T-3080

PRELIMINARY INVESTIGATIONS OF AN INTEGRATIVE GAS GEOCHEMICAL TECHNIQUE FOR PETROLEUM EXPLORATION

by

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A thesis submitted to the Faculty and Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science (Geochemistry).

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Date Nov. 24, 1986

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ABSTRACT

A new, innovative method of integrated gas geochemical exploration for petroleum has been tested and evaluated. The technique involves the shallow burial of a Curie-point wire coated with a small amount of activated carbon in a cylindrical container in the topsoil where the carbon interacts and adsorbs emanating soil gases. A collection period of several days to weeks was employed depending on soil conditions. After removing the wires from the support apparatus, analysis was conducted using a Curie-point pyrolyzer directly coupled to a quadrupole mass spectrometer. The resulting mass spectra were analyzed by multivariate statistics using the program, ARTHUR.

Experiments were undertaken in three different areas to assess the response of the system to various situations. Initial laboratory tests included optimizing the components and method for adsorption wire construction. A field test on the Dakota hogback in western Jefferson County, Colorado was conducted to identify potential variables that could influence signal response. Unique fingerprints associated with different subsurface sources of the vapor phase organics enabled discrimination and classification of those sources as a result of the second test in Weld County, Colorado. The third field study at Indianola, Utah revealed that fault systems in highly disturbed areas had associated fingerprints

with a considerably greater content of high molecular weight components. Finally, it was determined that the technique could generate greater quantities of information at a reduced cost as a result of the Patrick Draw, Wyoming test.

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ACKNOWLEDGEMENTS

I would like to dedicate this to my most patient and loving family: Mary, my wife, and daughters, Theresa, Jessica and Elizabeth, along with my parents and in-laws.

I would like to acknowledge and thank my advisor, Dr. Kent J. Voorhees and committee members, Dr. Ronald Klusman, Dr. Stephen Daniel and Dr. Gunther Holzer for their endless support and wisdom. In addition, Steve Durfee was the one person in our research group who not only played a major part in software development for our equipment, but became a boundless source of information, advice, discussion and friendship. Last but not least, I would like to acknowledge the help of Mr. Willis Alderman of Amoco Production Company for his aid in gaining permission to mimic the work of Richers, et al, 1982 for comparison sake.

CHAPTER I

INTRODUCTION

Detection of hydrocarbon leakage in petroliferous regions is the oldest exploration tool known to mankind (Link, 1952). Hunt (1979) notes the use of asphaltic seeps by many of the ancient peoples of the Middle and Far East dating as far back as 3000 B.C. It was an active petroleum seep in an area outside of Titusville, Pennsylvania that led to America's first oil well in the late 1800's. As man's technological advancements created an increasing demand for petroleum generated energy, greater exploration efforts left fewer and fewer of these visible targets untested.

It was at this point in the early twentieth century that several researchers proposed and tested methods for the detection of petroleum microseepages as a new, direct method of oil finding. These early researchers theorized that the light hydrocarbon components were migrating through the micro-fissures and inhomogeneities in the lithologies of petroliferous regions. Laubmeyer (1933) of Germany, Sokolov (1933) of the U.S.S.R., and Horvitz (1939) and Rosaire (1940) of the U.S.A. reported sampling and analytical techniques for the detection and quantitation of these micro-emissions from the subsurface. These early pioneers found both the soils and soil atmosphere sampled above a producing petroleum occurrence had significantly higher concentrations of hydrocarbons than samples collected over barren areas (Sokolov, 1933). The analytical methods used by these early workers involved the separation of the sampled gases into C_1 and C_2+ fractions using condensation followed by analysis via combustion and manometry (Philip and Crisp, 1982; Kartsev, et al., 1954). Field sampling methods followed two different philosophies in these initial studies. The Europeans, Laubmeyer and Sokolov, developed methods of soil gas sampling while their American counterparts, Horvitz and Rosaire, utilized the adsorbed fraction of hydrocarbons on soils. Teplitz and Rodgers (1935), working for Gulf Research and Development Corp. in the early 1930's, attempted vacuum desorption of ethane from soil samples.

A review of the Russian contributions through the mid-fifties is presented by Kartsev, et al. (1954), Sokolov (1959), Sokolov, et al. (1959), and Philip and Crisp (1982). Rosaire (1940), Pirson (1940) and Horvitz (1939, 1945, 1956, 1972) reviewed the American advances with respect to the hydrocarbon analysis of soils, soil gas, and groundwaters relative to terrestrial exploration efforts. Eventually, hydrocarbon gas prospecting even took to the air. Thompson (1979) reported of a helicopter-based reconnaissance technique that locates areas of higher gas flux.

Starting around 1950, workers began to develop sampling and analytical methods for the detection of the secondary effects of the petroleum microseepage. Isotopic ratio variations in the stable isotopes of both carbon and oxygen have been documented by several workers (Nisle, 1941; Rietsema, *et al.*, 1981; and Stahl, *et al.*, 1981). Davis (1967, 1969) reviewed the various microbiological prospecting techniques applied to petroleum exploration. The use of radiometrics as a petroleum exploration method began in the early fifties and continues today (Lundberg, 1952; Merrit, 1956; Armstrong and Heemstra, 1972a&b; Morse, *et al.*, 1982; Morse and Rana, 1983). Helium, an inert, highly mobile element that is commonly found in association with many petroliferous accumulations has also been used by many researchers as an exploration tool. Faul, *et al.* (1954) and Nikonov (1972) discuss the sources of the helium found in oil and gas pools. The development and application of the various forms of helium surveying have been reviewed by numerous people (Ball and Snowdon, 1973; Dikon, *et al.*, 1976; Holland and Emerson, 1979; Pogorski and Quirt, 1979; Roberts, 1979; Palacos and Roberts, 1980; Maddox, 1982).

The evaluation of the dissociation temperature of secondary carbonate cements derived from the oxidation of petroleum hydrocarbons is another technique currently being offered to the industry (Duchscherer, 1980, 1981, 1982).

Since the inception of the microseepage theories in the early twentieth century, there have been many methods developed for both the direct detection of the hydrocarbon cloud or emissions and the secondary phenomena associated with it. In the following sections, a synopsis of the various methods along with the many of the controversies which have evolved over time are reviewed.

Hydrocarbon Techniques

One of the first sampling methods documented in the literature is the free soil gas technique (Laubmeyer, 1933; Sokolov, 1933). In this method of sampling, a hole is drilled to a depth of several meters. The hole is sealed by means of an inflatible collar (packer) and after a period of equilibration the sample is drawn into a container (Philip and Crisp, 1982). Jones and Drozd (1983) outlined a modern analog used by Gulf Research and Development Corporation (GRDC). In the GRDC method, a hole four meters deep is augered, sealed and the gases are then pumped directly into a dual column gas chromatograph system for analysis. Kartsev, et al. (1954) describe the different sampling methodologies used by the Russians up through the mid-fifties. The "delay gas survey" incorporates the drilling of holes to the desired depth, hermetically sealing the hole for an equilibration period of up to twenty-four hours before the sample is withdrawn for analysis. In "deep gas surveying," a hole is drilled to several tens of meters and samples are collected at specific intervals along the bore. Where concentrations of the gaseous components are low, adsorbents such as silica gel were used to increase the hydrocarbon concentrations to suitable levels. Philip and Crisp (1982) conclude that the free soil gas techniques are preferred over other types of sampling systems due to the relative ease and lack of additional handling necessary in that methodology.

While the Europeans pioneered the free soil gas sampling methods, the American emphasis was on soil sampling and various extraction techniques to enable the analysis of the adsorbed hydrocarbon gases. One of the earlier soil extraction methods was developed by Horvitz using an acid/thermal extraction method (Philip and Crisp, 1982). Sokolov (1970) reported that desorption surveys yield greater concentrations of hydrocarbons than did the free soil gas methods. A review of the Russian desorption methods is provided by Kartsev, et al. (1954).

In a Canadian test of the hydrocarbon prospecting methods using soil as the sampling medium, Debham (1965) utilized a new approach to this technique in relation to analysis of the collected samples. A similar extraction process was used to that developed by Horvitz as described earlier. The off-gas was then drawn into a liquid nitrogen trap and later analyzed by gas chromatography (Debham, 1965).

Debham concluded that under the proper conditions, the information gained could be a valuable asset to be integrated with the geologic and geophysical data for a given study area.

A few years later, another test of the hydrocarbon prospecting technology was reported by McCrossan, et al. (1972). In this study, a similar extraction and analytical method was employed but the results were not as encouraging. It was found that the results yielded randomly scattered anomalies with little or no relation to any occurrence in the subsurface (McCrossan, et al., 1972). The greatest influence on the distribution of the anomalous samples was the amount of carbonate found in the soil samples. It seemed that the carbonates released greater quantities of hydrocarbons than did other soil components, and thus McCrossan, et al. concluded that the use of this technology in areas with soils containing variable amounts of carbonates would be fruitless (1972). Similar problems were encountered in several Australian surveys, but a correction factor where the summed hydrocarbon concentrations were divided by the acid soluble fraction of the soil was found to alleviate the problem (Devine and Sears, 1977).

Analytical Advancements

Until the development of the gas chromatograph in the early sixties, sample analysis was limited to a two-component system, the C_1 and C_2+ fractions (Jones and Drozd, 1983). This was accomplished either by condensation of the C_2+ portion or by the use of some chromatographic separation technique (Laubmeyer, 1933; Sokolov, 1933). After separation, the two fractions were analyzed by combustion and manometry from which the data generated could be mapped (Kartsev, et al., 1954). The importance of the introduction of the gas chromatograph as an analytical device cannot be over-emphasized. Along with the ability to separate the low molecular weight hydrocarbons, it added greater sensitivity than that provided by the old, classical analytical techniques (Debham, 1965; Horvitz, 1972). Wood (1980) reported a gas chromatographic method capable of analyzing ethane to 5 ppb, ethene to 5 ppb and propane to 20 ppb. The technique allowed for the rapid quantitative separation of the gas components from methane up to a C_5+ fraction, thus giving the hydrocarbon gas geochemist a greater discriminatory capability (Richers, et al., 1982; Jones and Drozd, 1983).

The added separatory capabilities of the new analytical advancements provided what some workers felt was an ability to better differentiate the type of source responsible for the gas anomaly (Pixler, 1969). Jones and Drozd (1983) indicated that certain ratios of the hydrocarbon components enable the probable distinction betweel oil, gas and condensate reservoirs (Table 1).

Table 1

Empirically Determined Composition Range for Soil-Gas Hydrocarbons over Different Reservoir Types

	C_1/Sum Cn	C_1/C_2	(C_3/C_1)x100
Dry Gas	100-95	100-20	2-20
Gas Condensate or Oil and Gas	95-75	20-10	20-60
Oil	5-50	10-4	60-500

Non-Hydrocarbon Quantitation Methods

Within fifteen years of the publication of the work by Laubmeyer and Sokolov on the detection of hydrocarbon micro-seepage anomalies, secondary phenomena associated with this leakage were recognized and documented. One of these phenomena was the presence of several different types of hydrocarbon oxidizing bacteria over the petroleum accumulation (Kartsev, et al., 1954; Davis, 1967; Davis, 1969). It was postulated that these bacteria consume the leaking hydrocarbons and the resulting hydrocarbon depletion is one of the factors in the formation of the classical halo type of surface anomaly pattern (Davis, 1967; Davis, 1969). Horvitz (1939) indicates that carbonate mineralization derived from the carbon dioxide generated by these bacteria is responsible for the minimal quantities of hydrocarbon gases directly over the accumulation. Davis (1969) elaborates on the direct effects of these organisms:

> Bacteria directly over the petroleum accumulation would consume the petroleum gases adsorbed to soil surfaces in this higher concentration zone, thus markedly decreasing the concentration of gas directly over oil, but bacteria would not be stimulated to utilize the lower "edge" concentrations.

These mechanisms would account for the typical halo anomaly shown in Figure 1. By specifically culturing for these hydrocarbon oxidizing bacteria another prospecting method was developed (Davis, 1967).

Radiometrics is another prospecting tool that evolved within the same general time frame (Lundberg, 1952). Although the nature of the cause is debated, the radiation minimum over the petroliferous zone is well documented (Lundberg, 1952; Merritt, 1956; Foote, 1969; Armstrong and Heemstra, 1972a&b; Morse and Rana, 1983). Foote (1969) provided an overview of various types of radiation surveys. Armstrong and Heemstra (1972a&b), Morse, et al. (1982), Morse and Rana (1983) have provided insight to the theory and technology of the method.

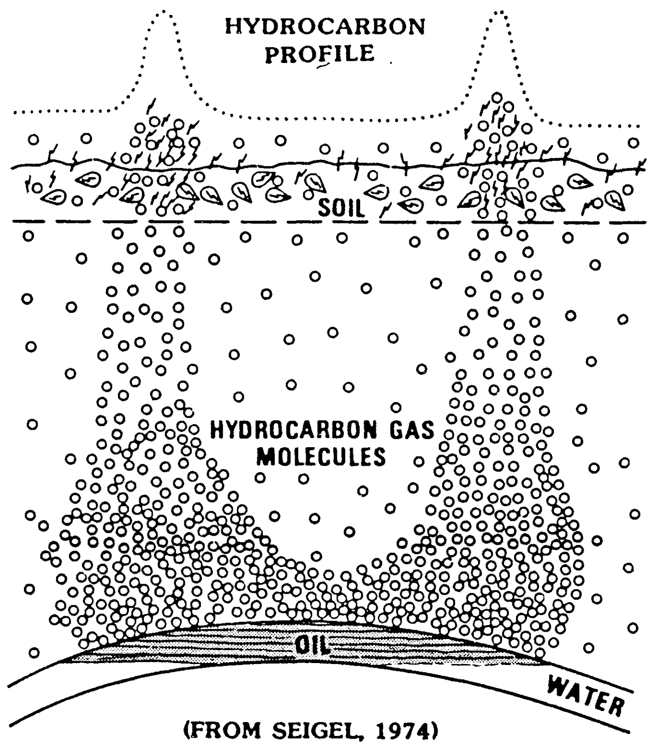

Figure 1. Halo Concentration Anomaly

An inorganic gas that is associated with petroleum accumulations is often targeted as a geochemical exploration pathfinder. Helium, because it is inert, of low molecular weight, gaseous and highly diffusive, has been the subject of extensive research in relation to exploration applications (Ball and Snowdon, 1973; Holland and Emerson, 1979; Porgorski and Quirt, 1979; Roberts, 1979; Palacas and Roberts, 1980; Maddox, 1982). Faul (1954) and Nikimov (1972) reviewed the sources of helium in petroliferous deposits. Sampling methods in helium prospecting range from free soil and gas to head space analysis of soil and water samplings. The analytical method is generally detection via a leak detector mass spectrometer (Porgorski and Quirt, 1979; Riemer, et al., 1979; Roberts, 1979).

The thermogenic and biogenic origin problem of methane and its use as an exploration pathfinder for petroleum has been recognized for many years (Kartsev, et al., 1954; Horvitz, 1956). Since methanogenic bacteria produce methane from the metabolism of organics in the anaerobic sedimentary environment, questions arise as to the source of the methane and methane anomalies. Some researchers even feel the majority of shallow natural gas found to date is biogenic in nature (Claypool and Rice, 1980). During this process, the bacteria's metabolic pathways result in methane generation where the methane generated is fractionated with the lighter

^{12}C isotope dominating (Tissot and Welte, 1979; Hunt, 1979; Kinghorn, 1983). The isotopic composition of the methane is felt to represent its source; therefore, analysis by mass spectrometry has been performed and the isotopic distribution is then related back and the nature of the source is identified (Fuex, 1977; Rietsma, et al., 1981; Stahl, et al., 1981). Isotopic ratios of other elements and compounds have been addressed by Donovan (1974) in a survey of secondary phenomena over the Cement Oilfield in Oklahoma.

Other inorganic and biogeochemical phenomena have been reported as pathfinders for petroleum exploration. The leaching of certain metallic ions from the leakage induced reducing environments overlying petroleum accumulations is reported by Donovan (1974) and Donovan, et al. (1981). It was reported in their study that the coloration of the outcrop over the Cement Oilfield structure changes from gray to red in the rocks adjacent to the producing area. This is due to the iron reduction and remobilization. With the remobilization of this and other elements, biogeochemical anomalies derived from greater plant uptake and use of these components has been proposed and researched (Dalziel and Donovan, 1980; Richers, et al., 1982; Alderman, 1982). Duchscherer (1979, 1980, 1981) reports on a method for the determination of the dissociation temperatures of the anomalous secondary carbonates. These carbonates are derived from carbon dioxide generated by the oxidation of the hydrocarbon cloud. Its use as an exploration tool is described through several case studies.

Advancements in both aviation and airborne microwave detection instrumentation has even put petroleum exploration into the air. Thompson (1979) discloses a helicopter-based sensing system to detect the hydrocarbon gases emanating from the soil into the atmosphere. Once several anomalies are located in the prospect area, ground verification by hydrocarbon gas surveying is used to prove the existence of these anomalies. Another method described by Barringer (1977) incorporates the inorganic analysis of airborne particulates which are collected and analyzed in an airplane or helicopter-based system. A comparison of the Barringer AIRTRACE (TM) results from a Mn/Fe airborne survey with results from a ground survey over the Cement Oilfield in Oklahoma has been provided in a USGS report by Barringer (1977).

The Controversy

Although much work has been done using hydrocarbon leakage detection for petroleum exploration, there have been many conflicting viewpoints concerning its usefulness. Hunt (1979) reported that most of the major oil company studies revealed no consistent or reproducible results. According to most of the service companies, lack of technological development and improper integration with known geology were the reasons for this confusion (Hunt, 1979; Philip and Crisp, 1982). The generation of certain hydrocarbon gases by plants was another potential problem that came to light in the early sixties. Smith and Ellis (1963) reported the extraction of petroleum-like hydrocarbons from soils with naturally occurring organics in proper quantity and ratios to be comparable to those reported in surveys by Horvitz (1956). Several years later, Horvitz (1972) presented data to support his previous findings.

Varying soil compositions in a study area also created problems that appeared to shed some doubt on the soil desorption technology's applicability in certain regions. McCrossan and Ball (1972) reported that soil samples with a high carbonate content had significantly greater yields of hydrocarbons than those with a smaller amount of carbonates. McCrossan and Ball's conclusions concerning the use of soil desorption techniques in areas of variable soil carbonate content was that the data generated were highly questionable. A few years later, workers in Australia found this problem could be alleviated by introduction of a total acid soluble correction factor (Devine and Sears, 1977).

Other apparent questions are derived from not understanding the transport mechanism by which these gaseous components pass through the overlying geologic environment to the surface. Questions relating to the quantities of material able to migrate through several thousand feet of overburden on the basis of mechanisms such as diffusion have been raised by many investigators (Seigel, 1974; Hunt, 1979; Philip and Crisp, 1982). Diffusion coefficients reported by Leythauser, et al. (1981, 1983) seem to indicate that this mechanism may play a part in the role of transport to the surface. Other parameters such as effusion, buoyancy and combined processes have been studied and reported (Stegna, 1961; Hunt, 1979; Davis, 1981).

Lateral displacement is another potential problem in the interpretation of gas geochemical data. Geologic structure and groundwater movement are the two potential mechanisms of lateral displacement (Hitchon, 1980; Jones and Drozd, 1983). It is often possible to determine the degree of offset by a fault or fracture zone; displacement by groundwater flow is a poorly understood process with conflicting reports as to its effect (Hunt, 1979; Hitchon, 1980; Philip and Crisp, 1982). In light of all this controversy, however, much research and even application of this technology is currently progressing in many of the oil companies in America (Jones and Drozd, 1983).

The Problem

Most investigators indicate that the sampling and analytical methods used by the early pioneers through the fifties was the probable cause of the inconsistencies of the early hydrocarbon gas geochemical work (Jones and Drozd, 1983). With the introduction of the gas chromatograph, many companies gained a new interest in the hydrocarbon gas techniques. Attempts to alleviate some of the variability derived from the field methods consisted of going deeper and deeper in the soil profile in an attempt to reduce the effects of changing soil composition and meteorologic variability (Horvitz, 1945; Kartsev, et al., 1954; Debham, 1965; Sokolov, 1972; McCrossan and Ball, 1971; Siegel, 1974). Hunt and Dickey (1972) and Hunt (1979) state that because of the high degree of variability reported in detailed exploration surveys, the technique is best suited as a regional reconnaissance tool.

Even with the introduction of the gas chromatograph, the analyst is still limited to a relatively small range of potential compounds which can be analyzed in a realistic period of time. Jones and Drozd (1983) state that due to the longer elution times of the larger molecules (greater than C_5), any information from that higher mass range is not practical and is reported as the C_5+ fraction. Based on these persistent problems, the author had proposed that a new method of integrative hydrocarbon gas sampling be combined with desorption mass spectrometry to provide a new method of geochemical exploration for oil and gas. Since the data collected are mass spectra of a mixture of components, the data processing and interpretive procedures were performed by applying multivariate statistics to each data set. Several researchers have reported excellent results in various situations after using this type of data analytical system (Voorhees and Hileman, 1982; Muesalaar, *et al.*, 1982; Voorhees, *et al.*, 1983).

CHAPTER II

RESEARCH OBJECTIVES

This project had several objectives addressing each of the aforementioned problems. The first of these involved the duplication and adaptation of the adsorbent Curie point wire apparatus described by Twibell and Home (1977) and Twibell, *et al.* (1981) as a surficial sampling device for collection of the hydrocarbon gases. The advantage in the use of this apparatus was the collection of gases emanating at a sample location over a period of time and on a common substrate. This integrative nature allowed much shallower sampling depths due to a reducing of the variability caused by meteorologic fluctuations (Klusman and Webster, 1981). The combined integrative sampling and mass spectral analysis also enhanced the collection and identification of the lower volatility compounds. Tests by Colenut and Thorburn (1979) have demonstrated pyrolysis effects to be minimal when using a similar type of system. Since the adsorption wire served as its own sample support and heating mechanism, the added risk of sample contamination during sample preparation was greatly reduced.

Application of the mass spectrometer as an analytical device offered a potential solution to the low molecular weight limitations of gas chromatography raised by Jones and

Drozd (1983). The mass spectrometric method of sample separation by molecular weight rather than on the type or nature of the components being analyzed or the nature of the column is of great importance. This enabled any component which was collected in a mass range of m/z 10 through m/z 800 to be analyzed, resulting in greater quantities of information that could be attained. An added advantage is that the computer interfaced mass spectrometer enables rapid, repetitive sample analysis. One apparent drawback of the system is that the sample mass spectrum is a mixture. This makes individual compound identification difficult at best. For this reason the utilization of the pattern recognition procedures and other data handling methods available in the multivariate statistical program ARTHUR (Harper, *et al.*, 1979) are incorporated.

CHAPTER III

EXPERIMENTAL PROCEDURE

This study has provided the basic information necessary to judge the adaptability of the Twibell/Home (1977, 1981) adsorption wire technology combined with desorption mass spectrometry and pattern recognition procedures as a soil gas tool for petroleum exploration. The different experimental sections of the project fall into five main categories:

1) Adaptation of the Twibell/Homes wire and sampler design
2) Initial field adaptability test; Dakota hogback
3) Weld County, Colorado test; Discriminatory capabilities
4) Indianola frontier area test; Non-producing area test
5) Patrick Draw, Wyoming test; methods comparison

The following text provides a description of the experimental procedures used in the various phases of the project.

Reproduction and Testing of the Adsorption Wire

The initial segment of this phase was the determination of the binder most suitable for this geochemical application. Three compounds, sodium silicate, zinc chloride, and aluminum oxide, along with one commercial dental cement, were chosen for the test. In order to prepare the sodium silicate solution from the crystalline compound, several steps were necessary. An unspecified quantity was dissolved in deionized water with several hours of stirring and heating. The solution was then evaporated until saturation was noted. Then the liquid phase was drawn off and stored in a clean vessel.

In the case of zinc chloride, aluminum oxide and dental cement, mixtures were attempted using deionized water with thermal enhancement, followed by evaporation. It was found that the last three binder materials yielded a pastey mixture. The binders that produced the pastey texture were found inadequate for this purpose. Based on these results, sodium silicate was chosen as the binder in all future tests.

Carbon was chosen as the adsorption medium because of its relatively high adsorption affinity for hydrocarbons, the organic compound class most likely to emanate from subsurface petroleum accumulations. In this phase, three different carbons were tested to determine which is most appropriate for this application. The three types were: (1) a carbon sample provided by Dr. Twibell--assumed to be a coconut charcoal; (2) SKC coconut charcoal; (3) a wood charcoal. All three were ground by mortar and pestle then sieved to a 120-200 mesh size range to insure an approximately constant surface area. Wires were constructed using each of the three carbon types and then exposed to various crude oil and reservoir rock samples. Any differences in the characteristics of the fingerprints generated from these tests were so noted.

Colenut and Thorburn (1979) reported the results of experiments using slightly modified adsorption wires and found the results were independent of the temperature of the Curie point wire used. In order to assure minimal pyrolysis effects, the lowest temperature (358 degrees Celcius) nickel wires were utilized.

The procedure described by Twibel, Home and Smalldon (1981) for the physical construction of the adsorption wires has been modified for this application. In order to minimize the potential for contamination, the wires are washed in a two-step hexane/methanol and ultrasonic cleaning process. After the second wash, the wires were then thermally treated at 150 degrees Celcius for 30 minutes. The wires were then stored in a similarly cleaned culture tube. Next, the wires were withdrawn from the tube and abraded on one end with extra fine emery cloth to enhance the surface for the carbon coating process. In order to coat the wires properly, the wires had to be dipped vertically into the sodium silicate solution. Rather than spreading the binder with a finger as described by Twibell, Home and Smalldon (1981), a cleaned spatula was used in order to avoid contamination from contact with body oils. Coating of the carbon on to the wire also required vertical dipping but with the added task of keeping the carbon level approximately equal. A 24 hour set time was then allowed to assure maximum binder stability. Figure 2 is a cross-sectional diagram of the adsorption wire.

Activation of the carbon surface was accomplished by employing a thermal-vacuum method where the wire was placed in the RF coil of the pyrolysis mass spectrometer. The pyrolyzer was triggered every 30 seconds for several minutes, thereby thermally desorbing any contaminants into the high vacuum system of the mass spectrometer. In order to evaluate the effectiveness of this method, the mass spectrometer was placed in scan mode to monitor the change in desorption with the number of times fired. When the wire reached a baseline (approximately machine background), the wire was considered to be active. The wires were then loaded into a cleaned 25 ml culture tube and stored in a dessicator that had been flushed with high purity nitrogen to minimize contamination.

The charcoal selection process included the exposure of several wires with the different carbon types to crude oil and reservoir rock samples under similar environmental conditions. A headspace environment was constructed by exposing the wires to a test specimen contained in a dessicator. All components of the headspace apparatus were thermo-chemically cleaned using the wire cleaning process described earlier. Upon introduction of the various crude

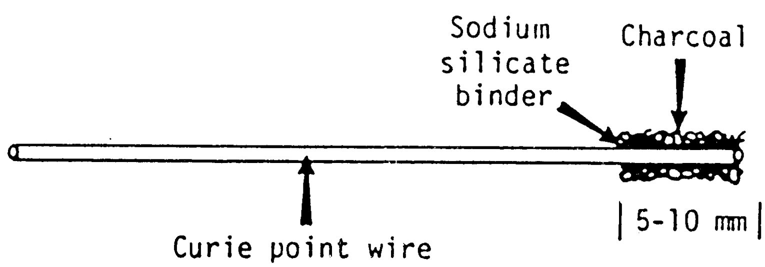

Figure 2. Cross-sectional Diagram of Wire

and reservoir rock samples into the headspace environment, an equilibration period of 72 hours was allowed. Adsorption wires with each type of carbon were then placed in the dessicator for a period of 90 minutes. The samples were then removed and analyzed by desorption mass spectrometry. The resulting data were then examined to identify and assess any differences between the various fingerprints. Because of the poor response of the wood charcoal and the potential availability problem with the English charcoal, the SKC coconut charcoal was selected.

Mass Spectrometry

The compounds collected on the adsorption wire were desorbed into the mass spectrometer utilizing a Fischer Curie-point pyrolyzer (1.5 KW @ 1.1 MHz) coupled to an Extranuclear Laboratories SpectrEL quadrupole mass spectrometer. A scan rate of 1150 amu/s with forty scans in the range of m/z 10 to 240 was used. In order to minimize fragmentation, electron impact ionization with an electron energy of 15 eV was utilized. The data were collected and stored on a DEC PDP-11/23 computer with RT-11 operating system. A schematic of the desorption mass spectrometry/data system is shown in Figure 3.

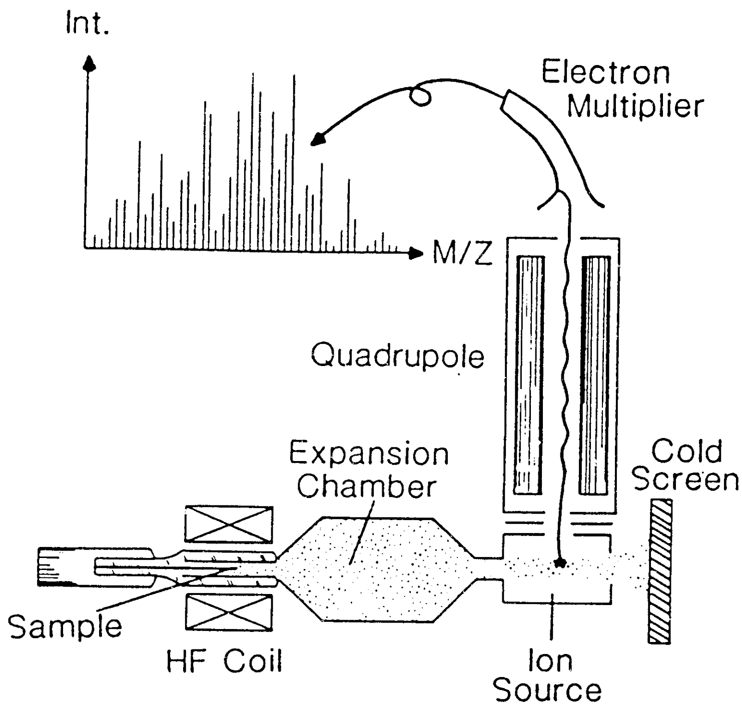

Figure 3. Py-Ms Schematic Diagram

Statistical Analysis

Pattern recognition procedures have been successfully applied to the desorption mass spectral data generated in this project. This approach has also been used in a wide range of fields from remote sensing to microbial characterization (Swain and Davis, 1980; Muezelaar, et al., 1982). Using a similar approach with the data generated from the integrative gas samples, the multivariate analysis has enabled the characterization of the "fingerprints" from the gases collected. This allowed the entire sample to be treated as its own signature and the assessment of correlation to the original organic source.

In order to transpose the data into a compatible format for input into the multivariate program ARTHUR, the data were processed through the Fortran program, ARTFIL. This reformatting program was written by Steve Durfee of the Colorado School of Mines. In addition to reformatting the data, ARTFIL also performs the initial normalization based on total ion current for the data file. The program was maintained on the DEC PDP computer system mentioned earlier. Once the output file from ARTFIL was complete, the new data file was transferred to the Colorado School of Mines DEC-1091 computer system via the communications program, CLINK. CLINK is an intercomputer communication program written by the staff of the National Institute for Health which allows communication and file transfer from the DEC 10 and DEC 11 systems and vice versa.

Once the transfer was complete, the new data file was copied to the standard ARTHUR input file: FOR001.DAT. The ARTFIL-generated file contains the necessary line information to instruct ARTHUR through its initial input mode of operation. The INPUT mode creates several output files in binary and Fortran code which contain all necessary information for future data manipulations. The FOR20.DAT file is the standard ARTHUR output file and contains pertinent data from both the ARTHUR INPUT and manipulative processing runs.

Upon initiating the multivariate subroutines of ARTHUR, many options are available to the user depending on the specific information or data display required. The unsupervised learning mode of ARTHUR was chosen to determine if unbiased discrimination of the various fingerprints was attainable. In order to utilize those specific features of ARTHUR, a series of control statements were established in the ARTHUR input file to control the manipulation segment. The commands and descriptions of their functions are as follows:

SCALE: Utilizes the autoscaling method of feature scaling. This step minimizes any inadvertent weighting based on the magnitude of the peaks. This results in a transposed data matrix where the features are assigned a mean of 0 and unit standard deviation.

DISTANCE: This option calculates the interpattern distance matrix in n-dimensional space. The Euclidean distance between any two samples in n space is a reflection of the samples similarity or dissimilarity.

UTILIT: Provides a line print output to the FOR20.DAT file of the distance matrix.

NLM (Non-linear Mapping): This option of ARTHUR allows a two-dimensional graphical display from the n space distance matrix. In doing so the method reduces the dimensionality of the data while preserving the interpoint distances thereby retaining as much of the original information as possible. It should be noted that from this point forth, the term cluster diagram will be used interchangeably with non-linear map.

VARVAR: Another utility option in ARTHUR that allows the two dimensional NLM to be displayed in the FOR20.DAT file for line printer output.

The data processing steps described in the preceding section were used in the last three field experiments: Weld County, CO; Indianola, UT; and Patrick Draw, WY. Interpretation of the data from the last three surveys was performed by determining whether several samples fell into a zone or cluster on the non-linear map. If a cluster or several clusters existed (determined by checking intersample distance in distance tables), the samples were compared to the known geologic conditions to identify any relationships that may exist.

Sampler Design and Preparation

In the first field test on the Dakota hogback, a 250 ml Pyrex beaker was employed as the apparatus cover and a piece of cork as the adsorption wire base support. Due to the problem of glass breakage and possible contamination from the cork, the decision was made to progress to an all metal system. A plain, non-coated aluminum can was selected for use as the cover. The adsorption wire support base was a one inch diameter aluminum disk that was 1/2" thick and had several holes drilled in it to act as wire receptacles. The disks were cut from an 8-foot rod. Both the disks and the cans were decontaminated by using the thermochemical cleaning process described earlier. Figure 4 is a cross-sectional view of the sampler in a field situation.

Field Tests

Dakota Hogback Experiment, Jefferson County, Colorado.
The purpose of this test was to gain insight into the effectiveness of the sampler in field situations. This site was chosen because of its close proximity to the Colorado School of Mines, minimal interference from underlying coal

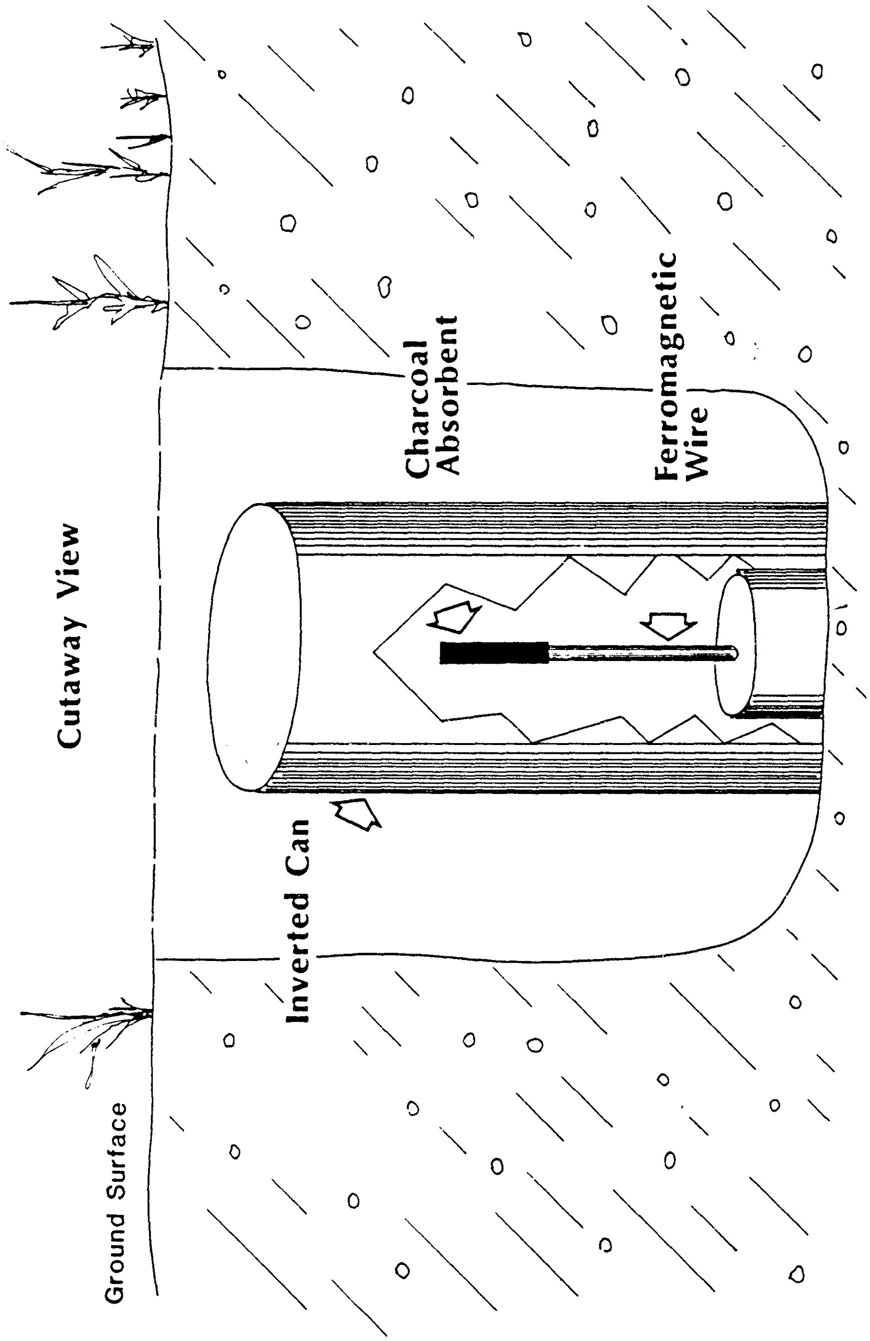

Figure 4. Cross-sectional View of Field Sampler

beds, and the topographic aspect. Three sites were selected, one each on the south and north facing slopes and the third on the flat between them. This permitted a test of the effect of soil temperature and topographic aspect on the flux rate of a given sample based on its location. Figure 5 shows a map of the area highlighting sample locations. The samples and soil temperature probes were implanted at a depth of approximately 8 inches. Four wires were placed in each sampling apparatus (described earlier). The close proximity also provided the opportunity to test the effects of sampling duration. Time and soil temperature were recorded at the sample emplacement and at each collection. Upon collection, the samples were returned to the laboratory and analyzed by the desorption mass spectral method described earlier.

Weld County Experiment, Colorado. Determination of effective sampling intervals and discriminatory capabilities of the technique for different organic sources of gases and vapors was the object of this test. Two sampling lines were selected for the sampling design, one with east/west and the other with north/south orientation. This allowed the experiment to be conducted over known background, coal and coal-oil-gas areas (Figure 6). A minimum of two wires were planted at each of the e/w line sample locations. This provided a test between two different sampling intervals at 9 and 16 days. The n/s line had a minimum of one wire per

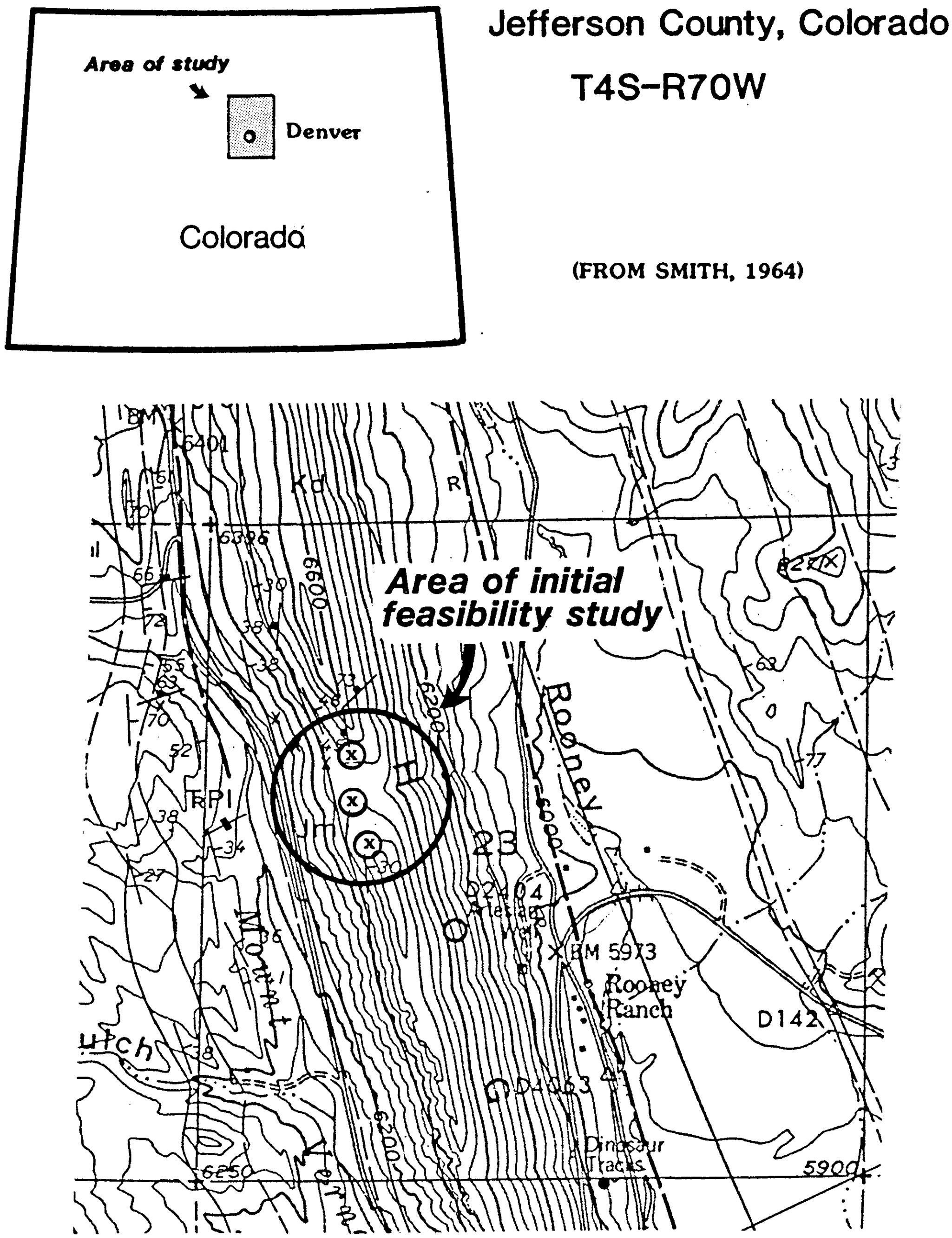

Figure 5. Dakota Hogback Area Map

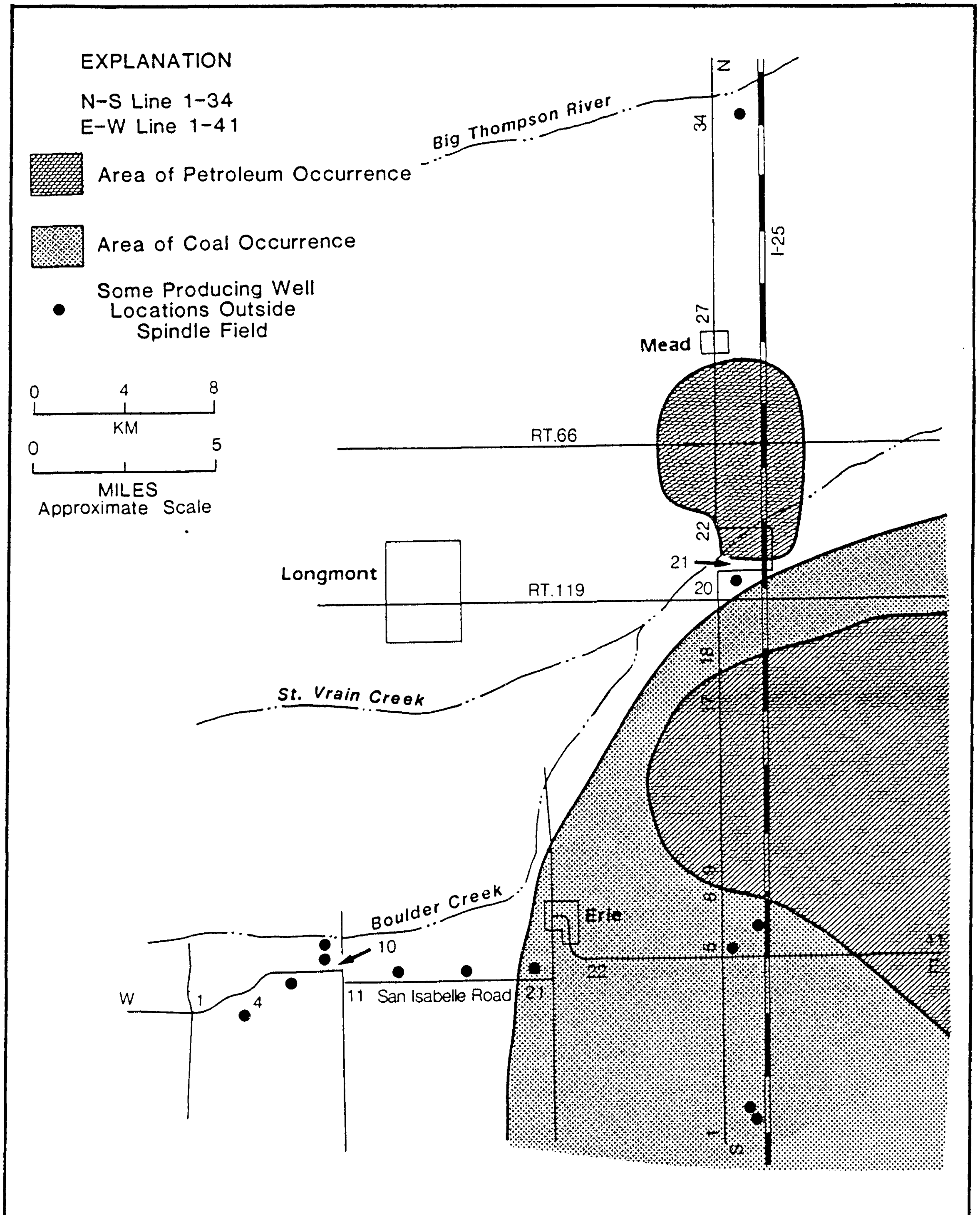

Figure 6. Weld County, Colorado Area Map

sampler and sample emplacement was offset several days to allow enough time for optimum sampling interval determination from the e/w line test. After collection of each phase of the experiment, the samples were returned to the laboratory for mass spectral and statistical analysis and subsequent data interpretation. The data processing and interpretation methods were described earlier.

Indianola Frontier Area Test: Sanpete County, Utah. The third field experiment was designed to test the method in an area of known petroleum occurrence and no production. Since the tectonic setting for the test area was related to the eastern edge of the southern Overthrust Belt, it also provided a test in an area where extensive faulting and fracturing occurs (Ritzma, 1981). Any unique fingerprints that may be associated with the faulting would then be detected and evaluated. The sampling design divided the area into two separate sub-areas, one consisting of 5 lines on the western flank of the Wasatch Plateau (Figure 7) and the second consisting of a single line along the plateau ridge (Figure 8). A total of 72 samples with a nine day integration time was utilized. The lower study radiated from a well drilled by Union Oil in section 24, R4E,T11S. The lines were set such that maximum exposure to the structural features was accomplished. The plateau line was centered on a well that was being drilled by the Energy Reserves Group (Indianola

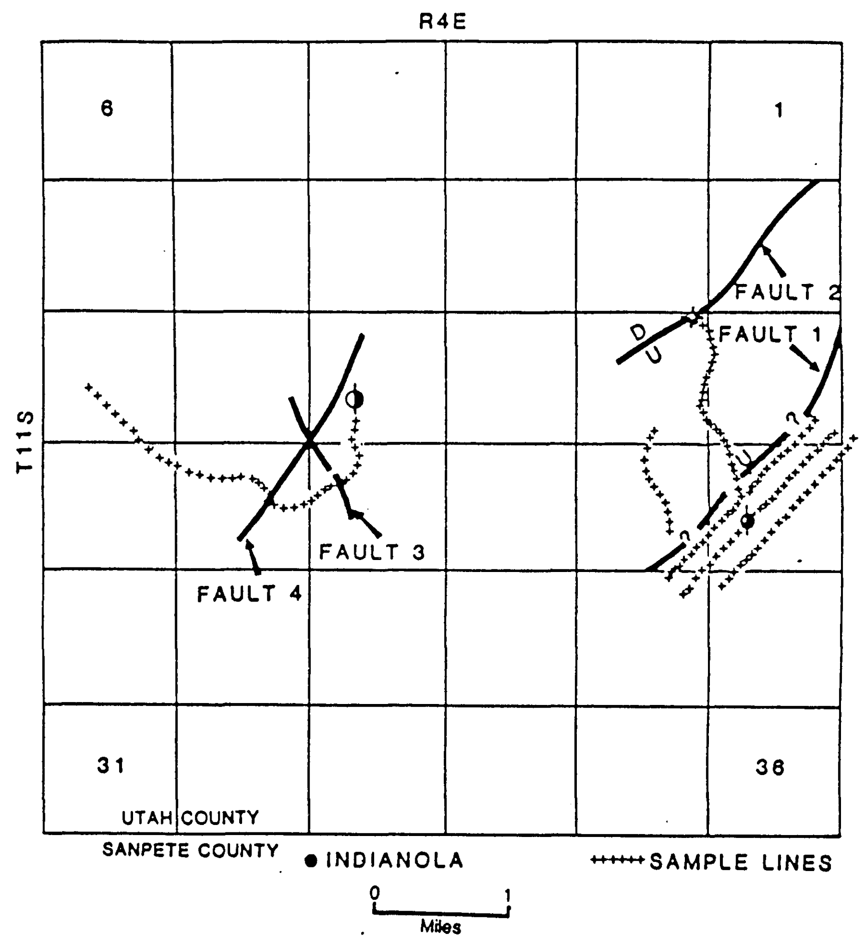

Figure 7. Lower Indianola Area Map

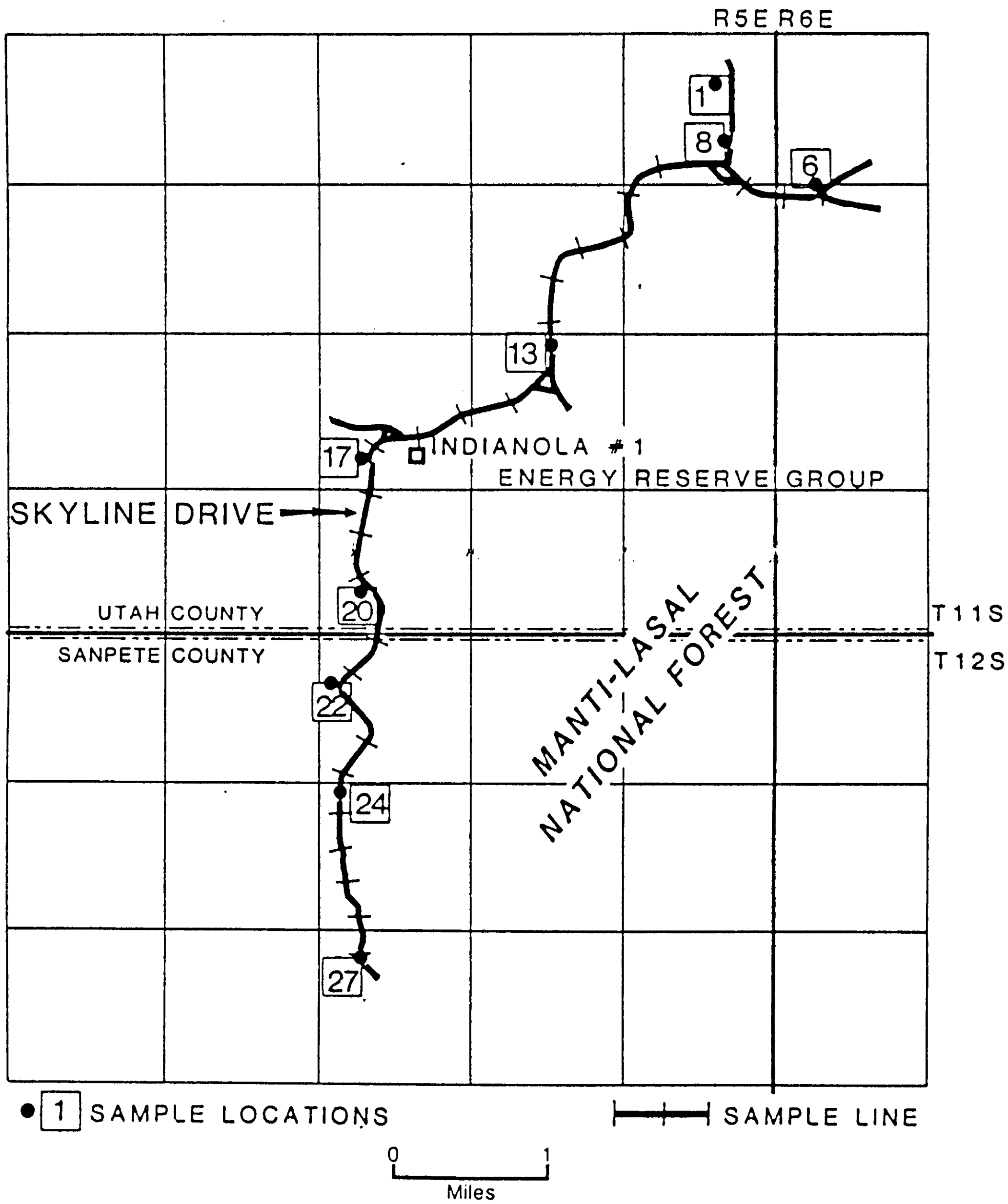

Figure 8. Upper Indianola Area Map

#1). This line permitted an evaluation of the site relative to a known petroleum occurrence in the lower area.

Patrick Draw Test: Sweetwater County, Wyoming. The final field test at Patrick Draw allowed for a comparison between the results of the new integrative technique and the data generated by conventional hydrocarbon gas geochemical methods. Richers, *et al.* (1982) reported the results of hydrocarbon gas geochemical surveys to evaluate leakage associated with Landsat delineated features in the area of the Patrick Draw Oilfield in Wyoming. In their study, all three of the commonly used soil gas sampling methods, free soil gas, headspace and desorption of gases from soils, were employed using gas chromatography as the analytical method. In order to allow for a representative evaluation, the sampling design used by Richers was followed as closely as possible. This resulted in a total of 107 sample sites with an integration time of 9 days (Figure 9).

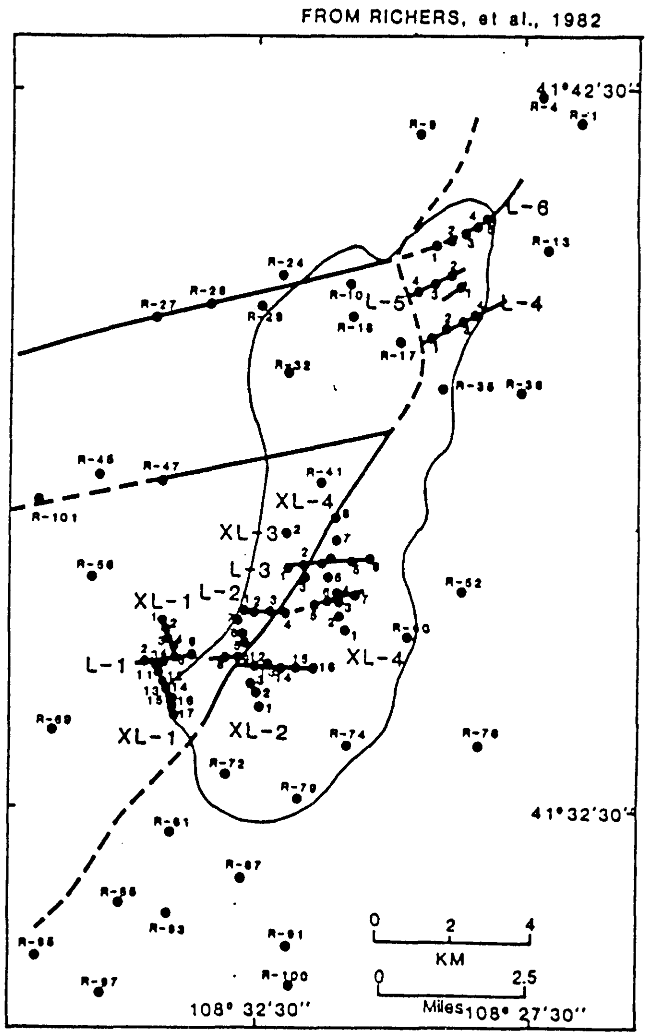

Figure 9. Patrick Draw Area Map

CHAPTER IV

FIELD TEST RESULTS AND DISCUSSION

Dakota Hogback Test

A map displaying the sampling area and individual site locations is shown on Figure 5. The positions of the three sampling locations were on the south and north facing slopes along with one in the saddle between them. The samplers and soil temperature probes were planted on March 11, 1982. The instantaneous soil temperature and peak counts for each sampling and analysis run are listed in Table 2.

Table 2

Temperature and Flux Comparison: Hogback Test

Date	3-11-82			3-18-82			3-25-82		
Site	1	2	3	1	2	3	1	2	3
Soil T C	4.2		0.8	4.6		1.6	6.5		0.8
Peaks**	-	-	-	61	19	144	99	67	87

** = number of peaks from sampler wire.

Note: Site #1 = north facing slope; Site #2 = saddle; Site #3 = south facing slope.

It appears that a trend may occur as indicated by the data generated at Sites 1 and 2, and it appears to be related to soil temperature. Site #3, on the other hand, does just the opposite of what the trend suggests. The fingerprint generated by the analysis of the sample from Site #3 looks very much like that of a vapor phase analysis of a reservoir rock as had been observed in the charcoal tests described earlier. It is believed that a phenomena like that of the breached oil pool in the "J" sand outcrop further to the south along Route 285 could be responsible for this occurrence. The higher temperatures occuring at Sites 1 and 2 are because of the solar influence of these relatively exposed areas. It should be noted that the 14 day sampling interval did not saturate the adsorption wire, and therefore no decision on optimum sampling time could be made. This, combined with the apparent increase in the number of peaks with increasing temperature, was considered in establishing all further exposure times for the duration of the project.

Weld County Field Test

A total of 75 sample locations were established on two lines (e/w=41; n/s-34) with 61 sites remaining intact for sample recovery and analysis. Two sets of wires were included in each of the samplers on the e/w trend allowing a comparison of 9 and 16 day sampling intervals to be conducted. Since the sampling duration of 9 days was determined to provide adequate flux for analysis, the presentation of the results will focus on the data from experimental phases using that interval. Figures 10 and 11 are the cluster diagrams for the 9 day interval samples on the e/w and n/s lines respectively. They have been interpreted by zoning the samples based on known or assumed subsurface occurrence of "background," coal and coal, oil and gas. Table 3 is a summation of the correlative success between fingerprint similarity and organic gas/vapor source type. It should be noted that the "fingerprints" from samples collected over the various organic sources were discriminated reasonably well. The representative fingerprints from two of the various cluster diagram zones associated with the different organic sources are found on Figure 12. The average 88 percent correct source prediction factor (calculated from Table 3) appears to provide an adequate foundation on which to base further tests of the technique.

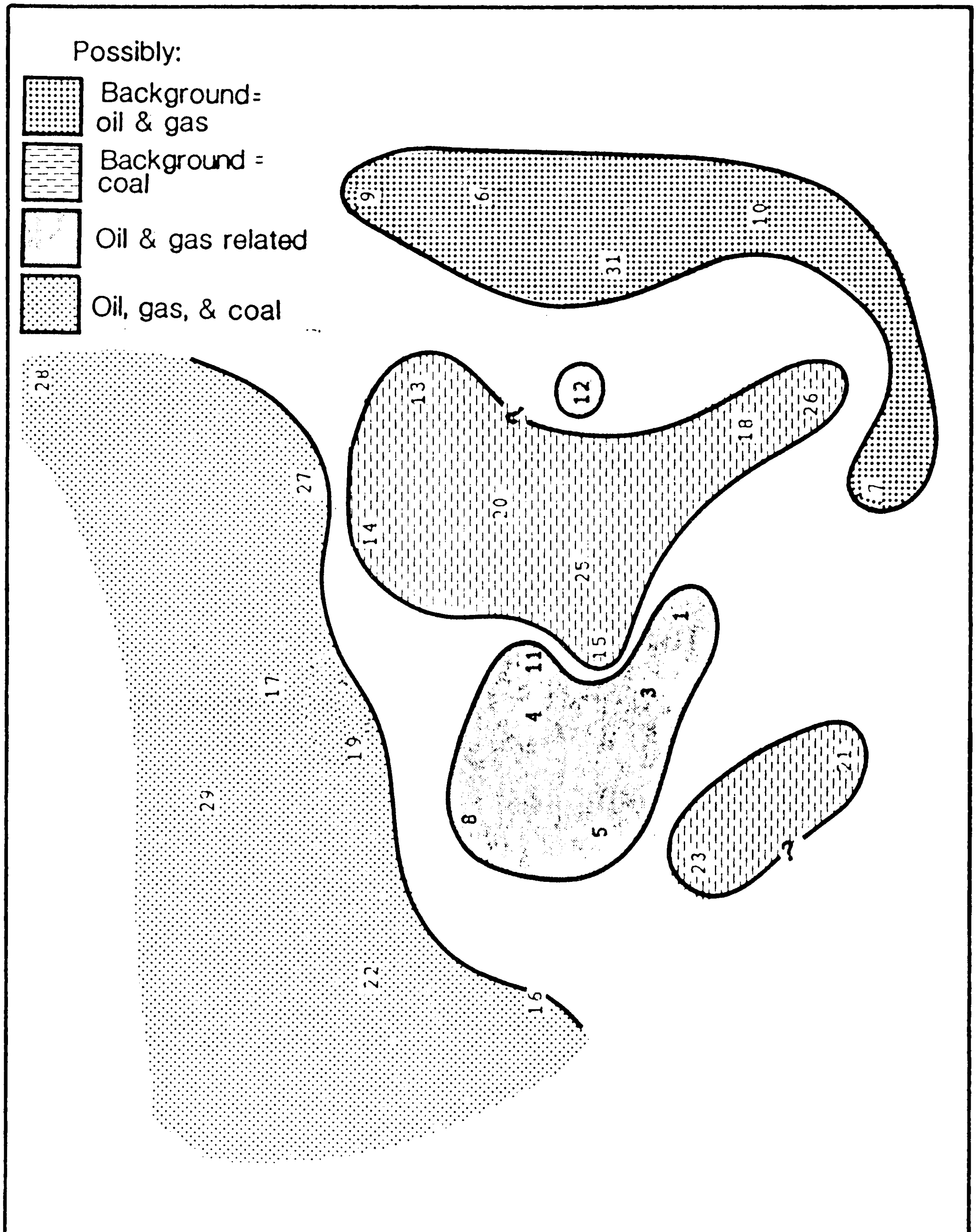

Figure 10. Cluster Diagram of Weld County E/W Line

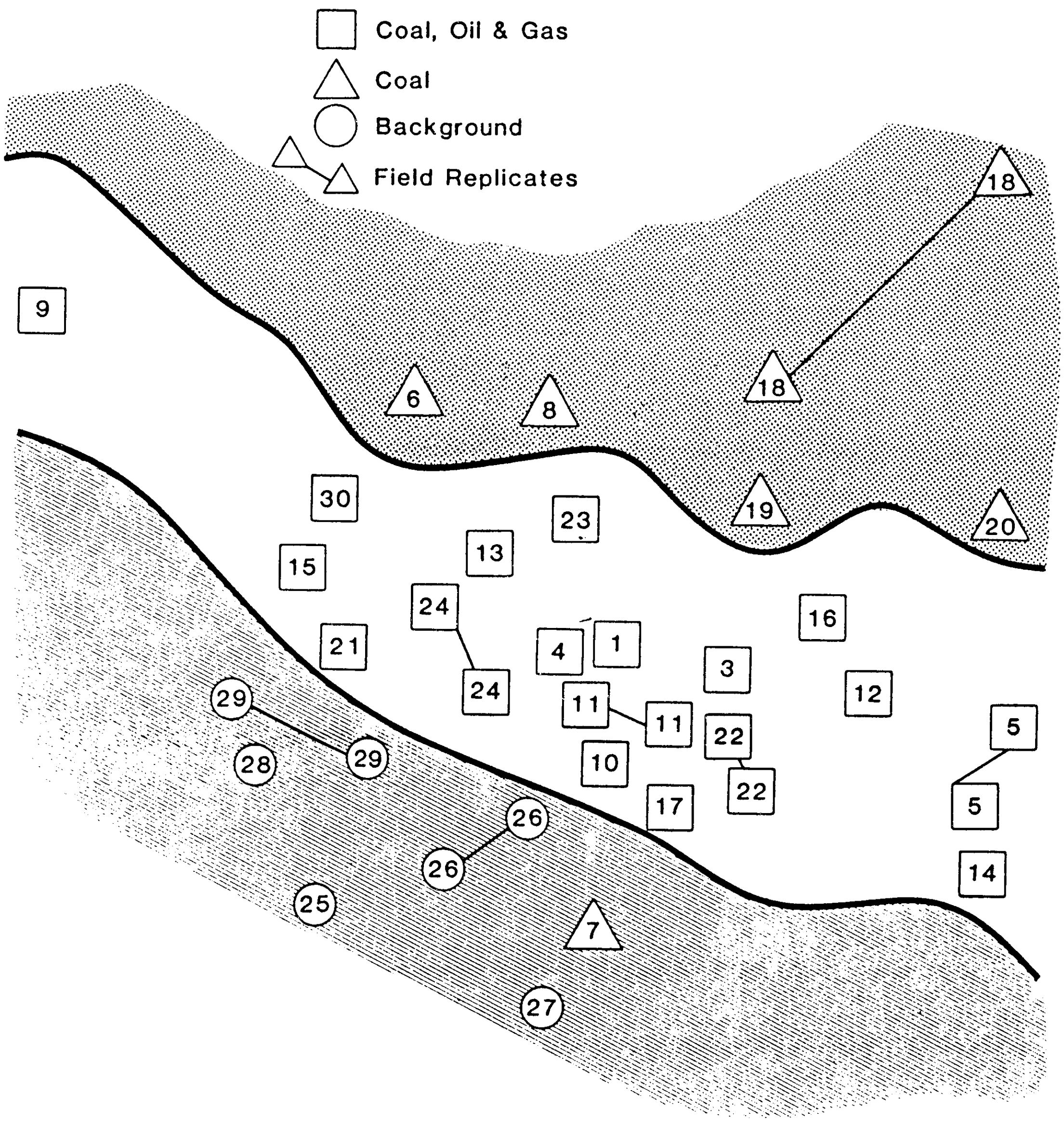

Figure 11. Cluster Diagram of Weld County N/S Line

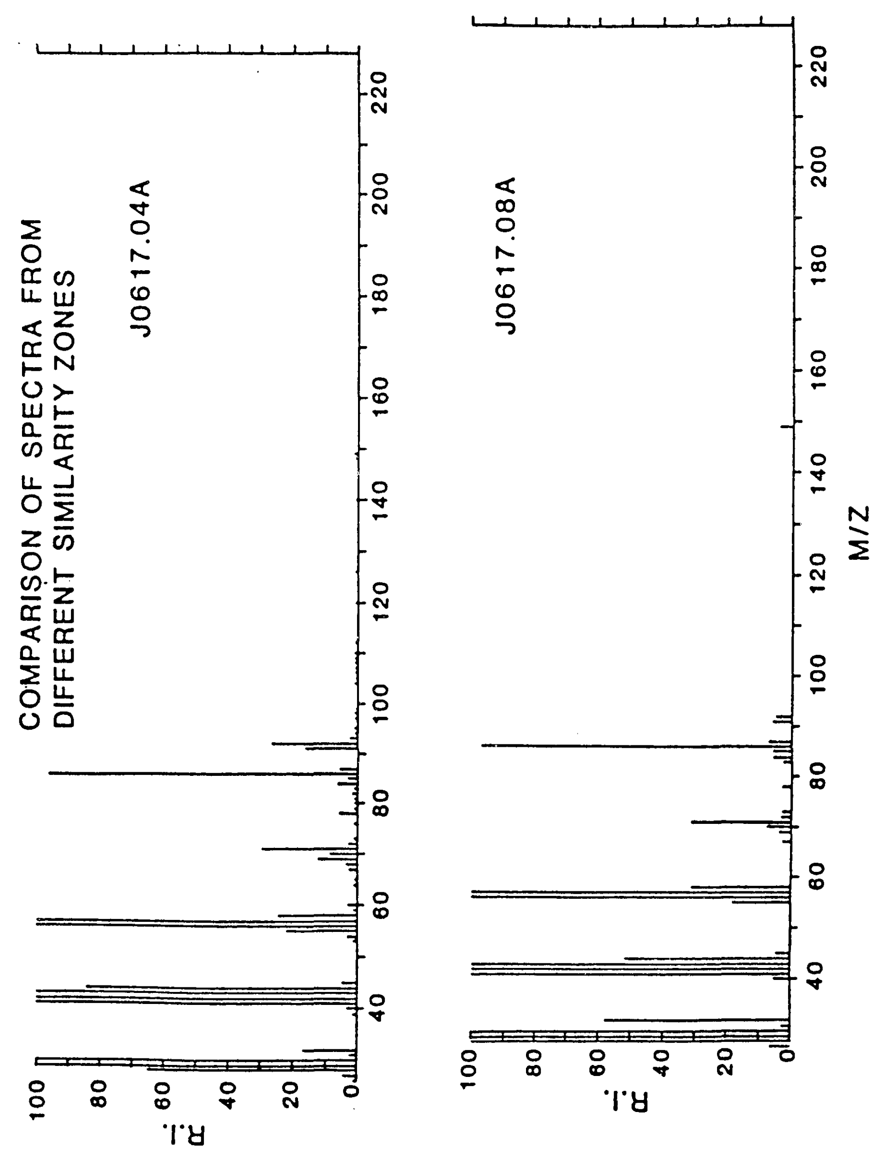

Figure 12. Representative Fingerprints (Mass Spectra)
from Weld County Test

Table 3

Table of Zoning Ability for Fingerprint Data from Weld County Test

Correlative Success by Fingerprint Similarity

Spindle Study

Occurrence Type	Samples	Similar Fingerprints
Background	10	9
Oil and Gas	30	29
Coal	17	13
Fault Controlled	4	4

Indianola Frontier Test

Since the previous test was conducted in an area of middle to late stage production, a question arose as to the effects of field production on the surficial hydrocarbon signatures that were identified. Upon initial visual interpretation of the mass spectra from this study, it became evident that there were several different signatures associated with this area. After completion of the computerized multivariate data analytical techniques, three distinct "clusters" were revealed on the non-linear map (Figure 13). Figure 14 shows a typical mass spectrum from each of these clusters. Figure 14a is a typical spectrum of the signature related to the samples over the well site in section 24, T11S,R4E. The two remaining fingerprints (Figures 14b and 14c) are representative of two different types of fault/fracture leakage that occur in the study area. Each of these sample types fall into one of the outlying clusters highlighted in Figure 13. Both of the fault/fracture signatures contain a significantly greater quantity of high molecular weight components (> m/z 120) than detected in the previous study. The samples collected over the well site were relatively similar in nature to those samples collected over known occurrences in the Spindle survey. Based on this, no apparent change to the fingerprint was identified due to the degree of production associated with the occurrence.

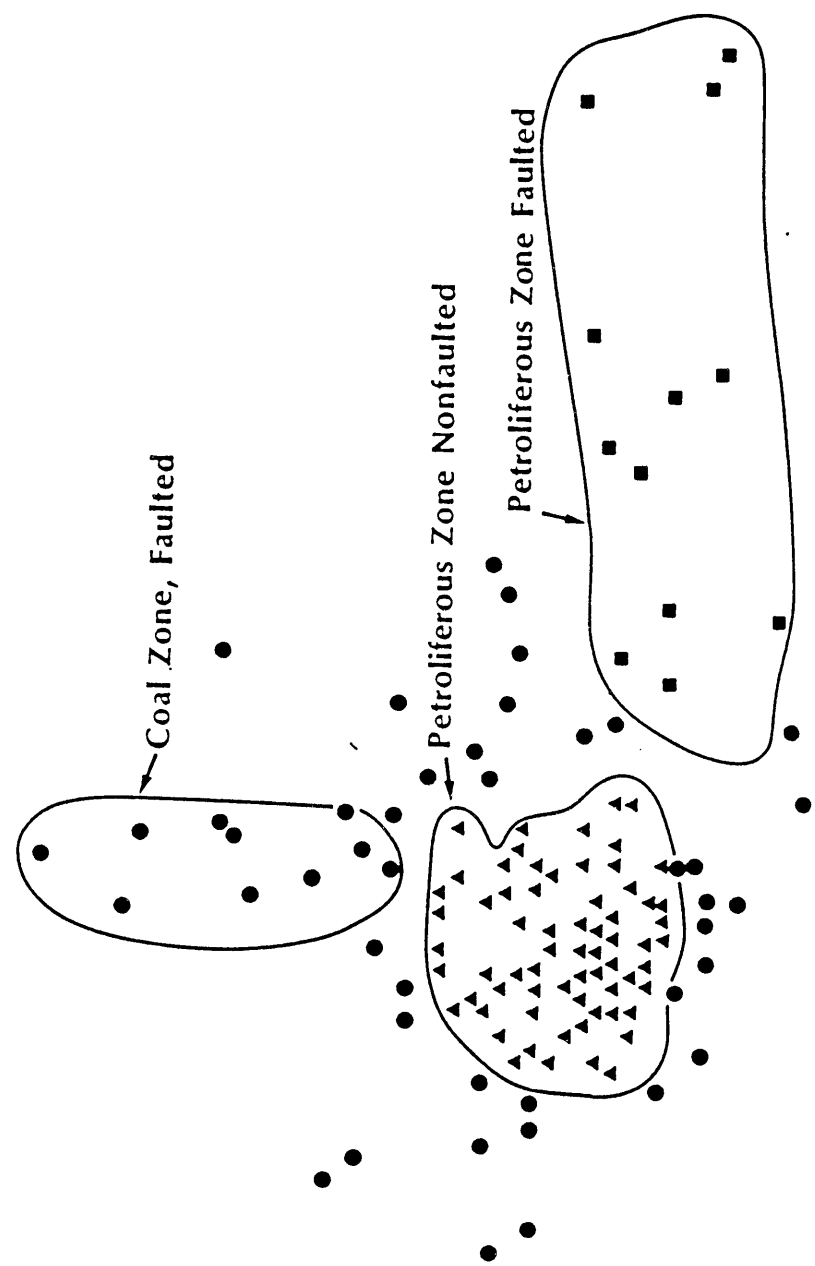

Figure 13. Cluster Diagram of Indianola Data

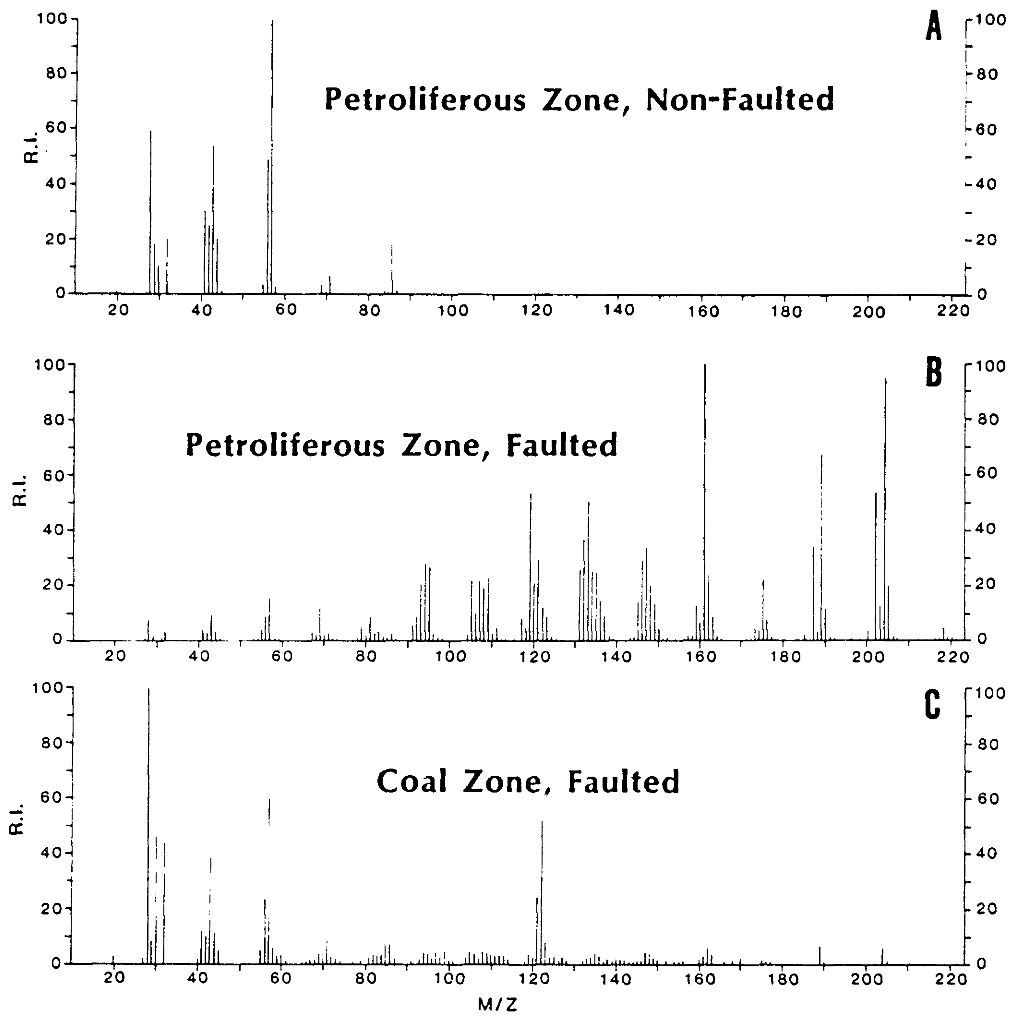

Figure 14. Representative Fingerprints from Indianola Frontier Study

Samples having a fingerprint similar to the fault/ fracture pattern similar to Figure 14b were found in faulted areas that were close to the known petroliferous occurrence. These samples displayed a greater intensity and quantity of the higher molecular weight components than did the samples with the fault/fracture pattern similar to that shown in Figure 14c. Several of the samples having the Figure 14c character were from sites along a fault near the Indianola #1 well that was being drilled at the time of the survey. The Indianola #1 was completed as a "dry hole" later that year. This would indicate that the fault/fracture fingerprint (Figure 14c) was probably associated with background fault/ fracture leakage for the area.

Patrick Draw, Wyoming Test

The sampling design used by Richers, *et al.* (1982) is depicted in Figure 9. In order to allow for as accurate a comparison as possible between the CSM integrative technique and the currently used gas geochemical methods, the same design was adhered to in the present study. In undertaking their study, Richers, *et al.* (1982) intended to determine if higher rates of gas emission were present and related to the linear features (faults) which crossed the study area (Alderman, 1982). Figure 15 shows the results of the Geosat study in a map depicting the combined significant anomalies of all three gas methods that they used. The basic

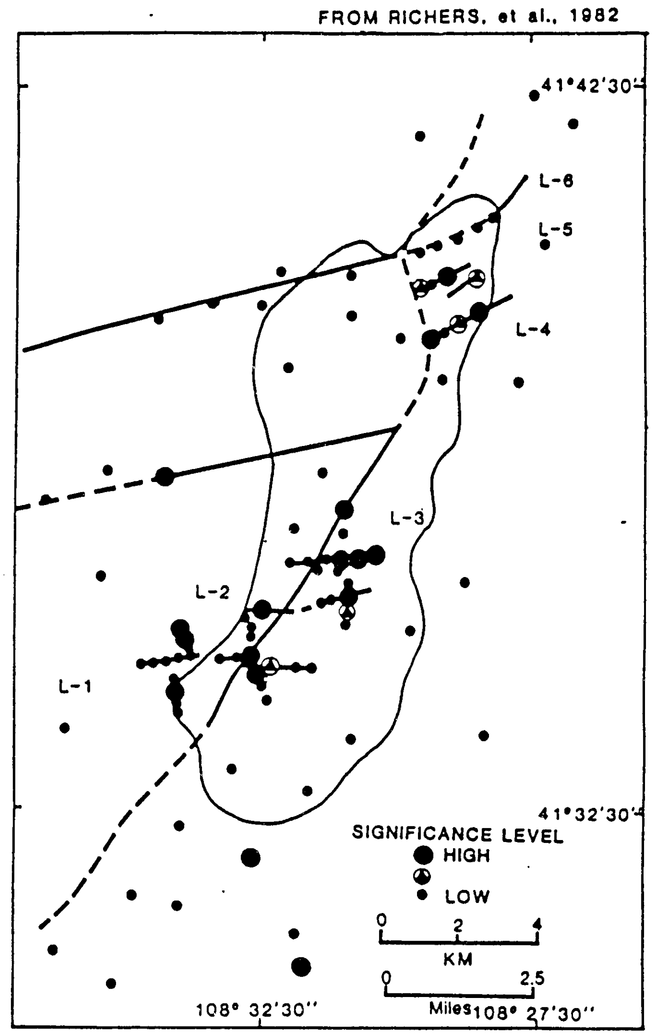

Figure 15. Results of Geosat Patrick Draw Survey

conclusions from the Geosat study were: (1) a micro-seepage of light hydrocarbon gases seems to exist over the field; (2) the linear features identified in their study leaked more profusely; and (3) gas geochemistry may be a very useful tool when used in conjunction with geologic and geophysical data.

After the field work, sample analysis and data processing, an important observation was made based on visual inspection of the mass spectra from the survey. Figure 16 shows the two predominant types of signatures generated through our survey. At first examination, both spectra look extremely similar. A closer inspection shows the lower fingerprint to contain a greater number of higher molecular weight peaks than in that of the upper fingerprint. The majority of those sample locations having a pattern similar to the lower example in Figure 16 are directly related to the lineaments in the Richers et al. (1982) study. This observation indicates that not only do such features offer the potential for higher fluxes of hydrocarbons at the surface, but also provide a path by which more complex organic compounds can migrate to the surface. This type of signature is subdued relative to those found in the Indianola study and is more likely to be a function of the tectonic setting which created the fault/fracture zones rather than being related to any type of production phenomena.

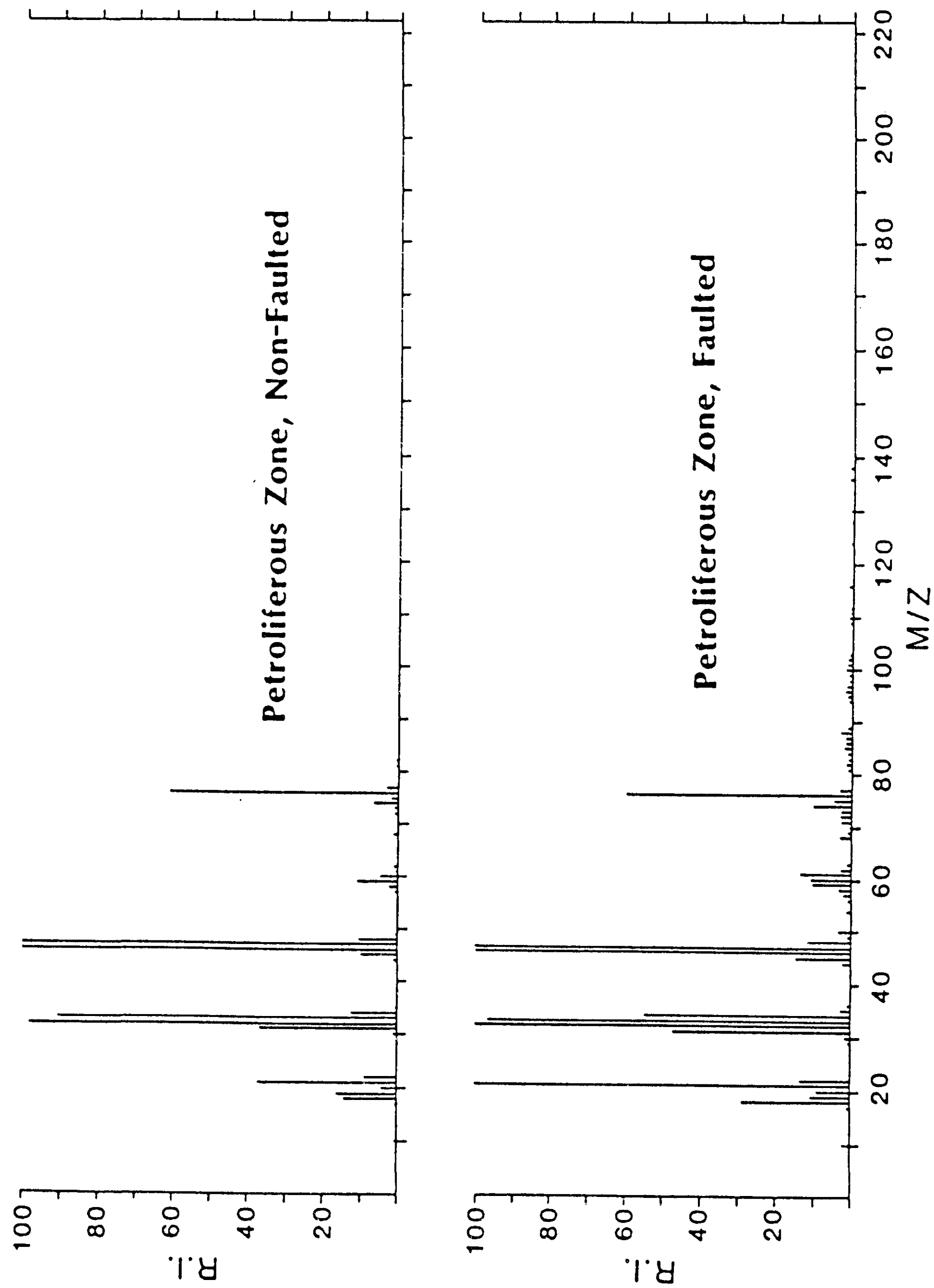

Figure 16. Representative fingerprints
from Patrick Draw tests

Several important advantages were realized during this survey. First, in using the mass spectral analysis system, a two minute analysis time was accomplished permitting a rapid, repetitive sample analytical method. Also, an increased ability in volatile compound collection, analysis and characterization was attained. This becomes particularly important when dealing with the higher molecular weight components found in the fault/fracture samples. Another factor was a substantial savings in field time and area accessibility (i.e., cost). Since sample placement occurs within the top foot of the soil horizon, no power equipment was necessary, thereby making the method much more portable in rough terrains. All of the above are important factors to consider since one of the main objectives of this project was to investigate the feasibility of the technique as an exploration method.

Reproducibility

An evaluation of the precision of the technique from a survey of the replicate samples from the field tests is the last subject of this thesis. In order to facilitate a quantitative assessment of the reproducibility, a parameter called the Similarity Index was calculated. The first step in this process was the extraction of the interpoint distances for each replicate pair (DIJ) from the multivariate distance table along with the maximum distance (DMAX) in each set. The similarity index (SIJ) was then calculated by the following formula:

$$SIJ = 1 - DIJ/DMAX$$

A listing of the pertinent data and results for the Weld County, Indianola and Patrick Draw Field Tests are found in Tables 4-6 respectively. Table 7 contains a compilation of the statistical results from each of the data sets. It should be noted that the average SI of the mean SI from each data set is 0.88.

Table 4

Weld County Replicate Data

Sample Pair	DIJ	DMAX	SIJ
4 A/B	0.77	5.75	0.87
5 A/B	0.78	5.75	0.86
19 A/B	0.76	5.75	0.87
21 A/B	2.10	5.75	0.63*
22 A/B	0.51	5.75	0.91
24 A/B	0.64	5.75	0.89
25 A/B	0.53	5.75	0.91

*Rejected with Q quotient of 0.82 (> 51 for 7 samples)

Table 5

Indianola Replicate Data

Sample Pair	DIJ	DMAX	SIJ
4 A/B	1.10	5.30	0.79
5 A/B	0.41	5.30	0.92
7 B/C	0.14	5.30	0.97
8 A/B	0.48	5.30	0.91
9 A/B	2.50	5.30	0.53*
10 A/B	0.31	5.30	0.94
11 A/B	0.26	5.30	0.95
12 A/B	0.34	5.30	0.94
13 A/B	0.63	5.30	0.88
14 A/B	1.40	5.30	0.74
16 A/B	0.22	5.30	0.96
17 B/C	1.10	5.30	0.79
18 B/C	0.67	5.30	0.87
19 A/B	0.85	5.30	0.84
20 A/B	0.14	5.30	0.97
21 A/B	0.33	5.30	0.94
22 A/B	0.28	5.30	0.95
24 A/B	0.20	5.30	0.96
25 A/B	0.13	5.30	0.98
26 A/B	0.12	5.30	0.98
27 A/B	0.87	5.30	0.84

Table 5 (continued)

Sample Pair	DIJ	DMAX	SIJ
28 A/B	0.15	5.30	0.97
29 A/B	0.14	5.30	0.97
30 A/B	0.13	5.30	0.98
31 A/B	0.30	5.30	0.94
31 A/C	0.13	5.30	0.98
31 B/C	0.28	5.30	0.95
32 A/B	0.38	5.30	0.93
32 A/C	0.37	5.30	0.93
32 B/C	0.21	5.30	0.96
34 A/B	0.85	5.30	0.84
35 A/B	0.28	5.30	0.95
37 A/C	0.47	5.30	0.91
38 A/B	0.76	5.30	0.86
39 A/B	0.98	5.30	0.82
40 A/B	0.45	5.30	0.92
41 A/B	0.47	5.30	0.91
57 A/B	0.17	5.30	0.97
63 A/B	1.00	5.30	0.81
66 A/B	0.29	5.30	0.95
67 A/B	0.44	5.30	0.92
69 A/B	0.39	5.30	0.93
75 A/B	0.14	5.30	0.97
76 A/B	0.74	5.30	0.86

Table 5 (continued)

Sample Pair	DIJ	DMAX	SIJ
80 A/B	1.20	5.30	0.77**
81 A/B	0.94	5.30	0.82
83 A/B	0.21	5.30	0.96
84 A/B	0.19	5.30	0.96
85 A/B	0.57	5.30	0.89
87 A/B	0.92	5.30	0.83
88 A/B	0.39	5.30	0.93
89 A/B	0.70	5.30	0.87
90 A/B	1.10	5.30	0.79**
91 A/B	0.26	5.30	0.95
92 A/B	0.81	5.30	0.85
93 A/B	0.22	5.30	0.96
94 A/B	1.50	5.30	0.72
95 A/B	0.61	5.30	0.88
96 A/B	0.92	5.30	0.83

*Rejected with Q quotient of .42 (> .41 value for 10+ samples).

**Rejected due to problems during analysis.

Table 6

Patrick Draw Replicate Data

Sample Pair	DIJ	DMAX	SIJ
2 A/B	1.40	3.53	0.60
5 A/B	1.00	3.53	0.71**
6 A/B	0.72	3.53	0.79**
7 A/B	0.56	3.53	0.84
9 A/B	1.90	3.53	0.46*
14 A/B	0.75	3.53	0.79
15 A/B	0.95	3.53	0.73
16 A/B	0.31	3.53	0.91
17 A/B	0.52	3.53	0.85
18 A/B	1.00	3.53	0.71
20 A/B	0.36	3.53	0.90
21 A/B	0.41	3.53	0.88
22 A/B	0.46	3.53	0.87
35 A/B	0.24	3.53	0.93
38 A/B	0.17	3.53	0.95
50 A/B	0.21	3.53	0.94

*Rejected with a Qu quotient of .52 (> .41 for 10+ samples).

**Rejected due to problems during analysis.

Table 7

Compilation of Replicate Statistics

Survey	Mean SIJ	Std. Dev.	RSD
Weld County	0.89	0.02	0.02
Indianola	0.91	0.06	0.07
Patrick Draw	0.84	0.10	0.12
Overall Average	0.88	0.06	0.07

CHAPTER V

SUMMARY

This thesis has dealt with the adaptation of the carbon adsorption wire previously used as a headspace sampling medium as an integrative gas geochemical sampling device. This was followed by adapting a pyrolysis mass spectrometer as the analytical instrument where the pyrolysis inlet was used as a desorption mechanism for sample introduction. The resulting data were processed using the cluster analysis (non-linear mapping) procedures available in the multivariate statistical program, ARTHUR.

Several laboratory tests were conducted on various types of binding media and charcoals to identify the optimum combination for use in adsorption wire construction. Sodium silicate and coconut based charcoal were selected based on overall performance and availability.

In order to assess the applicability of the sampler in field situations and response in a variety of exploration situations, four sites were chosen. The first test was located in a saddle area on the Dakota hogback in western Jefferson County, Colorado. Though the resulting data from this test were limited, a possible relationship between soil temperature/topographic aspect and overall fingerprint pattern became apparent.

Starting with the Weld County, Colorado field study, an evaluation of the technique in areas related to petroleum occurrence was undertaken. The ability to discriminate between different organic source materials was the outcome from that test. Though the results were inconclusive relative to the effects (or lack thereof) of non-production in the Indianola, Utah test, a different finding came to light. Several of the samples from that study displayed a unique character relative to the components that comprised their fingerprints (mass spectra). A shift in the molecular weight distribution from the low to high molecular weight components became apparent. The samples displaying this character were located in fault zones which occurred in the area. This indicates that the occurrence of this type of fingerprint character in other surveys may be indicative of and used as a pathfinder for delineating faults. The last study at the Patrick Draw Oilfield in Wyoming demonstrated that the integrative soil gas geochemical technique described above can provide greater quantities of data than conventional hydrocarbon gas methods at a highly reduced cost.

As a result of the aforementioned findings of this investigation, the author feels that the method is a viable tool with which further development could be extremely useful to the petroleum explorationist.

CHAPTER VI

RECOMMENDATIONS FOR FUTURE RESEARCH

The following research recommendations are suggested to further enhance the state of the technology:

1) Controlled laboratory loading experiments to assess the functionality preferences of carbon and other types of adsorbent media (e.g., Tenax, silica gel, etc.).

2) Evaluate the applicability of the supervised learning procedure (SIMCA) available in ARTHUR as a potential in the modeling of existing emanations overlying a petroleum occurrence for comparison with emanations in unknown areas.

3) Controlled laboratory experiments to evaluate the effects of static and dynamic flow conditions relative to the potential for replacement and/or stripping of components from the sorbent surface. The effects of these conditions could be important if timing is too long or inconsistent within a study.

4) Because of the ambiguous nature of the mass spectrum (fingerprint) representing a mixture of components, desorption/GC/MS analysis should be performed to identify the various compounds that comprise a hydrocarbon gas sample. This is especially important since many of the heavier molecular weight components have not been reported in the relevant literature.

5) Kartsev, *et al.* (1959) reported the seasonal effects on gas concentrations at a site. One would assume a similar effect would be detected in the fingerprint over various seasons. For this reason, a long term study to establish any type of seasonal effects on the fingerprint is suggested.

Many of the above suggestions have been undertaken by the author as possible research to be used in pursuit of his doctorate.

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