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dissertation entitled

DEVELOPMENT OF MULTIDIMENSIONAL HPLC AND
ATOMIC SPECTROSCOPIC METHODS FOR THE
SEPARATION AND DETERMINATION OF METAL COMPOUNDS IN PETROLEUM

presented by

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has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry

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Date 7/24/85

DEVELOPMENT OF MULTIDIMENSIONAL HPLC AND ATOMIC SPECTROSCOPIC METHODS FOR THE SEPARATION AND DETERMINATION OF METAL COMPOUNDS IN PETROLEUM

By

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A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1985

ABSTRACT

DEVELOPMENT OF
MULTIDIMENSIONAL HPLC AND ATOMIC SPECTROSCOPIC METHODS
FOR THE SEPARATION AND DETERMINATION OF METAL COMPOUNDS
IN PETROLEUM

By

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Fuels of all kinds are known to contain metals at low concentrations. Interest in trace metal analysis of fuels stems from their geochemical importance, and their deleterious effects. For example, iron and nickel act as cracking catalyst poisons, lead contributes to jet turbine corrosion, and chromium forms toxic combustion products. This topic is becoming increasingly important as petroleum resources dwindle and broadened-property, or alternate fuels, are put into use. These newer fuels contain higher concentrations, and a wider variety, of metals than are found in conventional fuels. Two questions are important: 1), what are the actual metal concentrations in the fuel; and 2), what is the chemical environment of each metal of interest?

The research presented in this thesis focused on two goals: 1), to develop a direct method for metal determinations in fuels; and 2), to utilize this method in conjunction with a chromatographic separation to produce metal

speciation information. A four step approach was taken to achieve these goals.

Initially a column chromatographic technique, sequential elution solvent chromatography (SESC), was employed to separate the residual fuel being studied into nine compound class fractions. The question of how the chromatographic behavior of metal-containing compounds compares to that of nonmetal-containing analogs was investigated by subjecting metal-containing complexes to SESC. The fuel fractions were then analyzed by a direct atomic absorption technique, which was developed as the second part of this research. These results were used to produce metal distribution profiles, according to compound class.

In the third part of this work, the SESC fractions were further characterized by HPLC techniques. This work included single-column, size-exclusion and normal phase separations. A computer-controlled multidimensional HPLC system, which was developed in this laboratory, was employed to develop methods applicable to this research. An example is the mode-coupling of a size-exclusion column with a reverse-phase column to produce a size-polarity matrix.

The final step of this project involved the interface of the HPLC to an element-specific detector. This was investigated for both an atomic absorption spectrometer and an inductively-coupled plasma optical emission spectrometer.

To Pat,

Christopher,

and my parents

ACKNOWLEDGMENTS

I would like to express my sincere appreciation to Dr. Stanley Crouch for all his guidance and support in my research endeavors, and his patience with my various family crises. I'm particularly thankful for the expediency with which he, and Dr. John Allison processed my dissertation.

I am also very grateful to my husband, Pat, for his scientific collaboration and advice, and for all the emotional support which he provided. I doubt whether I could have completed this degree without him. I also thank my parents for all their support, both emotional and financial. They were very patient, even though they could not understand why this took so long. I'm not sure if I should thank my son Chris for the part he played, or whether I should apologize for subjecting him to graduate school at such a young age. Hopefully, that experience will not deter him from a career in science.

Finally I'd like to thank all the members of the Crouch group, past and present, for being such a neat family. I'd especially like to thank Kim, who has been like a sister to me, and who is a great friend. Thanks to Frank and Keith who may be gone, but are not forgotten. Thanks to Helen for

getting John off my back, and thanks to John for showing me how peaceful working in a quiet lab can be. Thanks to Jimmy for all his generosity. Thanks to Max for the motivating influence which he provided. Thanks to all those in the third floor lab for putting up with my real chemistry (with nasty solvents), especially Paul who tried to get me to clean up my act (I did try). Thanks to Bob for being so kind as to let the whole mob into his house. Thanks to Tom for his good influence, the future of the group's reputation may well rest on his and Max's special abilities. Thanks to Cheryl for taking over as lab mom, good luck Cheryl. I don't want to leave out Mark, Mark, Ralph and good old Nelson who all contributed to my educational experience at MSU. Finally, I must acknowledge the support and help I received from Reptilian Lifeforms, Inc.

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I. INTRODUCTION

The research reported in this thesis focuses on the determination and speciation of metals in fuels. This is a very challenging area of research which is a topic of interest and study for many different types of researchers. The next two sections of this introduction present the basic reasons for the activity in these two areas of research. This provides a context in which to consider the goals of this research, which are presented in the final section.

A. Metals in Fuels

Metals in petroleum matrices have been a topic of study for quite some time for several reasons. Metals occur naturally in petroleum, and their determination can provide important geochemical information (120,135). However, the presence of metals is not desirable in either crude petroleum or refined fuels. In crudes, nickel, arsenic, titanium, vanadium and iron will poison or alter the behavior of cracking catalysts (110). Metals in refined fuels can lead to the production of toxic combustion

products, as is the case with chromium, lead, mercury, arsenic, cadmium, plus others (71). They can also significantly reduce fuel thermal stability (42). In addition, trace metals in fuels can be very detrimental to the combustion chambers in which they are used. For instance, it has been shown that lead in jet fuels accelerates the corrosion of jet turbines (42). Metals can also be introduced into petroleum matrices either during storage in metal containers, or during use due to the deterioration of metal engine components. Considering these various situations it is obvious why methods for accurate metal determinations in petroleum matrices are of interest to many different groups.

Unfortunately, analyzing petroleum for metal content is not a trivial exercise. The basic problems which accompany metal determinations in fuels can be summarized as follows.

1) Sensitivity.

The metals which are present in fuels are at low levels. This makes detection challenging.

2) Imprecision.

Intralaboratory studies show there is a serious lack of precision associated with the typical methods for metal determinations in petroleum matrices (41). This holds true for a variety of spectroscopic techniques and may well result from

the sample pretreatment, which typically involves acid digestion, followed by ashing.

3) Background interference.

The presence of metals other than the one being investigated can interfere with the analyte's spectroscopic determination. In addition, the petroleum matrix is quite complex and is often a source of background emission or absorption.

4) Physical interferences.

Often metals in petroleum matrices are found bound to large, complex species, which require a large amount of energy for decomposition before the metal is released for atomic spectrometric analysis. Secondly, the viscosity of petroleum samples often requires special handling, and can produce erroneous results if the procedure does not take changes in viscosity into account. In fact, matrix considerations, sample viscosity, and sample solubility often limit the analytical techniques which can be employed.

5) Representative sampling.

Sometimes the metals in fuels reside in suspended particulate matter, e.g. wear metals. The

analytical technique must sample this effectively and treat the sample so that these particles are analyzed along with the rest of the solution in a manner which will provide an accurate total metal value for the sample.

B. Metal Speciation

Obviously, the total level of metals present is important. Nonetheless, the chemical environment, or chemical species, which contains the metal is also of interest. Knowledge of the metal species, or metal speciation information, is valuable in several respects. It provides information concerning the geochemical history which introduced the metal into the petroleum (135). It also can aid the refiner in predicting the chemical consequences of these metals during the refining process. Similarly, the engineer can better determine which material would be best for engine construction, knowing the potential chemical interactions. In addition, such information is useful in evaluating the environmental impact of fuel usage. Finally, there is the hope that metal speciation knowledge will aid in the development of methods for removing deleterious metals.

Metal speciation is a very complex area of study. The major problems stem from the fact that the petroleum matrix

is so chemically complex. Virtually no speciation information can be obtained using physical methods without prior separation, or some other type of matrix simplification. Liquid chromatography, both classical column techniques and HPLC, is generally the technique of choice. However the interpretation of the resulting separations is often not simple, and can require a variety of techniques. Once such a separation is achieved, metal determinations must be done to complete the speciation study. The problems accompanying these metal determinations, which have just been outlined, are often accentuated by the fact that the chromatography further dilutes the already low metal concentrations. This can result either from the separation of various metal-containing species, or from simple diffusion and mixing.

C. Research Goals

The goals of this research were twofold. First a method was desired for direct metal determination in a petroleum matrix, in order to eliminate some of the imprecision associated with the conventional ashing procedures. Secondly, a method was needed to provide information about the chemical environment of the metals in the fuel. Linked, these two methods can both determine and

speciate the metals residing in a petroleum matrix. It should be stated that this approach is only appropriate for petroleum samples which have been proved to be particulate-free. We propose that the ideal approach to meet this goal is to interface a multidimensional high performance liquid chromatographic (MHPLC) system to an element-specific detector. This system could provide fairly detailed chemical information and component separation for this complex matrix. Then the metal content of these components can be determined sequentially. As stated, this is set forth as the ideal approach; it is the end goal, not the starting point for this research. Instead, this study began by implementing some classical techniques, adapting them to approach our goals. This provided chromatographic background to begin the work with the MHPLC once it was constructed. At this point the interfacing of this system to an element-specific detector was also investigated.

The research presented here represents a very complex and challenging problem. In order to understand and better appreciate the numerous problems associated with this field of study, it is appropriate to review what other researchers in this area have reported. Thus, we will now turn to a historical perspective on the following four topics: metal determinations in petroleum matrices, the chemical characterization of petroleum constituents, previous

speciation studies, and highlights of the development of MHPLC.

II. HISTORICAL

A. Introduction

The goal of this chapter is to present a literature overview which will be sufficient to provide suitable background for this research project. This review is divided into four parts for the sake of clarity. Each section deals with a specific area; these are: 1) metal determinations in petroleum matrices; 2) chemical characterization of petroleum components; 3) previous metal speciation studies; and 4) highlights of the development of multidimensional high performance liquid chromatography (MHPLC).

Several other techniques, which are often used for metal determinations in fuel matrices, will not be considered in depth because they do not lend themselves to the approach taken in this research. Examples of these techniques include atomic fluorescence (13,152), x-ray fluorescence (43,79,119,150), and neutron activation analysis (146).

B. Metal Determinations in Petroleum Matrices

Methods development for metal determinations in petroleum is a very active field of research. These determinations are not trivial, as is reflected in the variety of approaches which have been reported. An overall comparison of the more common techniques has been given (71).

Atomic absorption spectroscopy (AAS) is widely used for metal determinations in petroleum matrices. The various AAS methods reported in the literature can be divided into two basic categories; those which employ sample ashing, and those which analyze the fuel directly. The first type involves ashing of the fuel, often with an acid as an ashing aid; followed by aqueous/acidic dissolution of the ash (57,112,156). This solution is then aspirated into the AA spectrometer. There are two basic problems associated with ashing techniques. One is imprecision, either due to the loss of volatiles during ashing, or due to sample loss during the required transfers. Although authors have recently reported good reliability and reproducibility with ashing techniques (112,156), a NASA interlaboratory study reported poor laboratory-to-laboratory agreement (47). The other general problem with ashing techniques is the lengthy analysis times. Ashing of fuels often requires several days to a week (46).

In response to these problems many researchers have worked to develop AAS methods for the direct analysis of fuels without preliminary ashing. This is done by dissolving the fuel in an organic solvent, or solvent mixture, and then aspirating this solution directly into the AA spectrometer. The most common solvents reported are kerosene, white spirit, methyl isobutyl ketone (MIBK), and toluene (15). Common mixtures are MIBK/xylene and xylene/MIBK/methanol (113).

The direct approach to petroleum analysis is becoming more and more common. However, there are three critical points which should be made concerning these techniques. The first is that without preliminary ashing the flame must provide the energy to destroy the matrix which contains the metals, before the metal can be atomized. Thus, there can be serious problems with matrix interferences. One study which dealt with the determination of iron and copper concluded that petroleum samples need to be acid ashed as there was evidence of transport interferences in xylene solutions, and matrix interferences even in a nitrous oxide flame (117). However, another study reported that such interferences can be avoided by careful adjustment of flame composition and characteristics (132). The method of standard additions can also be used to overcome some matrix interferences. For instance, this approach can eliminate viscosity effects, which could produce inaccuracies when

using a calibration curve produced by standards in a different matrix. However, it is important that the standard additions do not greatly change the viscosity of the sample. Appropriate standards for this technique are avaliable from the Conoco Oil Co., Ponca City, OK. These Conostan standards consist of metal dialkylbenzenesulfonates dissolved in a paraffinic oil (25).

A second problem is that the direct method of analysis dilutes already low metal levels. Thus low detection limits are a necessity. One group studied the effect of various organic solvents and water on the flame geometry of an air/acetylene flame (133). They found that there was a higher level of metal vapor, or better atomization efficiency with organic solvents. This would predict an increase in detectabilty. However, the increase was not as large as expected because the flame volume at the optimal observation height was larger with the organic solvent than with water. Detection limits comparable to those obtained for aqueous systems, and sometimes even better, have been reported (15).

One approach which is used to improve the sensitivity of AAS determinations is the production of volatile hydrides (44). This is done particularly in arsenic and antimony determinations. The hydride technique provides advantages in that once the hydride is formed it is quite easy to introduce all of the vapor into the flame. Since the metal

now exists as a vapor, flame energy is only needed to atomize the metal. In addition, since all the metal exists in the same form there is no matrix interference due to varying atomization behavior of different ligands. However, hydride generation is a multistep process. All of the metal must be converted to the proper oxidation state in order for the reaction to proceed (89).

The third point to be considered is that simple dilution of the fuel with an organic solvent may result in inaccurate metal determinations if some of the metal is present in the sample in particulate form (109,110). This is often the case in wear metal determinations in lubricating oil. The general approach which has been reported to remedy this situation is to use a dilute acid/organic solvent mixture for sample dissolution (2,31,75,107,151). This technique has been termed 'particle size independent' (17). Acetic, hydrofluoric, nitric, and hydrochloric acids have been used. A surfactant is often added to produce a uniform emulsion (6,29,108). In one study of this type, the fuel sample was emulsified in isobutyric acid, and the metal content was determined by comparison to aqueous standards (62).

Graphite furnace atomic spectroscopy (GFAA) has been employed by many researchers in response to the problems associated with AAS (24). Electrothermal atomization is very effective for matrix decomposition, and thus the

removal of many matrix interferences. In addition, this atomization process produces a more concentrated metal vapor than that produced in a flame system. In this way, lower detection limits can be attained with GFAA than with flame AAS. Another advantage is that organic solutions can be analyzed as easily as aqueous solutions, and in fact sometimes it is not necessary to dilute the sample at all. This technique also has its limitations. For instance, the precision is often poor, due to variations in atomization rates from one heating cycle to the next. Variation in total residence time for the sample in the graphite tube can also contribute to technique imprecision. Fabec (33) reported good precision and accuracy in GFAA determinations of shale oil for arsenic. However, this report also detailed several experimental problems common with this technique. For instance, careful optimization of the solvent system was necessary to produce a solvent mix which would result in the same signal for the same level of arsenic contained in different arsenic compounds. The mixture which was used contained water, THF, sulfuric acid and medium neutral oil. Variation in the proportions of these components greatly effected arsenic recovery. This is a major problem associated with GFAA. Acid works to improve the recovery rate, but too high of an acid level results in rapid aging of the graphite which will produce erratic absorbance values. Another study reported atomization

interference in the analysis of petroleum samples for nickel and lead (73). The sample was introduced in an organic solvent. The interference was attributed to the types of ligands which were bound to the metal. Heteroatoms of the same type had a consistent effect. Nitrogen donors appeared to allow atomization to the free metal; whereas, sulfur- and oxygen-containing ligands tended toward the production of sulfides and oxides.

GFAA has also been used in the development of a 'particle size independent' method (101). These researchers used Smith-Hieftje background correction. GFAA has also been used in conjunction with other sample treatment techniques. One example is the extraction of copper from lubricating oil by a complexing agent, followed by GFAA analysis of the organic solution containing this complex (32). The advantage of this type of technique is that all the metal is contained in the same type of complex, thus resulting in consistent atomization behavior.

Inductively-coupled plasmas (ICP) are being used more and more for trace metal determinations in petroleum matrices (7,18,41,51,52,74,88,100). The plasma is ideal for this type of analysis in that it is a very high energy source in an inert atmosphere. As a result, the ICP can atomize nearly all elements which emit in easily observable regions of the spectrum, and do so with fewer matrix interferences than in the previously discussed techniques.

In addition, the argon atmosphere reduces the formation of many molecular light-emitting species (18). The multielement capability of the ICP technique is also an important asset, since many metals exist in petroleum matrices.

However, the ICP technique is not without its problems. ICP analyses are easiest to perform with aqueous samples, as the fundamental properties of the plasma are well characterized with water, and water is less volatile than many organic solvents (11). Some workers have employed ashing techniques for ICP analyses, just like those used for AAS analyses (100). However, most researchers would like to avoid the problems associated with ashing techniques, and do direct analyses of petroleum samples dissolved in organic solvents. This requires special modifications of typical ICP techniques (7). Analyzing organic solutions is not trivial since the plasma is very sensitive to changes in solvent delivery, solvent compositon, and solvent volatility (51). Vapors from volatile solvents absorb rf power and lower the plasma temperature (11). This makes it necessary to increase the incident rf power when using organic solvents. In addition, it is often necessary to adjust the analytical viewing height, as the signal is often larger at distances higher above the load coil than than with aqueous samples. It is postulated that the higher optimum distances are a result of the change in plasma temperature due to the

presence of organic solvent vapors which is thought to increase the enthalpy and thermal conductivity of the plasma gas (8). The introduction of organic vapors also results in the formation of a plume within, and extending out of, the plasma (51). This plume is caused by C_2 molecular emission (8). The plume is undesirable in that it can interfere with the measurement of atomic emission. The use of organic solvents also tends to produce a carbon deposit on the torch due to the presence of organic vapors in such a high temperature region. This carbon build-up also tends to destabilize the plasma.

The effects of organic solvents can be minimized when using a conventional torch assembly by lowering the flow rate of the organic solution into the nebulizer. Suitable flow rates can vary between 0.1 ml/min to 5.0 ml/min depending on the solvent (11). However, since the ICP is a mass-sensitive detector, this approach will result in a higher limit of detection. The detection limits obtained in organic solvent are generally worse, or just comparable to those obtained in water (11). This is somewhat surprising considering the enhancement seen in some AAS studies with organic solvents.

The problems noted with organic solvents have led to the design of a modified torch (12), and the design of a special spray chamber to enable efficient analysis of organic samples (51). The modified torch design provides

for efficient gas flows and reduction of carbon deposit (12). The new spray chamber is cooled and condenses some of the organic vapor, thus keeping it out of the plasma. With these types of modifications workers have reported sub-ppm determinations (41). Nonetheless, the organic solution limits of detection are not comparable to those of aqueous solutions (51). The organic solvents reported to be the most successful are MIBK, toluene, xylene, and even pyridine. Mixtures are often used as in AAS studies. Another modification which is reported is the use of a nitrogen-cooled argon plasma (16,101). This also acts to eliminate carbon deposition. Another interesting approach which has been reported is to vaporize the sample in a graphite cup, and then introduce this vapor into the ICP (126). This works to both minimize matrix effects and avoid the previously mentioned problems. Continuous hydride formation for arsenic and tin has also been reported as a highly efficient way to introduce these metals (102).

C. Chemical Characterization of Petroleum Constituents

Researchers have been interested in separating and characterizing petroleum constituents for as long as petroleum has been considered useful. The most basic separations are done by distillation. There is an enormous amount of literature recording attempts to further

characterize these distillate cuts. Altgelt and Gouw (5) have published a comprehensive review of the various classical column chromatographic methods which were developed between 1950 and the mid 1970's, for petroleum characterization. These generally involved either extractive separations based on solubility, or acid/base behavior, or chromatographic separations on silica or alumina. The fractions produced by these methods are very broad groupings, and the methods provide little detailed chemical information. In the early 1970's the American Petroleum Institute Research Project 60 group developed a separation scheme which produces more specific fractions, e.g. saturates, aromatics, neutral nitrogens, and so forth (89). Unfortunately, this method requires about a week to complete. Once this method appeared in the literature many researchers began to publish modifications of the API-60 scheme, which were faster (48). Beginning in 1965 L.R. Snyder began to report compound class separation schemes for medium and heavy distillates (67,122). Another compound class separation scheme of particular interest to this work is that reported by Farcasiu in 1977 (122). This scheme is known as sequential elution solvent chromatography (SESC). It was developed for the separation of solvent refined coal (SRC). The SESC scheme produces nine fractions which are of different compound classes. The procedure is discussed in

further detail in a later section of this thesis. A variation of this technique has also been reported (66).

More recently there has been a great deal of interest in using HPLC techniques to execute compound class separations comparable to those just mentioned. Vogh and Thomson (145) reported a preparative HPLC technique which produces fractions equivalent to the API-60 approach, in approximately three hours. The columns can also be regenerated by backflushing, and reused several times. Several other authors have reported similar separation schemes on a nonpreparative scale (82,129,130). An interesting variation employs a silver nitrate-treated silica column (22). Miller and others have studied the use of a perfluoroheptane mobile phase to develop an analytical HPLC silica column for compound class separation (91,131). Some of the separations reported are specific to a particular type of compound such as porphyrins (87), or carboxylic acids (115). Several groups have studied the usefulness of various bonded stationary phases to achieve compound class separations (1,26,27). Matsunaga (85,86) employed amino and cyano bonded-phases to produce saturate, aromatic and polar group separations. Miller (90) also used the same stationary phases and dual functional material consisting of alkylnitrile-substituted secondary alkylamine groups to achieve a similar separation. In addition, he employed backflushing to shorten the overall analysis time

and to improve quantitation. Some of these bonded-phases are particularly good at separating compounds by ring number. Studies which have investigated the separation mechanism, indicate that it is due to charge-transfer between the bonded functional group and the aromatic pi cloud (94,134). Due to the specific nature of this interaction this type of separation is useful for fairly highly-resolved chromatographic fingerprinting (94). Reverse phase separations have also been utilized for fingerprinting and were found to be superior for acidic fractions which require a high water content in the mobile phase (61). Probably the best resolved fingerprint is that reported by Novotny via capillary HPLC (60).

There are some very interesting characterization studies which involve HPLC interfaced to selective detectors which can provide very specific information. These include HPLC/IR (40,114) and HPLC/FTIR (20,68), HPLC/NMR (55), and HPLC with a post-column reactor (PCR) (120).

It should be noted that not all chemical characterization procedures involve HPLC. Many extraction procedures are still used (58,104). In addition, there are some characterization procedures which do not require preliminary separation (155), however these do not usually produce very detailed information.

D. Metal Speciation Studies

Metal speciation is of interest for several reasons, which were detailed in the introduction. The most common speciation studies are those concerning petroporphyrins (63,87). This is due to the valuable insight which this information provides concerning the geochemical origins of the metals, and the geochemical history of the petroleum itself (137,153). Most other speciation studies are less specific in nature and results. The least specific employ size exclusion chromatography (SEC) with an off-line element-specific detector (23,24). Studies which employ SEC with an on-line element-specific detector are more informative since this approach retains all the chromatographic information, some of which is lost with fraction collection. Examples of this are two studies reported by Hausler; the detector is an ICP (49,52,53). Graphite furnace AA has also been used (36,37). Unfortunately, the particular experimental conditions used in these studies leave the interpretation of the results obtained somewhat in question. The use of other chromatographic modes of separation provides more specific information. Partition chromatography has been used with off-line detection by AAS (45), GFAA (135), and ICP (50) for speciation of crudes and SRC. Once again on-line detection is more informative and is particularly pertinent to this

research. General discussion of this approach has been presented by van Loon (140,141). High performance liquid chromatographs have been interfaced to several different element-specific detectors. The list includes AES, although this is not too useful in fuel applications due to the wide variety of species which are present in this matrix (72). Atomic absorption techniques are more common, including flame AAS (35,69), and GFAA (14,36,37,77,143). Graphite furnace AAS techniques are more common due to the advantages enumerated earlier, however the limitations discussed also apply (143). In one study the GFAA signal was clearly shown to be species dependent (14). The chromatographic modes coupled to the GFAA include ion-exchange chromatography (14), bonded-phase chromatography (BPC) (36), and reverse-phase chromatography (RPC) (14,37). One of these studies is particularly interesting because of the use of a rapid scan UV-visible detector in series with the GFAA, and the correlation of SEC and BPC (aminocyano stationary phase) behavior (36). Perhaps the most promising approach is that of HPLC/ICP. This has been investigated by several different researchers (15,38,39,42,78,93).

E. Multidimensional HPLC Techniques

Multidimensional HPLC (MHPLC), or column switching techniques, have become very common since the advent of the

first high pressure, low dead-volume valve in 1973 (63). Most applications of column-switching fall into three categories: 1) sample clean-up, 2) trace enrichment, and 3) compound class separation (92,81,83). A more complete historical discussion of these techniques is contained in the PhD thesis by P.M. Wiegand (148). Multidimensional HPLC is especially useful for complex samples such as petroleum. Some researchers have developed on-line MHPLC methods for petroleum samples. One uses a two column medium-pressure LC system to affect class separations on a preparative scale (105). This method also employs backflushing and flow programming to shorten the analysis time. Alfredson (3) reported an automated three column system for compound class separation. Another three column system utilizes a low-resolution RPC separation, followed by a SEC separation, ending with an analytical RPC step (98). Several of the compound class separation schemes mentioned in the chemical characterization section of this paper involve off-line multidimensional techniques (82,90,130,145).

III. EXPERIMENTAL

A. Introduction

The research goals presented earlier are to develop methods for direct determination and speciation of metals in fuels. This work approaches these goals in a stepwise manner. The fuel studied is a residual fuel, NASA Residual Fuel #3. This fuel was chosen for its relatively high metal concentrations. In addition, this fuel provides a very complex matrix, which can be considered a 'worst case' for chromatographic method development. The first step in the study of this complex fuel involves a gross scale separation into compound classes. The sequential elution solvent chromatographic (SESC) technique was chosen because it produces nine well defined fractions (34). The resulting fractions are then further separated by size exclusion chromatography and the metal content is determined. This sequence provides preliminary, broad scale speciation information. The next step is the exploration of various HPLC techniques for further characterization of both the whole fuel and the compound class fractions.

Multidimensional HPLC (MHPLC) proves particularly applicable to this work due to the complexity of the sample matrix. The final step in this work is the interface of the HPLC/MHPLC system to an element-specific detector for on-line speciation information/analysis.

This section presents descriptions of the instrumentation and experimental techniques employed. It has been broken into six parts, for clarity. The first and second parts cover the column chromatographic separations and direct metal analyses which provide preliminary speciation; the next three parts present the HPLC and MHPLC methods which were developed; and the last part reviews the HPLC/element-specific detector studies. The results of these experiments, and their interpretation are the topic of the next chapter.

B. Column Liquid Chromatographic Separations

1. Introduction

The SESC procedure was developed for solvent-refined coal. Nonetheless, thin-layer chromatographic studies, which were done as part of this research, demonstrated its applicability to the separation of the residual fuel. In addition, the first SESC fractions collected were subjected to infrared analysis. The resulting spectra are different

for each fraction and contained features which would be expected for the various compound classes.

2. Apparatus and Supplies

The column liquid chromatographic (CLC) separations are run on a 450 mL J.T. Baker 'Flash' Chromatography column (product no. 7022-4 J.T. Baker Research Products, Phillipsburg, NJ), with a 500 mL reservoir (product no. 7092-4). The sorbent used is 40 μm 'Flash' silica (product no. 7024-5). This is a low pressure chromatographic system (2 to 5 psi), which allows rapid preparative separations. The pressure is supplied by a tank of dry, compressed nitrogen (Linde Corp.). The solvents used are either distilled in glass (Burdick & Jackson Laboratories, Inc., Muskegon, MI), or reagent grade materials (Fisher or Mallickrodt) which are then specially purified.

3. Experimental Procedure

The first column SESC separation of this fuel was done under gravity feed on a 4% deactivated silica (60-200 mesh) column. The reagent grade solvents used, are purified in-house in the following manner (106). Ethanol-preserved chloroform is washed five times with half its volume of water to extract the ethanol. It is then distilled in glass over calcium chloride. The ethyl ether is distilled over

potassium and benzophenone. The pyridine is dried over calcium hydride, and then distilled. Two hundred proof ethanol is used after drying over Drierite (W.A. Hammond Drierite Co., Xenia, OH). The remaining solvents were UV-grade materials; these were dried with 4Å sieves. In the SESC procedure the column is sequentially eluted with two column-volumes of nine solvents, or solvent mixtures, which produces nine compound classes fractions. Table 1 lists these solvents and fractions.

Table 1. Sequential Elution Solvent Chromatography

Fraction	Solvent	Compound Class
1	Hexane	Saturates
2	Hexane-15%Benzene	Aromatics
3	Chloroform	Polar Aromatics; non-basic
4	Chloroform-10%Ether	Monophenols
5	Ether-3%Ethanol	Basic Nitrogen Heterocycles
6	Methanol	Polar Heterocycles
7	Chloroform-3%Ethanol	Polyphenols
8	THF-3%Ethanol	Polars; High -O, -N
9	Pyridine-3%Ethanol	High Molecular Weight Polar Heterocycles; High -O, -N

The gravity feed approach requires two days for completion. Therefore, the procedure has been adapted to the 'Flash' setup. This reduces the time required for a complete run to about four hours. The 'Flash' column is packed with a 17 cm bed of activated 40 μm 'Flash' silica. This is sufficient to separate 0.5 g of fuel, which is deposited on approximately 20 g of 'Flash' silica, via THF.

The fractions are once again eluted with two column volumes, which is equivalent to 300 mL. The fractions are collected in 250 mL round-bottom flasks. In this way, the fractions can be concentrated on a Rotovap without transfer. It is necessary to combine the fractions from three to five runs in order to obtain enough sample for subsequent metal analysis. The column packing cannot be reused without regeneration with an acid wash and reactivation. The sample silica is reserved for metal mass balance determinations. Blank determinations are also necessary.

Model compound studies have been done to investigate the behavior of particular types of compounds when subjected to SESC. These include hydrocarbons such as naphthalene, furan, quinoline, various carbazoles and indoles. These studies validated this technique for the production of the predicted compound classes from a matrix other than solvent-refined coal (SRC). Several metal-containing porphyrins have also been subjected to SESC to determine whether metal-containing compounds chromatograph in the manner predicted by nonmetal-containing analogs. Copper(II), zinc, nickel(II), and colbalt(II) 5,10,15,20-tetraphenyl-21H,23H-porphines (TPP), as well as the nonmetal-containing porphine have been studied. Nickel and cobalt acetylacetonates (acac) and diethyldithiocarbamates (dtc) were also studied in this way. In addition, some less stable metal-containing complexes,

such as ferric phenolate and dibenzene chromium, were studied in a similar manner.

C. Metal Analyses

1. Introduction

Initially, the metal analyses were attempted using the miniature nanosecond spark source (MNSS) developed in-house (136). Even though the MNSS is highly energetic, it is not capable of desolvation, atomization, and excitation of these solutions. This, no doubt, is due to the short duration and low duty cycle of the spark. In light of this, atomic absorption spectrometry (AAS) was chosen for the metal analyses.

2. Apparatus and Supplies

The AA analyses were carried out on a Varian AA-5 spectrometer (Varian Associates, Inc., Palo Alto, CA). Both air/acetylene and nitrous oxide/acetylene flames were used; these gases were supplied by high pressure tanks purchased from the Linde Corp. Background correction was achieved with a deuterium continuum hollow cathode lamp (HCL). The first eight fractions were redissolved in methyl isobutyl ketone (MIBK) purchased from Fisher Chemicals. The ninth fraction requires a 3:1 MIBK:pyridine mixture. Two standards were used for the method of standard additions.

One is an NBS standard, Standard Reference Material 1078b, which is tris(1-phenyl-1,3-butanediono)chromium(III) (NBS, Washington, D.C.). This was prepared in the prescribed manner with the necessary reagents (Aldrich Chemical Co., Millwaukee, WI), in a paraffinic base oil, purchased from Conoco Inc. (Ponca City, OK). The other standard is actually a blend of twelve metal-organic sulfonates in a paraffinic hydrocarbon oil matrix; this is known as Conostan-S12 and is available from Conoco Inc.

3. Experimental Procedure

The method of standard additions was found to be necessary for these metal determinations, due to the complexity of this matrix. The amount of sample for each determination is quite limited since the initial SESC sample is only 0.5 g of fuel, which is subsequently divided into nine parts. In addition, the metal levels in this fuel are no higher than 20 ppm; thus, each fraction contains a very small absolute amount of any metal. Even though fractions from several runs were combined, it is still necessary to keep the dilution with MIBK to a minimum. The resulting sample size was generally 3-10 mL, and so the standard additions were done in a serial fashion. Due to this fact, and because the standards did not pipet well, it was necessary to make these additions on the basis of weight. They must also be done rapidly due to the volatility of

MIBK. Once an initial concentration was calculated for a given fraction, the concentration in the original fuel must be calculated based on the sum of the absolute amounts of metal in each fraction sample. This was necessary because it was impossible to remove all the SESC solvent from each fraction by Rotovapping. No other method of solvent removal was desirable as it might destroy the original metal species.

The total amounts of metal which were obtained in this manner were then compared to an expected value obtained by a traditional ashing procedure conducted either in this laboratory, or elsewhere in laboratories which took part in the NASA interlaboratory study (47). The ashing procedure used was that prescribed in the NASA study. This involves the ashing of 3 g of whole fuel in a Vycor crucible with 1 mL of concentrated sulfuric acid, as an ashing aid. The crucibles were heated by means of a hot plate and an infrared lamp until the sample was charred. This took a week to ten days since the application of heat must be slow in order to avoid any loss of this very viscous material. Then the charred material was placed in a muffle furnace and heated at 450° C for two days. The ash was then dissolved in 1.5 mL hydrochloric acid plus 0.2 mL nitric acid, and diluted to 10.0 mL with purified water. This solution was analyzed by AAS, and the concentration was determined according to a calibration curve of aqueous standards. The

method of standard additions was not necessary since most of the sample matrix was destroyed by the ashing procedure.

The operating parameters for the AAS fuel determinations are given in Table 2. Many of these determinations could be done with an air/acetylene flame, with carefully determined flame conditions. However, a nitrous oxide/acetylene flame was necessary for chromium analysis due to its refractory nature. There was a problem with carbon build up when MIBK was aspirated into a nitrous oxide/acetylene flame. Use of the Varian's Auxiliary Gas Flow decreased the build up to some extent. The Auxiliary Gas provides a stream of oxidant around the nebulizer capillary, which helps to produce a more uniform aerosol and also decreases the residence time of the sample. However, this resulted in a loss of sensitivity and so was not advantageous in these studies. The best solution was to work quickly.

Another problem which has already been alluded to, was the necessity for background correction. Apparently there is some molecular absorption associated with the combustion of these fuel samples. Thus, the absorbance readings without background correction were too high, and resulted in an overall metal concentration which was much too high (as compared to the whole fuel values obtained by ashing). For some samples the background values varied as the standard additions were made. This has been attributed to both a

Table 2. AAS Parameters for Direct Fuel Analysis

Analysis	Flame	Slit Width (μm)	Lamp Current (ma)
Whole Fuel			
Cr (ashed)	A/A-O	70	5
Cr (@387.9nm)	N/A-R	70	5
Fe (@248.3nm)	A/A-O	50	5
Ni (@232.0nm)	A/A-R	75	5
SESC Fractions			
Cr (@387.9nm)	N/A-R	70	5
Fe (@248.3nm)	A/A-O	50	5
Ni (@232.0nm)	A/A-R	75	5

A/A=air/acetylene; N/A=nitrous oxide/acetylene
R=reducing stoichiometry; O=oxidizing stoichiometry
Slit height=5 for all experiments
Viewing height=15 mm except for Cr, viewing height=7mm

change in matrix composition, and an accompanying change in viscosity, which influences uptake rate. However, the use of background correction was found to produce reasonable values and log absorbance versus log concentration plots with slopes of 1-1.1, which indicate the absence of such physical effects. All readings were taken as percent transmittance, to avoid the possible introduction of inaccuracies by hardware logarithmic conversion.

An experiment was done to determine if there was any particle-size dependence in the analyses of these fuel samples. This was done by adding 10 mL of aqua regia to the fuel/MIBK samples with shaking (17). The results for these

samples were then compared to the results of analogous untreated samples.

D. Size Exclusion Chromatography (SEC) of SESC Fractions

1. Introduction

Size exclusion separations of the SESC fractions are useful from several standpoints. Obviously, these provide relative size information about the components of the different fractions. This is only relative size information as it is impossible to match an unknown matrix with appropriate standards. The elution profile also indicates whether any small components have been trapped within larger, highly functionalized components. This is extremely important in metal determinations since there is evidence that some small metal complexes exist in fuels (153); a specific example is aryl arsenic compounds. Thus, size exclusion is a particularly useful separation technique when the liquid chromatograph is interfaced to an element-specific detector. This type of experiment is discussed in a later section of this chapter. In addition, different elution patterns for the various fractions are further proof that some actual separation has indeed taken place, versus a simple dilution effect.

2. Apparatus and Supplies

These separations were done on a 500 Å Ultragel column, purchased from Analytical Sciences Inc. (Santa Clara, CA). This column contains a highly-crosslinked polystyrene-divinylbenzene (PS-DVB) stationary phase, which was packed under high pressure with chloroform. This column is reported to have a 500-10,000 molecular weight range. Chloroform is the mobile phase used in these experiments. Chloroform was chosen because it exhibited less absorptive effects than THF in model compound studies and provides UV-transparency which is necessary with a UV-detector. The chloroform was purchased from Burdick & Jackson Laboratories, Inc. (Muskegon, MI). It was filtered before use by means of a Millipore (Waters Associates) 47 mm diameter filter with 0.45 μm pore Nylon-66 filters (Rainin, Woburn, MA). Monodisperse polystyrene standards having nominal molecular weighs of 17500, 9000, 7500, 4000, and 2000 were used for calibration. These were purchased from either Waters Associates (Milford, MA) or the Pressure Chemical Co. (Pittsburgh, PA). The column efficiency of the Ultragel column was determined repeatedly to monitor column deterioration. This was done by making plate count measurements. These were done with a 2% solution of o-dichlorobenzene (Mallinckrodt).

The HPLC pump/solvent delivery system used in all the HPLC experiments reported in this paper was the

Spectra-Physics SP8700 (Spectra-Physics, San Jose, CA). This is an intelligent solvent delivery system which consists of a dual-piston reciprocating pump with a ternary proportioning valve at its inlet. This allows mobile phase mixing for both isocratic or gradient operation. A Rheodyne injection valve (Rheodyne, Berkeley, CA) equipped with a 20 μL sample loop, was used with this system. The detector was a Chromatronix 220 (Chromatronix Inc., Berkeley, CA). This is a mixed-wavelength UV-absorption detector, equipped with a 20 μL flow cell. It was used at 254 nm in all experiments reported here.

3. Experimental Procedure

The PS-DVB packing of the Ultragel column was found to be extremely fragile in that in cannot withstand any pressure shocks. This extends even to column start-up. The column must be brought up to the desired flow rate gradually. In order to avoid column damage the solvent was initially pumped at 0.1 mL/min; this was increased in 0.1 mL/min increments, every two pump cycles, until an operational flow of 1.0 mL/min was reached. This process takes approximately 45 min under manual control.

The whole fuel was dissolved in chloroform, and then filtered through a Nylon-66 filter to remove any undissolved material. The SESC fractions were first Rotovapped and then allowed to air dry for several months, in an effort to

remove all of the SESC solvent. These fractions were then dissolved in either chloroform, or a chloroform/THF mixture, before injection. Injections were performed by filling the injector's 20 µL sample loop.

E. Other Single-Column HPLC Separations of SESC Fractions

1. Introduction

One approach to more complete speciation of the metals present in the SESC fractions, is to do further chromatographic separations which provide additional chemical information. The initial studies of this type involved single column separations of the SESC fractions. Three types of stationary phases were tried: a silica, an amino-bonded phase, and an octadodecylsilane (ODS) bonded phase.

2. Apparatus and Supplies

Two different silica columns were employed. One is a 5 µm Perkin-Elmer (Norwalk, CT) High Speed column, 14 cm x 0.25 " x 4.6 mm (i.d.). The other is a 5µm Hibar-II purchased from EM Reagents (Cincinnati, OH), which is 25 cm x 0.25 " x 4.6 mm (i.d.). An Applied Science (State College, PA) pre-SAT column was used with these columns, both to dry and condition the mobile phase. This column (25 cm x 0.25 " x 4.6 mm) was dry packed with 50 µm

pellicular silica. The amino-bonded phase and the ODS bonded reverse-phase columns are 5 μm Spherisorb packings in 25 cm x 0.25 " x 4.6 mm (i.d.) columns from Alltech Associates (Deerfield, IL). All solvents were LC/UV-grade from Burdick & Jackson Laboratories, Inc. (Muskegon, MI). These are filtered before use as described above. Model compounds were purchased from the Aldrich Chemical Co. (Millwaukee, WI).

3. Experimental Procedure

Various chromatographic conditions were tried in an effort to affect the best separation for the SESC fractions. Generally, the fraction was dissolved in the mobile phase being used. Long-term solubility tests were necessary in some cases as there was a concern that some of the material would be insoluble. Particulates would be caught by the frit at the inlet of the column resulting in an increase in backpressure. Gradient elution was necessary with most of these samples due to the presence of components having widely varying polarity. Model compounds were subjected to the same chromatographic conditions to investigate the separation mechanism on the amino column in particular, and to aid in the interpretation of the fuel chromatograms. Sample chromatograms are presented in the 'Results' section of this thesis.

F. Computer-Controlled Multidimensional HPLC Separations

1. Introduction

Figure 1 is a single-column chromatogram of the second SESC fraction. The envelope structure which underlies the prominent peaks is typical of fuel separations. It is no doubt due to the existence of many isomers and homologues which exhibit similar chromatographic behavior. Unfortunately, this behavior prevents the analyst from extracting specific chemical information from these chromatograms. Further separation is necessary to obtain this information, but this is difficult to obtain with a single-column separation. Therefore, an automated multidimensional HPLC system has been implemented as part of these fuel studies. Several different column-switching techniques have proved applicable.

Mode-coupling refers to a technique which connects two columns of different separation modes. This technique is useful in providing additional information about the fuel samples. In one experiment a normal phase column and a normal-bonded phase column were coupled to provide improved resolution of a fuel sample. In another case, the multidimensional system has been configured for heartcutting. Heartcutting is the technique in which a specific fraction of the effluent from one column is

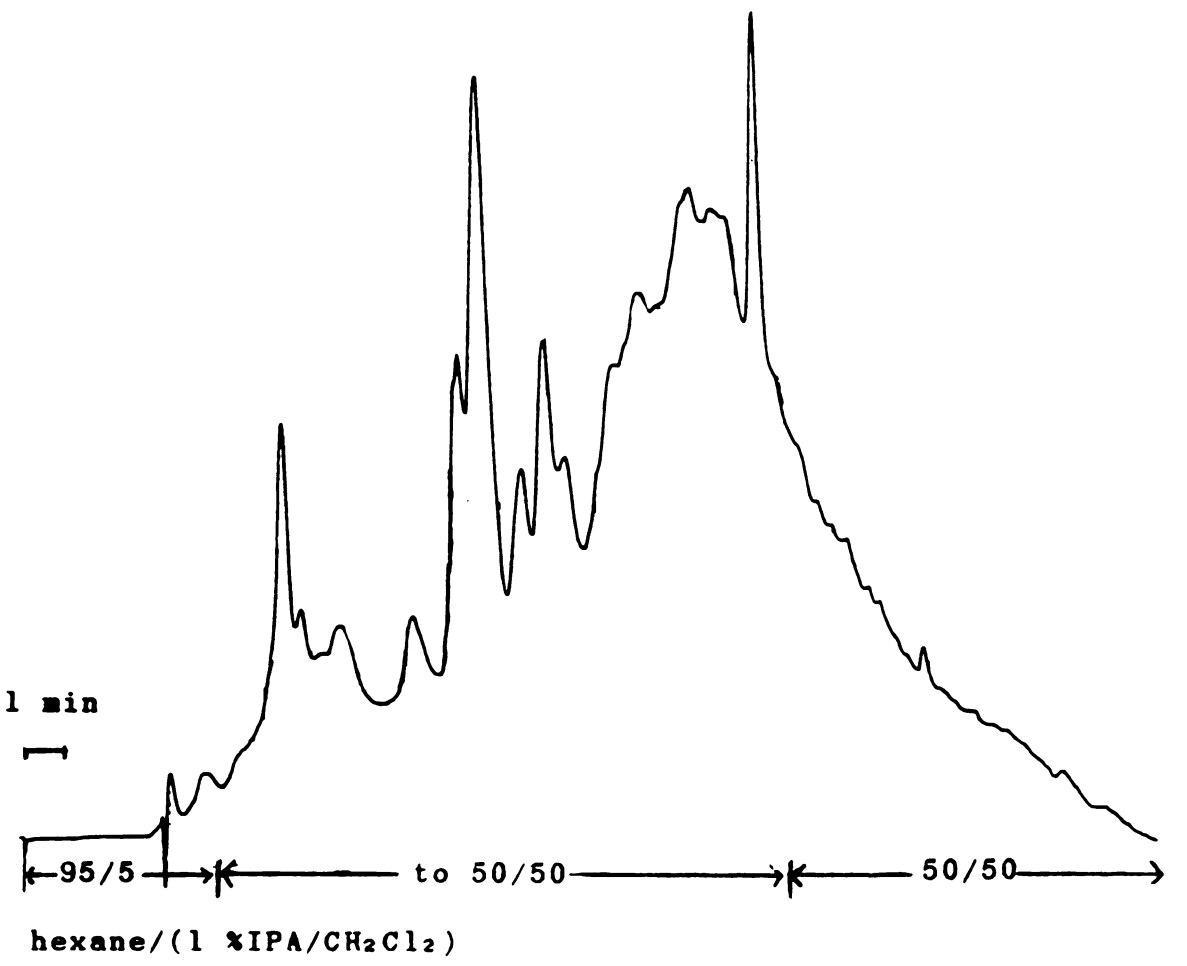


Figure 1. Single-column separation of SESC fraction 3; amino column.

directed onto another column, for further separation. This technique has been used to study SESC fractions 2 and 3 by coupling a silica and an amino column. A similar arrangement has been employed to perform a size exclusion separation, on the Ultragel column, in conjunction with a polarity separation, on the ODS column. This produces a size-polarity matrix to characterize the fuel. In addition to the column-switching hardware necessary for this experiment, another valve was configured to create an autoinjector. This executes repeated injections without operator intervention and thus speeds up the analysis.

Backflushing refers to the technique of reversing the flow in a chromatographic column. It is not a true multidimensional technique, since only one mode of separation is employed, but is a useful column-switching technique. Backflushing has been successfully applied to these fuel studies in several ways. First, it is good for column clean-up. Second, all components which are backflushed off a column generally elute in twice the backflush time; thus the analyst knows when all components which will elute, have eluted. This is particularly helpful when studying samples with an unknown number of constituents. Backflushing can also reduce analysis time, and improve the peak shapes of late eluters. This is illustrated in figures contained in the 'Results' section of this paper. Gradient elution can also shorten analysis time

and improve peak shapes of late eluters; however, it necessitates column reequilibration (which is often time-consuming), before the experiment can be repeated, and it does not provide the analyst with any indication of when all components have eluted. Finally, backflushing with a stronger mobile phase can be used to remove highly retained materials from one column so that they can be separated on a second column with a more appropriate stationary phase. This technique has been entitled 'Selectivity Programming with Backflush'.

2. Apparatus and Supplies

a. HPLC Components

The columns and solvents used were those described above. It should be noted that all the columns contain spherical packings. This type of packing is recommended for backflushing to avoid the formation of voids and channels upon flow reversal. The 0.25 " x 4 cm x 2.1 mm (i.d.) precolumn used in the 'selectivity programming with backflush' experiment was purchased from Upchurch Scientific, Inc. (Oak Harbor, WA). It was dry packed with 40 µm pellicular amino-bonded phase packing, purchased from The Anspec Co., Inc. (Ann Arbor, MI). The tubing used in the multidimensional system was either 1/16 " x 0.030 " (i.d.), x .010 " (i.d.) purchased from The

Anspec Co., Inc., or 1/16 " x 0.009 " (i.d.) purchased from Waters Associates (Milford, MA). Upchurch Scientific 'Fingertight' fittings were used whenever possible. A Gilson FC-80 Micro-Fractionator (Gilson Medical Electronics, Inc., Middleton, WI) automatic fraction collector was used in the autoinject experiments.

b. Instrumentation

The computer-controlled multidimensional HPLC system is depicted in Figure 2. It consists of four basic components: a microcomputer based on the 8085 microprocessor (Intel Corp., Santa Clara, CA); the SP8700 solvent delivery system; a flexible valving arrangement consisting of one to three 6-port, 2-position, low dead-volume Rheodyne valves with air actuators; and the Chromatronix 220 UV detector. The SP8700 solvent delivery system has two attributes which make it ideal for multidimensional experiments. One is that it can handle multiple mobile phases. The other is its ability to respond quickly to changes in back pressure which accompany column switching. The heart of the multidimensional system is the microcomputer which was designed and constructed in-house (95). The microcomputer functions in three capacities. The microcomputer is used to acquire data. Therefore, it is interfaced to the Chromatronix detector and to an LSI 11/23 minicomputer (DEC, Merrimack, NH). The latter interface is part of a

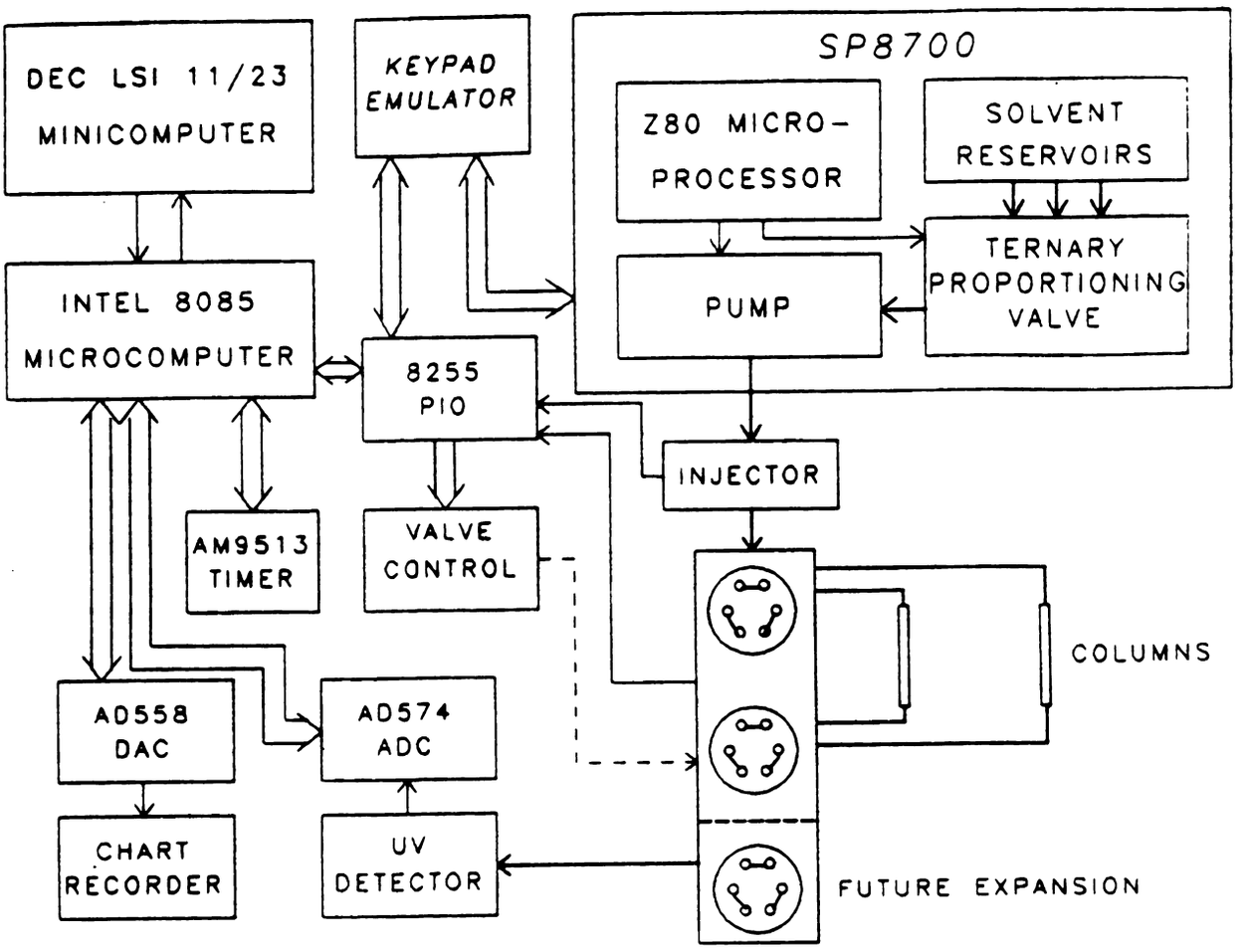


Figure 2. Block diagram of the multidimensional HPLC instrument.

hierarchial computer system; the minicomputer provides software storage, data storage, and data manipulation. The microcomputer also controls the column switching valves. This is accomplished by an optically-isolated relay circuit, which controls the operation of the air actuators via a solenoid. Finally, the microcomputer controls the SP8700 by way of a novel interface known as keypad emulation (149). The keypad emulation circuit allows the microcomputer to simulate a keystroke on the the SP8700's keypad. Thus, the microcomputer can order and synchronize MHPLC experimental events, such as valve switching and mobile phase changes. The interface in no way interferes with the SP8700's stand-alone capabilities. For further detail concerning these circuits see reference (149).

c. Software

P.M. Wiegand wrote the microcomputer operating system (148) using the polyFORTH (FORTH, Inc., Hermosa Beach, CA) version of FORTH. FORTH is a computer language which is designed for instrument control. It is a threaded language, and allows the construction of high level command words from basic kernal commands. This combination produces a powerful control language which is tailored to the application. The operating system which P.M. Wiegand designed includes mnemonics which are the same as the labels on the SP8700's

keypad; Table 3 summarizes the basic control words which are available.

Table 3. Multidimensional HPLC FORTH Control Words

Valve Control	
n CCW, n CW	Turn valve n and check validity (n=1 to 4)
SP8700 Communication	
k PRESS	Presses one key with code k
k1, k2, kn ENTER	Presses series of keys, then ENTER
n ENTER#	Converts number to key codes, then presses the keys and ENTER
Synchronization	
CLOCK	Starts micro clock counting from zero
INJECT	Starts micro clock upon injection
SYNC	Starts micro clock and SP8700 clock synchronously upon injection
Event Sequencing	
m,s EVENT	Delays m minutes and s seconds after inject
h WAIT	Delays h hundreths of seconds
#PEAKS	Variable which contains the peak count since inject
n +%FS, n -%FS	Delays until signal rises/falls to n% full scale
n %FSCHG	Delays until signal changes by n% full scale

The FORTH routines for multidimensional experiments are easy to write, read and change. In addition, since the microcomputer's operating software is stored on disc by way of the LSI 11/23, these routines can be stored and reused. The Ultragel start up routine, which is displayed in Figure

3, is a prime example of a routine that is often reused, even within other multidimensional programs.

This is a very user-friendly system which requires a minimum of computer expertise to use. Nonetheless, the user still has access to the full power of a computer language which provides capabilities such as conditional execution (also illustrated in Figure 3).

3. Experimental Procedure

a. HPLC Sample Preparation

Sample and mobile phase preparation were identical to that described previously.

b. HPLC Plumbing and Procedure

Figure 4 presents a variety of ways in which the column-switching valves can be configured. These can be used individually or in selected combinations to execute a number of different multidimensional experiments. It is important to keep the length of connecting tubing to a minimum, in order to minimize band-broadening. The need for this was investigated by a band-broadening experiment. The band-broadening experiment compared the peak shape for a single component eluted from an analytical column, to the peak shape for the same component when two valves, with

```
Block Number:  48
0   ( STYRAGEL STARTUP )
1
2 : STY SETUP EDFI #0 ENTER 7 0 DO DELI PRESS \/ PRESS LOOP
3   %C #1 #0 #0 ENTER EDRU PRESS
4   INIT #0 ENTER #9 #8 #7 #6 #5 #4 #3 #2 #1
5   9 0 DO FLOW PRESS #. PRESS PRESS ENTE PRESS PRES PRESS
6   I 0= IF ." Waiting for cam" CR CAM THEN 30 SEC
7 ." Waiting for cam" CR CAM 5 DELAY CAM 5 DELAY LOOP
8   FLOW #1 #. #0 ENTER  FLOW? ;
9  ( NOTE -- ASSUMES THF IS IN RESEVOIR C
10          Uses file # 0, clears file first.
11          Raises flow in 0.1 ml/min increments every 30 sec
12          plus one cam marker.
13          Waits for flow ready @ 1.0 ml/min.
14 Instrument should be in edit mode.  Type STY to start.)
1538 LIST
```

Figure 3. FORTH Routine for size-exclusion column start-up.

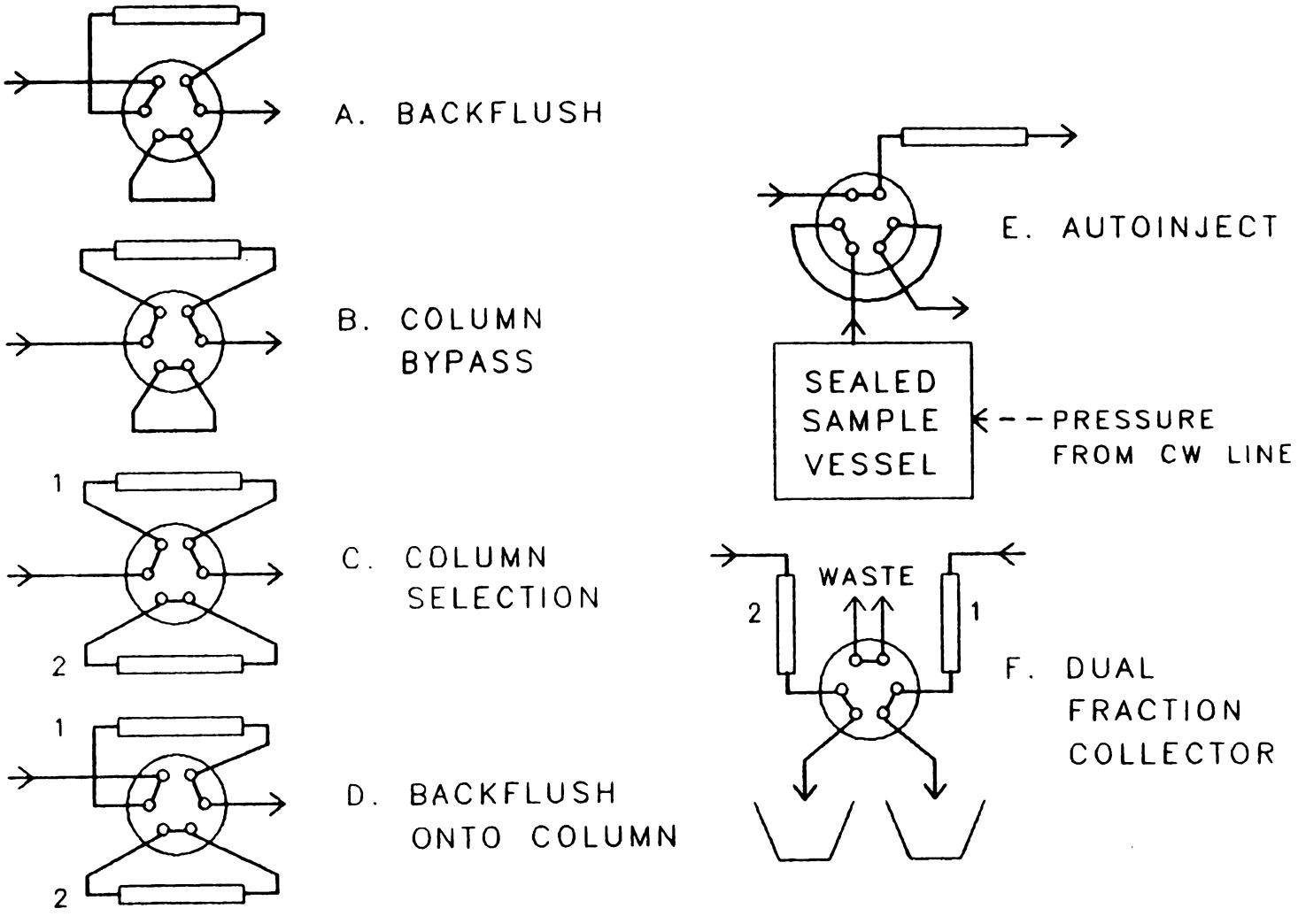


Figure 4. Possible configurations of a 6-port, 2-position valve.

their full complement of tubing, were in-line after the column.

The results of a number of single valve experiments are presented in the next chapter. These include autoinjection, heartcutting and backflushing. The column switch times were determined by preliminary separations and were done on the basis of elapsed time. Solvent changeover is often necessary before the development of a heartcut. This will lengthen analysis time; however, since this is an automated system, the chromatographer is free to pursue other activites during analysis time.

A two valve MHPLC system is much more powerful and often more convenient than a single-valve system. For example, solvent changeover time can be much faster when directed through a bypass loop, and column reequilibration can often be avoided completely. The two-valve experiments conducted include mode-coupling with backflush, selectivity programming with backflush, and two valve heartcutting. Once again the column-switching times for these experiments were determined by preliminary separations.

The two valve heartcutting experiment, discussed in the next chapter, coupled the Ultragel column with the ODS column to produce a size-polarity matrix. This involved directing 0.5 mL cuts of the Ultragel effluent onto the ODS column. Either chloroform or THF could be used to develop the Ultragel column. Correspondingly either a

water/acetonitrile(AcN), or water/THF, mixture was used for the ODS column. The strength of the reverse-phase eluent had to be adjusted so that the components of the cut eluted after the detector output disturbance, which occured at the ODS void volume. This disturbance was apparently a result of transfering such large cuts onto a column equilibrated with different mobile phase (148). Care was necessary when writing the experimental operation routine to ensure that none of the aqueous mobile phase (water/THF or water/acetonitrile) was left in the connecting tubing when the flow was redirected to the Ultragel column. The PS-DVB packing cannot tolerate water. In addition, PS-DVB cannot withstand pressure shocks. Therefore, it was necessary to insert a pressure restrictor into the bypass loop of the column bypass valve, which approximated the backpressure of the ODS column. This way the Ultragel column saw little change in backpressure when the heartcut was made. In addition it was necessary to bring the Ultragel column up to flow gradually, as discussed earlier, and to reinject each time another cut was desired. Thus, this is a very lengthy experiment, which is greatly facilitated by this microcomputer-controlled system.

G. HPLC(MHPLC)/Element-Specific Detector Interface

1. Introduction

There is a great deal of interest in interfacing HPLC systems to element-specific detectors, as is discussed in the historical chapter of this paper. It is a promising means for obtaining metal speciation information for fuels and other complex samples. Unfortunately, achieving such an interface is not trivial. Nonetheless, it was possible to interface the SP8700 solvent-delivery system to the Varian AA-5, atomic absorption spectrometer. However, this technique met with a limited amount of success for fuel analyses. Atomic absorption detection limits were not low enough to measure the metal concentrations present in the fuel. An HPLC/ICP interface has also been investigated. This is more promising since ICP detection limits are generally lower than AA detection limits. However, there are several experimental considerations discussed previously, which make a useful interface difficult to achieve. Even so, this should be a promising technique with some modification of the existing ICP.

2. Apparatus and Supplies

a. AA Experiments

Teflon tubing was used to direct the HPLC effluent into the AA nebulizer. The 'dripping cup' interface, Figure 5, consists of a Teflon pipet tip, which is connected to the nebulizer capillary by a piece of Teflon tubing. The nickel diethyldithiocarbamate ($Ni(dtc)_3$) used in the band-broadening and sensitivity studies was synthesized in this laboratory.

b. ICP Experiments

The ICP consists of a Plasma-Therm, Inc. (Kresson, NJ) ICP 25100 torch. This is used with a Plasma-Therm RF Generator type HFP 2500D. Both a concentric nebulizer and a crossed-flow nebulizer have been employed. Aqueous solutions were prepared from water that was distilled in glass, while nonaqueous solutions were prepared from reagent-grade solvents. Reagent grade iron(III) chloride (Fisher Chemicals) and the Conostan S-12 standard were used for detection limit determinations. The SP8700 effluent was directed into the nebulizer with Microline tubing (Thermoplastic Scientifics, Inc., Warren, NJ).

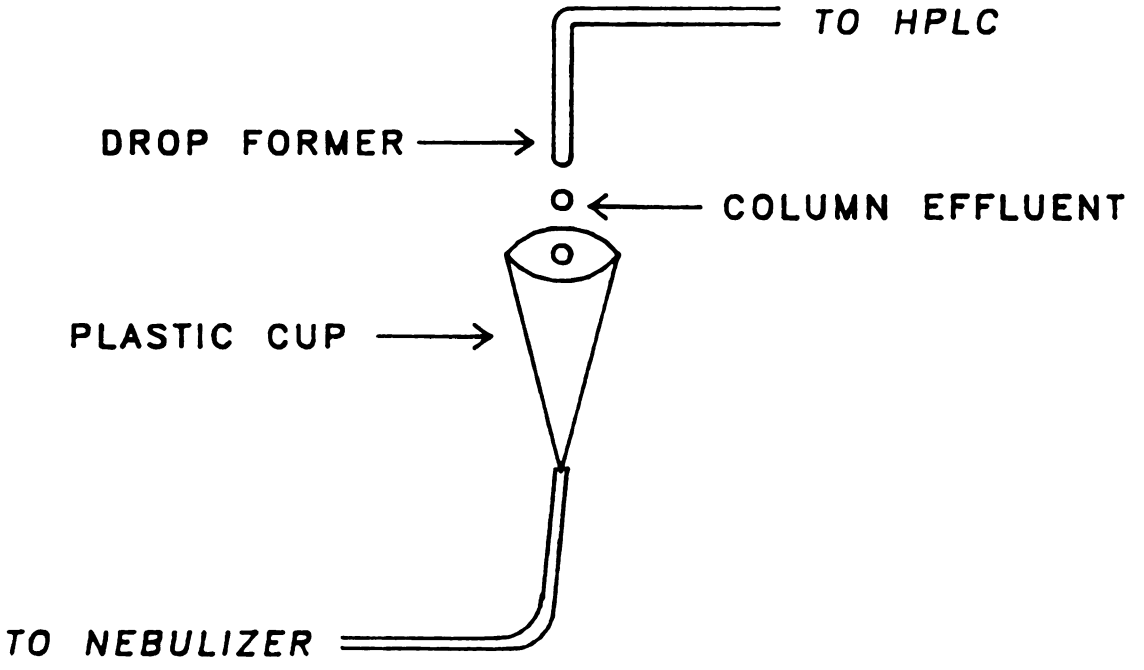


Figure 5. Dripping cup HPLC/AA interface.

3. Experimental Procedure

a. AA Studies

The $Ni(dtc)_3$ was synthesized from nickel(II) nitrate and sodium diethyldithiocarbamate in a warm (60° C) aqueous solution. The product was filtered, washed with water to remove any unreacted ligand, and recrystallized from chloroform.

Band-broadening was investigated by injecting an aliquot of $Ni(dtc)_3$/methanol solution onto the ODS column. The mobile phase was also methanol. The HPLC effluent was fed into the AA nebulizer, and the AA output was followed on a recorder. A similar study was done using a 'dripping cup' interface. With this interface, the HPLC effluent drips out of the end of the column, into the cup; the drop is then swept into the AA nebulizer. This technique produces a series of spikes. Thus, a band-broadening experiment was not possible with this interface. The object of the 'dripping cup' interface is to allow both the HPLC and the AA nebulizer to function at their optimum flow rates. In addition, this 'starvation' mode of nebulizer operation has been reported to be more efficient, which should improve detectibility (121). However, there is a trade off between this effect and the fact that small drops often do not introduce enough metal into the flame to be observable. The AA technique is mass sensitive.

The detectability of the HPLC/AA technique was determined with the direct interface. This was done by injecting a series of $Ni(dtc)_3$/methanol solutions in the concentration range from 80 to 8 ppm Ni.

The direct interface was also used to determine chromium in SESC fraction 6. This fraction was separated on the ODS column with methanol. This setup was also applied to the determination of nickel, iron and chromium in the whole fuel after it had been eluted from the Ultragel column with chloroform.

b. ICP Studies

The band-broadening introduced by the interface of the ICP to the HPLC was investigated in a manner similar to that for the HLPC/AA setup. However, it was not possible to use an actual HPLC peak as was done in the HPLC/AA study. This was due to the problems associated with introducing an organic solvent such as methanol into the plasma; these problems are detailed in a later section. In addition, a water-soluble metal complex which could be eluted off the ODS column was not readily available. Instead, the SP8700 was used to pump water through a pressure restrictor which was installed before the injector. An aqueous solution of ferric chloride and acetone was then injected. This plug then passed through the UV-detector and on to the ICP for analysis.

The detectability of the ICP technique for both aqueous and organic solutions was determined and compared. The aqueous solution was the ferric chloride solution. The organic solution consisted of Conostan S-12 diluted with MIBK. MIBK was chosen for this study because it afforded the greatest plasma stability of all the organic solvents which were tried. These include ethanol, methanol, and chloroform. A sensitivity for the aqueous HPLC/ICP was determined in much the same way as for the HPLC/AA setup. However, the organic versus aqueous study was done by aspirating the solutions directly into the nebulizer. This was necessary because of the poor detection limits observed for the organic solution, and due to the fact that the plasma was not stable indefinitely. The concentric nebulizer was used as it demonstrated the most stable uptake rate. The plasma parameters for the organic solution studies were 2.0 kV, 19 L/min 'plasma gas' (tangential support gas), 1.6 L/min 'auxiliary gas' (central plasma support gas), 0.6 on the flow gauge for the nebulizer gas (4 psi on the pressure gauge). The uptake rate was about 0.5 mL/min. The plasma parameters for the aqueous solutions were 1.5 kV, 12 L/min 'plasma gas', 1.4 L/min 'auxiliary gas' and 0.8 on the nebulizer flow gauge (20 psi on the pressure gauge). The argon tank pressure was set at 50 psi.

IV. RESULTS AND DISCUSSION

This chapter is divided into six major sections. Each deals with a different phase of this investigation, delineated along the same lines as the previous chapter. The experimental results are presented along with a discussion of their significance.

A. SESC Separations

1. Verification of the Appicability of the SESC Procedure to Residual Fuel #3

Since SESC was developed for solvent-refined coal, it was important to verify that the SESC procedure would fractionate the residual fuel being studied into the expected compound classes. Two means of verification were employed. One involved subjecting model compounds to the SESC procedure, and monitoring their elution behavior. The other involved infrared studies of the compound class fractions produced by the SESC separation of the residual fuel.

a. Hydrocarbon Model Compound Studies

The elution behavior for the model compounds was determined by either infrared, or UV-visible spectroscopy. The results were then compared to the behavior predicted for these compound types by the SESC procedure. Table 4 summarizes these results.

Table 4. Hydrocarbon Model Compounds and Their SESC Behavior

Compound	SESC Fraction		Method of Verification
	Observed	Predicted	
tetradecane	1	1	IR
octene	1	1	IR
naphthalene	2	2	HPLC
furan	3	3	HPLC
indole	3	3	HPLC
dibenzothiophene	3	3	HPLC
phenol	4	4	IR
cholesterol	4	4	IR

b. Infrared Studies of the Residual Fuel SESC Fractions

This study involved the infrared analysis of the fractions produced by the first SESC separations of the residual fuel. The results of this study are displayed in Figures 6, 7, and 8. As can be seen, the spectra are different for each fraction, indicating that a chemical separation has taken place. In addition, these spectra do contain some features specific to the type of compounds which should be present. For example, the spectra for

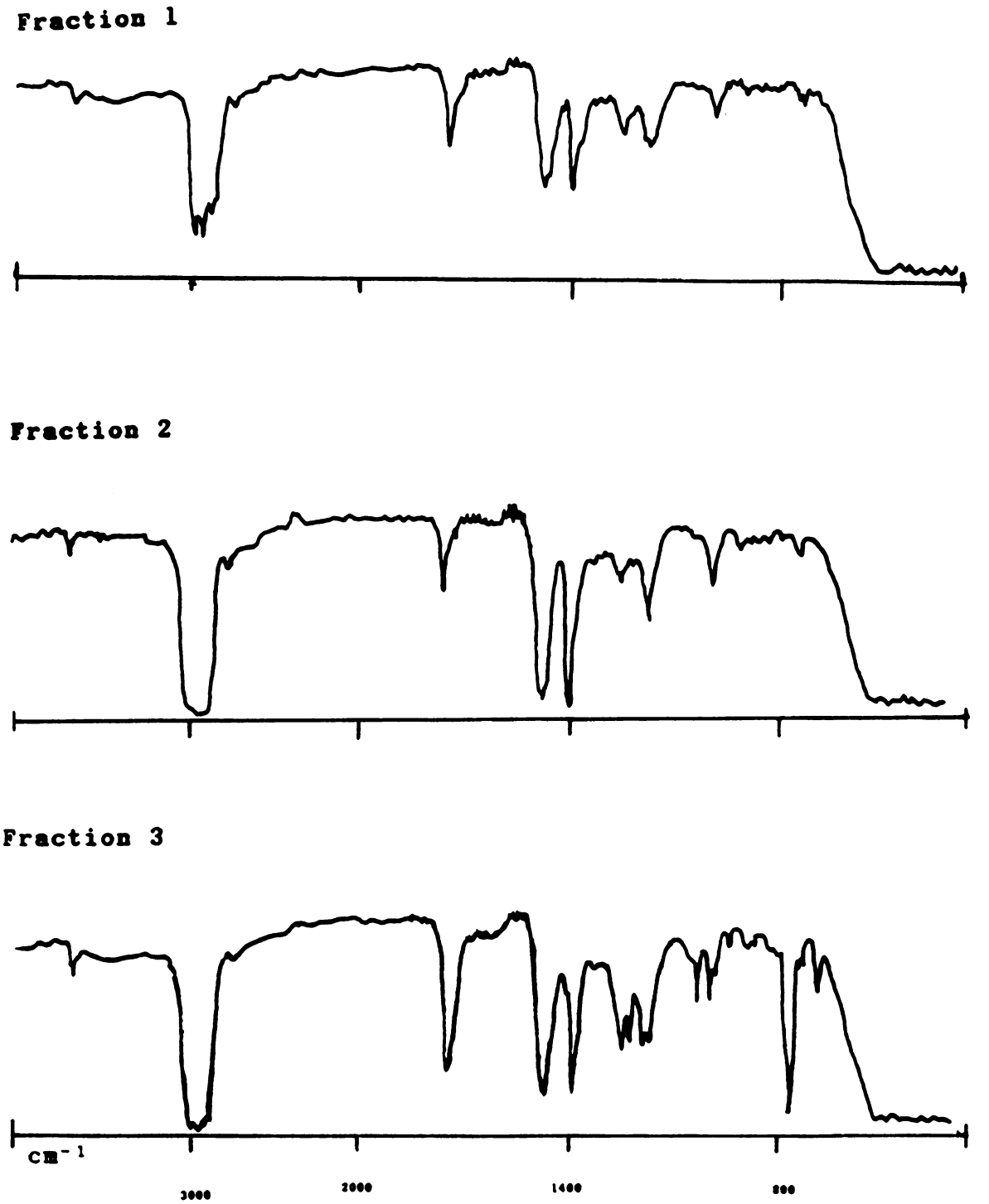


Figure 6. Infrared spectra of SESC fractions 1-3.

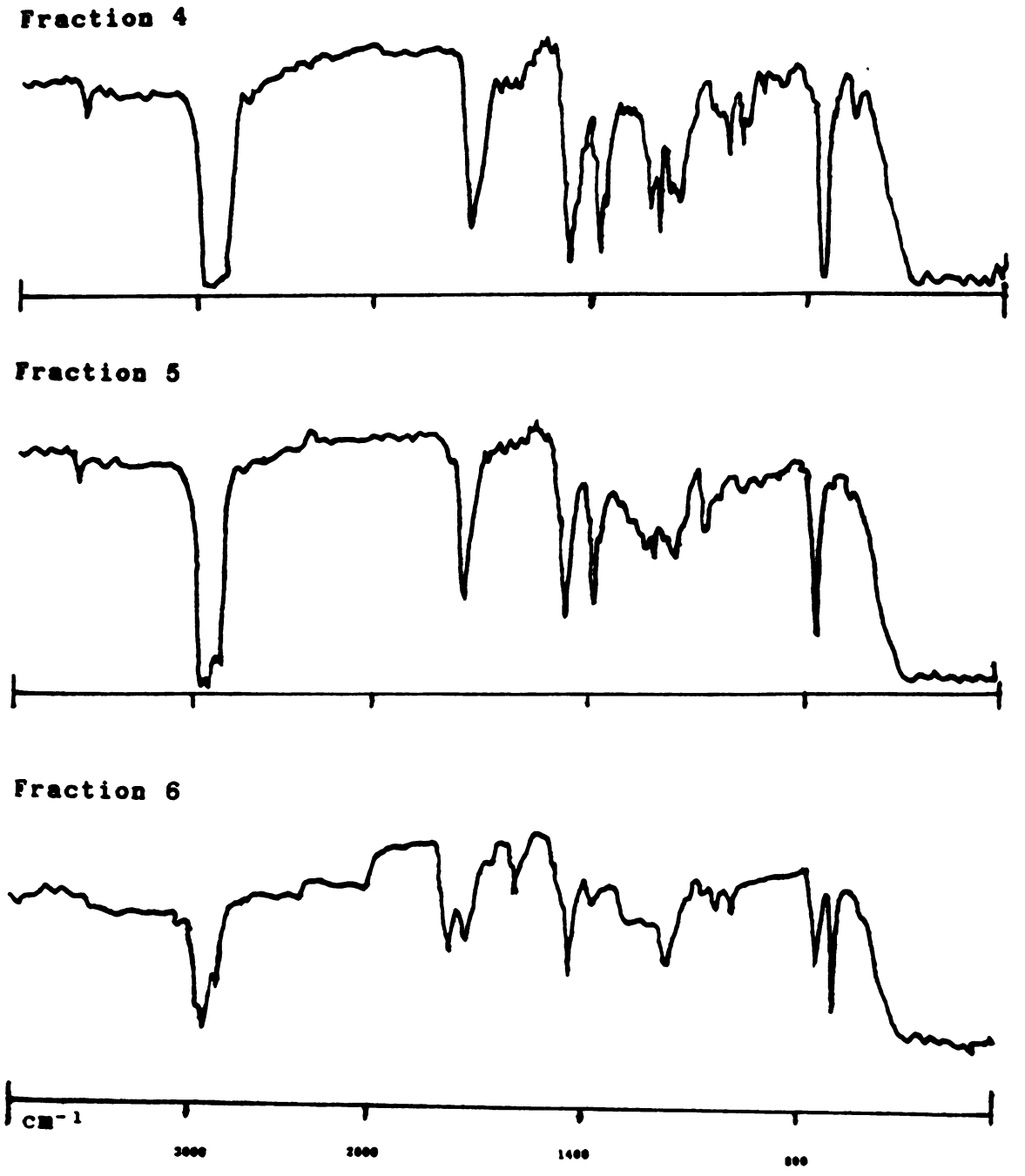


Figure 7. Infrared spectra of SESC fractions 4-6.

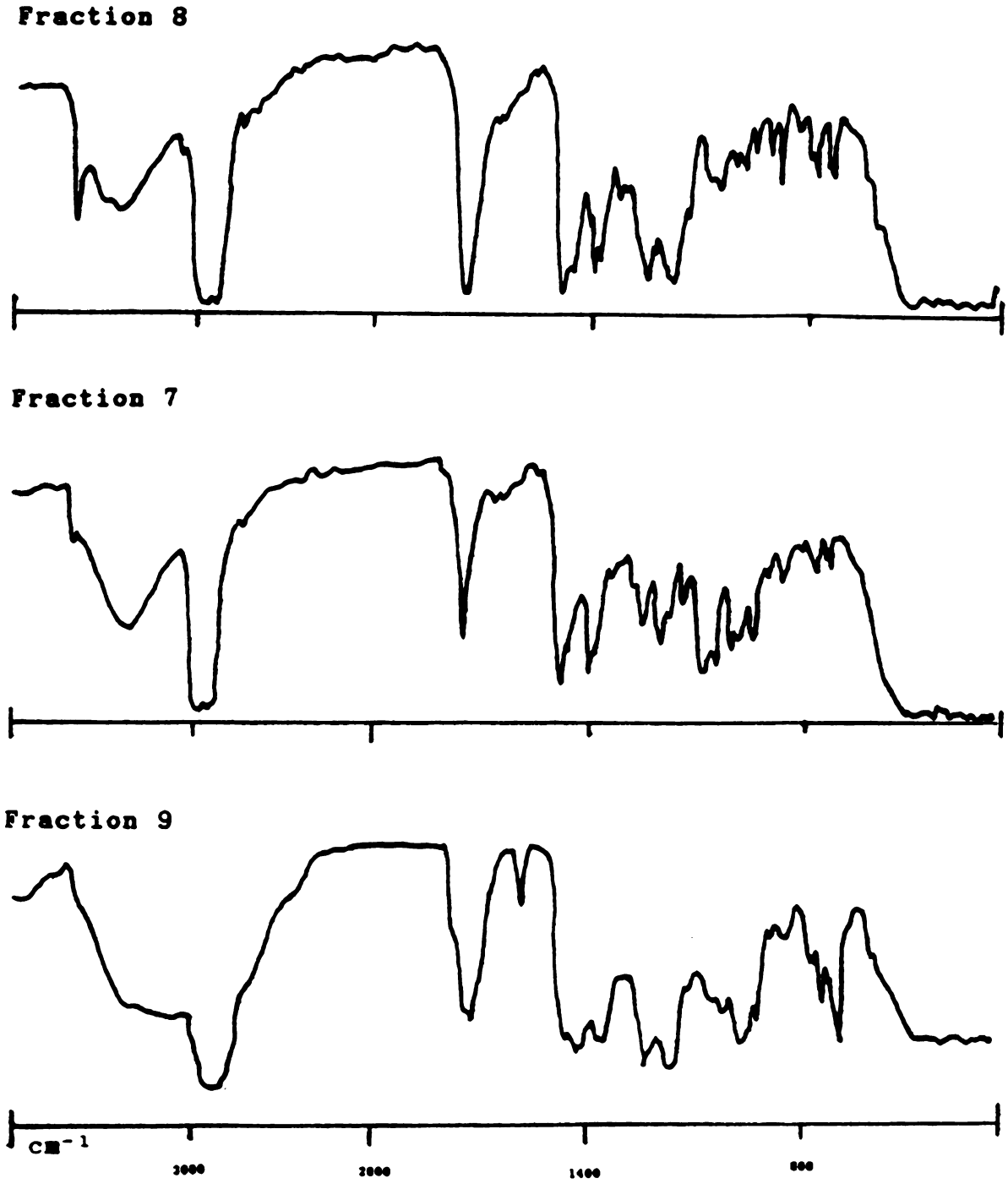


Figure 8. Infrared spectra of SESC fractions 7-9.

fractions 7 and 8 exhibit phenol bands in the 3300-3500, 1050, and 1150 cm^{-1} regions. These fractions are expected to contain polyphenols. There are 1150-1240 cm^{-1} ether, 1060 cm^{-1} amine, and 750 cm^{-1} halogen absorptions in the spectra for fractions 3, 4, and 5, but not in the preceding spectra. The spectrum for fraction 9 exhibits very broad, strong absorbances as might be expected for highly functionalized compounds. There is some overlap observed when the spectra for adjacent fractions are compared. This is due to the fact that the gravity-fed system did not produce compact bands. Also the eluent volumes and collection technique employed were not optimized at the time this first experiment was run.

2. SESC Behavior of Metal-Containing Model Compounds

a. Results

Another important question in this research is whether the SESC chromatography of the metal-containing species in the fuel is determined by the organic part of the complex. This was investigated by chromatographing a series of metallated tetraphenyl porphines (TPP), and the nonmetallated analog. These were chosen because they exist naturally in petroleum, and they are one of the few types of complexes in which the nonmetal-containing version has

approximately the same shape, size, and chemical configuration, as the metal-containing species.

The results of the SESC separations of the porphyrins are depicted in Figure 9. In addition, this figure contains the results of the SESC separation for some other metal complexes. UV-Visible absorption spectroscopy of the SESC effluents was used to determine into which fraction each complex eluted.

b. Discussion

The metallated porphyrins did not all chromatograph into the same SESC fraction as the nonmetallated TTP did. This indicates that the metal does influence the chromatography of these complexes, even in a gross scale separation. However, the discrepancy is not large. When the complexes do not elute as predicted, they do elute in an adjacent fraction. In some cases this can be explained by considering the metal's coordination number, and most commonly associated complex configuration, e.g. whether the complex readily distorts its structure to add solvent molecules. For example, the nickel acac and dtc complexes are both square planar and readily take on solvent molecules.

The behavior of the loosely associated complexes is quite pertinent because some of the metals in petroleum may well be of this type. It is reasonable that this type of

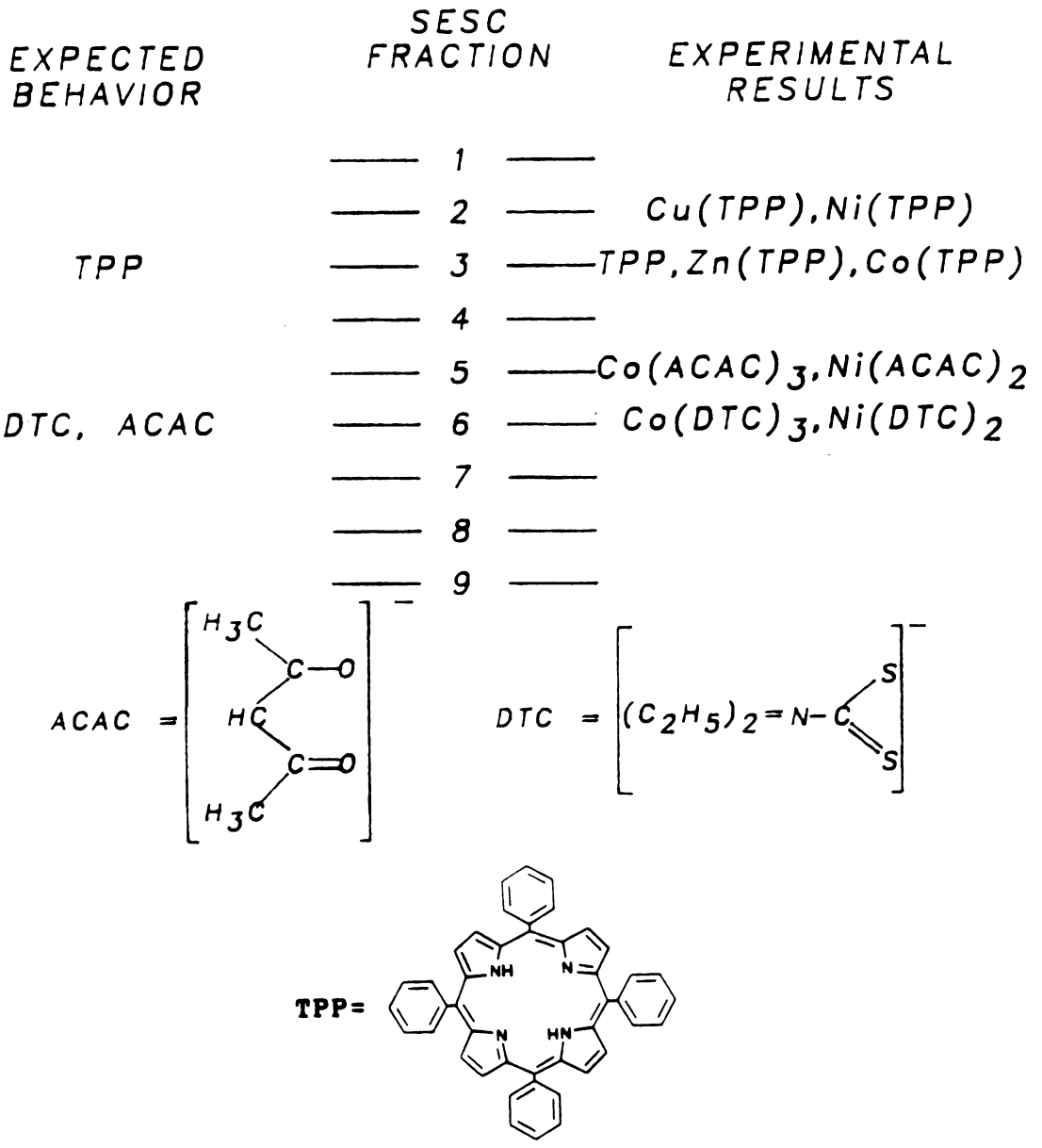


Figure 9. SESC behavior for stable metal complexes.

species is less apt to chromatograph as predicted. This was investigated by subjecting two fairly unstable metal complexes to SESC. These were dibenzene chromium and ferric phenolate. Neither eluted as predicted, however, there is a difference in their behavior. The chromium dibenzene was visually observed to begin eluting with the third SESC solvent mixture. The UV-spectra of the eluent provided evidence that some of the chromium dibenzene did elute off the column with this solvent. The fact that this was one fraction late is not surprising as the aromatic rings would definitely be affected by the associated metal, possibly in somewhat the same manner as a heteroatom. More colored material eluted with the next two solvents. These colored species were assumed to contain chromium since the uncomplexed ligand would be colorless. Atomic absorption confirmation would be appropriate. The exact nature of the chromium's chemical environment was not certain. However, the UV-spectra determined that it is different from the original complex. Apparently the dibenzene chromium did interact with the chromatographic solvents to a considerable extent. However, the iron present in the ferric phenolate did not spread. This species did elute a fraction early. This could be explained in a couple of ways. The iron may possibly tie up the phenolic group, interfering with its interaction with the silica silanol groups. Another possibility is that the metal complex interacted strongly

with the chloroform mobile phase and so did not interact with the silica.

Thus, metal speciation information and distribution profiles, based on a separation of this type, must be interpreted very cautiously. Elution of metal-containing species with the fourth fraction does not ensure that they are associated with monophenols. They may well be associated with neighboring type compounds instead.

Obviously, further study of the actual species present would be necessary. It is possible that not only the metal, but also the chromatographic mobile phase, influences the elution behavior of metal complexes. This could possibly be studied by substituting mobile phases which have the same elutropic strength, but different selectivity, e.g. different dipole or proton-donating capabilities. Such pairs could be chosen based on the Snyder solvent classification scheme (124).

There is a great deal of band spreading observed with these model compounds. This means that the fractions containing metal complexes may require an unusually large amount of solvent for complete elution. This may indicate that silica is not an ideal stationary phase for the separation of these types of materials. Nonetheless, some useful information can be obtained by this method as is illustrated below in the discussion of the fuel separations.

B. Metal Determinations in SESC Fractions

1. Experimental Results

The amount of chromium, iron, and nickel in each SESC fraction was determined by AAS. The chromium determination was done at 387.9 nm with a reducing nitrous oxide/acetylene flame and the NBS standard previously described. The iron determination was done at 248.3 nm with an oxidizing air/acetylene flame. The nickel determination was done at 232.0 nm with a reducing air/acetylene flame. The standard additions in both these determinations were done with Conostan S-12. Three standard addition plots, representative of these determinations, are presented in Figures 10, 11, and 12. These plots are one each from the chromium, iron and nickel determinations. Each data point is denoted by an asterisk. The pair of dotted lines on either side of the solid linear regression line represent the 95% confidence limit associated with the regression. The origin for each of these plots is at a negative concentration value due to the nature of the standard addition method. Figure 13 is a composite of the log absorbance versus log concentration plots associated with the previous three figures. Linear regression of the log concentration versus log absorbance data produces lines having slopes of 0.98 for chromium, 1.1 for iron, and 1.1 for nickel. These values indicate that there are no major

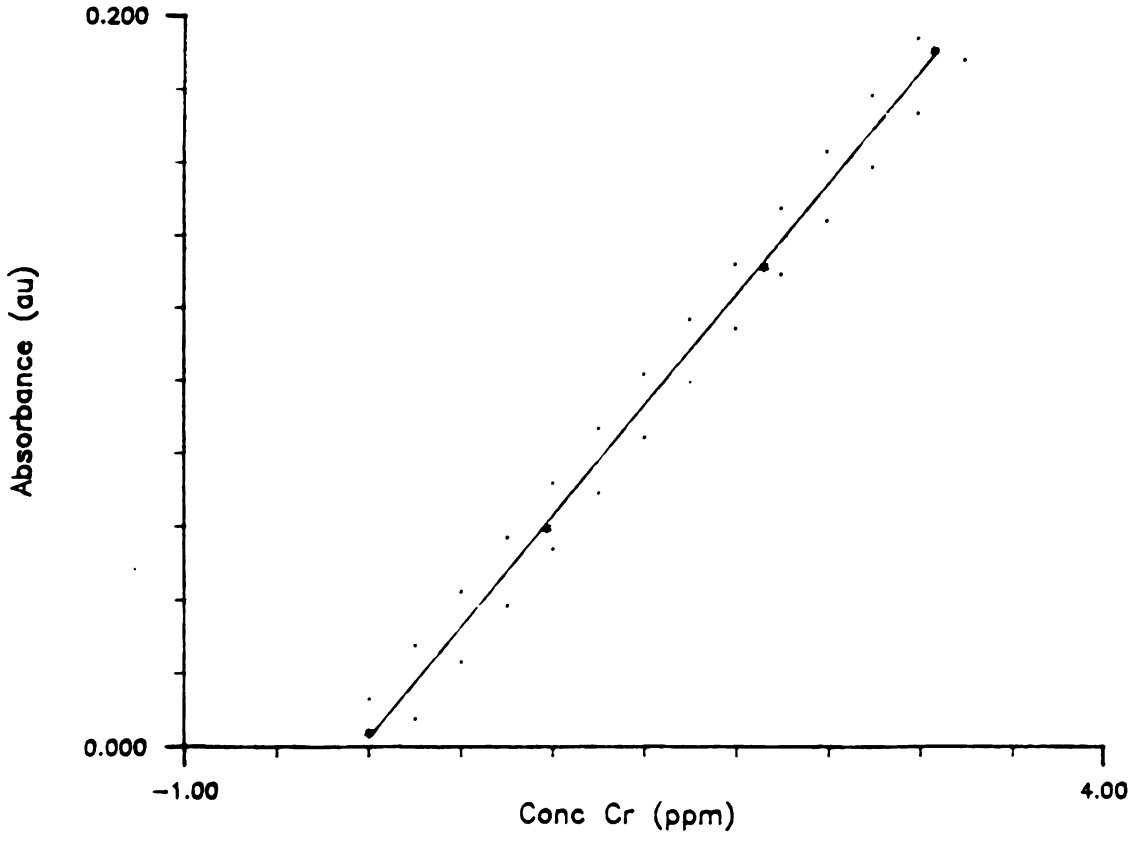


Figure 10. Chromium determination in SESC fraction 9.

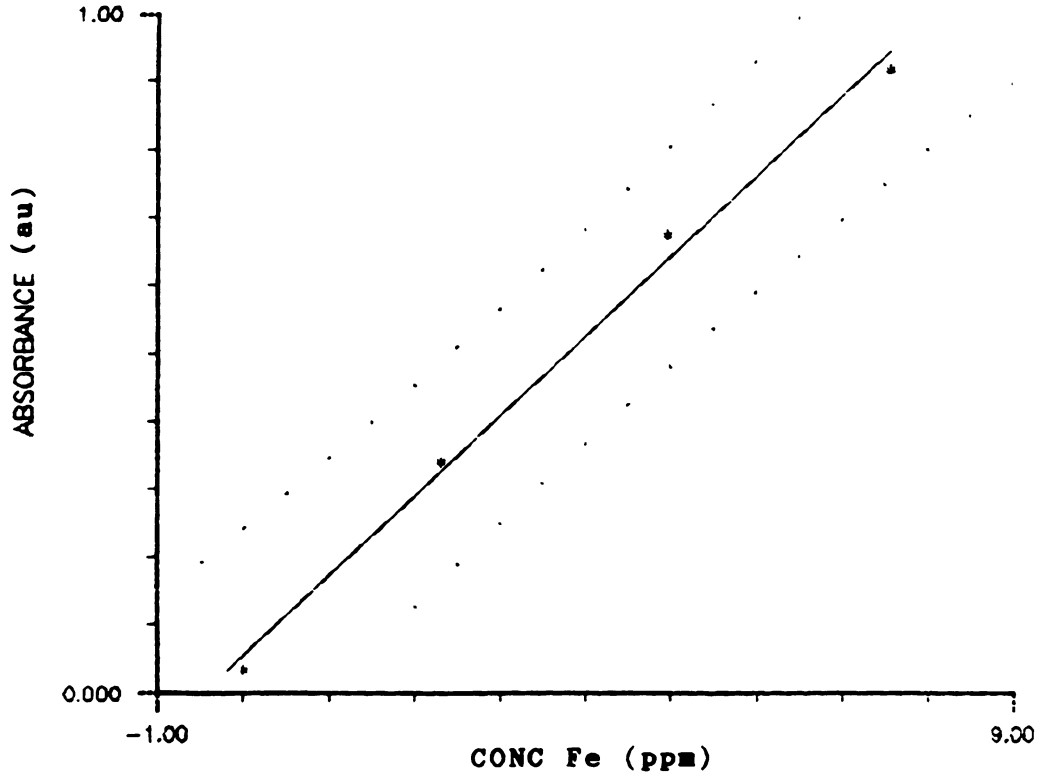


Figure 11. Iron determination in SESC fraction 2.

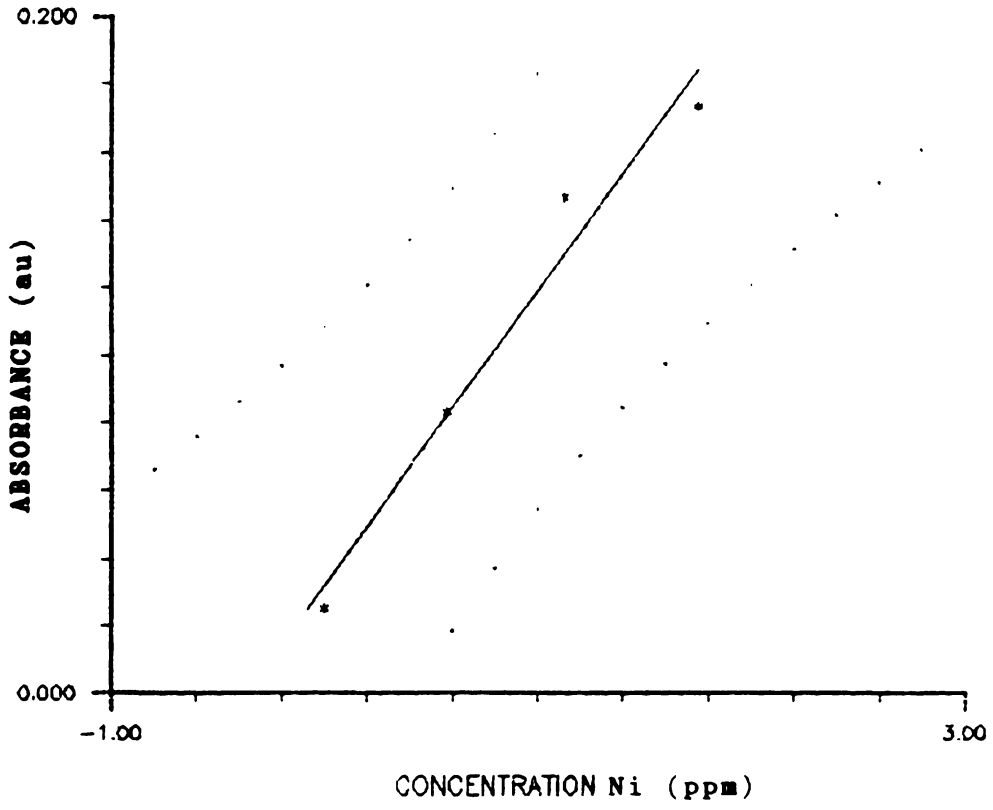
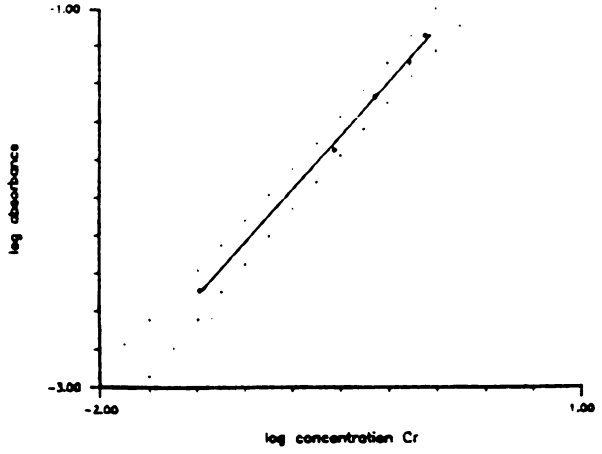


Figure 12. Nickel determination in SESC fraction 7.

log/log of Cr in SESC 9



log/log plot of Fe in SESC 2

log/log of Ni SESC 7

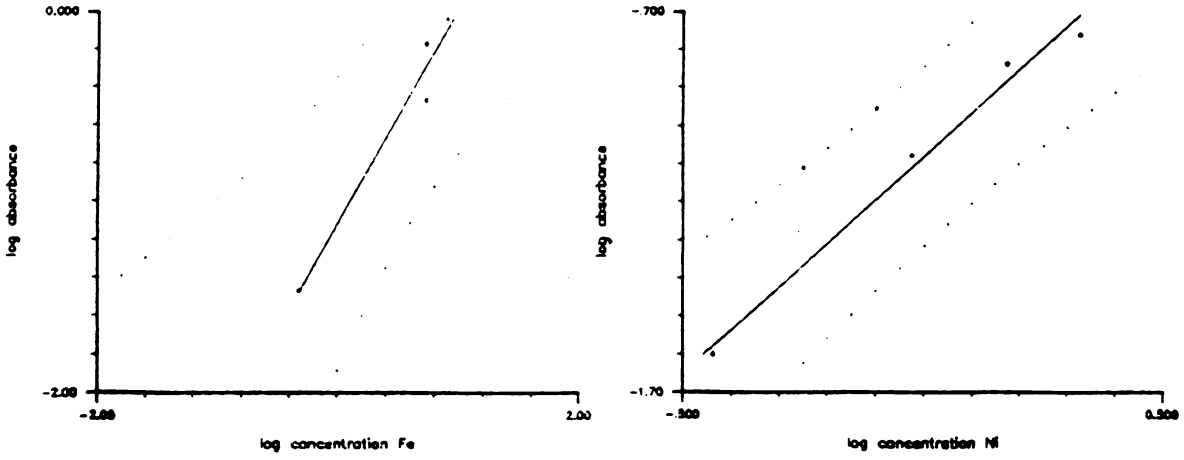


Figure 13. Log concentration vs. log absorbance plots.

deviations from Beer's law, from either chemical or physical sources. The absolute amounts of metal present in each fraction, as determined by these experiments, are tabulated in Table 5, along with the results of the mass balance and blank studies. In Table 6 the total metal concentrations, calculated from the sum of the SESC values, are compared to the whole fuel concentrations obtained from either the direct metal analyses in this laboratory, or the NASA interlaboratory study. The metal distribution profiles for these three metals, which are based on the SESC fraction determinations, are displayed in Table 7.

Table 5. Metal Present in Each SESC Fraction

SESC Fraction	Absolute Metal Present in Micrograms		
	Cr	Fe	Ni
1	0.000	0.00	0.00
2	0.374	6.17	3.02
3	0.089	3.42	3.60
4	0.115	6.49	0.70
5	0.165	8.36	2.70
6	1.36	3.43	0.13
7	0.752	3.73	0.34
8	0.465	5.46	0.33
9	0.080	7.62	7.60
Sample Silica	0.0	0.0	0.0

2. Discussion

As discussed in the previous section, these metal distribution profiles must be interpreted with caution. The

Table 6. Comparison of Metal Determinations of Residual Fuel #3

Metal	Concentrations in ppm Sum of SESC Fractions	Whole Fuel by Direct AAS	Interlaboratory NASA Study (AAS)
Cr	1.70	1.72	0.71 1.34*
Fe	31.5	30.1	21.5
Ni	18.4	20.5	15.0

* This value was obtained by ashing in our laboratory.

Table 7. Metal Distribution Profiles by Compound Class

SESC Fraction	Compound Class	Percent of Total		
		Cr	Fe	Ni
1	Saturates	0.0	0.0	0.0
2	Aromatics	11.0	13.8	16.4
3	Polar Aromatic	2.6	7.6	19.4
4	Monophenols	3.4	14.5	3.8
5	N-Heterocycles	4.8	18.7	14.7
6	Polar Heterocy.	40.0	7.7	0.7
7	Polyphenols	22.0	8.3	1.8
8	High O,N-Polars	13.7	12.2	1.8
9	High O,N-Polars	2.4	17.1	41.3

sixth SESC fration contains the majority of the chromium which exists in the fuel. Most of the remaining chromium appears in the second, seventh, and eighth fractions. The sixth compound class contains polar heteroaromatic

compounds. It is reasonable that metals would be associated with this type of compound. The fact that the next two fractions also contain significant chromium, could be interpreted in two ways. One is that this indicates the existence of two other types of chromium complexes, polyphenols and highly polar, functionalized compounds. The other possibility is that the amount of solvent six used was insufficient to remove all of the polar heteroaromatic complex, and so this complex carried over into the next two fractions. This would be plausible if this compound exhibited excessive tailing as was observed in some of the porphyrin studies. This could be determined by rerunning the experiment with a greatly increased amount of solvent six. The significant amount which appears in fraction two definitely indicates that another type of chromium species was present in the fuel. Whether this was really an aromatic complex, as would be expected for the second fraction, or not requires further investigation.

The interpretation of the iron results is somewhat different. The iron is distributed throughout the fractions more uniformly than is the chromium. This may indicate that most of the iron exists in a loosely associated complex. The higher amounts in fractions five and six may again be due to too small an elution volume; most of the iron may actually exist in a type five complex.

Another point of interest is the results of the blank studies. These indicate that negligible amounts of metal are introduced into these determinations by the silica. This is not what was found by Squire et al. (127) in their SRC studies. This group also found that in each of their profiles the sixth fraction contained the large majority of the metal. That this is not the case here is possibly due to the use of the 'Flash' silica, which is both carefully sized and carefully cleaned. Perhaps this process removes unwanted metal from the silica.

The SESC procedure does not necessarily provide absolute metal speciation information, but it provides a useful first step. In addition, it does serve to concentrate the metal species, which may may prove useful as a means of removing unwanted metals in fuels.

C. Size Exclusion Chromatography of SESC Fractions

1. Experimental Results

A plate count for the Ultragel was used as a means to monitor column deterioration. The original values were on the order of 7000 theoretical plates. The column was calibrated as described in the experimental section. The resulting nominal molecular weight/retention time plot is shown in Figure 14. The SESC fractions were separated on the Ultragel column for further chemical characterization of

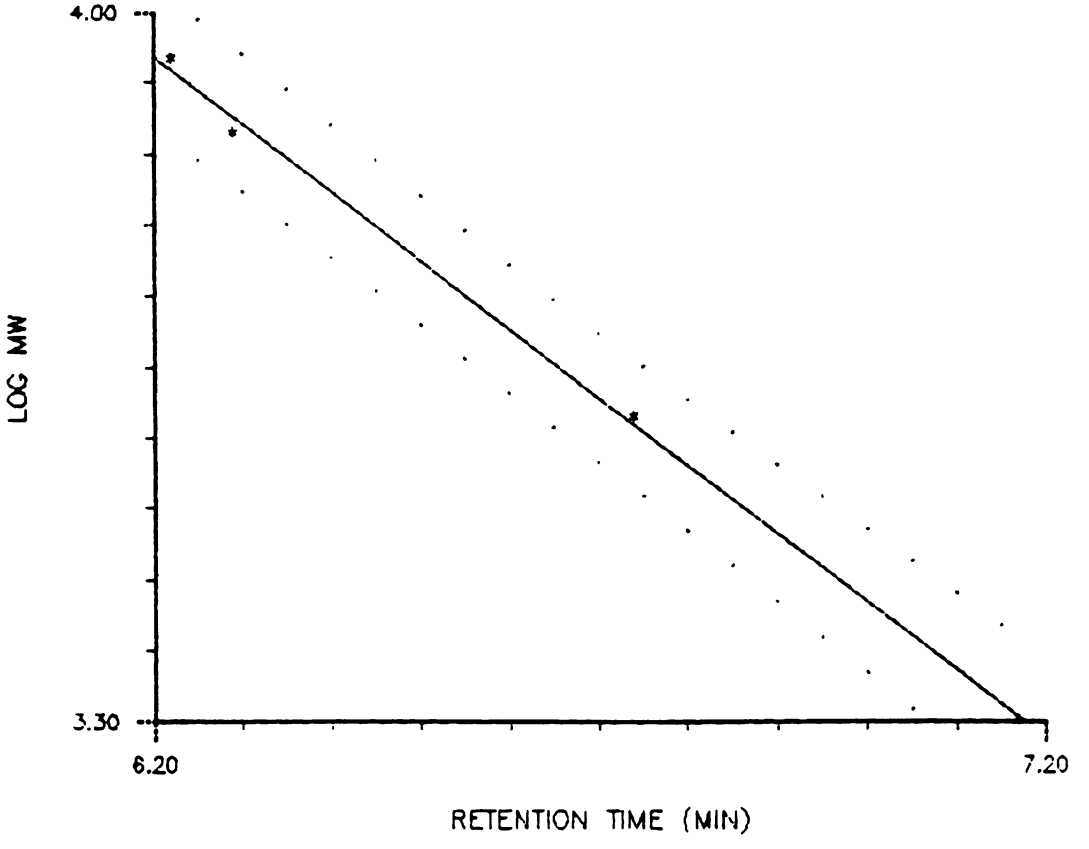


Figure 14. Ultragel column calibration, retention time vs. log nominal molecular weight for polystyrene standards in chloroform.

the fuel. Figure 15 is a composite of the resulting chromatograms.

2. Discussion

The SEC chromatograms of the SESC fractions provide two kinds of information. The first is relative size information. The elution patterns could be compared to the polystyrene calibration curve. However, since these standards are not necessarily representative of the fuel constituents, this would not be reliable. There is a trend for the elution to occur earlier in time when comparing the first fractions to the later ones. This indicates that the later fractions contain increasingly larger components. The other interesting point is seen in the later fractions. These contain not only early eluting components, but also late eluting ones which is indicative of small molecules being trapped in the larger, more highly functionalized components. Thus the iron which was observed in the ninth SESC fraction may actually have been bound to a small molecule. It should be mentioned that the detector used in these experiments is a UV-detector. As a result, the relative intensities of the elution patterns cannot be interpreted quantitatively.

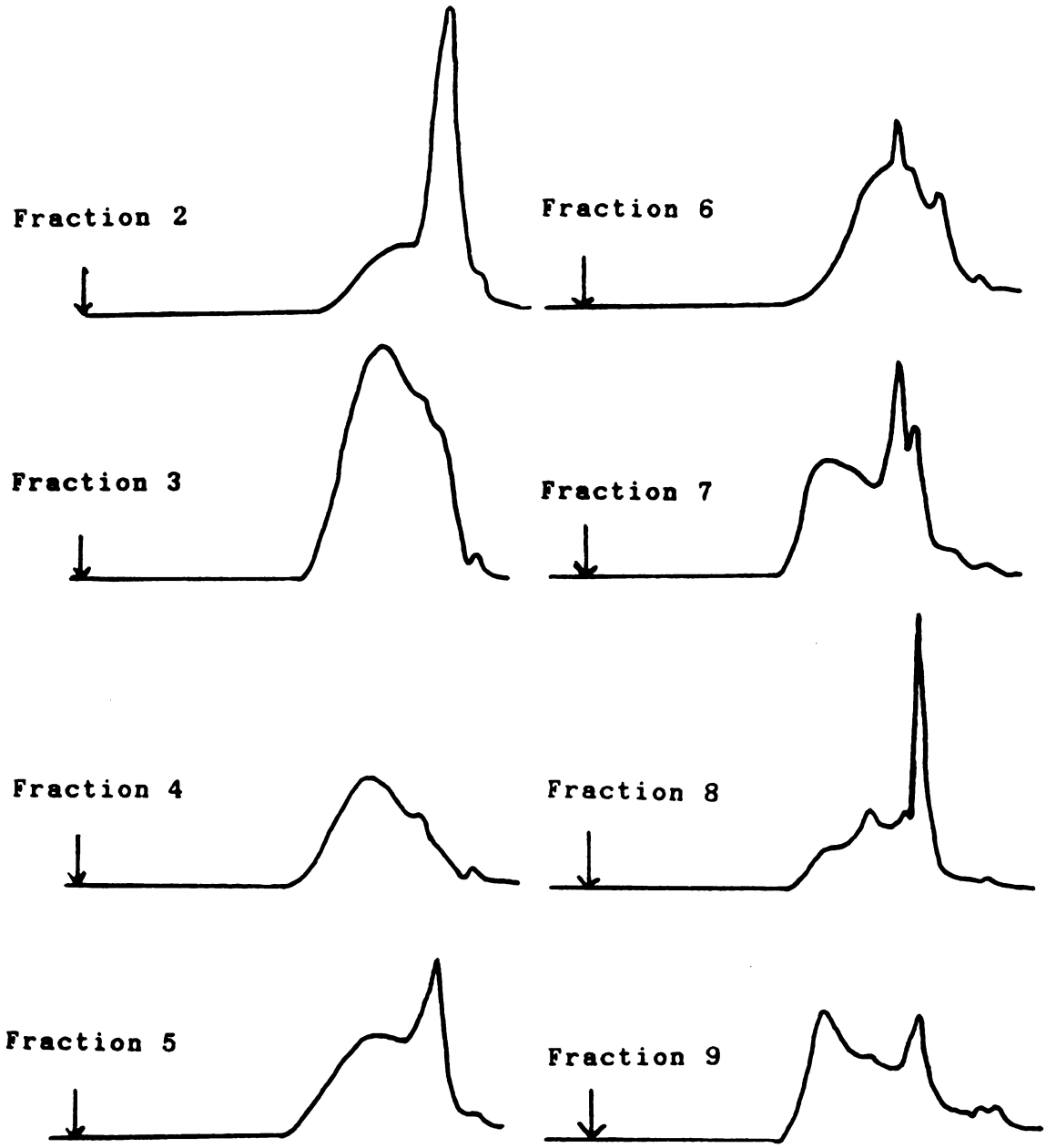


Figure 15. Size-exclusion separations of SESC fractions 2-9.

D. Other Single-Column HPLC Separations of the SESC Fractions

Since there are several possible interpretations of the SESC metal distribution profiles, it is important to obtain more specific information about the components of these fractions. Further chromatographic separation of these components should aid in determining what is actually present in each fraction. The initial separations of this type were done with single-column HPLC.

1. SESC Fraction 2

a. Experimental Results

The second SESC fraction should be composed of aromatic constituents. An amino-bonded phase was chosen to separate this material because this type of column has been shown to be effective at separating by ring number. The resulting chromatogram is shown in Figure 16. Model compounds, varying in ring number, were also separated on this column to provide a standard by which to interpret the fuel separation. Figure 17 allows easy comparison of the fuel to these models when they are separated under the same chromatographic conditions. The chromatographic parameters are specified with the figure.

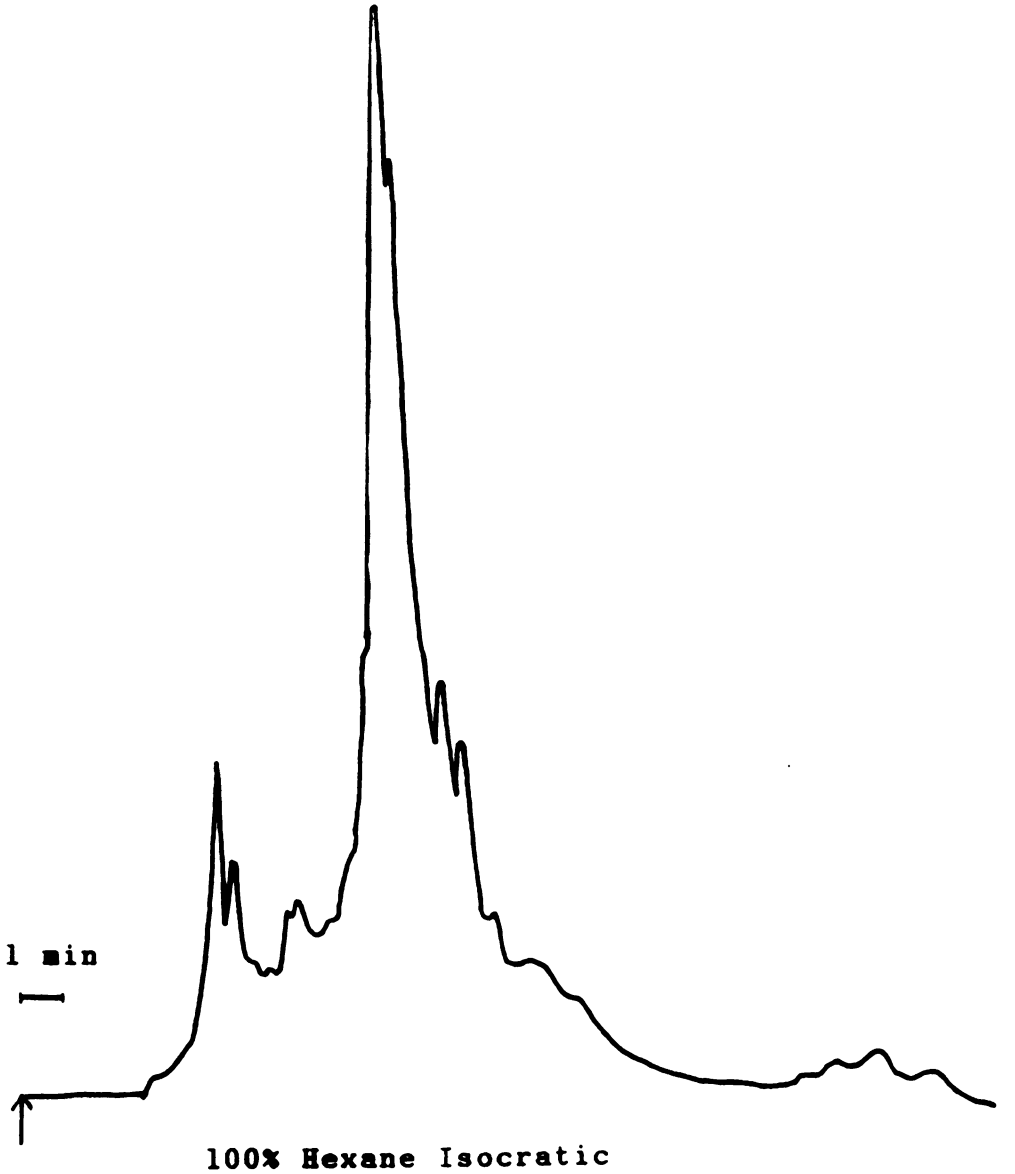


Figure 16. Single-column separation of SESC fraction 2; amino column.

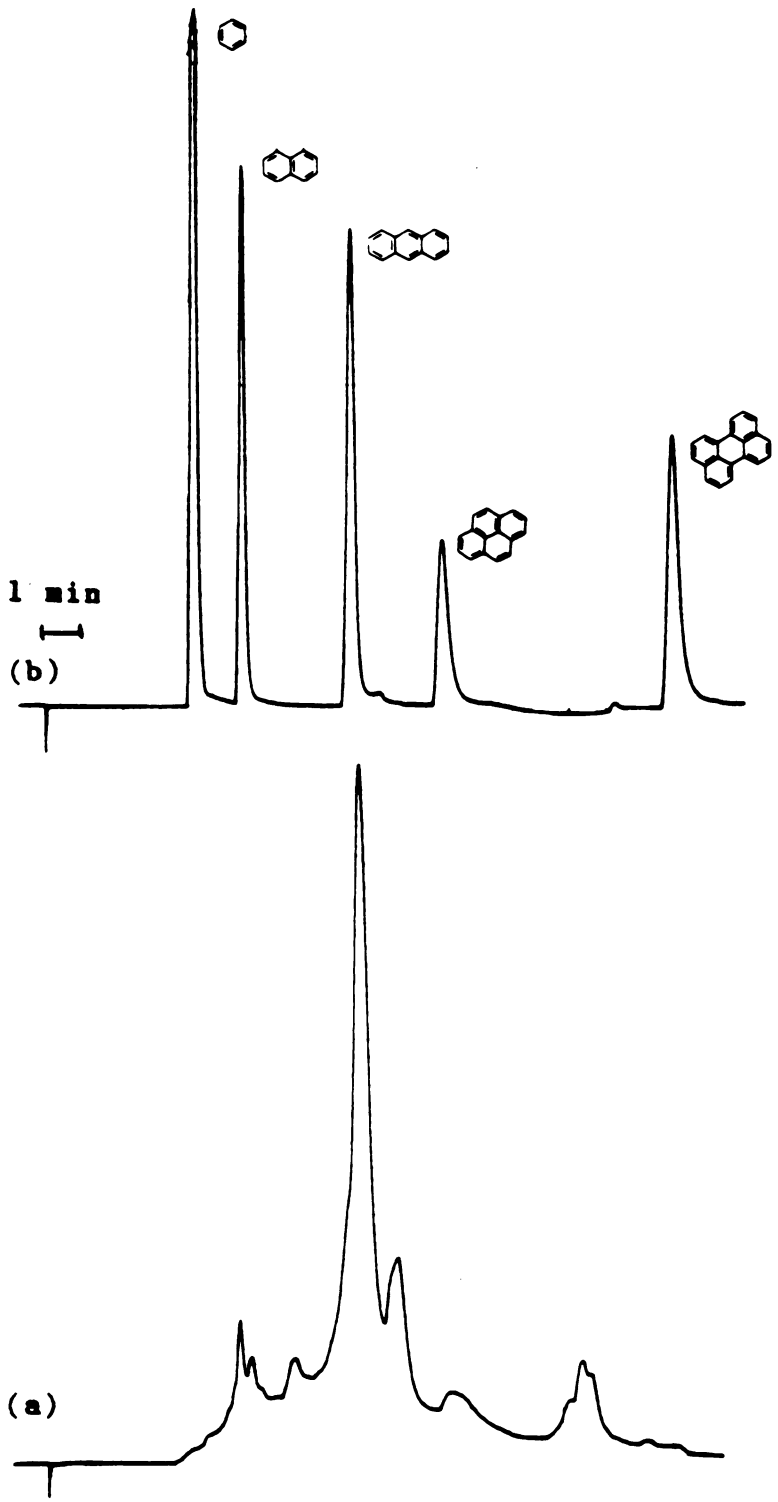


Figure 17. Single-column separations, amino column: (a) SESC fraction 2, (b) model compounds.

b. Discussion

The comparison shown in Figure 17 indicates that the components which make up fraction 2 contain between four and five rings. The extreme amount of overlap seen in Figure 16 is no doubt due to the presence of isomers and similar ring structures with slightly different substitution. These factors would also prevent clear ring number separation. Gradient elution was employed in these chromatograms to provide the best possible separation. Several gradients were tried without success in an effort to better resolve this mixture. Model compound studies in which various aromatic compounds and simple heteroaromatic compounds were separated on the amino column, show that it is possible that this fraction may contain simple oxygen-containing compounds. This is illustrated in Figure 18. If all five compounds were in the same sample, the heteroaromatic compound would coelute with the pure aromatic compounds. Similar studies which employed a nitrogen heteroaromatic compound verified that nitrogen-containing compounds would not coelute. Therefore, it is unlikely that any nitrogen-containing heteroaromatics are present in this fraction. Neither of these types of heteroaromatic compounds should be present according to the SESC procedure, but it is plausible considering the gross scale of that separation.

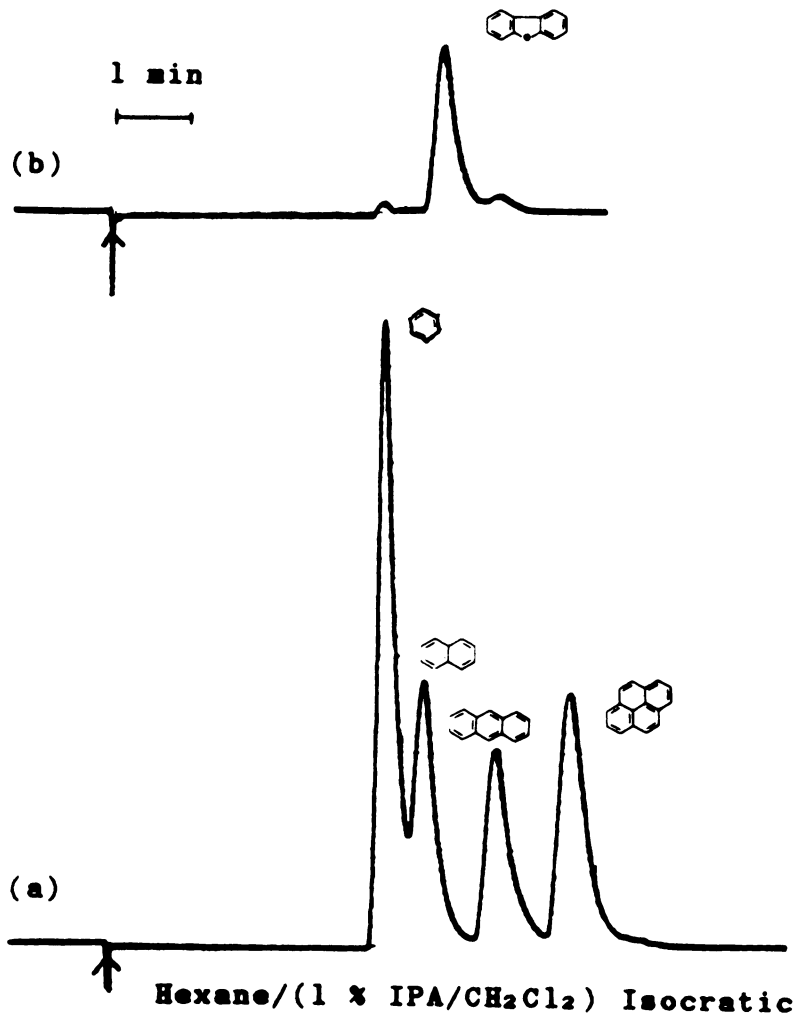


Figure 18. Amino column separation of (a) aromatics and (b) dibenzofuran; amino column.

2. SESC Fraction 3

a. Experimental Results

The third SESC fraction should consist of non-basic heteroaromatics, having one heteroatom. The actual compounds identified by Farcasiu (147) in this fraction, contained the heteroatom in a five-membered ring. Therefore, model compounds of this type were employed. These include a nitrogen-containing series, indole, carbazole, and diphenyl carbazole; an oxygen-containing series, furan and dibenzofuran; and a sulfur-containing analog, dibenzothiophene. The model compounds were used to evaluate the amino column's ring separating capability for such heterocyclics. Figure 19 displays one of the resulting chromatograms. The separation by ring number was quite good for any series of heteroaromatics. The next question was whether analogous ring structures, with different heteroatoms, would coelute. This question is answered by the chromatogram shown in Figure 20. The solvent strength could be adjusted so that the oxygen- and sulfur-containing compounds coeluted. However, the nitrogen-containing compounds would not coelute, even with a solvent mixture strong enough to prevent any ring number separation for these model compounds.

Single-column separations for this SESC fraction were achieved using the amino column. One such separation is

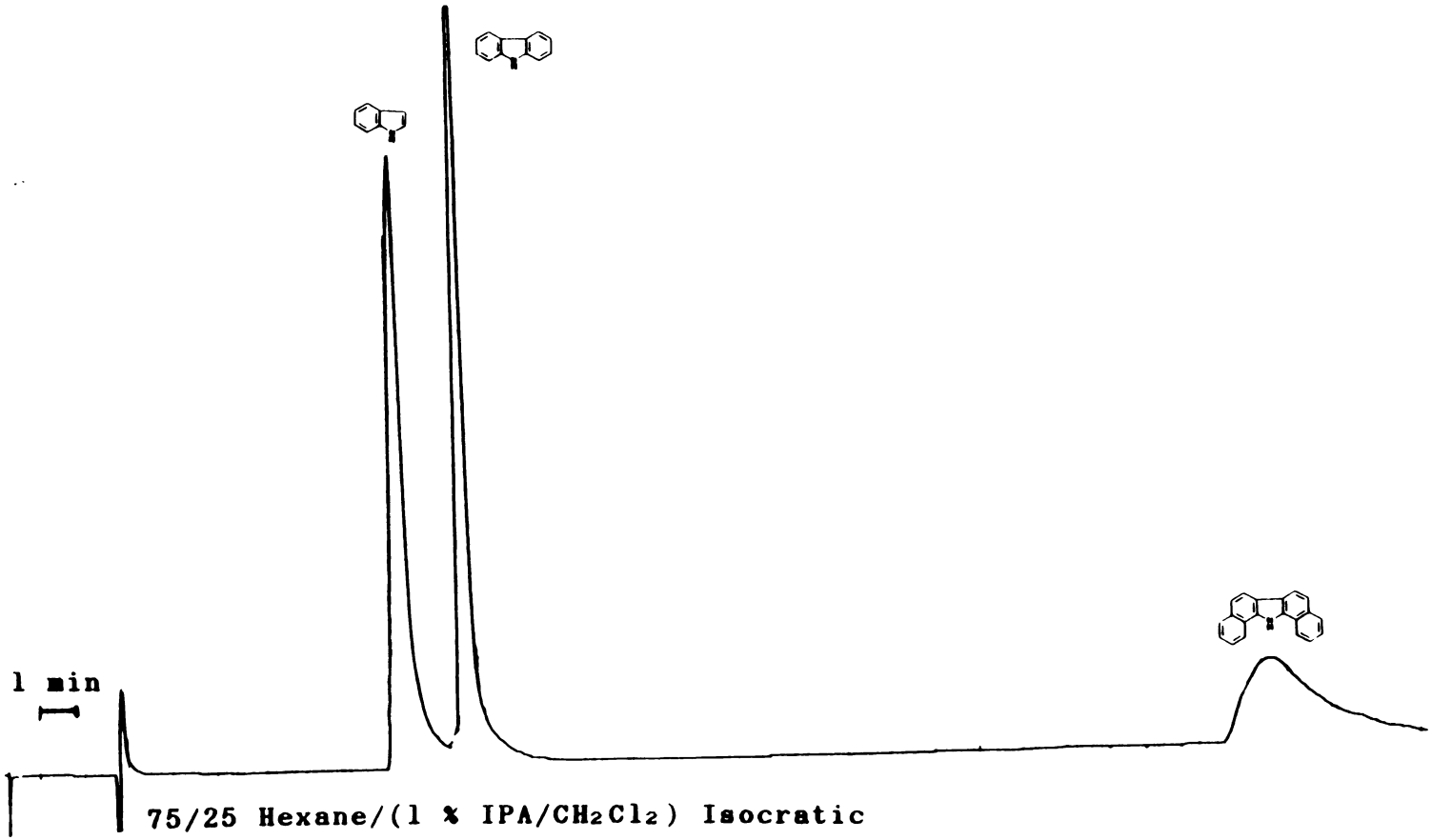


Figure 19. Separation of N-heteroaromatics by ring number; amino column.

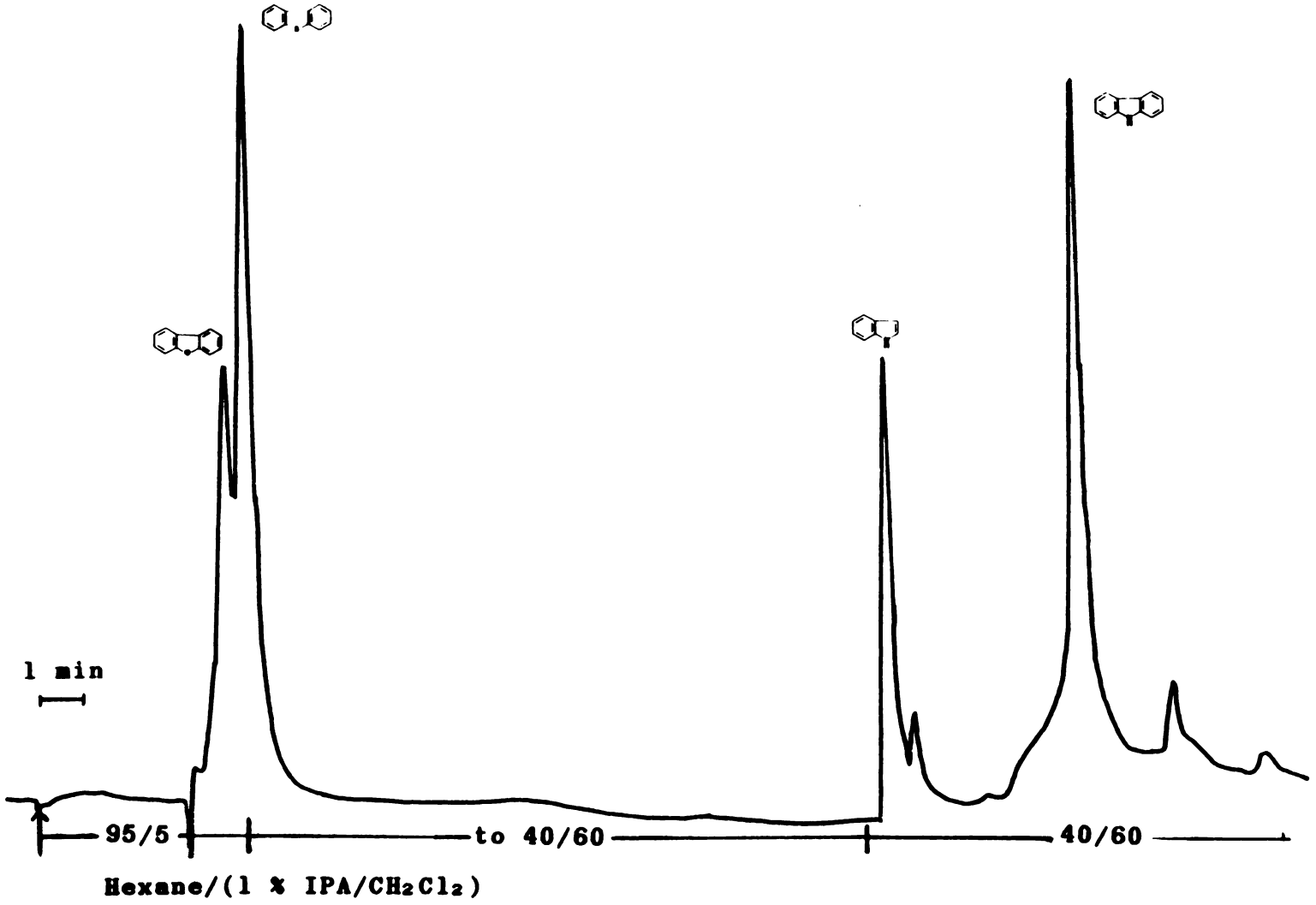


Figure 20. Separation of analogous heteroaromatics; amino column.

shown in Figure 21. This is a gradient elution separation, and is one of the most reasonable in terms of resolution achieved and time required. Further resolution is definitely desireable in this separation as the overlap 'envelope' conceals many components. Often times the resolution of a gradient-elution separation can be improved by employing a slower gradient. Figure 22 is the chromatogram obtained with a slower gradient. Unfortunately, this is not much of an improvement over that seen previously. Figure 23 is a composite of the faster gradient applied to the separation of Fraction 3, and some model compounds.

b. Discussion

The model compound studies indicate that the elution of heteroaromatic compounds off an amino bonded-phase is determined by both the ring structure of the compound, and the nature of the heteroatom. Nitrogen-containing compounds are much more highly retained. Unfortunately, this means that the interpretation of chromatogram a in Figure 23 is not straightforward. The early-eluting components are probably one- to three-ring O- or S-containing heterocycles, considering that the elution time of even a very simple N-heterocycle is shown to be much later with this gradient. The components which do elute later in the SESC fraction chromatogram could be either larger S- or O-containing

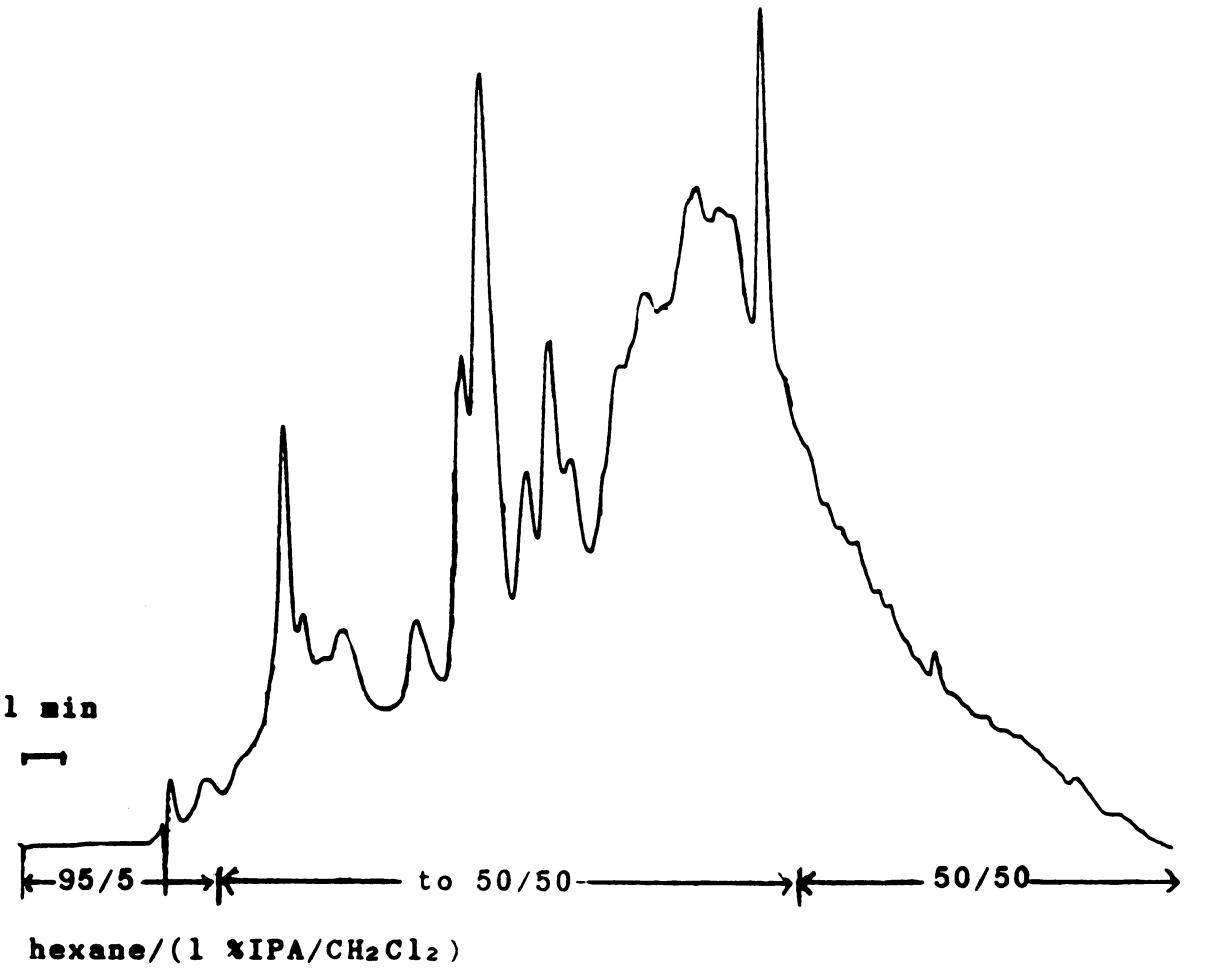


Figure 21. Single-column separation of SESC fraction 3; amino column.

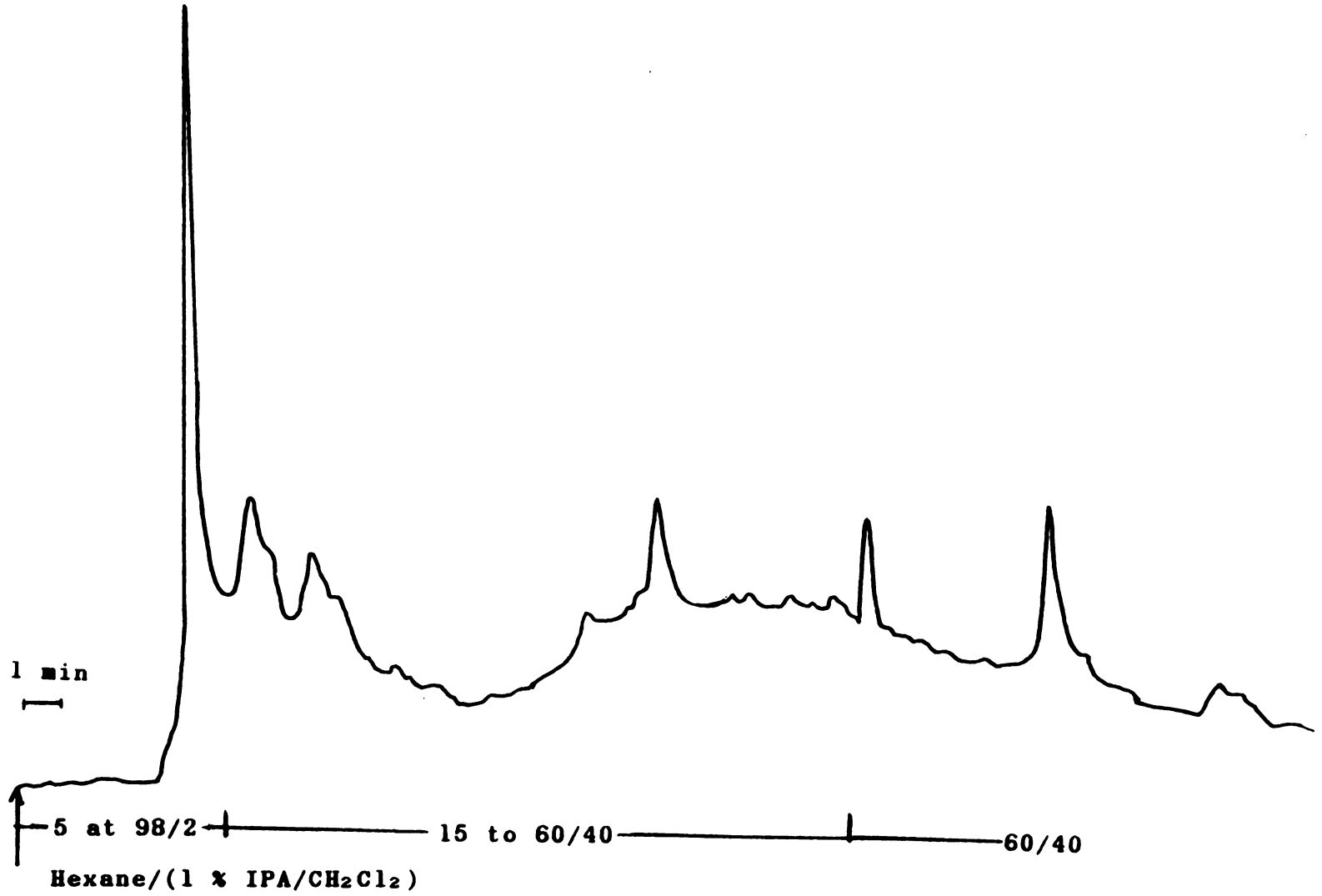


Figure 22. Separation of SESC fraction 3 with slower gradient; amino column.

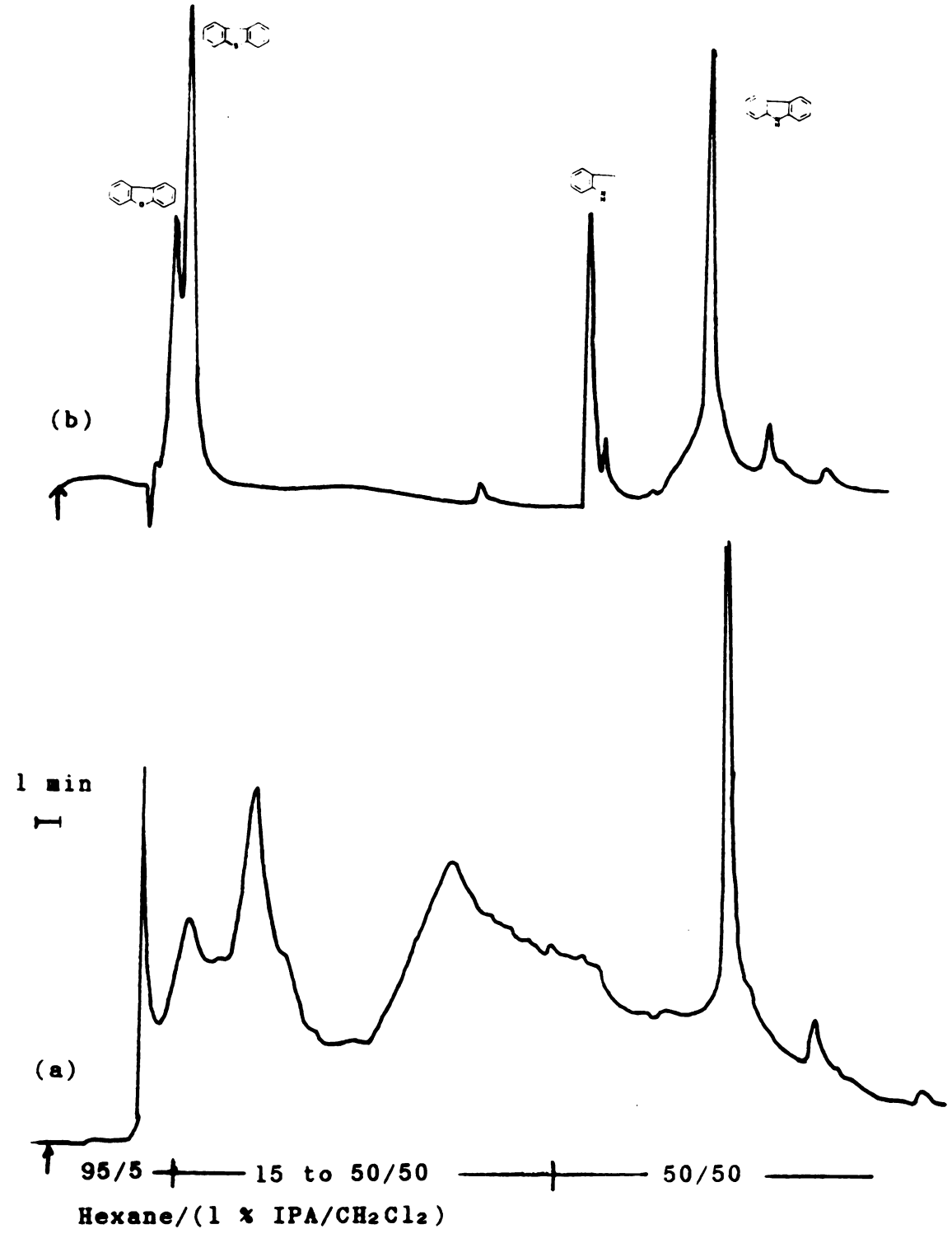


Figure 23. Single-column separations: (a) SESC fraction 3, (b) model compounds; amino column.

components, or they could be N-containing compounds. It seems reasonable that at least some of the components in this fraction would be N-containing. A simple backflushing experiment, which is detailed later, provides some additional information. Whether these are sulfur, oxygen, or nitrogen heteroaromatics must be determined by another technique. One technique which would provide further information would be a multidimensional separation which correlated the size of these components, with their amino column behavior.

In a similar study of the ring-separating behavior of an amino bonded-phase, Miller (89) found that S-containing compounds would sometimes coelute with pure aromatics, but that N- and O-containing compounds were more highly retained. Miller's results do not completely agree with the results of this study where O- and S-containing compounds were seen to elute in much the same manner. However the trend is the same in that heteroaromatic analogs do not all exhibit the same chromatographic behavior on an amino column. Whether the O- or S-containing compounds are more highly retained may be a function of packing preparation.

Another study which provided information about the components of this fraction, involved the substitution of chloroform for the methylene chloride used in most of these separations. Chloroform is in group VIII of the Snyder solvent classification scheme, while methylene chloride is

in group V (124). The goal of this study was to improve the separation by modifying the mobile-phase selectivity, while holding the solvent strength constant. This is based on Snyder's (125) idea that the polarity of a solvent mixture is the arithmetic average of the polarities of the pure solvents; the polarity index for methylene chloride is 3.1, chloroform is 4.1. However, chloroform acted as a weaker solvent in this application. Apparently, chloroform's proton-donating character was not appropriate for this sample. Thus, this fraction must indeed contain non-basic nitrogen heteraromatics.

3. SESC Fraction 4

The fourth SESC fraction was also separated on the amino column with gradient elution. The resulting chromatogram is shown in Figure 24. This chromatogram is similar to those for the earlier fractions, in that it also contains an envelope of overlapping components. However, this fraction does contain a component, or components, which is more highly retained and required a gradient to a very strong mobile phase for its elution. The highly-retained component is either much larger than the others, or contains polar substituents, in addition to the phenol group. It is also possible that more than one phenol is present, which would result in strong retention. Fraction 4 should be composed of monophenols. However, the SESC separation is on

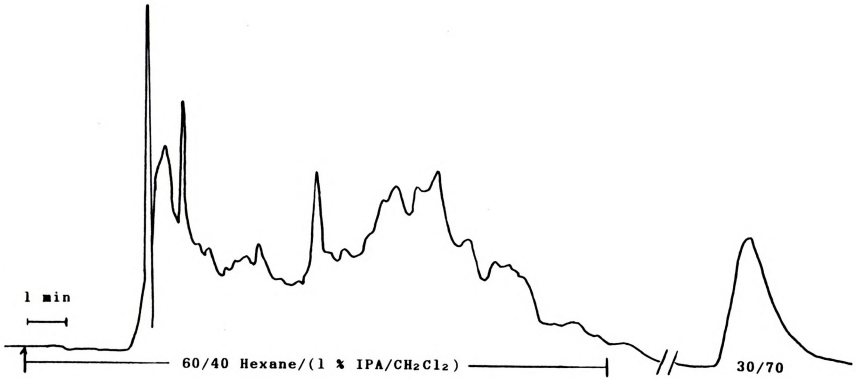


Figure 24. Single-column separation of SESC fraction 4; amino column.

a gross scale and as such this possiblily cannot be ruled out. Unfortunately, appropriate model compounds to test this idea were not available. Thus, detailed interpretation is not possible.

E. Multidimensional HPLC Separations

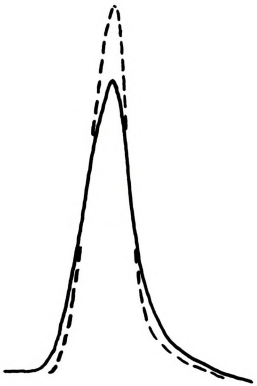
The single-column HPLC separations of the SESC fractions have been shown to be very difficult to interpret. In addition, it was not possible to achieve very good component resolution with a single-column approach. Multidimensional HPLC techniques should provide improvements in both these areas. Several of the multidimensional HPLC techniques which were investigated are reported in this section. The FORTH programs used to execute these multidimensional experiments are contained in Appendix A.

1. System Characterization

Several initial experiments were done to characterize the advantages and problems with the multidimensional HPLC system that was constructed in this laboratory. The results of these experiments provide insight into how this system can be most advantageously employed.

a. Band-Broadening

The amount of band-broadening introduced into a chromatographic separation by the system's hardware is an important consideration in the configuration of any chromatographic system. This is especially true for a multidimensional HPLC system since it includes column switching valves and a large amount of complementary tubing. The amount of band-broadening inherent in this multidimensional system was investigated by comparing the peak shape for a single component injected onto an analytical column, both when the effluent was sent directly to the detector, and when the effluent passed first through both valves, with their full complement of tubing. Figure 25 displays the results of this experiment and several expressions of the resultant band-broadening. The fact that there is some band-broadening is not surprising considering that about 30 cm of tubing and two fittings are necessary to connect a 25 cm column to a valve. Further study showed that the majority of this band-broadening was indeed introduced by the tubing. The amount of band-broadening associated with the valves themselves is negligible, as has been observed by other workers (30,63). Thus, it is very important to minimize the tubing used to configure a multidimensional system, and to use small diameter tubing, such as 0.009".



18% INCREASE IN W1/2

19% DECREASE IN PLATES

6% INCREASE IN PAF
(PAF=Peak Assymetry Factor)

11% DECREASE IN RESOLUTION

(VALUES QUOTED PER VALVE)

Figure 25. Multidimensional HPLC band-broadening;--- = without valves, ___ = with valves.

b. Baseline Disturbance Associated with Multidimensional Experiments

Any fluctuation in the chromatographic flow rate, and consequently the system backpressure, is reflected in the instrument's detector output. This is due to the detector's flow cell design, which consists of a quartz plate pressed against a Teflon block, that has a flow channel cut in it. The reference flow cell is similar in design, but it is not in-line in these experiments; instead, it contains air. Therefore, the reference cell does not respond to backpressure changes as the sample side does. It was necessary to determine what changes in flow rate, and detector output, accompanied air-actuated valve switching. This experiment was done by switching a short, second column in and out of line. The results of this experiment can be seen in Figure 26. When the second column was introduced, the flow momentarily decreased, which resulted in an upward drift of the detector output. The opposite was true when the second column was taken out of line. The solvent delivery system adjusted to this change fairly rapidly, in about 5 to 10 seconds. Generally, the larger the backpressure a column has associated with it, the greater the baseline disturbance will be. However, the solvent delivery system's response is so quick that this change appears as a spike which does not usually hamper chromatographic interpretation.

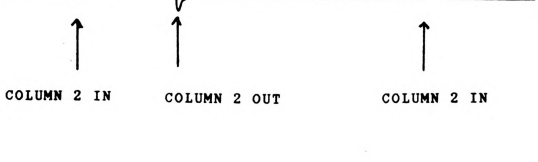


Figure 26. Baseline disturbance due to column switching.

A second type of baseline disturbance can occur in multidimensional experiments. This is associated with making heartcuts of the effluent of one column onto another, which has been equilibrated with a different mobile phase. The baseline disturbance occurs when the heartcut solvent plug elutes from the second column. Apparently, this disturbance is not due to a flow rate variation accompanying the heartcut process, because the disturbance is not seen instantaneously. Also, no disturbance occurs when a large heartcut is made onto a column that is equilibrated with the same mobile-phase. Instead, it appears as though the heartcut solvent plug has incompletely mixed with the eluting mobile-phase, creating zones of differing refractive index. The type of disturbance that results is illustrated in Figure 27. This figure presents the results of a baseline disturbance investigation which involved a series of hearcuts of increasing length, and thus volume. The mobile-phases used were water and THF, which are completely miscible. These results indicate that even when the two mobile-phases are miscible, a heartcut of one half of a milliliter, or more, will result in a baseline disturbance which is great enough to obliterate the chromatogram at that point. Thus, one must allow for this effect when designing a heartcut experiment.

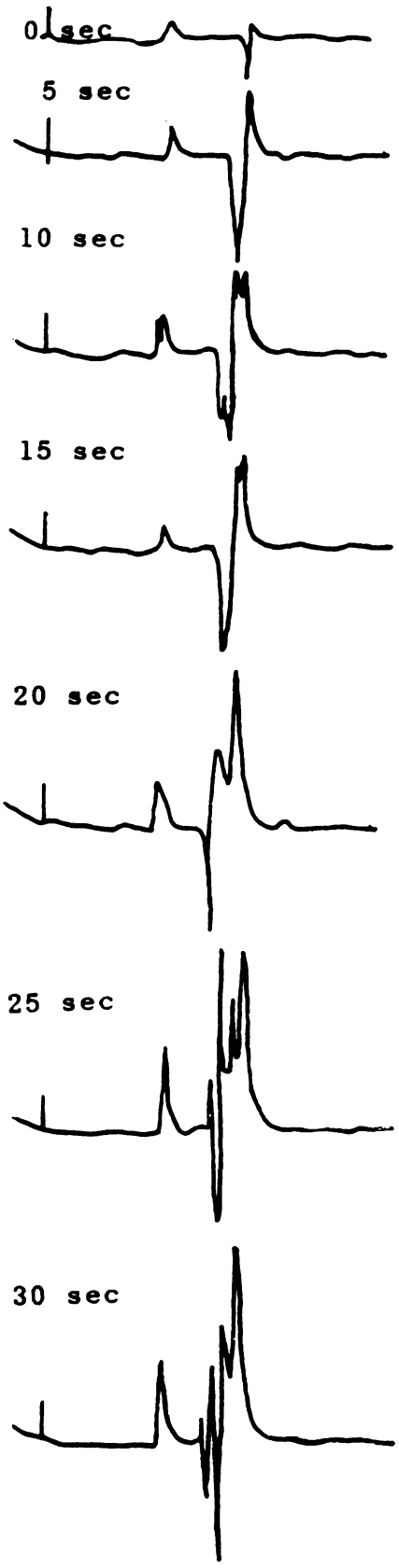


Figure 27. Baseline disturbance related to the length of heartcuts.

2. Simple Backflush Separations

a. General Discussion

Simple backflush experiments are those which involve the forward elution of a single column, followed by a flow reversal. This is not a true multidimensional technique, as discussed earlier; but is included here since it involves column switching. Figure 28 illustrates the effectiveness of this technique for reducing analysis time and improving the peak shape of late eluting components. The valving configuration necessary for this type of experiment is shown in Figure 29.

b. Simple Backflush Separations of Fuel Samples

Figure 30 presents simple backflush chromatograms for the third SESC fraction, and for aromatic and heteroaromatic model compounds. Chromatogram (b), the model compound separation, indicates the region of this mobile-phase scheme where aromatic compounds elute, and where nitrogen heteroaromatics begin to elute. When chromatogram (a) is compared to chromatogram (b), the conclusion is that the third SESC fraction does not contain any pure aromatic components. Secondly, it is apparent that Fraction 3 contains a lot of highly retained materials since all the backflushed components do not coelute. The materials which elute after twice the backflush time, could be termed

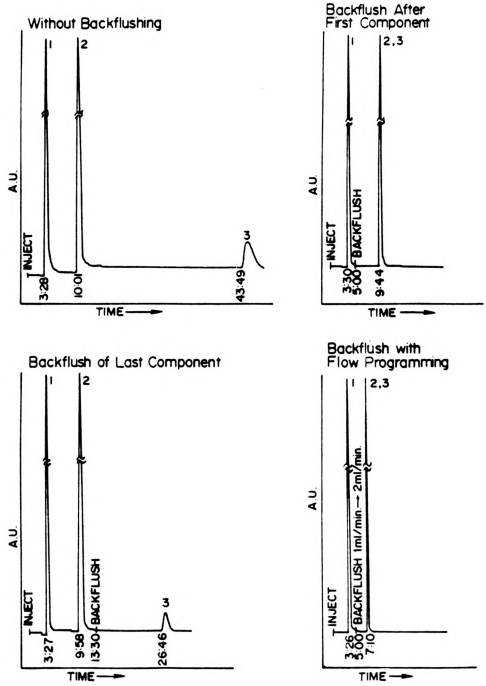


Figure 28. Backflush chromatograms.

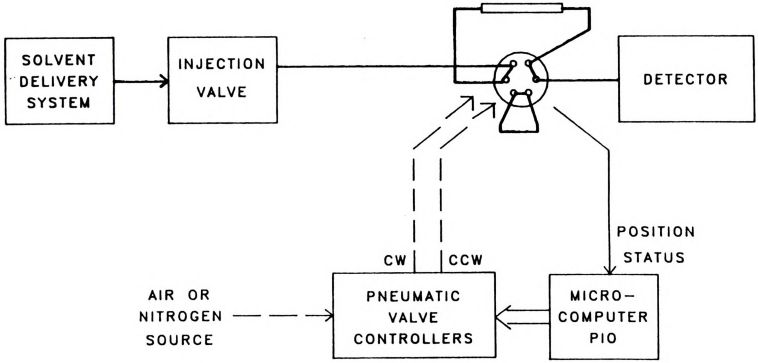


Figure 29. Single-valve backflush configuration.

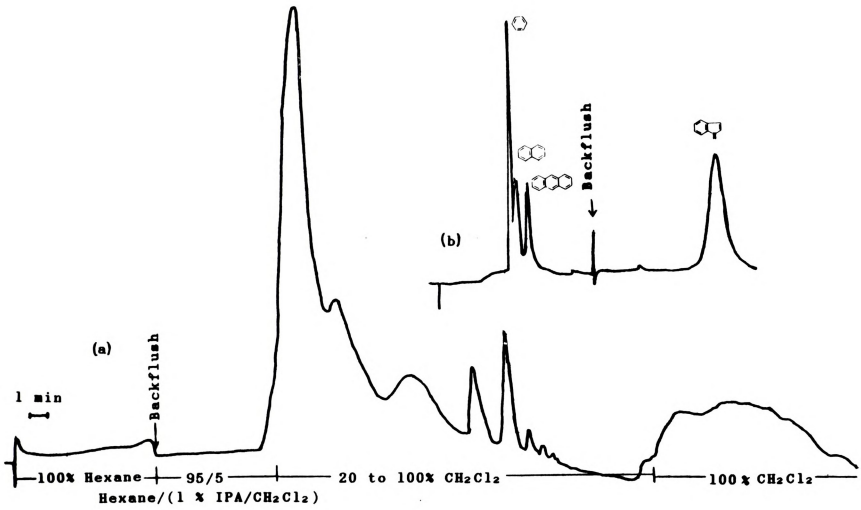


Figure 30. Single-column separations with backflush: (a) SESC fraction 3, (b) model compounds; amino column.

irreversibly adsorbed with respect to the initial mobile-phase. It should be noted, however, that the initial mobile-phase was 100 % hexane, which is weaker than the mobile-phase used for the single-column separation of this fraction (Figure 21). This was done to provide a period of time in which only aromatics could elute, in order to test for their presence. Therefore, a gradient to a very strong mobile-phase is necessary to remove all of these materials. This technique has been termed solid-phase extraction (125). The gradient used does go to a stronger mobile-phase than that used in the separation of Figure 21. This indicates that all of this material was not eluted from the column in the earlier experiment; backflushing is a good way to test for this. Thus, this SESC fraction must contain components of widely varying polarities. In addition, the poor resolution and peak shape of the components which eluted last, indicate that the amino stationary phase is not ideally suited for the separation of all the components in this fraction. A multidimensional technique was developed in response to these results. This technique is presented in a later section.

Figures 31 and 32 present single-column and simple backflush separations of an alternate jet fuel known as ERBS-5 (Experimental Referee Broadened-Specification). This is a fairly 'clean' alternate fuel in that it contains a relatively small amount of highly functionalized components

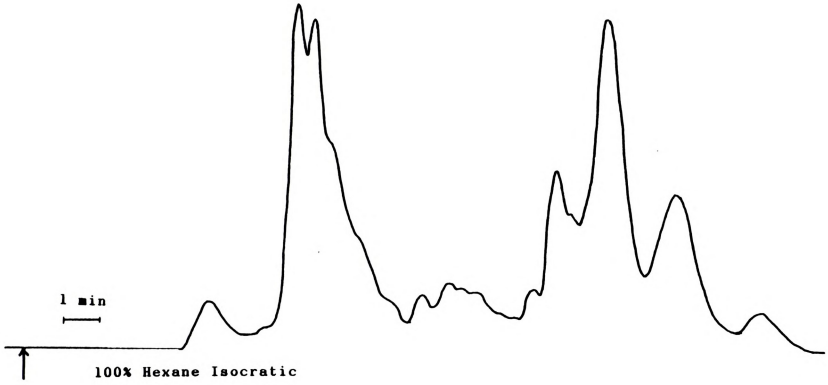


Figure 31. Single-column separation of ERBS fuel; amino column.

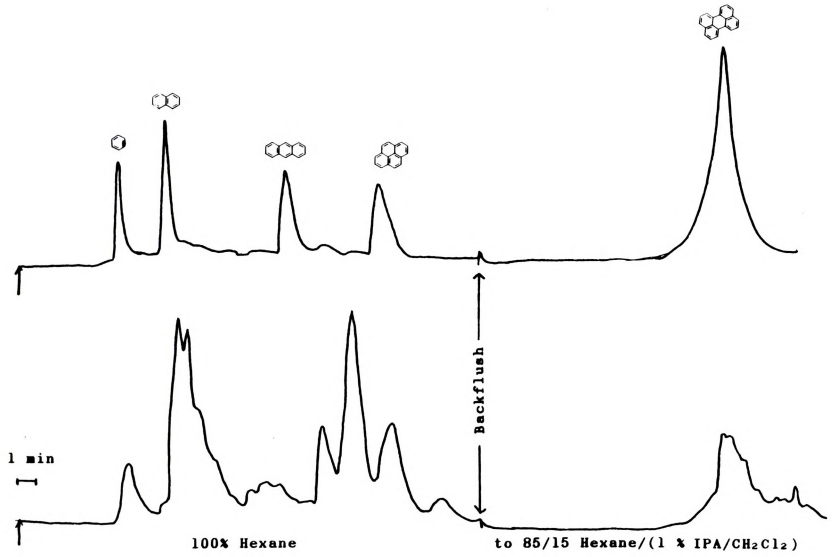


Figure 32. Single-column separations with backflush: (a) ERBS, (b) model compounds; amino column.

(see Appendix B for ERBS analysis). The single-column chromatogram is fairly well resolved, for a fuel separation, and appears to be complete. However, the backflush experiment shows that some highly retained components had not eluted. The model compound chromatogram of Figure 32 (chromatogram b) provides a means for interpreting the ERBS separation. Apparently, this sample consists of mainly one to four ring components. The backflushed materials could be either larger components, like the five ring model, or polar materials, which is more likely considering the NASA analysis of this fuel (Appendix B).

3. Multidimensional HPLC Separations with Backflush

a. Multidimensional Backflush

Multidimensional HPLC separation with backflush is a title that can be applied to several different techniques, as discussed earlier. The separation which is depicted in Figure 33 is one in which two components, which were poorly resolved by the first column, were backflushed onto a second column having a different selectivity for further separation. The compounds involved were anthracene and dibenzothiophene. These two three-ring compounds coelute from the amino column, but are separated by the silica column due to their difference in functionality. This model study was done to illustrate the usefulness of this technique to provide further information about the

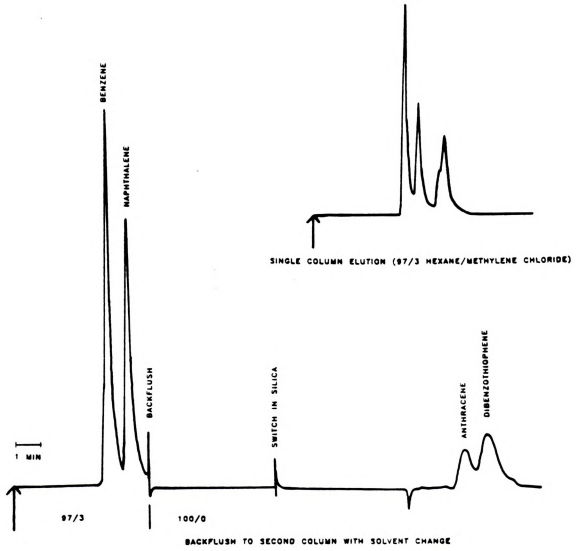


Figure 33. Multidimensional backflush separation of model compounds.

heteroaromatic compounds of the third SESC fraction. The valving configuration used is shown in Figure 34.

b. Selectivity Programming with Backflush

Selectivity programming with backflush was developed to handle the wide range of polarity of the components of the third SESC fraction. The approach of this technique is to combine two stationary phases with different selectivities so that all of the components can be separated even though they vary greatly in polarity. A precolumn is packed with the more retentive stationary phase. The sample is injected onto the precolumn which serves to separate the sample into two parts. One part consists of materials which are nonpolar enough to be separated on this stationary phase. The second part consists of more polar compounds which require a less retentive stationary phase, and thus will be highly retained on the precolumn. The materials which pass through the precolumn are sent onto an analytical column, containing the same packing, for actual separation. The components which are retained on the precolumn are backflushed off and sent onto a different analytical column for separation.

The valving setup for this experiment is shown in Figure 35. A chromatogram produced in this way is presented in Figure 36. The two analytical columns used were the amino column, which is more retentive for polar compounds,

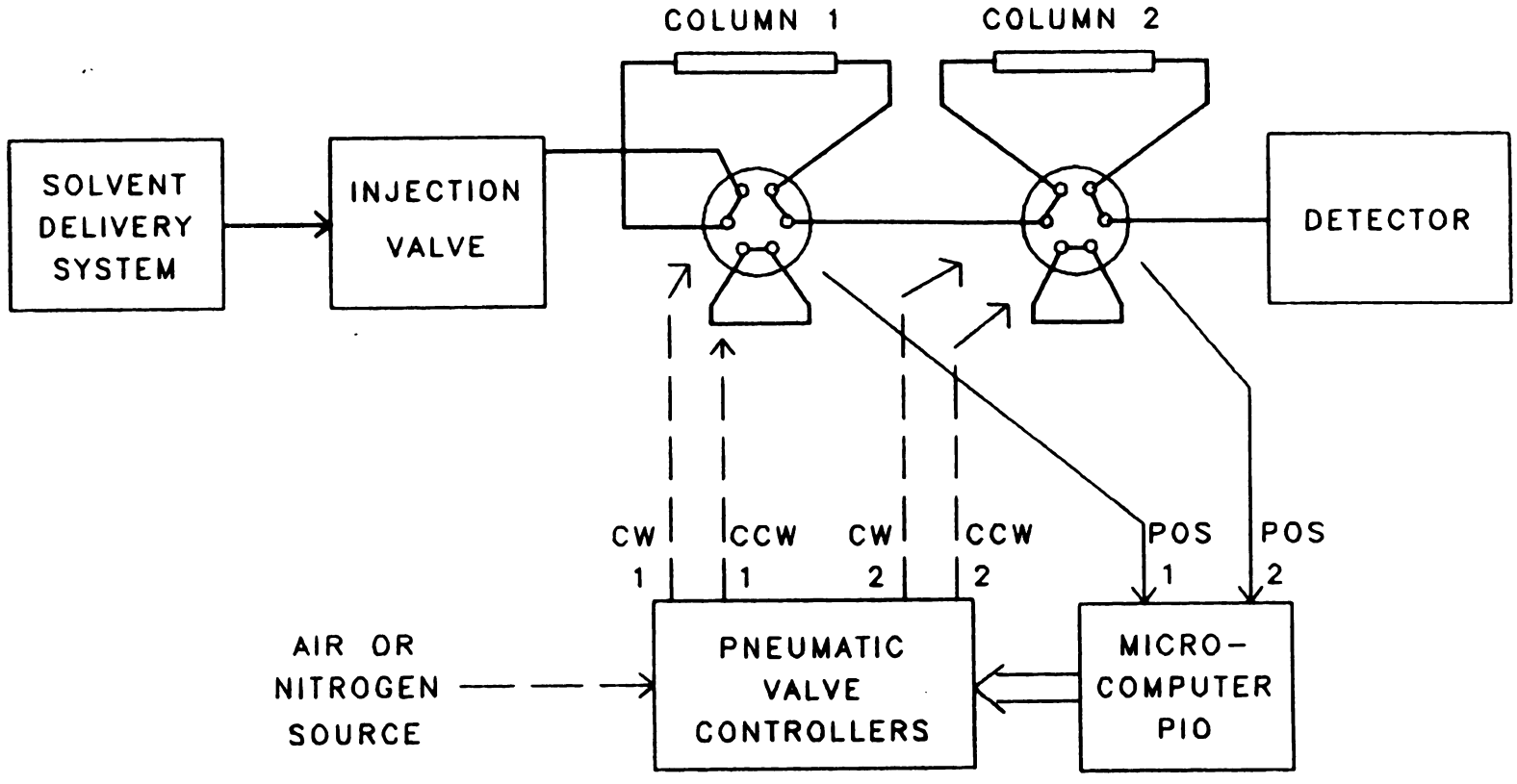


Figure 34. Valve configuration for multidimensional backflush.

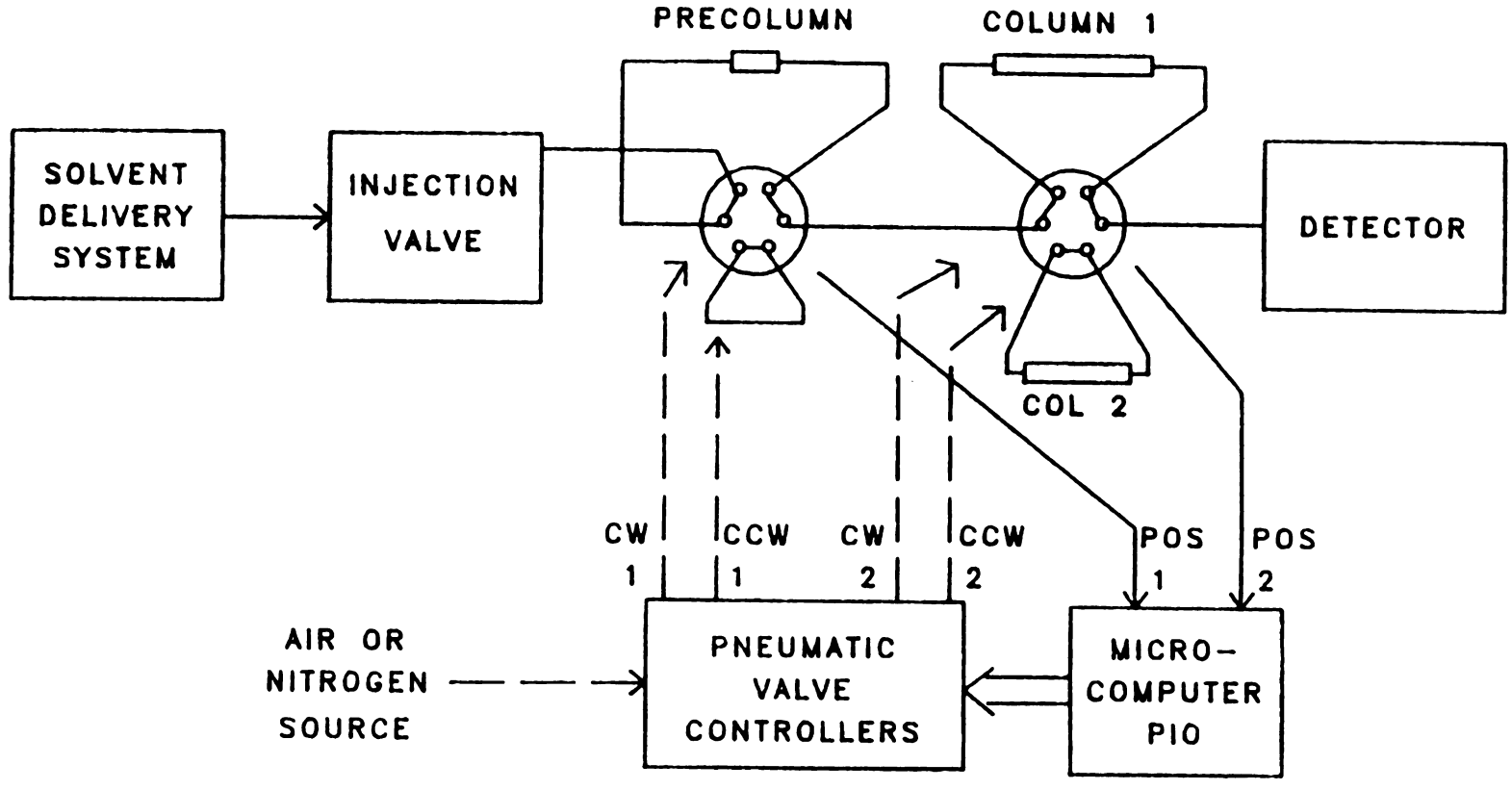


Figure 35. Valve configuration for selectivity programming with backflush.

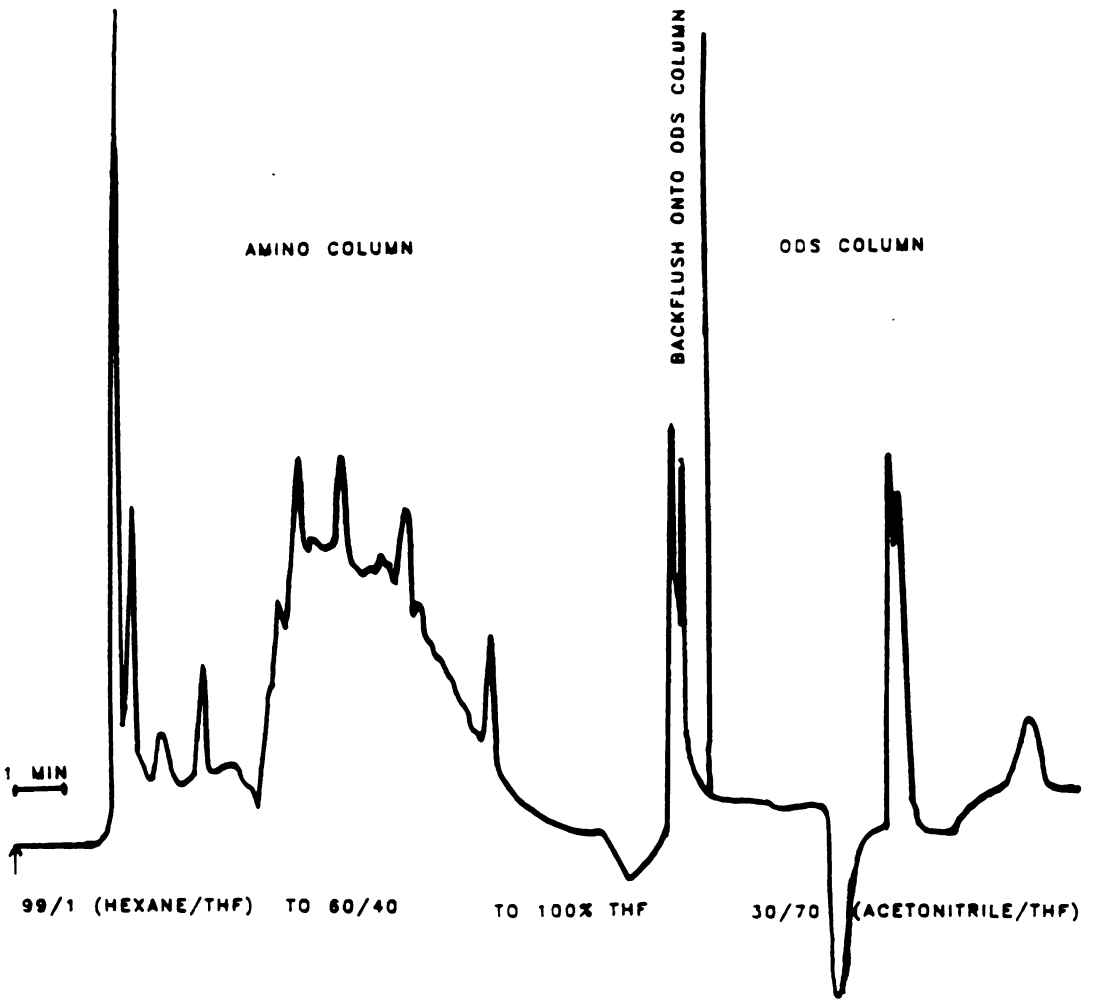


Figure 36. Selectivity programming with backflush separation, SESC fraction 3.

and the ODS column, which is less retentive. The precolumn was packed with pellicular amino stationary phase. The mobile-phases for the two separations were hexane/THF on the amino column, and THF/acetonitrile on the ODS column. Thus, this was a nonaqueous reverse-phase separation. Nonetheless, the partitioning on the ODS column followed a reverse-phase separation pattern, in which the more polar materials eluted earlier in time. A later backflush of the ODS column (not part of this experiment) indicated that all of the fraction 3 components were eluted from the column by this multidimensional technique. Thus, this technique successfully dealt with a sample containing constituents having widely varying polarities, while providing reasonable resolution of these components in a fairly short analysis time of twenty-one minutes.

4. Multidimensional Separations with Heartcut

a. One-Valve Heartcut Experiments

Figure 37 depicts the valve configuration used for single-valve heartcut experiments. Two separations of this type are presented in Figures 38 and 39. Both of these separations are ones in which an SESC fraction, either 2 or 3, was first separated on the amino column. Then part of the effluent was directed onto the silica column to see if more components could be resolved. In the case of the

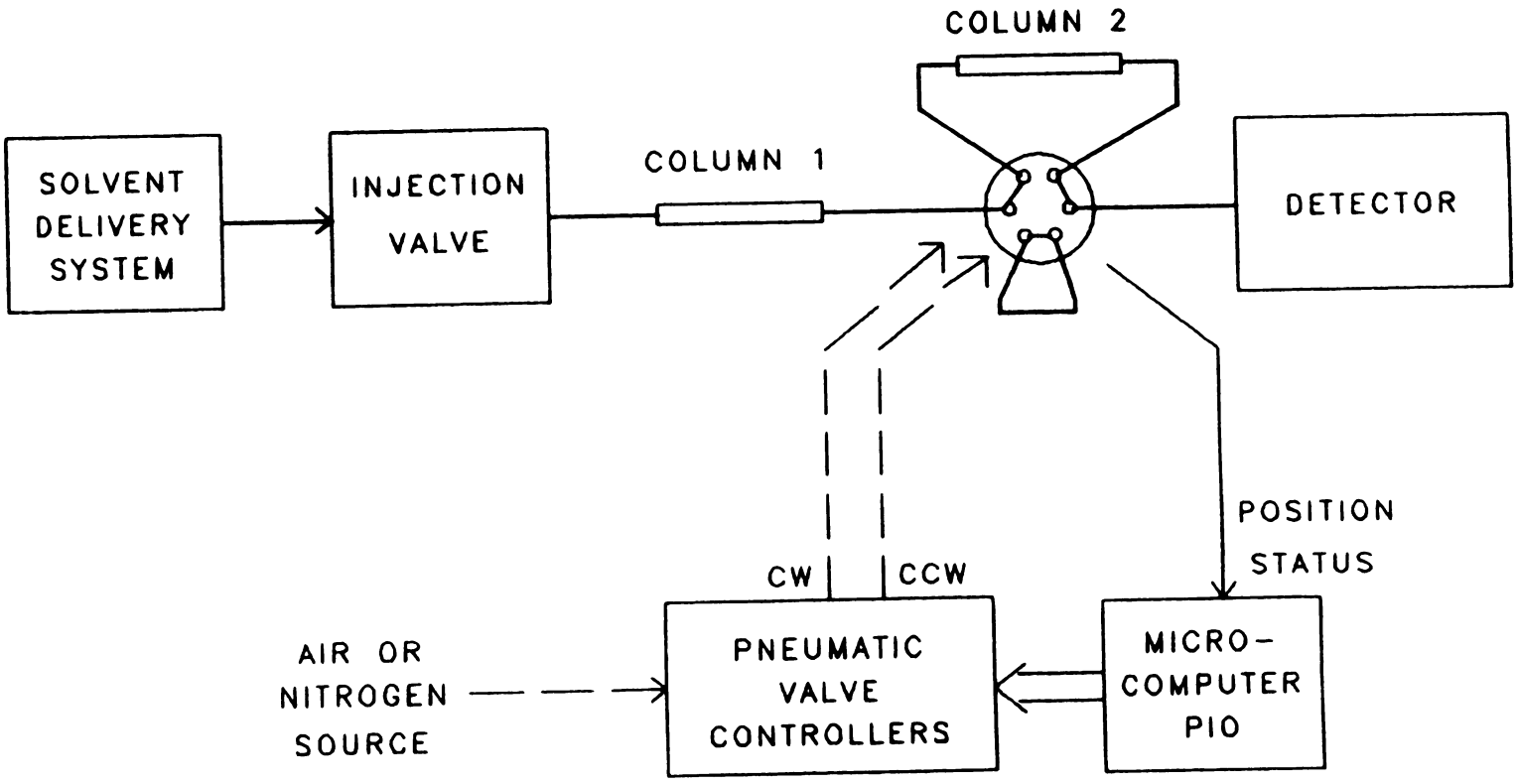


Figure 37. Valve configuration for single-valve heartcut.

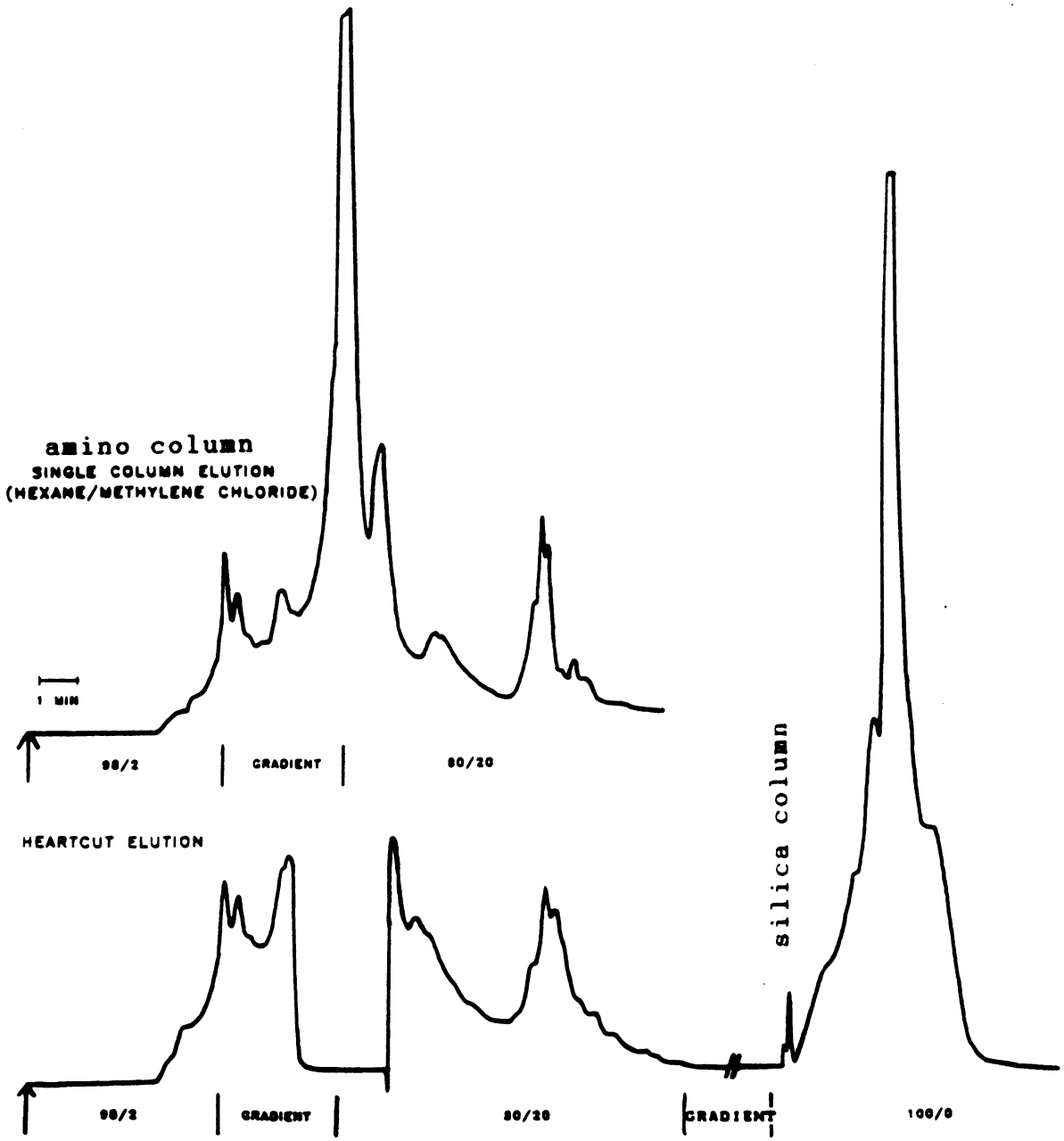


Figure 38. Single-valve heartcut separation, SESC fraction 2; amino column to silica column.

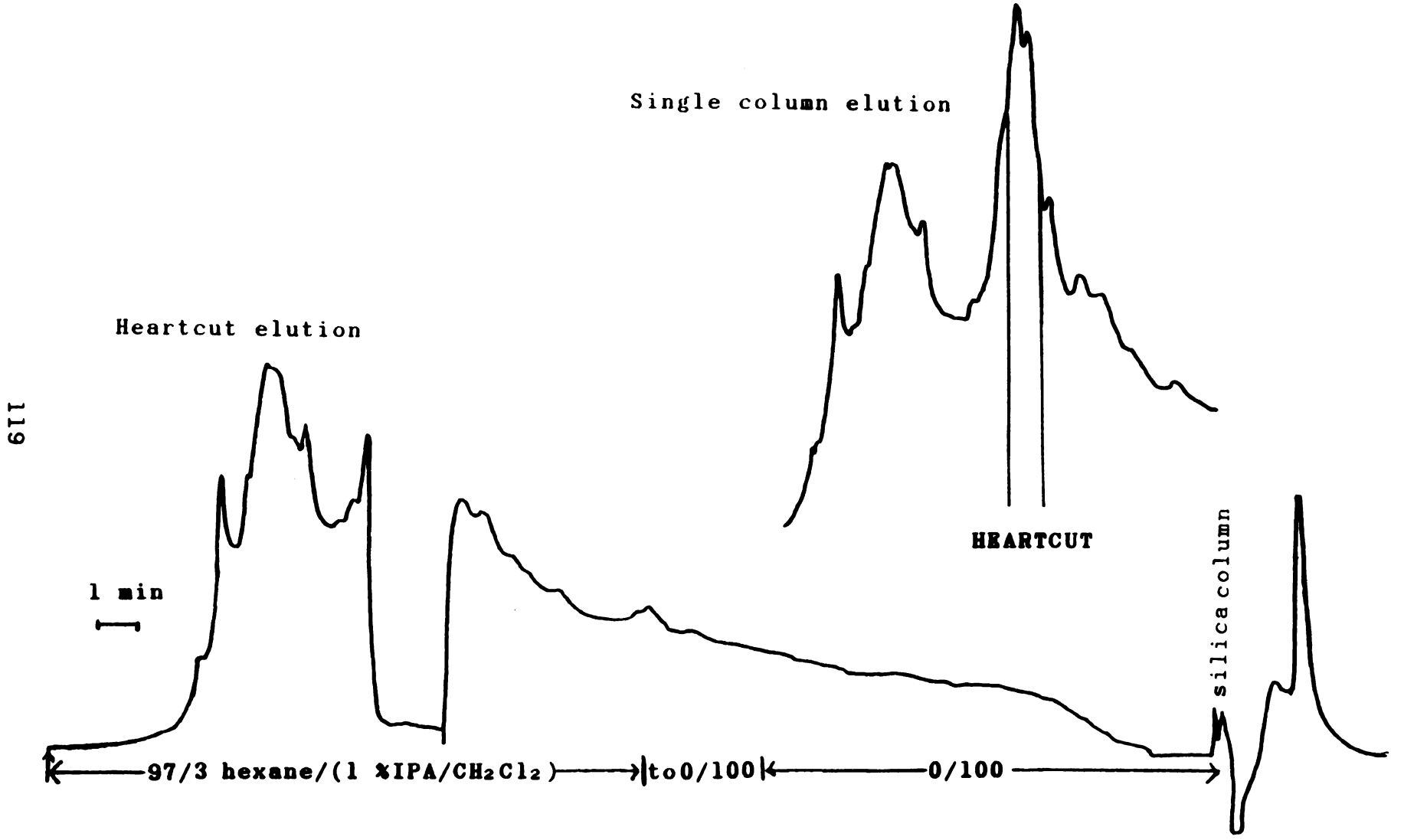


Figure 39. Single-valve heartcut separation, SESC fraction 3; Amino Column to silica column.

second SESC fraction, a portion which eluted off the amino column, was cut onto the silica column. When this cut was separated on the silica column, some further resolution was achieved. The same is true of the cut of the third SESC fraction. These separations served to demonstrate this technique was possible with this instrument. The results were not as good as expected due, no doubt, to the fact that the silica column's efficiency had deteriorated because of deactivation and irreversible adsorption of some fuel components.

b. Two-Valve Heartcut Separation

As discussed earlier, the use of a two-valve configuration produces a much more powerful heartcutting system, as compared to a one-valve configuration. A simple two-valve multidimensional configuration is depicted in Figure 40. A specialized version of this, which was discussed in the experimental chapter of this dissertation, is shown in Figure 41. This experimental setup was used to obtain correlated size and polarity information about the residual fuel, by coupling the Ultragel, size-exclusion column, and the ODS column. For this to be possible a pressure restrictor was placed in the by-pass loop of the second valve to keep the backpressure of the system constant for the sake of the polystyrene-divinylbenzene gel of the size-exclusion column.

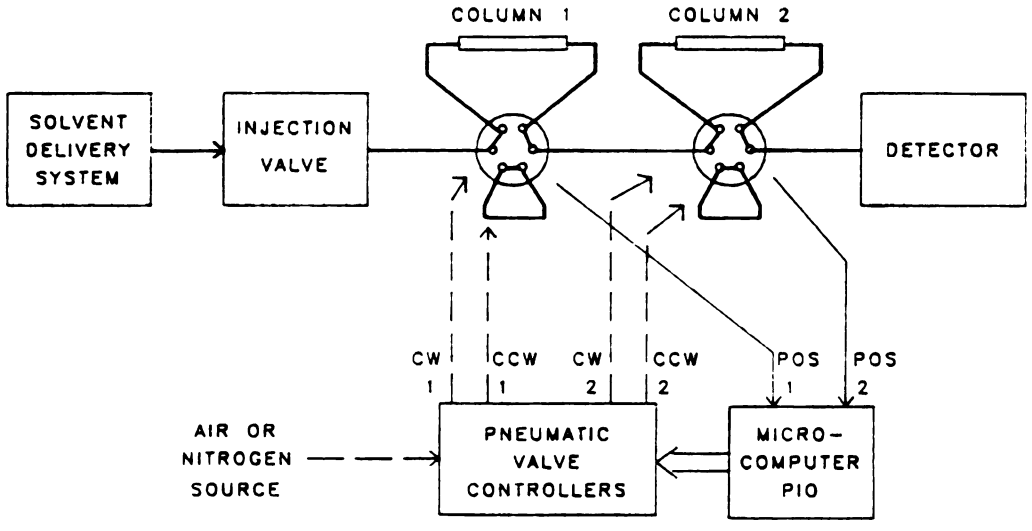


Figure 40. Two-stage valve configuration for multidimensional HPLC.

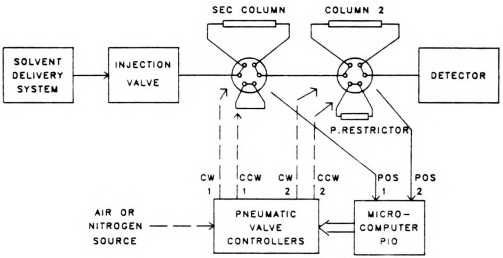


Figure 41. Valve configuration for size-exclusion separation with heartcut.

The size exclusion chromatogram of the whole fuel (chromatogram 1) and then the reverse-phase separations of two heartcuts (chromatograms 2 and 3), made at the absorbance maxima of the SEC chromatogram, are shown in Figure 42. This experiment illustrates this technique and provides some broad-scale information concerning the fuel. The cut that was taken earlier in time (chromatogram 2), elutes later in time from the Ultragel column. This seems to indicate that these larger components are also less polar, than the components of the second heartcut. These elute later in time from the Ultragel column and so are smaller in size. This is surprising as the larger components are also expected to be more highly functionalized. There may be some other factors which should be considered when interpreting these chromatograms. For instance there is a great deal of overlap exhibited by the components as they elute off of the ODS column. This may be due to the fact that a very large cut (1/2 mL) was taken in order to provide enough material for detection. There may not have been good enough zone compression of the cut occuring at the head of the ODS column. If this was true, resolution would be poor. The other possibility is that another stationary phase would be more effective. The best route for further investigation of this topic would be more complete size separation on a PRP1, microparticulate size-exclusion column (Hamilton or Perkin-Elmer), which

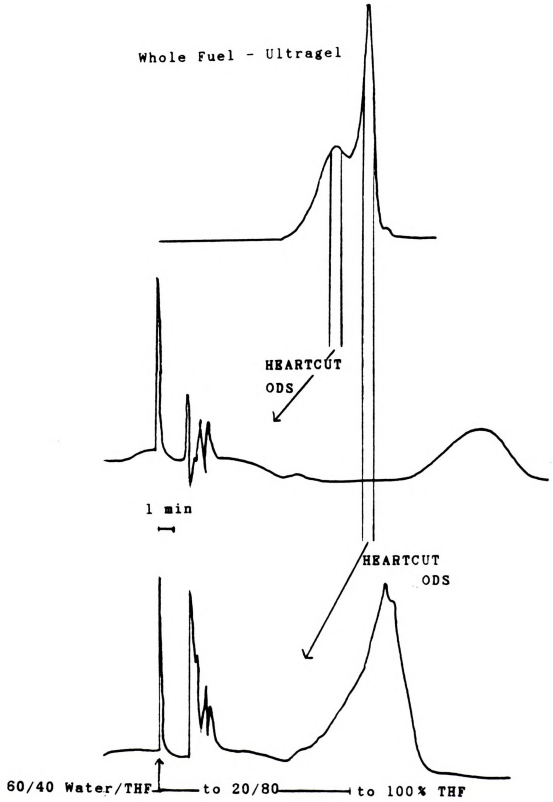


Figure 42. Size-exclusion separation with heartcut, whole residual fuel.

would lend itself more readily to multidimensional experiments.

F. HPLC(MHPLC)/Element-Specific Detector Interface

1. HPLC/AA Studies

a. Interface Development and Evaluation

The first interface used between the SP8700-based HPLC and the Varian AAS was a direct interface, in which the HPLC effluent was sent through a minimum length of Teflon tubing, directly to the nebulizer intake capillary. This interface was characterized by the reverse phase separation of a solution containing 80 ppm of $Ni(dtc)_3$ in methanol, on an ODS column. The nickel complex synthesized by this researcher contained a major contaminant as seen in Figure 43. The use of an element-specific detector was ideal for determining which peak, or if both peaks, contained the nickel complex. Figure 43 displays the response of the UV-detector, and the AAS detector, at 230.2 nm, for both peaks. Apparently, the first peak contained the nickel complex.

Two important aspects of this interface can be evaluated by considering the results of this experiment. One is how much band-broadening was introduced by the interface. Comparison of the peak shapes and peak widths

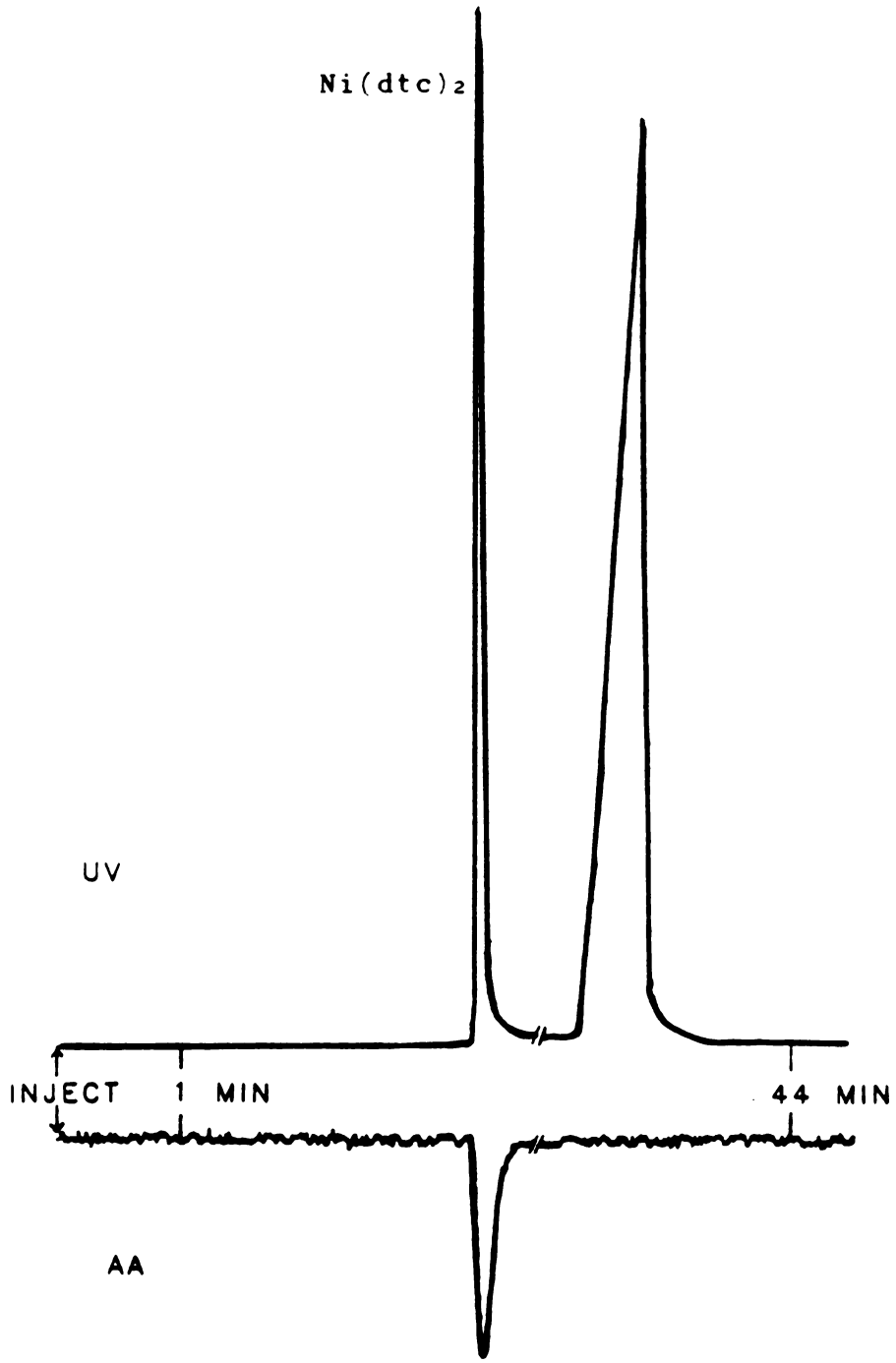


Figure 43. HPLC/AA: $Ni(dtc)_2$ purity test; separation on ODS column with methanol at 2 mL/min; air/acetylene flame, 232.0 nm.

produced by each detector indicates that there was some band-broadening introduced by this interface. This is discussed in more detail later in this section. The second important aspect to be considered is the detection limit which can be achieved with this technique. There is a definite difference in signal intensity obtained by the two detectors. This is partly explained by the fact that there is a larger percentage of chromophore in this peak, which is what determines the UV-detector response, versus a relatively small amount of metal, which determines the AA detector response. In addition, this small amount of metal is contained in a fairly complex matrix which the flame must first decompose in order to form free atoms. A third point is that the concentration of the metal is quite low by the time it reaches the AA due to chromatographic dilution. This is the essence of the HPLC/AA sensitivity problem. The limit of detection was determined by injecting 20 μL aliquots of a series of $Ni(dtc)_3$/methanol solutions having different concentrations. The results of this study are displayed in Figure 44. The limit of detection, which is defined as a signal-to-noise ratio of two, was reached when an 8 ppm solution was injected. Chromatographic dilution dilutes this 8 ppm solution to about 0.3 ppm by the time it reaches the AA. This is a reasonable AA detection limit, especially considering factors such as flame volume, which were discussed in the historical chapter. The problem with this detection limit is that it requires a higher metal

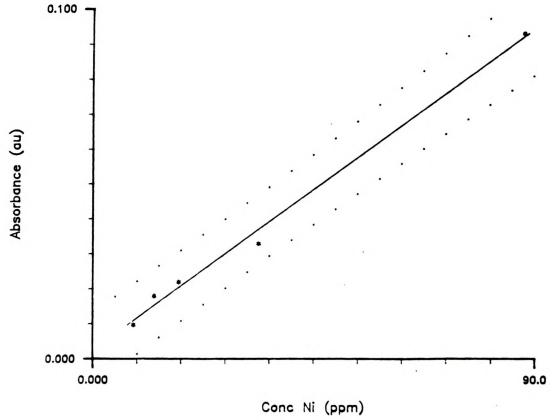


Figure 44. HPLC/AA: sensitivity and limit of detection; $Ni(dtc)_2$ on ODS column, methanol at 1 mL/min; air/acetylene flame; 232.0 nm.

concentration in the injected sample than is usually possible in fuel studies.

An alternate interface was tested to see if it could improve this situation. This was the 'dripping cup' interface, as illustrated in Figure 5. This interface should improve the detectability of this technique since the 'starved mode' of nebulization has been shown to be more efficient. The type of peak obtained with this interface is presented in Figure 45. This is a noisy signal due to the intermittent nature of sample introduction; however, acceptable peak shapes are possible. The important aspect of this figure is that the peak intensity is flow rate dependent. This is due to the mass sensitivity of the detector. Thus, there is a certain drop size required to achieve full signal intensity. If the drops are not this large, then an increase in drop introduction frequency results in an increase in signal intensity. Unfortunately, the drops produced in this experimental setup were limited in size by the surface tension of the mobile-phase. Therefore, this was not a variable which could be modified. However, controllable drop size will not necessarily produce the ideal interface. A drop which is big enough to produce a full signal, will also be large enough to result in some loss of chromatographic resolution.

The band-broadening introduced by both the direct and dripping cup interface was investigated by comparing the

Figure 45. Peak shape with dripping cup interface; $Ni(dtc)_2$ on ODS column with methanol; air/acetylene flame; 232.0 nm.

number of theoretical plates associated with the peak shapes produced by each detector. This relationship, plus the relationship of band-broadening and chromatographic flow rate, are depicted in Figure 46. At the lower flow rates, which are ideal for HPLC, there was a large amount of band-broadening introduced by the nebulizer. The situation was somewhat better for the cup interface, as compared to the direct interface, but was still not ideal. At high flow rates there is a great loss in chromatographic efficiency, but the relative amount of band-broadening introduced by the nebulizer is less. This illustrates the basic flow incompatibility of HPLC systems and AA spectrometers which have concentric nebulizers.

b. Chromatographic Results

Regardless of the limitations of HPLC/AA, some useful data was produced. One study involved the separation of two nickel model compounds, $Ni(acac)_2$ and $Ni(dtc)_2$, by reverse-phase chromatography on an ODS column. Figure 47 depicts the chromatogram as seen by both detectors. The band-broadening introduced by the AA is evident. Nonetheless, this illustrates the usefulness of AA for samples with relatively high metal levels.

The analysis of a size-exclusion separation of the whole residual fuel was possible, due to the fact that the natural uptake rate for chloroform, by the nebulizer, was

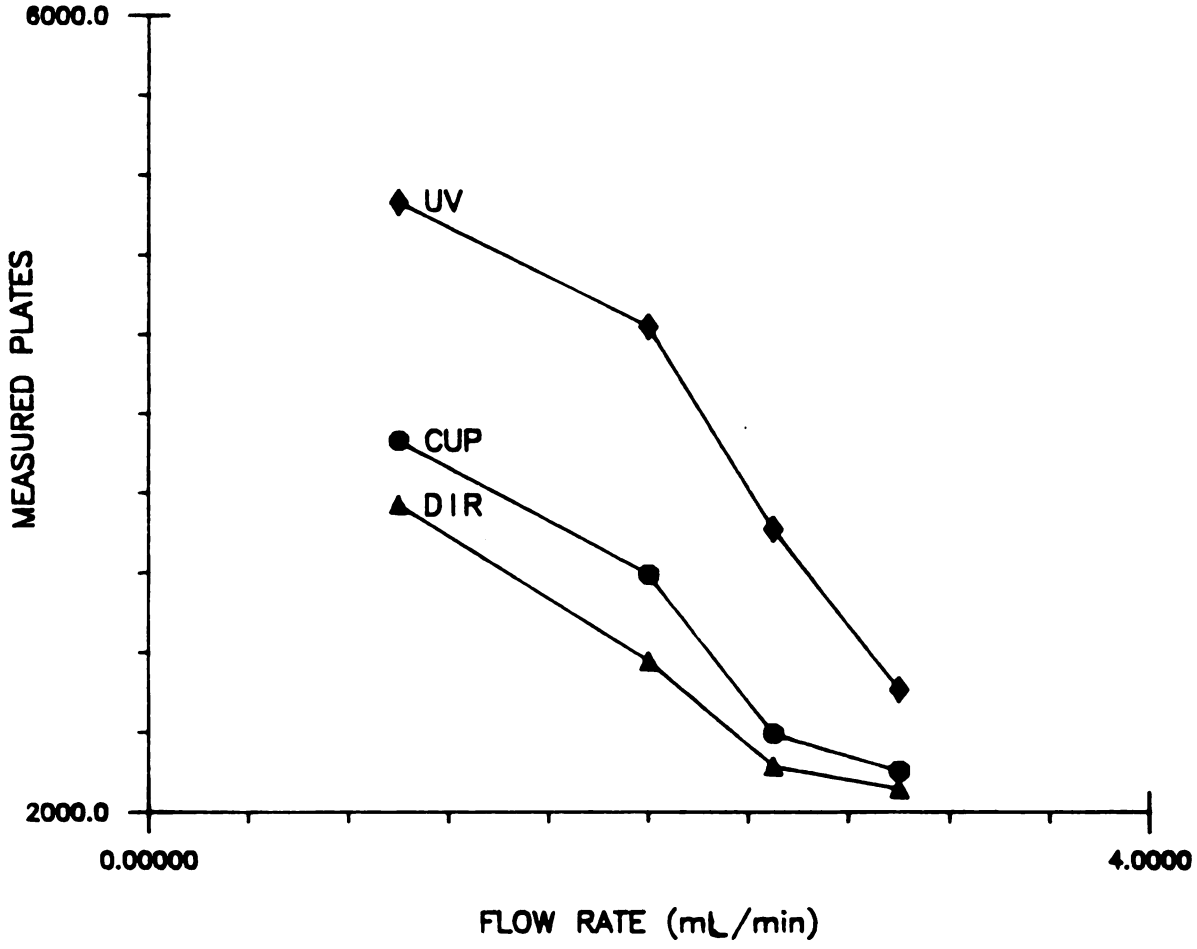


Figure 46. HPLC/AA: band-broadening introduced by different interfaces.

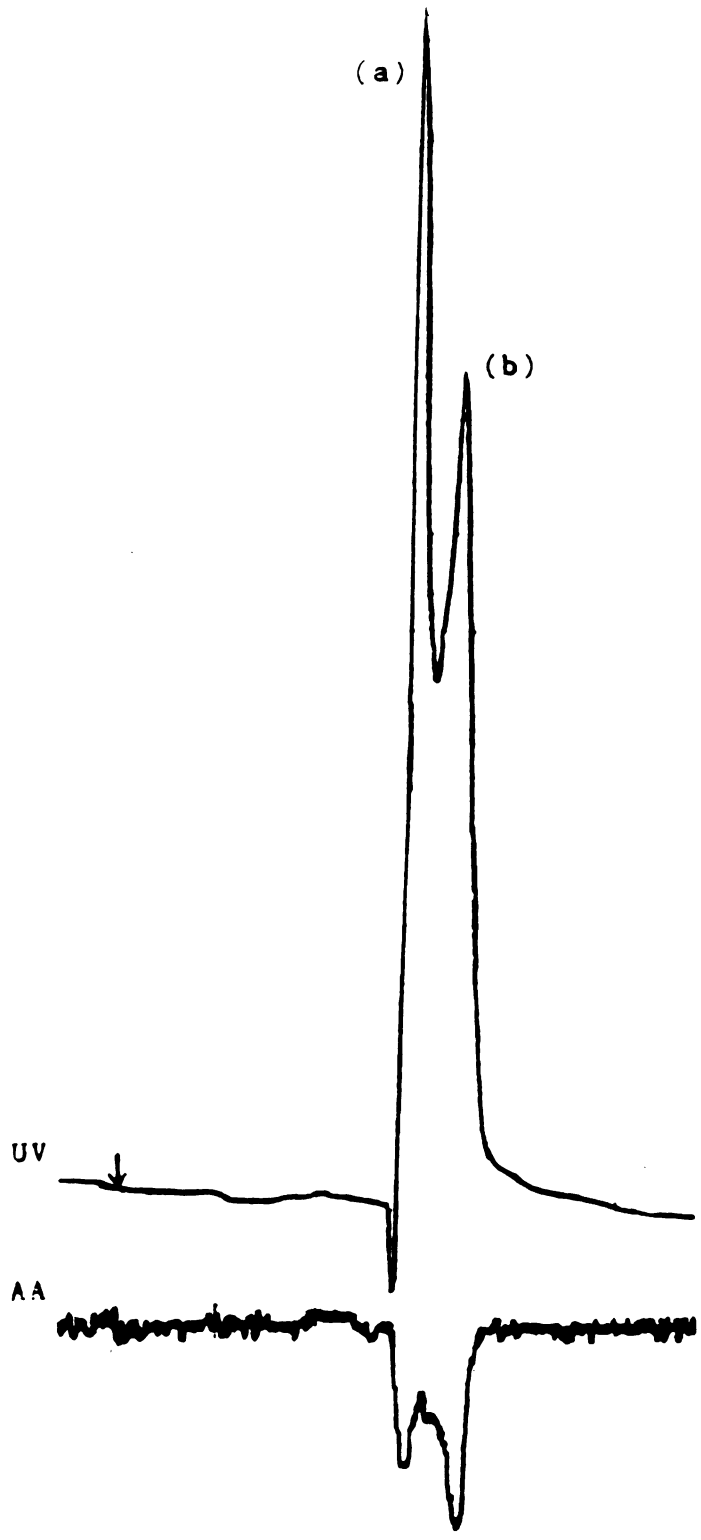


Figure 47. HPLC/AA: separation of (a) $Ni(dtc)_2$, and (b) $Ni(acac)_2$, ODS column with methanol at 2 mL/min; air/acetylene flame, 232.0 nm.

about 2 mL/min. This is an acceptable HPLC flow rate. Therefore, if chloroform was used as the mobile-phase, the size-exclusion effluent could be analyzed in this manner. The results are shown in Figure 48. Atomic absorption was monitored at both the nickel (232.0 nm) and the iron (248.3 nm) line, since these metals are present in the residual fuel at relatively high concentrations. The signal intensities which were obtained are much less than were hoped for. Nonetheless, the signals are reproducible, and were confirmed by off-line fraction collection studies. These results are useful in that they provide evidence for the localization of the metal which is present in this fuel. This indicates that the metal must exist in specific complexes, as opposed to being spread throughout the sample, either in a loosely associated form, or due to the action of the chromatographic solvent. These areas of localization can be correlated to relative size by referring to the UV-detector trace. Unfortunately, the limit of detection has obviously been reached in the AA analysis. Thus, much information can not be obtained. For instance, possibly these areas of localization may exist on top of a background resulting from the spreading out of the rest of the metal by the chromatographic solvent. This discussion pertains to the results presented in Figure 49 for the determination of chromium in the reverse-phase separation of the sixth SESC fraction by the ODS column.

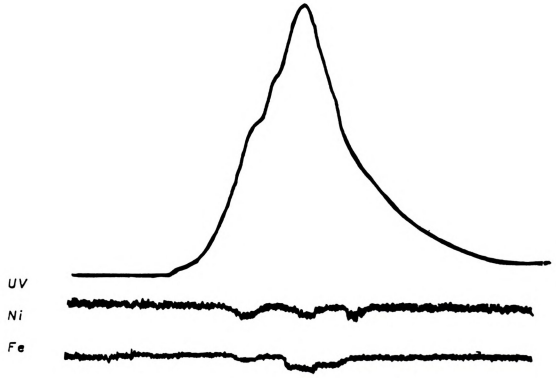


Figure 48. HPLC/AA: size-exclusion separation of whole residual fuel; Ultragel column with $CHCl_3$ at 2 mL/min; air/acetylene flame, Ni at 232.0 nm, Fe at 248.3 nm.

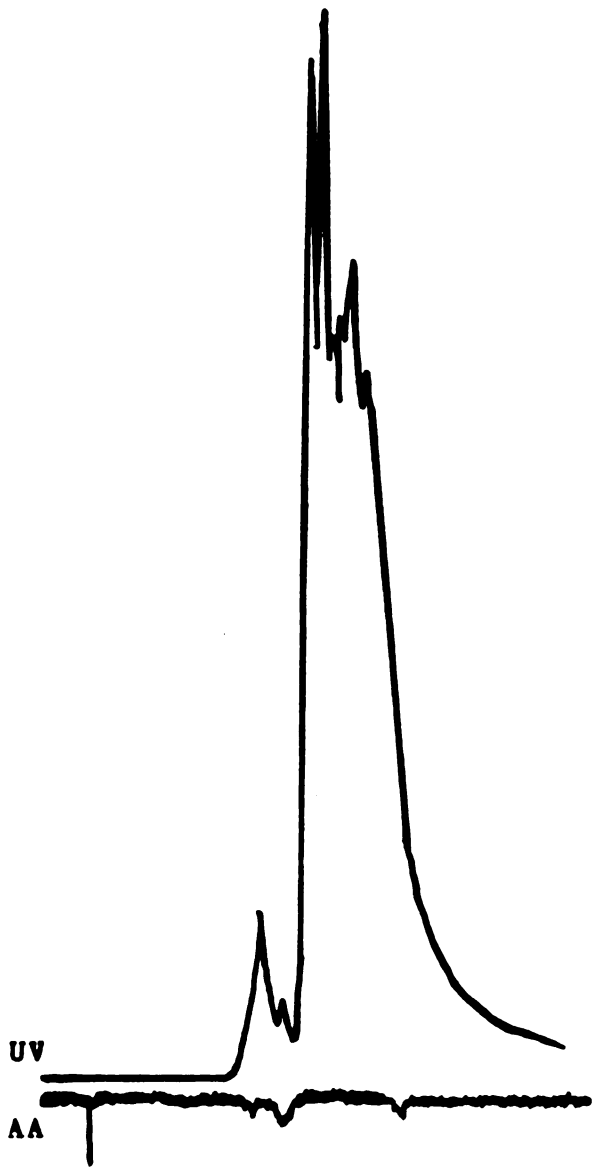


Figure 49. HPLC/AA: reverse phase separation of SESC fraction 6; ODS column with methanol at 2 mL/min; nitrous oxide/acetylene flame, 357.9 nm.

2. HPLC/ICP Studies

The detectability of the AA technique was not good enough to detect very much of the metal that was present in the SESC fraction. Therfore, an HPLC/ICP interface was attempted. This decision was based on the lower limits-of-detection which the ICP technique can provide.

a. Determination of Operating Parameters

Special conditions are required for the operation of an ICP with organic solvents, as was discussed earlier. The actual operating parameters which are discussed here, were listed in the experimental chapter. It was necessary to initiate the plasma and then aspirate an aqueous solution before the organic solvents could be introduced. This introduction was made gradually, usually by way of water/ethanol mixtures. At the same time the rf power, and gas flow rates were adjusted to the values appropriate for operation with organics. In order to aspirate organic solutions successfully, it was necessary to use a very low nebulizer flow to decrease both the associated solvent emission plume, and carbon deposition. A high tangential flow, or plasma gas flow, was necessary to keep the discharge away from the quartz tubes; this also helps to reduce carbon deposition. Unfortunately, these conditions

all decrease the amount of a sample which can be introduced into the plasma in an organic solvent. The organic solvents which were evaluated for use with the ICP include chloroform, methanol, ethanol, and MIBK. Chloroform was of particular interest as this was the mobile-phase used in the SEC/AA studies. However, it produced an extreme emission plume, and the plasma was very unstable. The same was true for methanol, which was unfortunate for the same reasons as for chloroform. The most successful organic solvents were ethanol and MIBK, both of which are poor HPLC solvents.

b. Sensitivity Studies

The limit of detection in an organic matrix had to be detemined by nebulization, instead of sample injection. It was not possible to simulate the AA sensitivity study due to the plasma's lack of stability with organic solvents. Thus, solutions having various concentrations of iron were prepared by diluting Conostan S-12 with MIBK. The detection limit determined in this way was 3 ppm iron. The aqueous limit of detection for iron was determined for comparison. This was done by injecting a 60 µL sample of an aqueous ferric chloride solution into a flowing stream of water. The limit of detection was determined to be 0.6 ppm, which corresponded to an injection of a 3 ppm solution, diluted five times by the flowing stream of solvent.

c. Band-Broadening Study

The band-broadening introduced by the interface through the concentric nebulizer, standard spray chamber, and the ICP itself, was investigated. This was done by injecting 60 μL aliquots of the ferric chloride solution into a stream of water flowing at 2 mL/min. The corresponding UV-detector peak shape was obtained by the addition of a trace amount of acetone to the iron solution. The experiment had to be performed in this way for reasons enumerated in the experimental chapter. The results of this experiment are shown in Figure 50. As can be seen a large amount of band-broadening was introduced. This is no doubt mainly due to the type of spray chamber employed.

The HPLC/ICP technique shows promise with the following modifications. The torch needs to be redesigned in the manner discussed in the historical chapter, to allow more efficient rf coupling when organic solvents are used, and to minimize carbon build up. It is also important that a more efficient spray chamber design be implemented. This will probably have to be cooled to remove solvent vapor. A special interface may also be necessary to allow the pumping of some HPLC solvents.

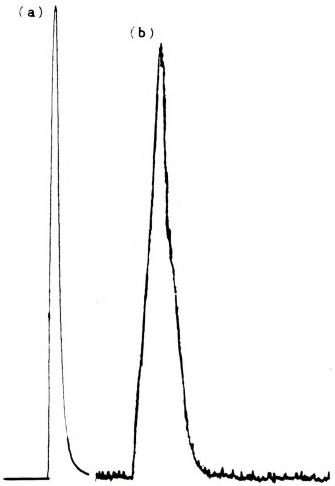


Figure 50. HPLC/ICP: band-broadening investigation; ferric chloride/acetone peak by (a) UV-detector and (b) ICP.

V. CONCLUSIONS AND FUTURE PERSPECTIVES

The research reported in this dissertation, has developed and evaluated several techniques which can aid petroleum metal speciation. The results of these studies have clearly demonstrated the complexity of the metal speciation endeavor. The following sections review the results of this work with respect to what further modifications should be made, or what additional techniques should be evaluated in the future.

A. Column Chromatography for Compound Class Separation and Preliminary Metal Speciation

The SESC separation scheme was shown to be effective for the compound class fractionation of the residual fuel being studied. Atomic absorption spectroscopic metal determinations of these fractions demonstrated that in some cases SESC separation resulted in the localization of the metal in specific fractions. When more than one fraction contained significant percentages of the metal, as was the case for chromium, this was interpreted as evidence that the

metal resided in one or more stable complexes. These complexes were either of the class specific to that fraction, or of a type whose chromatographic behavior is influenced by the metal in such a way that it elutes in a manner similar to the compounds of that class. Model compound studies demonstrated that stable metal complexes can behave in both ways. In some cases, the metal's preferred coordination number and complex structures, can be used to explain, or predict, deviate elution patterns. The true nature of the complex may be postulated on this basis.

Cases in which only one fraction contains a significant concentration of a metal may mean that most of the metal exists in one species. However, it is also possible that the chromatographic solvent used to elute that fraction, acted to concentrate the metal, which originally existed in a loosely associated complex. This is feasible since some of the SESC solvents are fairly good complexing agents. Substitution of a different solvent or a solvent mixture having an equivalent strength, might be useful for evaluating this effect. Conversely, the SESC solvents could also spread loosely associated metals throughout several fractions. Thus, the interpretation of metal distribution profiles which do not contain regions of significant concentration is quite difficult. Generally, the only reliable conclusion which can be drawn is that the metal probably exists in a loosely associated complex, whose original nature must be determined in some other manner.

Some alternatives for this are discussed later in this chapter.

Further investigation into the chromatographic behavior of metal-containing compounds would be most interesting and useful in the continuation of this research. Future work could test more types of stable metal complexes, containing a wider variety of metals. The chromatographic behavior of loosely-associated metal complexes could be explored using synthetic petroleum samples, in which the complex is used to spike a model petroleum matrix. In addition, extraction techniques could be employed in conjunction with chromatographic techniques to explore what fraction of the metals in a fuel exist as loosely-associated metal complexes. For instance, comparing the chromatographic behavior of a sample of untreated fuel with that of an extracted sample, would indicate which metal-containing chromatographic components are not due to stable metal complexes. Furthermore, such experiment would provide information about the interaction of these types of complexes with chromatographic solvents and stationary phases. More indepth study of the metal complex-chromatographic solvent interaction is of interest, and could generally be done with molecular spectroscopic techniques. Another appropriate study would be a quantitative investigation of how various metal complexes chromatograph on silica.

The large degree of tailing exhibited by the porphyrins subjected to SESC, suggests that silica may not be the best stationary phase for the compound class separation of metal-containing materials. Thus, it may be worthwhile to evaluate other stationary phases to achieve this type of separation. Bonded phases which exhibit less adsorptive properties may be more suitable, such as a cyano or C_8 bonded-phases. Another possibility is a resin stationary phase such as PRP1 (Hamilton). The manufacturer reports that this material exhibits reverse-phase behavior, which might be effective in eliminating the observed band-spreading. However, PRP1 has also been reported as an effective size-exclusion material. It is unlikely that any material will function well in two such different capacities.

A further improvement would be to adapt the SESC technique to preparative HPLC, as was done for the API-60 technique (137). Preparative HPLC would not only facilitate the separation process, but would also provide an opportunity for on-line element-specific detection. On-line detection would be much more efficient, and possibly more informative than the off-line technique, due to the elimination of sample transfers and delayed metal determination.

B. Multidimensional HPLC Applied to Fuel Characterization

HPLC is a logical technique for acquiring further information about the constituents of the SESC fractions. However, the single-column separations of the fractions exhibited such a large degree of overlap, that they provided little specific information. The HPLC model compound studies provided insight into the separation mechanisms of the stationary phases employed and, more importantly, demonstrated the difficulty of interpreting fuel separations based on retention time. In addition, single-column techniques were generally inadequate at handling the wide range of polarities evidently present in most of these fractions.

The multidimensional HPLC techniques developed provide a much more effective means for obtaining information about the SESC fractions. These techniques can provide a correlated matrix of information, (e.g., size and polarity), which is extremely useful for characterizing such complex analytes. Multidimensional HPLC is also capable of more complete component resolution than single-column HPLC. This was demonstrated by the heartcut experiments. Generally, the resolution achieved in these examples was not optimal due to the limited number of stationary phases available and the column deterioration which is often a consequence of methods development work. None of the reported separations

led directly to component identification. However, this was not the goal of these studies, nor is it likely to be possible solely with HPLC . Techniques to meet this goal are discussed later.

C. HPLC with Element-Specific Detection for Metal Speciation

The ideal method for metal speciation in fuel would characterize the species by a chromatograhic separation, and then determine the metal content of each species in an on-line fashion. In this way the metal content could be directly correlated to a particular fuel component. The results of the HPLC/element-specific detector investigations reported here demonstrate that this is not a simple task. There are three basic problems. One is interface inefficency. Most conventional nebulizers are no more than ten percent efficient. Therefore, most of the metal which is present in the sample never reaches the analytical zone of the spectroscopic detector. This compounds the effect of the second problem which is the dilution of the originally low metal concentrations, by virtue of the chromatographic separation. The third problem is the loss of chromatographic resolution which generally occurs in the nebulizer spray chamber. In some cases, band-broadening may spread the metal-containing component to where it is below the limit of detectability. Therefore, both an efficient,

low dead-volume interface, and a very sensitive element-specific detection technique are necessary.

This work employed and evaluated two simple interface schemes; a piece of Teflon tubing which connected the HPLC column to the nebulizer capillary, and the dripping cup interface. Each met with limited success. An alternate interface, which deserves investigation, is the isolated-droplet generator constructed in this laboratory (139). This device may well improve sample introduction efficiency, while conserving chromatographic resolution, since the effluent is converted to a droplet stream.

The ICP technique was the most promising of the metal detection methods investigated in this research. The modifications detailed in the last chapter are definitely necessary to achieve the detectability and compatibility necessary for metal determinations in fuel components present in organic HPLC effluent. There are two options if the detectability of the modified instrument is still not sufficiently low for this application. One option is to try a different technique with lower limits of detection, such as atomic fluorescence. This could even be done using the ICP for sample desolvation and atomization. An array of pulsed hollow cathode lamps could be used to provide multielement capabilities. Needless to say, this approach is complex and would no doubt be accompanied by its own special problems and limitations.

The second option is to employ a special chromatographic technique, which can relieve the stringent detectability requirements for the element-specific detector. One possibility would be to concentrate the metal by repeatedly heartcutting the suspected metal-containing peak onto a special column. This column might be packed with a conventional stationary phase which is particularly retentive for that type of compound. Special stationary phases do exist which can extract and retain the metal, pulling it out of its complex. These materials usually consist of a ligand or clathrate bonded to the stationary support material.

Another potentially effective chromatographic technique is supercritical fluid chromatography (SFC). This may offer two advantages. First it is theoretically possible to introduce all of this chromatographic effluent into an atomic detection device. This would greatly reduce the detectability requirement for the detector, while also increasing the efficiency of the detection technique as no energy would be necessary for desolvation. However, actually executing a SFC/element-specific detector interface is not simple. The desolvation process is accompanied by a tremendous amount of expansion. Therfore, either the interface will have to be able to accomodate this expansion, and somehow retain all of the solute material, while also being able to handle the solute in its desolvated form; or

the detector will have to be modified to operate at supercritical conditions. Researchers at VPI are investigating such an interface with the hopes of applying it to fuel studies. Supercritical fluid chromatography may well be ideal for fuel separations in that it may eliminate the problems associated with conventional HPLC mobile-phases interacting with the the metals and metal complexes present in the fuel.

A final comment should be made concerning the actual identification of the metal-containing species as they exist in fuel. Chromatographic techniques, even SFC, which is less likely to alter the original nature of the complex, can only separate and characterize the metal-containing species. This is sufficient for applications solely concerned with removing unwanted metal species. However, actual speciation will only be possible by the combination of HPLC, element-specific detection, and molecular spectroscopic techniques such as IR, UV-visible, molecular fluorescence, NMR, or mass spectroscopy. Each of these techniques have been successfully used in conjunction with HPLC. Considering recent technological advances, the possiblity of combining one or more of these techniques on-line with an HPLC/element-specific detector is quite real. Only when this becomes a reality, will complete metal speciation in petroleum matrices be possible with a single system.

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APPENDICES

APPENDIX A

FORTH Programs for Multidimensional HPLC Experiments

Multidimensional Backflush

```
Block Number:  47
0    ( BACKFLUSH WITH FLOW PROGRAM; SOLVENT CHANGE )
1    CVARIABLE FILE
2    : 2MDBF SETUP FILE C! 1 CW 2 CCW EDFI FILE C@ ENTER
3    %A #9 #7 %C #3 FLOW #1 ENTER TIME #5 #. #5 ENTER
4    TIME #5 #. #6 %A #1 #0 #0 FLOW #1 ENTER
5
6
7    TIME #9 #0 ENTER
8    EDRU PRESS INIT FILE C@ ENTER PRES PRESS
9    FLOW? SYNC 5 30 EVENT 1 CCW 9 0 EVENT 2 CW 90 0 EVENT ;
10
11
12
13   ( INCLUDE FILE # BEFORE 2MDBF -- EXAMPLE: #1 2MDBF)
14   ( INSTRUMENT MUST BE IN EDIT MODE TO BEGIN)
15
```

Selectivity Programming with Backflush

```
( 2SELPROG -- THIS ROUTINE ALLOWS ELUTION OFF PRECOLUMN PLUS)
(    AMINO COLUMN, THEN BACKFLUSHES PRECOLUMN ONTO ODS )
 CVARIABLE FILE  CVARIABLE 2FIL
: 2SELPROG SETUP 1 CW 2 CW 2FIL C! FILE C! EDFI FILE C@ ENTER
  %A #9 #9 %C #1 FLOW #1 ENTER TIME #3 ENTER
  TIME #1 #2 %A #6 #0 %C #4 #0 ENTER TIME #1 #8 ENTER
  TIME #2 #4 %C #1 #0 #0 ENTER TIME #2 #8 ENTER
 EDFI 2FIL C@ ENTER %C #1 #0 #0 FLOW #1 ENTER
 TIME #2 #8 ENTER TIME #2 #8 #. #1 %B #4 #0  %C #6 #0 ENTER
 TIME #7 #0 ENTER
  EDRU PRESS INIT FILE C@ ENTER PRES PRESS FLOW? SYNC
  27 0 EVENT CONT 2FIL C@ ENTER
  28 6 EVENT 2 CCW 1 CCW 90 0 EVENT ;
```

Heartcut and Heartcut Development with Gradient

```
Block Number:  29
0    ( MULTIDIM GRADIENT III-17)
1    CVARIABLE FILE CVARIABLE 2FIL
2    : 17GRADIII SETUP FILE C! 1 CCW EDFI FILE C@ ENTER
3     %A #9 #7 %C #3 FLOW #1 ENTER TIME #1 #8 ENTER
4    TIME #2 #1 %A #1 #0 #0 ENTER TIME #6 #0 ENTER
5     EDRU PRESS INIT FILE C@ ENTER
6      PRES PRESS
7     FLOW? SYNC 8 0 EVENT  1 CW 10 0 EVENT  1 CCW
8     30 0 EVENT 1 CW 90 0 EVENT ;
9    ( BE SURE TO INCLUDE FILE #  BEFORE 13GRADIII-- EXAMPLE:)
10   ( #1  13GRADIII )
11
12
```

Ultragel Heartcut onto ODS Column with Gradient

```
(ROUTINE FOR HEARTCUTS OFF STYRAGEL ONTO ODS;
 ODS DEVELOPED WITH STY OUT OF LINE;
 STY USES THF, ODS  WATER/THF; REEQUIL GOES TO ORIGINAL COND)
:STYHRT SETUP EDFI #1 ENTER %C #1 #0 #0 FLOW #1 ENTER
 TIME 6 ENTER#
 TIME 20 ENTER# %A 60 ENTER# %C 40 ENTER#
 TIME 25 ENTER# TIME 35 ENTER# %A 20 ENTER# %C 80 ENTER#
 TIME 45 ENTER# %C 100 ENTER# TIME 60 ENTER#
 STY SYNC 5 30 EVENT 2 CCW 3000 WAIT 2 CW 1 CCW
 CONT #1 ENTER 25 00 EVENT 2 CCW
 55 00 EVENT STP PRESS EDITMODE REEQUIL ;
 ( STYHRT USES SP8700 FILES 0, AND 1, REEQUIL USES FILE 2;)
 ( SP8700 MUST BE EDIT MODE TO BEGIN)
```

APPENDIX B

ERBS-5 Characterization Results*

Property	Result	Test
Hydrogen, Wt. %	12.80	ASTM D-3701
Sulfur, Total, Wt. %	0.14	NDXRF
Sulfur, Mercaptan, Wt. %	< 0.0003	D-3227
Nitrogen, ppm by Wt.	82	Chemiluminescence
Oxygen, Wt. %	< 0.1	Unterzucher
Arometics, Vol. %	30.2	D-1319
Olefins, Vol. %	0.6	D-1319
Naphthalenes, Wt. % (Vol. %)	16.0 (13.5)	D-1840
Specific Gravity (15°C/15°C)	0.8415	Pycnometer
Freezing Point °C (°F)	-28.9 (-20)	D-2386
Viscosity, CS, at 21°C	2.06	D-445
0°C	3.30	D-445
Flash Point, °C (°F)	51.1 (124)	D-56
Net Heat of Combustion, KJ/Kg (BTU/lb.)	42.44 (18,244)	D -2382
Smoke Point, mm	15	D-1322
Thermal Stability, JFTOT		D-3241
Spun TDR	9.6	
Spot TDR	12.2	
Δ P (mm Hg)	0.0	
Distillation		D-86, D-2887

GROUP TYPE	WT % (BASED ON 100)	WT % OF TOTAL SAMPLE
ALKANES	0.0	0.0
CYCLOPARAFFINS	0.0	0.0
ALKYLBENZENES	20.1	6.6
INDANES-TETRALINS	17.3	5.7
INDENES-DIHYDRONAPHTHALENES	6.6	2.2
NAPHTHALENES	1.8	0.6
ALKYLNAPHTHALENES	42.1	13.9
BENZOTHIOPHENES	3.9	1.3
ACENAPHTHENES	1.1	0.4
ACENAPHTHYLENE-FLUORENES	2.5	0.8
PHENANTHRENES	4.6	1.5
DIBENZOTHIOPHENES	0.0	0.0
TOTALS	101.0	33.0

*Provided by Dr. Gary Seng of NASA