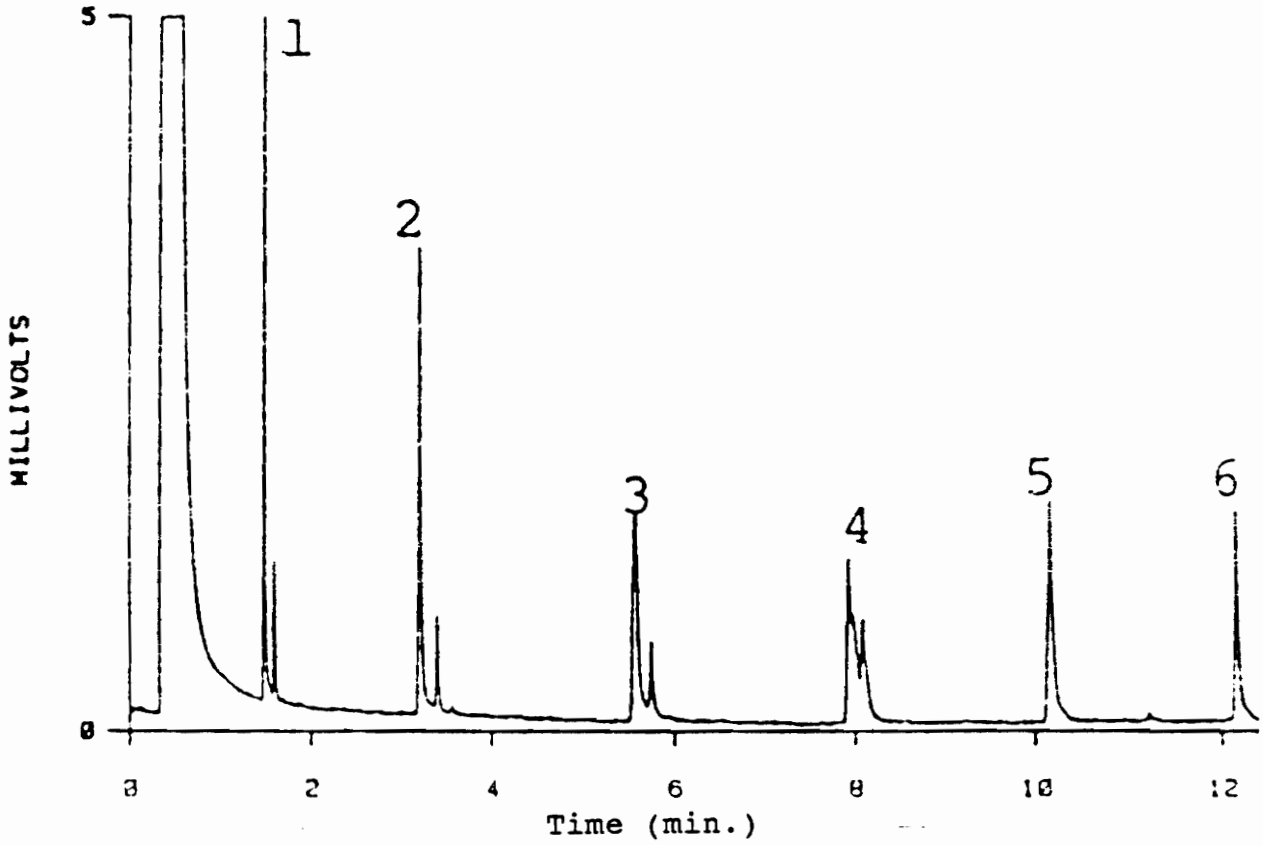


FIGURE 6. Low Levels of Primary Amines (1-ethyl to 1-heptyl) on a Deactivated Capillary Column [7].

chromatography and/or CGC :

a. thermally labile compounds cannot be flash-vaporized,

b. flash vaporization discriminates against non-volatile components,

c. samples eluting near the solvent are obscured by the large solvent peak,

d. identification by retention time is not conclusive.

The development of Gas Chromatography/Mass Spectroscopy (CG/MS) overcame limitation (d) above. CGC was particularly well-suited to the GC/MS interface due to the small volume of gas eluting from the column. Grob & Grob in the early 1970's investigated splitless hot injection (the injector is in splitless mode for a set time, then via a solenoid, switched to split mode during a chromatographic run) as a way of overcoming limitation (c). The principle involved is known as the SOLVENT EFFECT and shall be discussed later. Grob & Grob investigated this technique more as a tool for trace analysis than as a method for resolving peaks from the solvent peak, and found that the technique caused both sample concentration and improved resolution behind the solvent peak [8]. However, there seemed to be some loss of precision when one uses the splitless technique (see Table 1), though this investigation indicates otherwise.

Schomberg et. al. investigated and developed the cold on-column injector to overcome limitations (a) and (b) [9]. This design shows the best precision of any of the injec-

TABLE 1. RSDs of Various Injection Techniques[11].

	SPLIT		SPLITLESS		ON-COLUMN*	PV*
RSD	manual	auto	manual	auto	manual	auto
abs.	2-5	0.5-1.5	3-5	1-3	>1	0.5-0.7
rel.	0.5-1	0.2-0.3	1-1.5	>1	0.1-0.3	0.1-0.3

* only technique with available data

tion techniques (see Table 1), but has limitations of it's own. Automating this design is impractical, it requires syringes with special capillary needles, large volumes (several uL or more) of liquid solvent might damage the column, and non-volatile contaminants are placed into the column (permanently).

Hence, Vogt & Jacobs designed an off-column, programmed-vaporizing injector (PV) [10], which is shown in Figure 7. The PV injector allowed sample to be injected (using an ordinary syringe) into a cold injector off-column. The injector is then ballistically heated (from ambient to 350°C in 20 seconds or less), thus rapidly vaporizing the sample in the glass-lined injector. The sample never encounters hot metal surfaces that cause degradation of thermally labile samples, and shows precision nearly equivalent to that of on-column injection.

The above injection techniques show RSDs as listed in Table 1. These RSDs are only rough averages since they were reported by different sources, under nearly ideal, though very different conditions (clean sample matrices, easily analysed samples, and research-grade instrumentation). RSDs larger and smaller than these can be found throughout the literature.

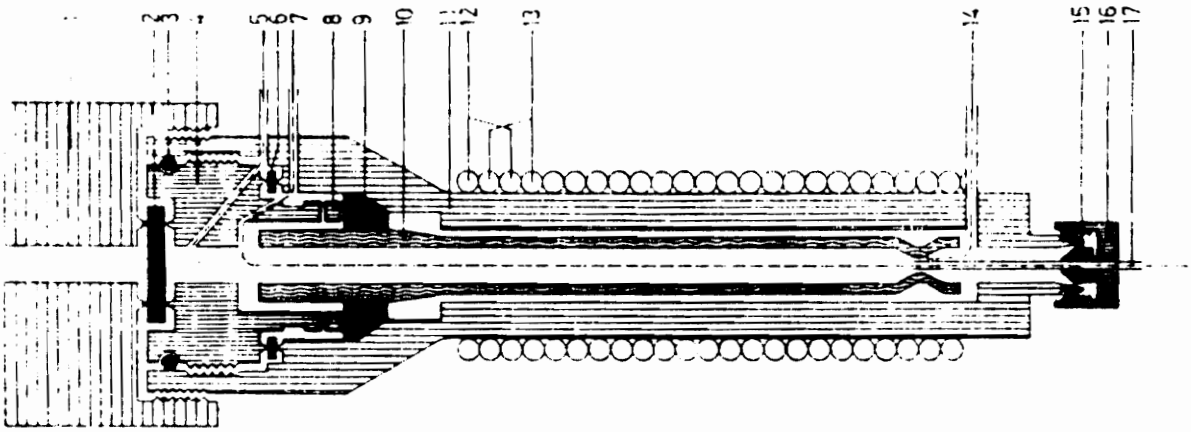


Fig. 1. Cross-sectional view (schematic) of the split–splitless injector. 1 = Injector cap; 2 = septum; 3 = silicone O-ring; 4 = insert holder; 5 = septum cleaning; 6 = aluminium washer; 7 = gas; 8 = back ferrule (1/4 in.); 9 = graphite ferrule (1/4 in.); 10 = glass insert; 11 = injector (stainless steel); 12 = Thermocoax heater; 13 = carrier gas; 14 = split exit; 15 = graphite (1/16 in.); 16 = nut (1/16 in.); 17 = glass capillary column.

FIGURE 7. Vogt's Programmed-Vaporizing Injector [10].

Currently, all of the aforementioned injectors are commercially available. Capillary columns are available in a wide range of different polarities, in I.D.s of 0.10 to 0.75 mm, in lengths of 10m to 100m. Presently, commercial capillary columns are very reproducible, highly efficient, and very inert. The future direction of CGC will probably involve the practical application of ultra-microbore (below 0.10 mm I.D.) columns for ultra-high resolution needs in research and methods-development, the replacement of packed columns with thickly coated megabore columns in many applications, the development of low-temperature column deactivation techniques (especially for polar stationary phases), the development of ultra-high temperature (450-500°C) columns, and the continued development and acceptance of supercritical fluids as the mobile phase.

EXPERIMENTAL

In this study, the following analytical system was used:

1. a Hewlett-Packard (Avondale, PA, USA) 5890A Gas Chromatograph equipped with an FID,
2. a Hewlett-Packard 3396A integrator,
3. a Hewlett-Packard 7673A autosampler equipped with a 10uL Hamilton (Reno, NV, USA) 80377 syringe,
4. Hewlett-Packard 10m x 0.20mm I.D. crosslinked methylsilicone (d_f = 0.30 um) Ultra-performance column, never removed during the course of the investigation,
5. 1.0 uL brown vials with replaceable orange silicone septa (Supelco, Bellafonte Park, PA, USA),
6. Supelco Thermogreen septa pre-conditioned @225^{0}C,
7. Precision Sampling (Baton Rouge, LA, USA) 1.0ml syringe for dilutions.

The integrator and GC were connected via the INET loop. The autosampler was connected to the integrator and the GC via the REMOTE plug.

The GC parameters were (unless otherwise noted):

1. Split Ratio = 50:1
2. $T_{injector}$ = 170^{0}C
3. $T_{detector}$ = 300^{0}C
4. equil. time = 0.50 min.
5. attenuation = 0
6. range = 4
7. *$\underline{u}$ = 50 cm/s helium
8. F_{air} = 480 ml/min
9. F_{H2} = 28 ml/min
10. F_{aux} = 30 ml/min N_2
11. F_{purge} = 2 ml/min

*measured at 70°C with butane.

The autosampler parameters were:

1. sample pre-wash: 2x
2. solvent post-wash: 6x
3. amount injected: 1.0uL

The integrator parameters were:

1. peak width: 0.04 min. (data sampling rate)
2. threshold: same integer value as attenuation
3. attenuation: set so smallest peak of interest is easily discernable from the baseline.

The samples used were as follows:

1. CONTROL MIX (in toluene):
   a. PGDN = 4500 ppm wt./wt.
   b. DEP = 1800 ppm "
   c. 2-NDPA = 80 ppm "
   d. DBS = 1600 ppm "

2. OTTO FUELS STD., A, B, C, D, (in CH_2Cl_2): Their respective concentrations are similar to the Control Mix and to each other.

3. NAVY SAMPLE 1 & 2 (in 1,2-dichloroethane):
   a. Nitroglycerine (NG) = 20 & 10 ppt wt./wt.
   b. DEP = 1 & 0.5 ppt
   c. 2-NDPA = 1 & 0.5 ppt

4. SPLIT/SPLITLESS (SP/SPLS) SAMPLES (C-9, C-14, C-15, C-16 normal hydrocarbons, equal volumes each):

a. 300iso = 300 ppm v/v in iso-octane.

b. 30iso = 30.0 " " " "

c. 3iso = 3.00 " " " "

d. 30hex = 30.0 " " " hexane

The glass injector liners were: a H-P split-only injector (with a floating cup), and an HP split/splitless injector. The split-only liner was tightly packed with about 3mm of silanized glass wool directly above the floating cup. The split/splitless liner was packed with about 3 mm of silanized glass wool located at about the center of the liner. The RSDs that are reported are for 6 to 9 replicate injections. No data points were rejected. Injections were made in blocks of three usually (never more than four), that is, for 9 replicate injections, A was injected three times, B three times, and C three times, then A three times, B three times, etc. Procedures which were compared were performed no more than 24 hours apart (though usually the procedures were performed the same afternoon or evening). The statistical significance when RSDs are compared is determined using the F test (90% confidence level). When split vs. splitless injection RSDs are compared, the standard deviation of the area for split injection is multiplied by the **measured** split ratio (area using splitless injection/area

using split injection) to make the standard deviation of split injection comparable to that of splitless injection. This investigation will have two parts: the OTTO FUELS investigation and the SPLIT/SPLITLESS (SP/SPLS) investigation. The Otto Fuels section is a methods-development investigation to try to determine optimal conditions for a rocket propellant sample. The SP/SPLS section is an in-depth investigation into one particular methods-development step: employing splitless injection. The Otto Fuels analysis investigated relative standard deviations (RSDs) of the Otto Fuels samples and a sample referred to as the Control Mix. The Control Mix was the residue in the waste vial on the auto-sampler during the second trial of the Otto Fuels reproducibility study: since it sat unsealed for several days, all of the CH_2Cl_2 evaporated, leaving only the four major components and the non-volatile impurities. The residue was diluted with toluene until the solution's concentration was similar to the Otto Fuels samples. This yielded a sample without the volatile CH_2Cl_2 as a solvent. Toluene was chosen as a solvent because it evaporated more slowly than CH_2Cl_2. One step in this investigation compares the RSD using CH_2Cl_2, THF and toluene each as the dilution solvent. Some physical properties for these solvents are listed in Table 2.

The Otto Fuels samples were analysed according to the U.S. Navy's standard method [17], which henceforth shall be called the NORMAL method. Various parameters were changed to try to improve the precision as well as the speed of analysis of the method. These parameters include: solvent used, the linear flow rate of the carrier gas (u), initial temperature of the column (T_{init}), column temperature program rate, use of split vs. splitless injection, and injector liner design. The conditions used were:

1. NORMAL method {u = 50 cm/s, split-ratio = 50:1, split-only liner, 70°C (0min.) to 250°C at 15°C/min.}, using the NAVY 1 & 2, Otto Fuel STD., A, B, C, D, Control Mix

2. FAST method {u = 75cm/s, 105°C (0.30 min.) to 250°C at 50°C/min.) using A, A x 1/10 in toluene, Control Mix,

3. NORMAL method, using Control Mix diluted 10x with CH_2Cl_2, THF, and toluene

4. NORMAL method, using splitless injection (0.40 min. splitless) or split 50:1, using split/splitless and split-only liners in both techniques, using the Control Mix x 1/10 in toluene

5. NORMAL method, using the Control Mix, except varying the splitless time (0 min. to 1.2 min.)

SP/SPLS investigated various parameters and their effect on RSD, peak shape, and/or retention time shifting. These parameters are: sample concentration, solvent used, splitless time, T_{init}, u, & split ratio according to the following conditions:

1. NORMAL method (u = 50 cm/s, split/splitless liner, split ratio = 50:1, 70°C {0.4min.} to 240°C at 15°C/min.) using 300iso, 30iso, 3iso, 30hex,

2. NORMAL method, except splitless time is varied and optimized for C-15 using 30iso, for u = 50, 75 cm/s,

3. NORMAL method, except T_{init} = 40°C, using 30hex,

4. SP/SPLS method (NORMAL method, except splitless time of 0.40 min.), using 300iso vs. 30iso,

5. SP/SPLS method, except T_{init} = 70, 80, 85, 100, 110, 120, and 130°C, using 300iso, 30iso,

6. SP/SPLS method, except T_{init} = 40, 60, 70, 85, and 100°C, using 30hex,

7. SP/SPLS method (T_{init} = 85°C, 0.40 min. splitless time) except split ratio (**after** the split-vent has reopened) is set at 50, 100, and 200:1, using 30iso.

TABLE 2. Physical Data for Some Solvents [16].

	VAPOR PRESSURE at STP	**VISCOSITY** @25°C	**RELATIVE EVAPORATION RATE** butyl acetate=1	**POLARITY INDEX** pentane=0
CH_2Cl_2	350 torr	0.41cP	27.5	3.40
THF	145	0.46	14.5	4.20
TOLUENE	22	0.55	1.9	2.40
WATER	18	0.89	-----	10.2

RESULTS AND DISCUSSION

OTTO FUELS SECTION

The NORMAL method was dictated by the U.S. Navy's standard procedure [17]. This method was first used to analyse the Navy 1 & 2 samples. The results are in Table 3. Reproducibility is excellent despite the high concentrations of the solutes. The chromatogram in Figure 8 shows the distinctive fronting of column overload for the NG peak, yet reproducibility was not adversely affected. Peak shapes of the other solutes are excellent, even for the free amine (2-NDPA).

A sample chromatogram for the Otto Fuels using this method is shown in Figure 9. The chromatogram shows the solvent and the four major solute peaks are all very well resolved and also exhibit excellent peak shapes. The DEP and DBS peaks should be symmetrical, since they are simple esters. The 2-NDPA is a free secondary amine and the PGDN is a very polar (and fairly labile) nitrate-ester. One might expect these two compounds (due to their activity) to have non-Gaussian peak shapes on the thinly coated non-polar column if the column and injector liner are not well deactivated. The concentration of the sample is well above the detection limit for the FID. There is apparently no column overload (which would reveal itself as peak fronting). The peaks are actually over-resolved, costing time with no benefit. Thus, there seems to be considerable room for improvement in the method, **if** no other compounds of interest are present in

TABLE 3. RSD of Absolute Area and of Area Relative to DEP For NAVY #1 Using The NORMAL Method.

	NITROGLYCERINE		**DEP**	**2-NDPA**	
SAMPLE	Abs.	Rel.	Abs.	Abs.	Rel.
Navy #1	0.51	0.29	0.60	0.64	0.41
Navy #2	0.72	0.41	0.63	0.51	0.36

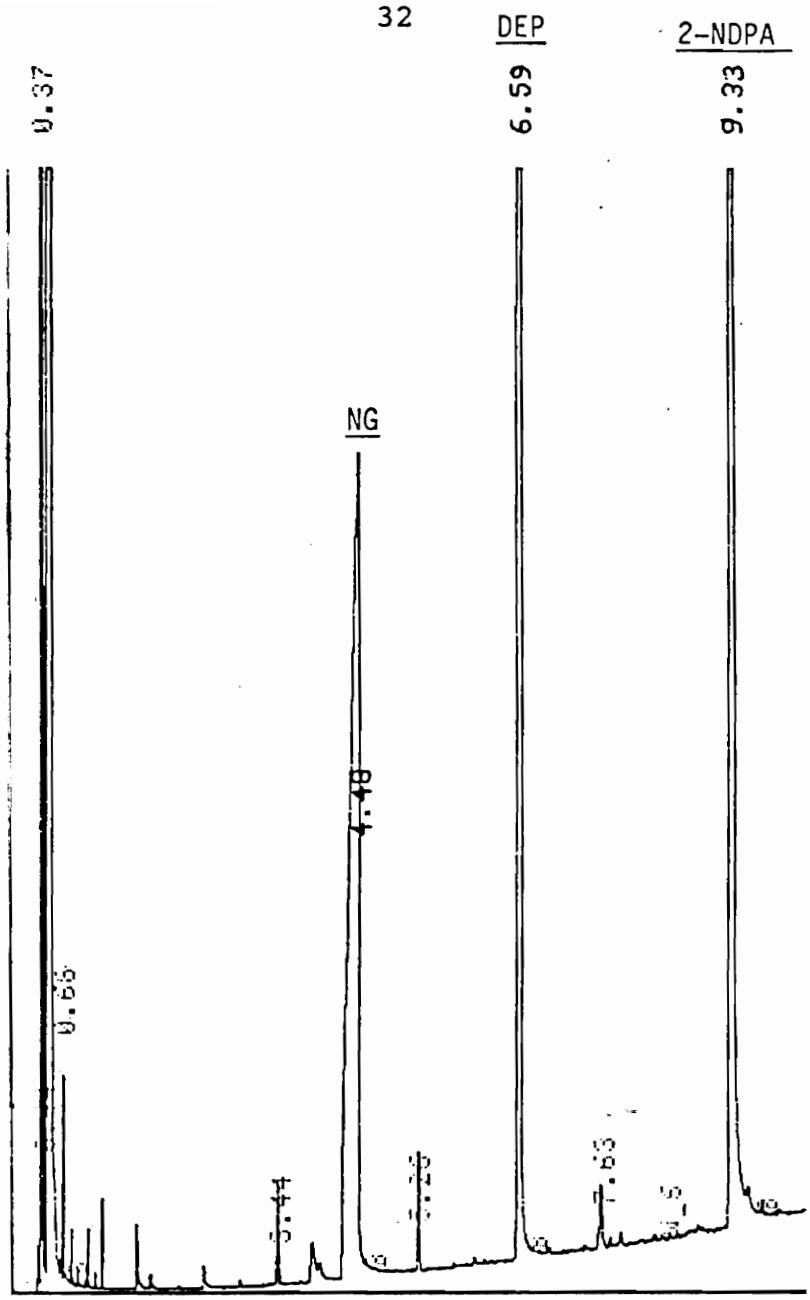


FIGURE 8. Sample Chromatogram For Navy #1 Sample, Using The NORMAL Method.

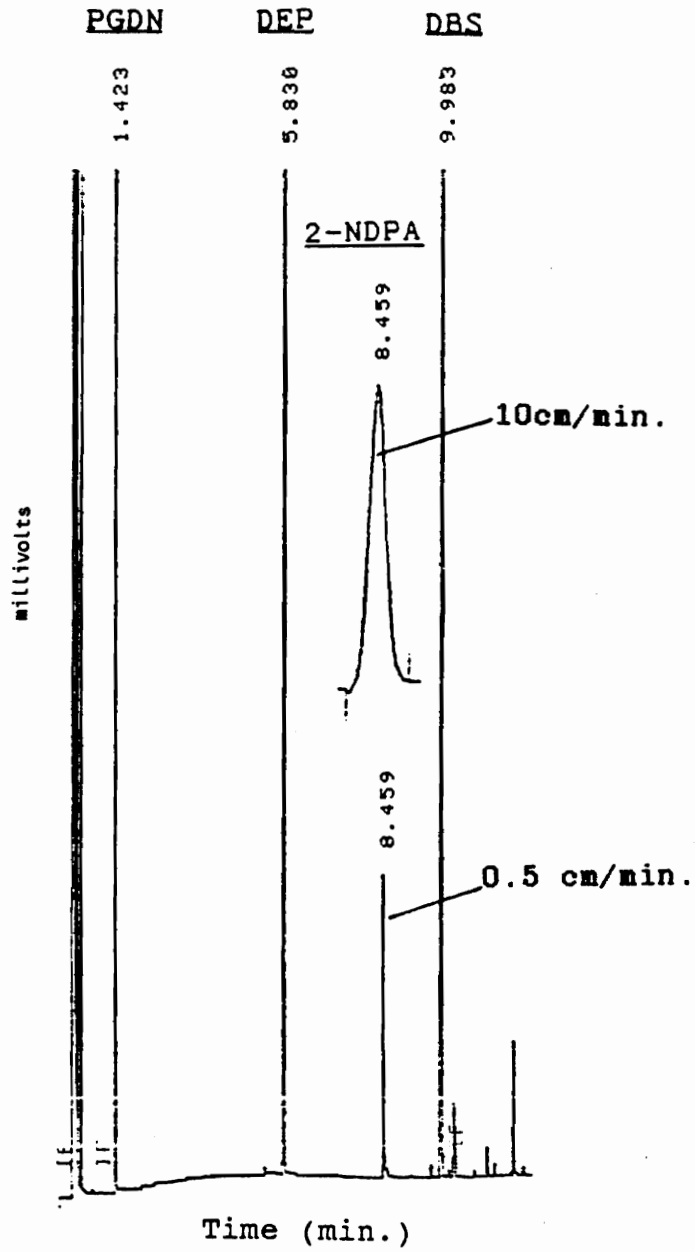


FIGURE 9. Sample Chromatogram For Otto Fuels, Using The NORMAL Method, Showing the Gaussian Peak Shape of the 2-NDPA At Two Different Chart Speeds.

the sample. The goal is to develop a more rapid method with a gain (or at least no loss) in reproducibility.

The five Otto Fuels samples and the Control Mix were analysed by the NORMAL method, 5 replicate injections each. The resultant reproducibility data is listed in Table 4. These RSDs are acceptable but not excellent for autosampler injection. The RSDs for areas normalized to DEP (the internal standard) were lower than RSDs of the absolute areas, as one might expect, since the use of an internal standard procedure compensates for error caused by solvent evaporation, changes in detector response, or other systematic factors that affect all peaks equally (by percentage).

The steps in improving the method were: increase the temperature program rate, then u and, lastly, T_{init} to obtain at least baseline resolution between all peaks while minimizing analysis time. Increasing the program rate preferentially accelerates the later eluting peaks. Increasing u accelerates all peaks by about the same amount. Increasing T_{init} accelerates all peaks by about the same absolute time. The maximum practical program rate is about 50°C/min. Further reduction in analysis time was accomplished by increasing both u and T_{init}. For helium, u can be increased to 75 cm/s without a significant loss of theoretical plates (see Figure 1). T_{init} was increased until PGDN was clearly baseline resolved from the solvent peak. This occurred at 105°C (0.35 min. hold). The resultant method was the FAST

TABLE 4. RSD of Absolute Area and of Area Relative To DEP of OTTO FUELS Using The NORMAL Method.

	PGDN		**DEP**	**2-NDPA**		**DBS**	
SAMPLE	Abs.	Rel.	Abs.	Abs.	Rel.	Abs.	Rel.
Std.	1.2	0.50	1.6	3.1	2.7	3.0	2.0%
A	2.9	1.2	2.4	3.7	3.1	2.5	0.79
B	1.8	1.1	1.2	2.4	2.3	0.88	0.32
C	1.1	0.67	0.98	2.4	2.1	0.90	0.31
D	2.0	1.2	2.4	2.7	1.5	1.9	0.55
C.Mix	1.7	1.0	1.6	1.5	0.64	1.4	0.50

method, and its effect on reproducibility is shown (for six replicate injections) in Table 5.

As one can see, reproducibility for the FAST method is generally superior to that for the slower NORMAL method. This is not surprising, since the peaks on the FAST method are sharper, therefore easier to integrate (i.e. smaller peak-widths-at-base, see Table 6). Thus, ambiguity about where a peak begins and ends is reduced. Curiously, the greatest improvement in reproducibility is seen with the PGDN, which is no longer baseline resolved from the solvent in the Control Mix. This improvement could be attributed to PGDN's thermolability: with the NORMAL program, the PGDN resides at elevated temperatures in the column much longer than with the FAST program, allowing more time for thermal decomposition. Another factor also seems to affect reproducibility: the rate of solvent evaporation. For all cases, sample A (100% CH_2Cl_2) has the worst reproducibility, followed by sample A/10 (90% toluene, 10% CH_2Cl_2), and finally the Control Mix (100% toluene) which shows reproducibility equivalent to or better than samples A or A/10 in virtually every case. This effect is attributed to differences in solvent volatility and not of viscosity differences (since all three solvents have similar viscosities, see Table 2).

An examination of raw area counts shows how area counts change over time more rapidly for sample A than for the Control Mix. Note that the areas of injections #5 and #6

TABLE 5. RSD (Absolute Area) of FAST vs. NORMAL Methods.

	PGDN		**DEP**		**2-NDPA**		**DBS**	
SAMPLE	NORM.	FAST	NORM.	FAST	NORM.	FAST	NORM.	FAST
C.Mix	3.1	0.4	0.9 *	0.7	1.4 *	1.7	1.4 *	2.4
				*		*		
A	7.6	1.2	6.1	1.2	4.8	2.3	5.6	0.9
		*		*	*	*	*	
A/10	3.4	0.6	2.6	0.9	2.8 *	2.5	4.1 *	2.3

#

* or # * #: no statisticallly significant difference

between these pairs at 90% confidence.

TABLE 6. Peak-Widths-At-Base of FAST vs. NORMAL Methods.

	PGDN		**DEP**		**2-NDPA**		**DBS**	
SAMPLE	NORM.	FAST	NORM.	FAST	NORM.	FAST	NORM.	FAST
A	24	11	31	11	28	10	30	12
A/10	14	7	24	9	28	11	25	11
C.Mix	26	8	33	12	28	10	31	13

TABLE 7. Raw Area Counts Using The NORMAL Method.

	PGDN			DBS		
Injection #	A	A/10	C.Mix	A	A/10	C.Mix
1	39698	4172	46883	130670	12137	146620
2	39409	4222	47677	132021	12117	148417
3	40091	4254	48948	136097	12158	151187
4	39942	4252	48696	132289	12385	150711
5	45705	4524	50977	145925	12749	151832
6	46250	4476	50071	148665	13400	148128

are internally consistent with each other, but are greater than the areas of injections #1 to #4 (which are internally consistent themselves), especially for sample A. The reason for this area discrepancy is that the samples were injected in blocks of four, then in blocks of two. The same procedure was used for the FAST method and the jump in areas between injections #4 and #5 was not observed. Thus, the individual samples must be changing (if the chromatographic system were changing, the areas of all three samples would be affected equally, i.e. by the same percent), and the longer run time (3 times longer) for the NORMAL method exacerbates the effect. The only difference between the samples is the amount of the volatile CH_2Cl_2 present in the sample. Thus, solvent evaporation over time explains NORMAL's lower reproducibility.

Thus, the FAST method has reduced the total run time from about 16 minutes to about 4 minutes with a net gain in (or no loss of) reproducibility. One step in improvement of the method has been accomplished, and a second step suggested, that is, using a solvent less volatile than CH_2Cl_2. Thus, the effect of solvent volatility was investigated using the Control Mix diluted 10x with CH_2Cl_2, THF, and toluene. The results (8 replicate injections per sample) are listed in Table 8. The data indicates that diluting the sample with the less volatile toluene clearly improves reproducibility for three of the four components.

TABLE 8. Absolute Area RSD For The Control Mix Diluted 10x With Three Different Solvents.

DILUTION SOLVENT	PGDN		DEP	2-NDPA		DBS
THF	2.0	*	1.7	5.4	*	3.1
	*		*	*		*
CH2Cl2	2.4	*	2.4	5.3		2.2
				*		
TOLUENE	1.3	*	1.1	4.0		1.3

#

* or # * #: no statistically significant difference

between these pairs at 90% confidence.

Another parameter investigated was the application of the split/splitless injection technique to the method. This technique utilizes the solvent effect as earlier described in the INTRODUCTION. There are several items that must be noted about this technique. First, the injection liner used for split/splitless injection is normally of a different design than is used for split injection. Therefore, the reproducibility of both injection techniques using both liner designs (each commercially available from Hewlett-Packard) for each technique will be investigated. Second, in order to correctly employ the solvent effect, the initial column temperature should be well below the boiling point of the solvent (in this case toluene). Therefore, the NORMAL method (T_{init} = 70°C, but with splitless time of 0.80 min.) was used. The Control Mix x 1/10 in toluene was the sample. The results (9 replicate injections) are shown in Table 9.

The results indicate that the split-only liner yielded equivalent or better reproducibility than the split/splitless liner, and splitless injection yielded equivalent or better reproducibility than split injection. Conventional wisdom has usually held that split injection was the more precise method (see Table 1). The improved RSD for splitless injection over split injection occurs throughout this investigation. The split/splitless liner was specifically designed to improve quantitation employing the split/splitless technique (it has a smaller internal diameter, hence a

TABLE 9. RSD Comparison of Split/Splitless and Split-Only Liners In The Split and Splitless Modes.

	PGDN			**DEP**			**2-NDPA**			**DBS**	
LINER	SPLT		SPTLS	SPLT		SPTLS	SPLT		SPTLS	SPLT	SPTLS
Split-only	0.9	*	0.7	1.4	*	0.8	1.5	*	0.9	1.1	0.5
				*		*			*	*	*
SP/SPLS	1.7	*	1.4	1.0	*	0.8	3.1		0.8	1.4	0.5

#

* or # * #: no statistically significant difference

between these pairs at 90% confidence.

smaller internal volume, and it doesn,t have a floationg cup, as does a split-only liner). Yet, the liner design seems to have no significant effect on quantitation.

The minimum splitless time required to cold-trap all solutes was determined to be 0.80 min. by increasing splitless time incrementally till all peak areas stopped increasing (areas for splitless times of 0.80, 1.00 and 1.20 min. were all about the same). What one observes at splitless times of less than 0.80 min. is that the more volatile solutes require less time in the splitless mode to achieve the maximum peak area than do the non-volatile solutes (see Figure 10). This seems to run counter to intuition, because one might think that non-volatile solutes would be the fastest to condense, therefore they would be more rapidly transferred onto the column. Assuming unidirectional flow (i.e. no back-flow from the column to the injector), Figure 10 seems to indicate that this is not the case. The non-volatile components seem to reside in the injector longer than volatile components.

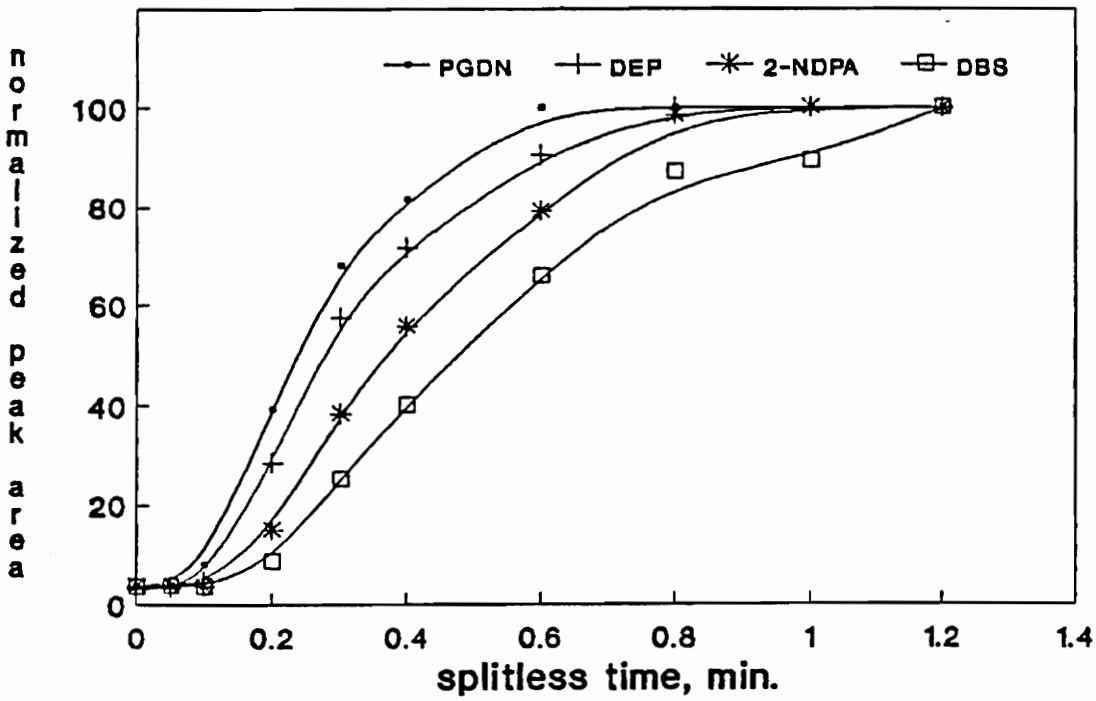


FIGURE 10. Plot of Splitless Time vs. Area For Control Mix's Four Major Components, Using The NORMAL Method.

SP/SPLS SECTION

The second part of this study investigates the solvent effect and its effect on quantitation when various parameters are varied. The standards used are a set of normal-chain hydrocarbons in a hydrocarbon solvent. The first comparison to be investigated is shown in Table 10, which compares the RSDs (of 8 replicate injections) of the four SP/SPLS standards when analysed in both split and splitless (0.40 min. splitless time) modes. Using 0.40 min. of splitless time gave the maximum response for all solutes for all standards. The column's initial temperature, T_{init}, was set to be 30°C below the boiling point of the solvent used, so T_{init} = 70°C for the standards in iso-octane (b.p. = 98°C) and T_{init} = 40°C for the standard in hexane (b.p. = 69°C).

The data shows, again, that reproducibility generally increased with the use of splitless injection. The C-9 peak was surrounded by smaller peaks that presumably were traces of isomers of octane or nonane, and the integration sometimes included them as if they were part of the C-9 peak, hence the high RSD for C-9. This illustrates a pitfall of using splitless injection in trace analysis: impurities are also concentrated on the head of the column along with the desired components. The data also indicates that the 30iso sample showed somewhat better reproducibility than 30hex. The slight increase in 30hex's RSD is probably due to it's solutes all eluting several minutes later than the corres-

TABLE 10. RSDs For Split vs. Splitless Injection.

	C-9		C-14		C-15		C-16	
	SPLT	SPTLS	SPLT	SPTLS	SPLT	SPTLS	SPLT	SPTLS
300iso	3.2	8.1	1.9	0.7	1.8	0.5	1.7	0.4
	*			*		*		*
30iso	1.8	4.1	1.0 *	0.7	0.7 *	0.8	0.5 *	0.8
				*		*		
3iso	obscured		9.9	0.4	1.4	0.5	2.1	0.3
30iso	1.8	4.1	1.0 *	0.7	0.7 *	0.8	0.5 *	0.8
	*			*		*		*
30hex	2.6	1.0	1.7 *	1.0	1.7 *	1.1	1.5 *	1.1

#

* or # * #: no statistically significant difference

between these pairs at 90% confidence.

ponding solutes in the 30iso (30iso's T_{init} was 30°C higher), thus they have more time to diffuse in the mobile phase. Hence 30hex's peaks aren't as sharp, as will be shown later in Table 16.

The data in Table 10 also shows that, in the splitless mode, 300iso's RSD is generally equal the RSD for 30iso and 3iso. This was not expected, because Figure 11 illustrates that, in the splitless mode, the 300iso sample shows column overload (i.e. peak fronting). 300iso's smaller RSD indicates that, as long as the peaks are well resolved and the baseline remains stable, overloading the column does not seem to affect quantitation. This was also seen in the Otto Fuels part of this investigation, where the Navy samples were analysed under similar conditions (see Figure 8).

Additional observations about the solvent effect can be gleaned from the same chromatograms that yielded the above RSDs. Thus, the following data was examined: absolute area counts, measured split ratio, retention times, and peak-width-at-base (actually area counts/peak width).

First, absolute area counts will be examined (actually area counts/100, see Table 11). Several phenomena are observed. Recalling that equal volumes of all four hydrocarbons were used in preparing the standard (using a 5.0uL zero-needle-volume syringe: 3.0uL/10ml solvent for 300iso), one sees that, for injection split 50:1, area trends are:

C-9 > C-14 > C-15 > C-16;

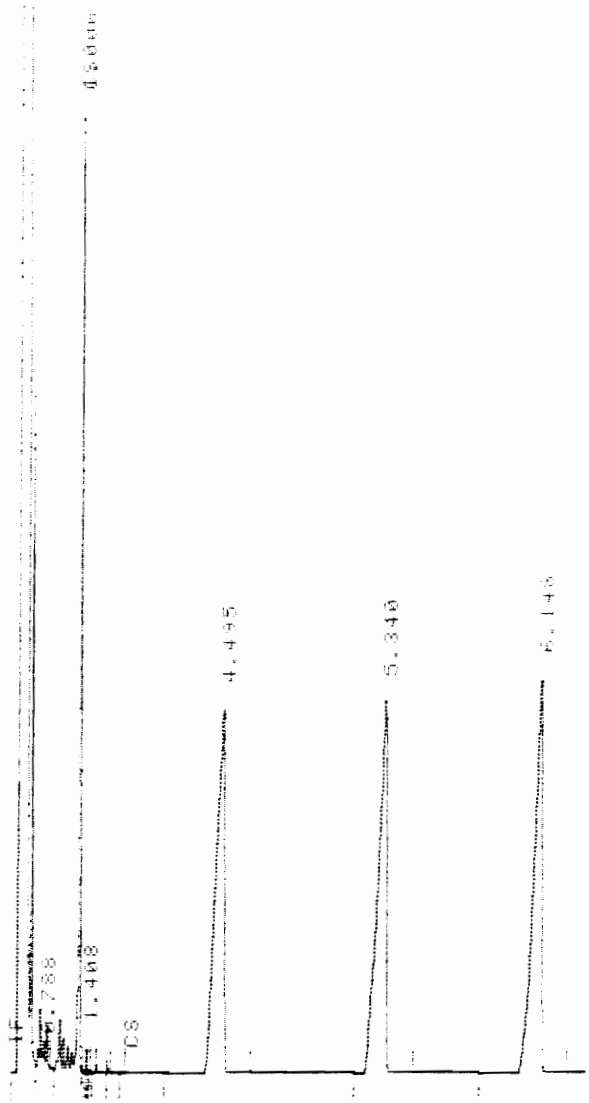


FIGURE 11. Chromatogram of 300iso In The Splitless Mode Showing Column Overload (0.40 min. Splitless Time, T_{init} = 70°C).

TABLE 11. Average of Absolute Area Counts ($x10^{-2}$) For 8 Replicate Injections of Split vs. Splitless Injections.

	C-9		**C-14**		**C-15**		**C-16**	
SAMPLE	SPLT	SPTLS	SPLT	SPTLS	SPLT	SPTLS	SPLT	SPTLS
300iso	230	6400	230	10000	220	10000	220	11000
30iso	28	980	29	1300	28	1400	27	1400
3iso	obscured		6.6	120	5.6	120	5.3	130
30hex	95	580	86	870	78	910	71	970

while for splitless injection, area trends are:

C-16 > C-15 > C-14 > C-9

The cause of the first trend is discrimination against non-volatiles in the splitting process. This is a well-documented phenomenon, and is not surprising. The cause of the second trend is the nature of the FID detector, which is essentially a carbon counter, therefore the component with the greatest number of carbons gives the greatest response (since there is little or no injector discrimination in the splitless mode). This, too, is a well documented phenomenon and is not surprising.

One more observation from this table is that 30hex showed a much greater response (roughly threefold) than 30iso in the split mode, but a much lower response (roughly 40% lower) in the splitless mode. This is surprising. Obviously, in the split mode, the solvent has a role in the amount of solute transferred to the column. Perhaps there is cold-trapping of the C-9, C-14, C-15, C-16 solutes even in the split mode and, at 40°C, there is more cold-trapping than at 70°C. Perhaps, also, injector discrimination against non-volatiles allowed more hexane and it's solutes onto the column than iso-octane and it's solutes. Neither conclusion is very satisfactory, and would need more work to verify or vilify. In the splitless mode, it is difficult to explain why 30hex is 40% lower than for 30iso One would expect a sample in the splitless mode to have about 50 fold greater

area counts than a sample split 50:1, without regard to solvent or initial column temperature. As shall be shown next, this was not the case for 30hex.

The next logical comparison is of the measured split ratio of each component in a mixture. The measured split ratio is defined as: area counts for splitless injection/area counts for split injection. The measured split ratio tells how much solute actually reaches the column, and is compared to the calculated split ratio (in this case 50:1). This is illustrated in Table 12, which shows that for 300iso and 30iso, C-15 and C-16 are indeed split about 50:1 while C-9 is split only about 30:1. For all cases, the higher the solute's boiling point, the closer the measured split ratio is to the calculated split ratio. However, the measured split ratios for 3iso and 30hex solutes are nowhere near the calculated split ratio. For 3iso, this is probably due to the low concentration. Apparently, under these chromatographic conditions, splitting doesn't occur linearly over a large range of concentrations. This conclusion is augmented by comparing area counts for 3iso vs. 30iso and 300iso in the split mode (Table 10). Here, one sees that 30iso is about $1/10^{th}$ the area of 300iso, but 3iso is not $1/10^{th}$ the area of 30iso, rather about $1/5^{th}$! The possible reasons for the 30hex showing a lower measured split ratio were discussed earlier when 30hex's greater response than 30iso in the split mode was considered.

TABLE 12. Measured Split Ratio (Splitless Area/Split Area).

SAMPLE	C-9	C-14	C-15	C-16
300iso	28	44	47	49
30iso	35	46	49	51
3iso	-----	18	22	25
30hex	9	10	12	14

The effect of molecular weight and split vs splitless injection modes on retention times (RTs) of the solutes is shown in Table 13. What is observed is that RTs increase when splitless injection is used, and the more concentrated the sample, the greater is the increase. This isn't surprising. The difference in RT between the split and splitless techniques is simply the time that the solute spent in the condensed state at the head of the column (i.e. when it wasn't moving). Also, the greater the amount of solute that is solvent trapped, the more time that is required to revaporize the solvent. 30hex shows greater difference in RT between the two modes than does it's 30iso counterpart, but this is reasonable since 30hex's initial temperature was 30°C lower than 30iso's, initial temperature, and the time required to traverse the extra 30°C would be reflected in the increased RT difference.

As mentioned earlier, a splitless time of 0.40min. was found to yield the maximun area for all solutes in this investigation. Adding more splitless time did not increase peak areas. This was shown by performing a split analysis, then increasing the splitless time incrementally till peak areas stopped increasing and the same peak area was seen for at least two different splitless times. The plot of peak area vs. splitless time for 30iso and 30hex is shown in Figure 12, which shows that 30hex reached it's maximun area at 0.25 min. followed by 30iso (0.35 min.). This trend

TABLE 13. Retention Times (minutes) For Split vs. Splitless Injection.

	C-9		C-14		C-15		C-16	
	SPLT	SPTLS	SPLT	SPTLS	SPLT	SPTLS	SPLT	SPTLS
300iso	0.85	1.00	4.45	4.50	5.28	5.33	6.08	6.15
30iso	0.85	0.99	4.44	4.45	5.27	5.29	6.07	6.09
3iso	obscured		4.37	4.38	5.21	5.22	6.02	6.03
30hex	1.77	2.00	6.45	6.74	7.31	7.60	8.12	8.42

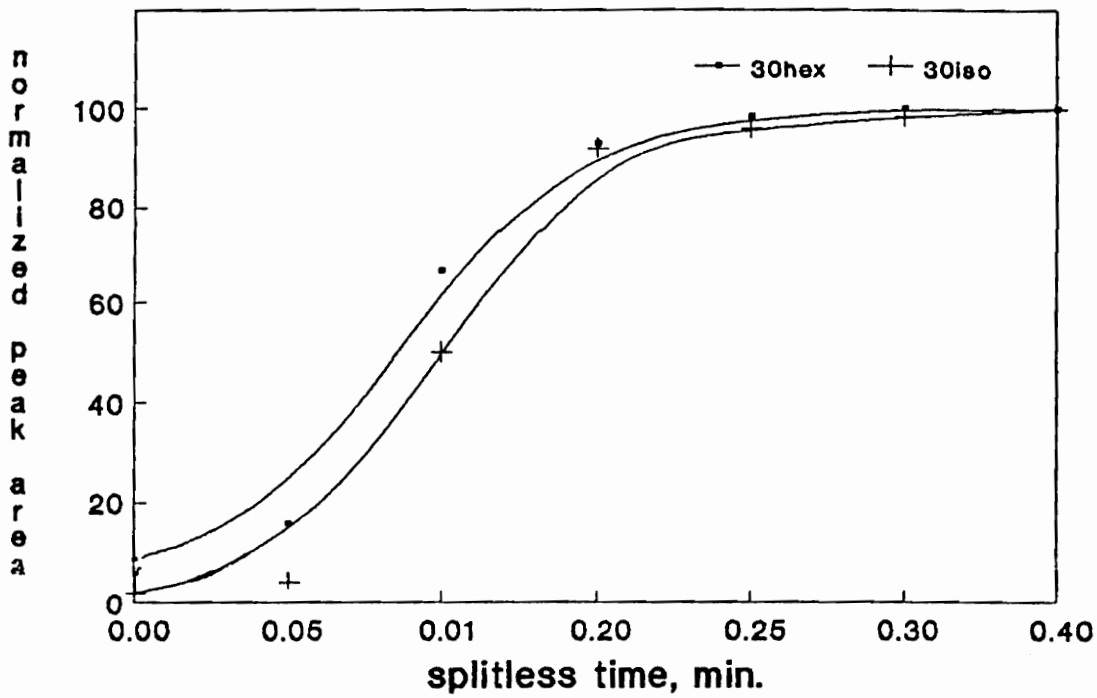


FIGURE 12. Plot of Splitless Time vs. Area For C-15 Hydrocarbon In 30iso (T_{init} = 70°C) vs. C-15 Hydrocarbon In 30hex (T_{init} = 40°C).

is probably caused by the lower initial temperature for 30hex, which should aid in trapping the non-volatiles. However, one could not use the initial temperature for 30iso since 70°C is the boiling point of hexane. As shall be shown later, the solvent effect deteriorates at the boiling point of the solvent. Since the solvent effect is, as the name implies, mostly dependent on vaporization and subsequent condensation of the solvent and not of the solute, it is more reasonable to select a temperature that is 30°C below each solvent's boiling point than to use the same temperature for two different solvent systems whose boiling points are 30°C apart. Thus, data using 40°C for 30hex and 70°C for 30iso are more comparable than if 70°C were used for both solvent systems. The phenomenon observed in the Otto Fuels section of the most volatile component requiring the least splitless time to reach the maximum peak area was not seen to a significant degree.

Using 30iso, the splitless time required to acheive maximum area using a new linear flow velocity ($\underline{u}$ = 75 cm/s). was determined (see Figure 13). The plot shows that maximum area is reached about 50% faster at $\underline{u}$ = 75 cm/s than at $\underline{u}$ = 50 cm/s. This is not surprising, since one would expect sample to be transferred onto (and through) the column much more rapidly at the faster flow rate. It is this effect that is augmented by using the narrow-bore split/splitless liner over the wider I.D. split-only liner. However, as was

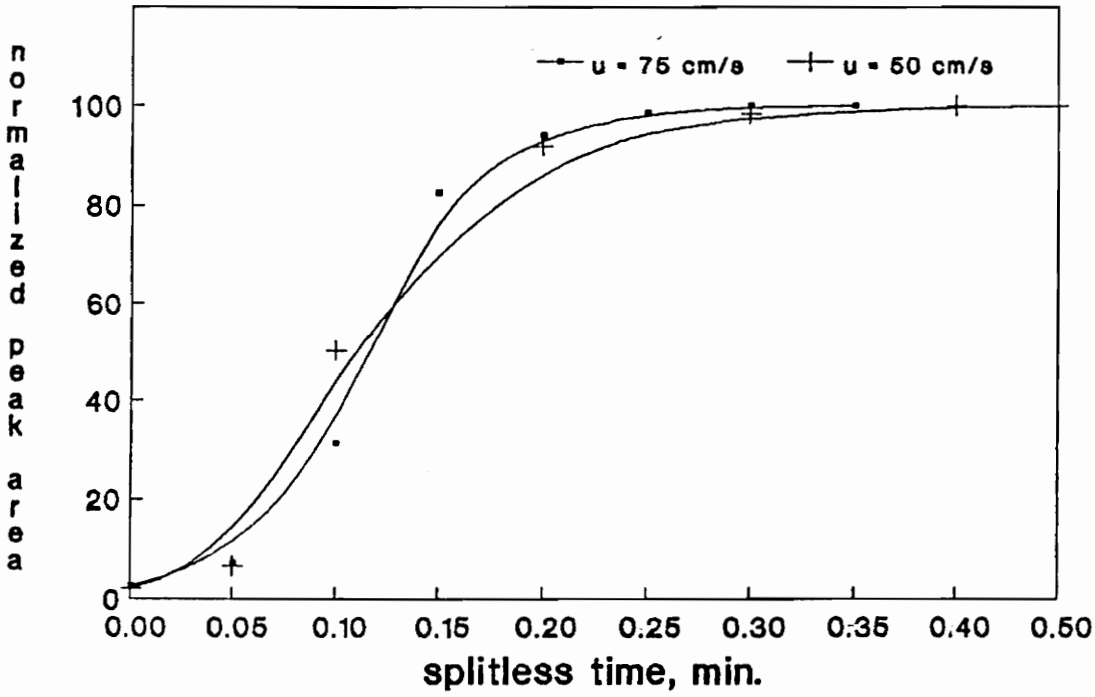


FIGURE 13. Plot of Splitless Time vs. Area For C-15 In 30iso, at u = 50 cm/s vs 75 cm/s, (T_{init} =70°C).

seen the Otto Fuels section, quantitation is not aided.

The next phenomenon to be investigated was the effect that varying the column initial temperature (T_{init}) has on the solvent effect. A tabulation of RSDs for 30iso and 300iso at four different temperatures (7 replicate injections) is listed in Table 14. The trend is a loss of reproducibility at higher initial temperatures, especially for 300iso, and for lower molecular weight solutes (also, the reproducibility of 300iso is significantly different from 30iso for C-14 and C-15 at 130°C only. The more dramatic effect of increasing T_{init} is seen in the peak shape. This is graphically demonstrated in Figure 14, which compares chromatograms of 30iso at 100°C and 130°C. The peaks don't just broaden, they also become non-Gaussian. This effect is more pronounced in 30iso than in 300iso, and is more pronounced in the lower molecular weight solutes.

Having compared one sample at several different initial temperatures, and two different concentrations at the same temperature, the next step is to compare one solute concentration in two different solvents, at the same initial temperature. Hence, 30hex and 30iso @85°C will be examined. Figure 15 shows that C-9 has poor peak shape in 30hex while it is very sharp in 30iso. All other peaks remain sharp. This indicates that band narrowing is a function of the solvent's state (at 85°C, iso-octane is below it's boiling point while hexane is above it's boiling point) and not of

TABLE 14. RSD of 300iso and 30iso At Four Different Initial Temperatures Using Splitless Injection.

INIT TEMP	C-9 300iso	C-9 30iso	C-14 300iso	C-14 30iso	C-15 300iso	C-15 30iso	C-16 300iso	C-16 30iso
70°C	8.1	4.1	0.65	* 0.71	0.49	* 0.81	0.44	* 0.80
		*	*	*	*	*	*	*
85°C	0.77	3.0	0.48	* 0.45	0.49	* 0.45	0.56	* 0.54
					*	*	*	*
100°C	in solvent		0.92	* 0.99	0.86	* 0.80	0.82	* 0.89
						*	*	*
130°C	in solvent		1.83	0.43	2.33	0.44	0.79	* 0.51

#

* or # * #: no statistically significant difference

between these pairs at 90% confidence.

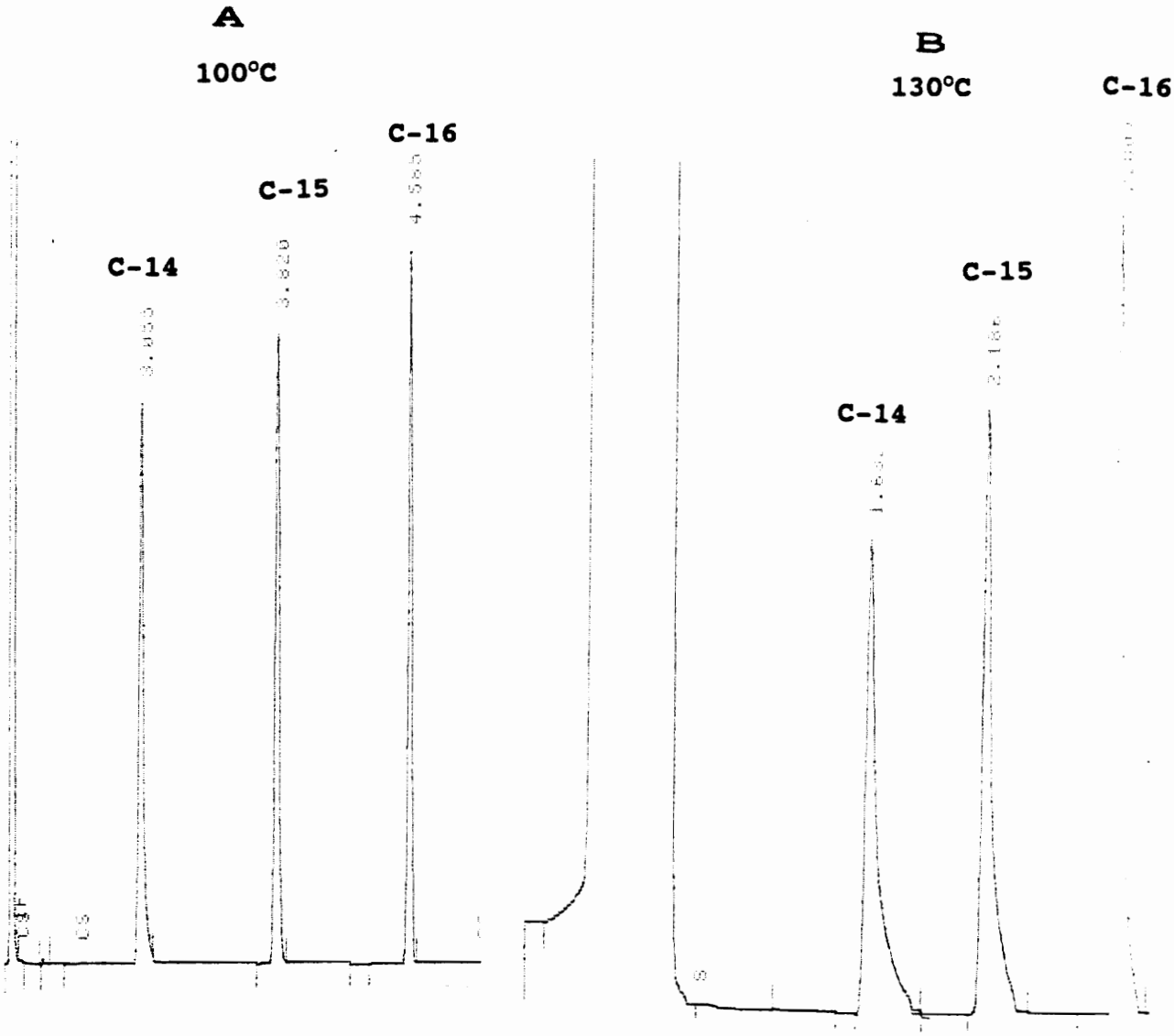


FIGURE 14. Chromatogram of 30iso at A): T_{init} = 100°C vs B): T_{init} = 130°C, (0.40 min. Splitless Time), Comparing Peak Shapes of All Components.

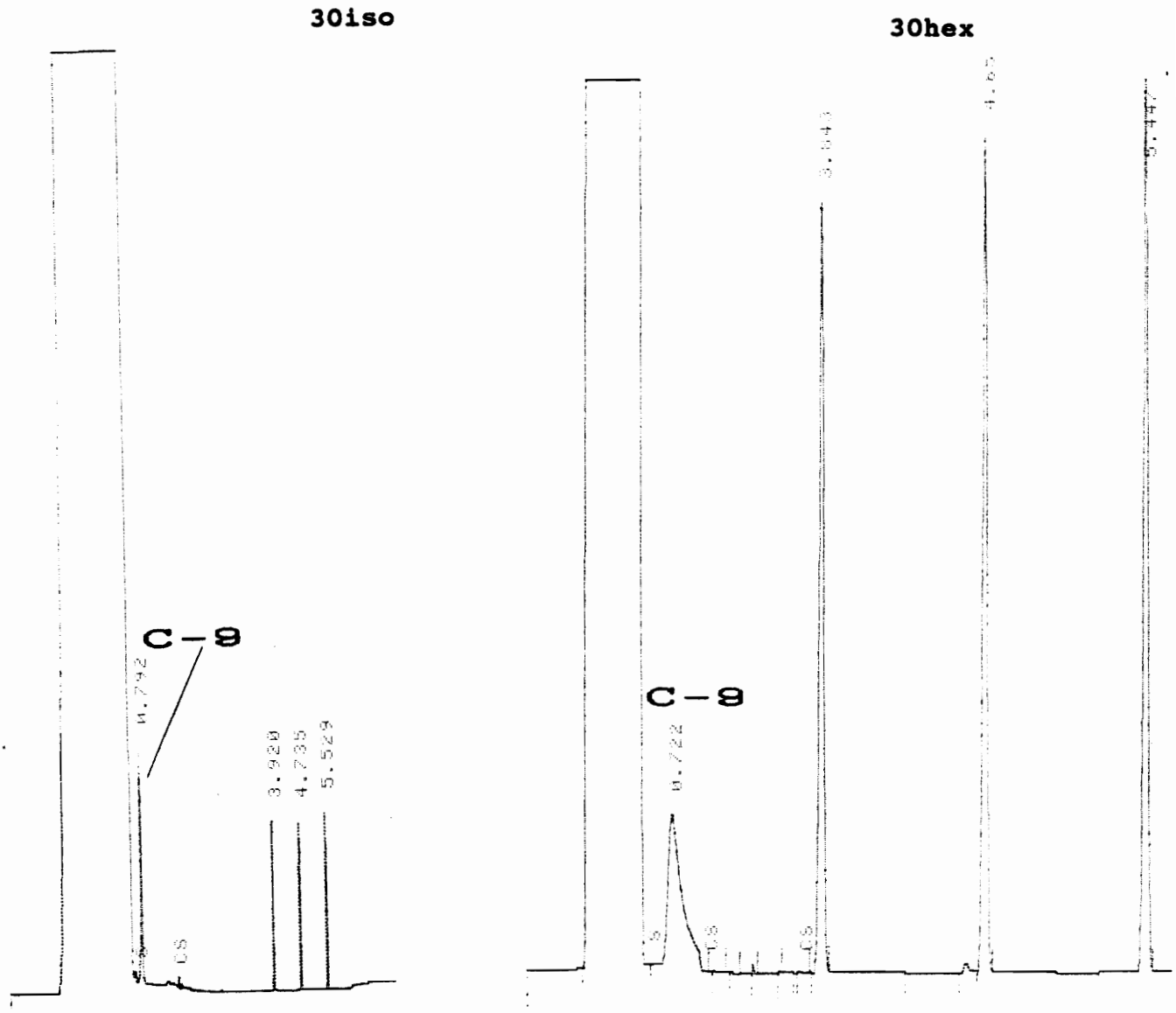


FIGURE 15. Chromatograms of 30iso vs. 30hex at T_{init} = 85°C, (0.40 min. Splitless Time) Comparing C-9's Peak Shape.

the solute's state or of the column temperature alone.

The final criterion to be investigated is the effect that varying the split ratio (after the split-vent has reopened) has on the resolution a peak that elutes very near the solvent peak. To do this, the initial column temperature has to be selected so that the C-9 peak is barely resolved from the solvent peak (at 85°C). The concept is that, if the split ratio is increased, the precipitous drop observed at the end of the solvent peak due to the opening of the split valve might become even more precipitous, with even less residual tailing. Figure 16 illustrates that there was no apparent change in the resolution of C-9 and solvent. Thus, one would want to keep the flow through the split-vent at some fairly low split ratio, say 30:1.

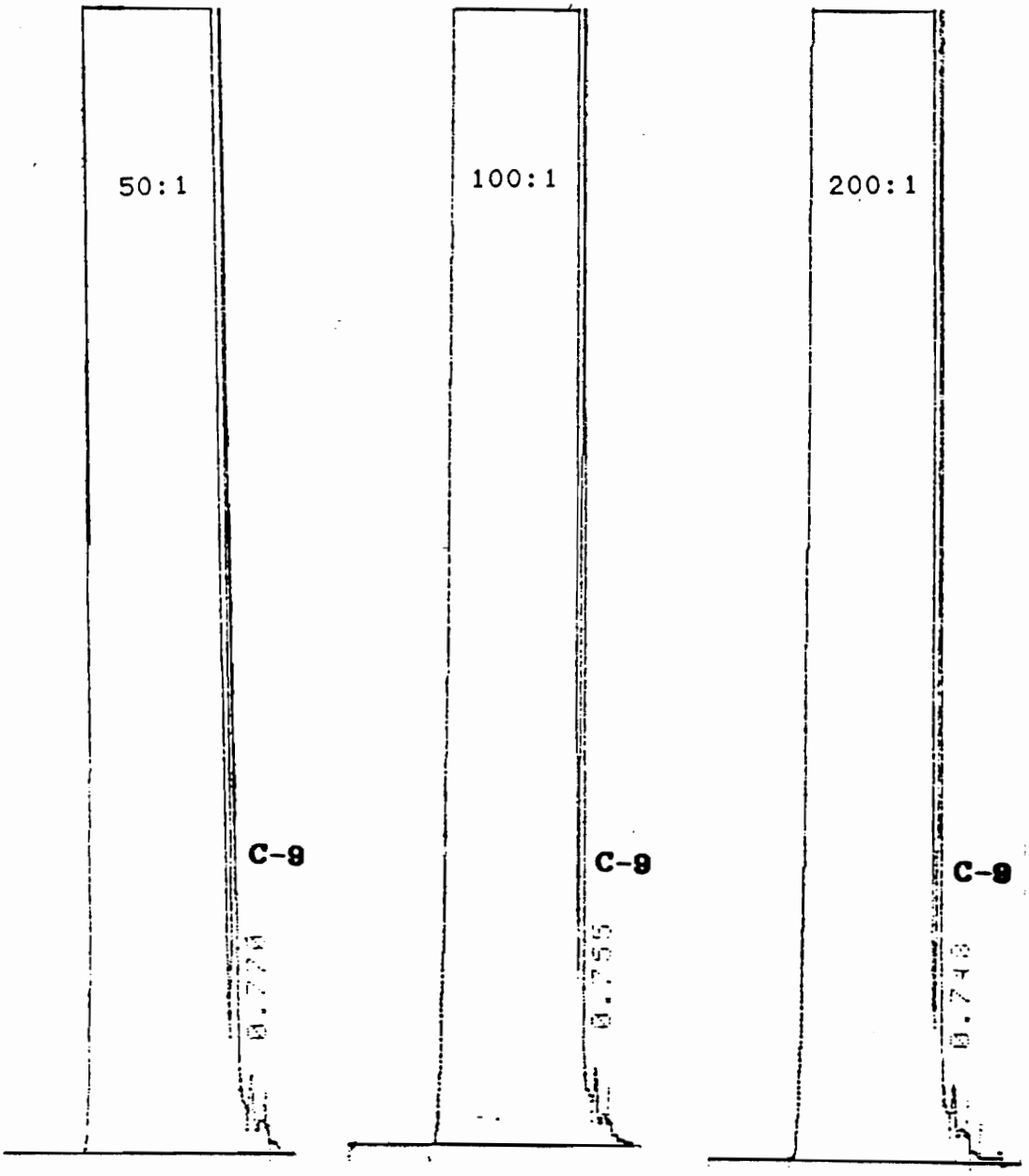


FIGURE 16. Chromatogram of C-9 on The Solvent Peak, Split Ratio (after reopening of the split-vent = 50, 100, 200:1 (30iso, T_{init} = 85°C, 0.40 min. Splitless Time).

CONCLUSIONS

The Otto Fuels section of this investigation yields some very practical conclusions in methods-development. First, using a temperature program and carrier gas flow rate that are as fast as possible, while maintaining the requisite resolution should improve time-efficiency at no cost to precision. In the case of thermolabile compounds, there may be a significant improvement in accuracy due to the shorter residence time of the sample in the heated system. Second, using the least volatile (though not too viscous) solvent improves quantitation. This is influenced by differences in boiling point between the solvent and solutes. Furthermore, using the splitless technique improves sensitivity, with a further net gain in reproducibility. Lastly, the design of commercially available the injector liners seems to have little effect on reproducibility in either the split or splitless modes.

The conclusions one can draw from the SP/SPLS section are manifold. First of all, making peaks sharper and more symmetrical generally improves precision. The splitless technique accomplishes this. Second, quantitation is not adversely affected by column overload as long as all peaks are well resolved and the baseline is stable. Third, the lower the solvent's boiling point, the less the sample is split. Why this is true is not entirely clear. Also, the

lower the solvent's boiling point, the less sharp the solute peaks are. Fourth, analysis above the solvent's boiling point causes peak shapes to rapidly deteriorate, though the higher the boiling point of the solutes, or the more concentrated the solution, the less the solutes are affected by the high initial temperatures. Fifth, changing the split ratio has no effect on resolution, peak shape, or area. The practical conclusion of all of this is, to optimize quantitation one would want to: use splitless injection, use the highest practical boiling solvent, keep the initial column temperature just below the boiling point of the solvent (unless the peaks of interest elute very close to the solvent, then one would lower the initial temperature to 30°C or so below the boiling point), use just enough splitless time to yield the maximum peak areas for all components (too much might obscure peaks that occur close to the solvent's tail), and use the fastest temperature ramp that will allow proper resolution.

In summary, both split and splitless injection techniques show precisions (RSDs) of less than 1% when the chromatographic conditions are optimized. In this investigation, splitless injection shows a small, but significant superiority in precision over the split mode of injection.

REFERENCES

[1] A. J. Martin, A. T. James, Analyst **77**, 915 (1952).

[2] A. J. Martin, A. T. James, Biochem. J. **50**, 679 (1952).

[3] R. D. Condon, Anal. Chem. **31**, 1717 (1959).

[4] L. S. Ettre, W. Averill, Anal. Chem. **33**, 680 (1961).

[5] D. H. Desty, et. al. Anal. Chem. **32**, 302 (1960).

[6] R. D. Dandeneau, E. H. Zerenner, HRC&CC **2**, 351 (1979).

[7] H. M. McNair, M. W. Ogden. HRC&CC **8**, 326 (1985).

[8] K. Grob, K. Grob, HRC&CC 1, **57** (1978).

[9] G. Schomburg, G. Husmann, J. Chromatog. **214**, 85 (1981).

[10] W. Vogt, K. Jacob, et. al., J.Chromatog. **186**, 197 (1979).

[11] H. M. McNair, "Quantitative Capillary GC", VPI&SU, Blacksburg Va. (1985), p. 82.

[12] H. M. McNair, E. J. Bonelli, "Basic Gas Chromatography", Varian Co., 1969, p 25.

[13] obsid. p.3.

[14] M. W. Ogden, "Deactivation and Preparation of Fused Silica Open Tubular Columns for Gas and Supercritical Chromatography" (Ph.D. Thesis), VPI&SU, 1985, p. 94.

[15] K. Grob, K. Grob, HRC&CC **1**, 57 (1978).

[16] J. T. Baker HPLC Solvent Reference Manual, J. T. Baker Co., Phillipsburg, N. J., 1985, pp. 9-2, 10-46, 10-61, 10-64.

[17] B. J. Alley, E. S. Hayes, "Capillary Gas Chromatography of Nitrocellulose-Base and Minimum Signature Propellants", 1984 JANNAF Propellant Characterization Subcommittee Meeting, CPIA Publication 413, pp 1-9, January, 1985.

VITA

Gregg Steven Sotack was born on December 12, 1960 in Hazelton, Pa. to George J. and Gloria Sotack. At the age of four, after the death of his father, he moved to Baltimore, Md. with his family, where his mother married Harry J. Bezold. He graduated from South Carroll High School in 1978. He was an undergraduate at Virginia Polytechnic Institute, working three years with Communications Satellite Corp. as a co-op student. As an undergraduate, he also worked for Dr. Tomas Hudlicky in organic synthesis. He graduated with a Bachelor of Science in Chemistry from VPI&SU in 1985. He spent a year as an environmental chemist with Olver, Inc. in Blacksburg, Va. before his graduate studies.

As a graduate student, he pursued his studies in quantitative GC under Dr. H. M. McNair, and aided him as a laboratory research assistant and sometime lecturer. He received his Master of Science in Analytical Chemistry in December, 1988.

His interests and hobbies include fishing, hunting, politics, theology, fine Canadian beers, and football.