

Case 8224

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Exhibits

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Exhibit # 1

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Hazardous Organic Compounds in Liquid Wastes from
Disposal Pits for Production of Natural Gas

by

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BRIEF

Hazardous organic compounds including volatile organic compounds (VOC) and a complex mixture of polycyclic aromatic hydrocarbons (PAH) and alkylated PAH have been identified and quantitatively determined in samples taken from waste disposal pits from natural gas production in northwest New Mexico. Results from these findings are discussed in terms of impact and consequences for pollution of aquatic environments.

ABSTRACT

Samples of liquid waste found in disposal pits from natural gas production were collected at sites selected in northwest New Mexico and were characterized for hazardous and other organic compounds using GC and GC/MS techniques. Purge and trap pretreatment was used in GC/MS determination of volatile organic compounds while solvent extraction, prefractionation and preconcentration were used for isolation of polycyclic aromatic hydrocarbons (PAH) and alkylated polycyclic aromatic hydrocarbons in the same waste samples. Benzene and alkylated benzenes were present at estimated concentrations of 10 to 50 mg/L in aqueous portions of pit wastes. Selected ion monitoring with capillary GC/MS with deuterated PAH as internal standards was used to quantify PAH in both aqueous and non-aqueous liquid phases. Over 50 PAH were detected at total concentrations of 130 $\mu\text{g/L}$ to 24,500 $\mu\text{g/L}$ for aqueous phases and 1055 mg/kg to 13,500 mg/kg for non-aqueous phases in pit wastes. In addition, total organic compounds detected in GC analyses of pit wastes were estimated as 200 $\mu\text{g/L}$ to 235 mg/L for aqueous phase and 11 g/kg to 402 g/kg for the non-aqueous phase. Consequences to aquatic environment from disposal practices in natural gas production are evaluated and discussed based on these results.

INTRODUCTION

Natural gas is believed to have origins similar to oil and is often but not always found in contact with oil and water at pressures between 100-2000 psig (1,2). Oil may actually be produced simultaneously with natural gas from the same well and in New Mexico a natural gas well is defined as a well in which the gas/oil ratio is over 100,000 cubic feet of gas per barrel oil. At high pressure wells, natural gas is not a pure substance but is typically a mixture of C_1 to C_4 alkanes, and several inorganic gases with methane at 70 to 95+% mole ratio (1). In addition, a complex mixture of minor components including C_5 to C_{10} alkanes and aromatic hydrocarbons including polycyclic aromatic hydrocarbons (PAH) have been found in natural gas (3-8).

In production and transport of natural gas, two major aqueous wastes are generated: produced water (or brine water) and discharge water from hydrostatic testing (DWHT) of natural gas pipelines (8,9). Produced water which is stored in open-air pits or holding reservoirs is the wastewater separated from natural gas and hydrocarbon condensate at well-heads. The volume of these wastewaters can be quite large. For example, from 31,172 wells producing water in New Mexico in an eleven month period of 1982, over six billion gallons of produced water were recorded (10). Wastes are disposed using underground injection and waste pits on land surfaces. While pits in the U.S. commonly are lined and discharge to unlined pits is now largely prohibited, in northwest New Mexico most waste pits in natural gas production are unlined. Eventual migration of aqueous contents of such pits into ground water has been observed (11-13). Even in pits which are lined with clays, formation of cracks or ruptured linings may develop from contact of clay with certain organic wastes (14). Since DWHT was found to contain hazardous

organic compounds at individual concentrations of 7 to 860 $\mu\text{g/L}$ in prior studies in this research program, presence of hazardous organic compounds in such pits was thought possible and considered potentially serious based on composition and magnitude of wastes and on the number, characteristics and locations of such waste pits near vulnerable aquifers.

The presence of high molecular weight organic compounds in produced water and DWHT can be attributed in part to a phenomenon termed retrograde condensation, which is defined as liquid formation by isothermal expansion of a fluid on a dew point gas stream (11). Formation of liquid by pressure reduction on a gas is a behavior for fluid peculiar to mixtures in the critical region and is unlike that for pure substances (11). Methane in natural gas can be considered a supercritical fluid at ambient temperature and under conditions of high pressure. An important consequence of this condition is increased solubility of large molecular weight compounds in the supercritical fluid (16-18). However, as natural gas is passed through a pressure drop in production equipment or pipelines, the solubility of larger molecular weight components is decreased and condensation occurs.

In waste disposal pits located near natural gas wells, produced water is often found with a hydrocarbon phase which is either originally present at saturation with the water or more likely is carried over with water due to imperfect control of flotation valve in separators at field-treatment units. Although water contamination by salts in brine has been reported (12,13), presence of high molecular weight toxic organic compounds in liquid wastes from these disposal pits is not widely known. An exception is work by Middleditch (15) in which near 200 volatile organic constituents including $\text{C}_3\text{-C}_{16}$ alkanes, benzene, alkyl benzene, naphthalene, and alkyl aromatic hydrocarbons were identified in the produced water effluent from the Buccaneer

Gas and Oil field in the Gulf of Mexico. The objective of this present work is to characterize and quantify when possible organic and toxic organic compounds in liquid wastes including produced water in disposal pit contents located in the San Juan Basin of northwest New Mexico. This work is also expected to provide a base of data for assessment of movement and release of toxic compounds into ground waters as well as into domestic atmospheric environments.

EXPERIMENTAL

Instrumentation

A Hewlett-Packard model 5880A gas chromatograph was equipped with flame ionization detector (FID), automated splitless injector, and DB-5, 10 m long, 0.25 cm ID fused silica capillary column. Conditions for analysis of all samples were: initial temperature, 30°C; program rate, 6°C/min; final temperature, 260°C; final time, 5 min; injector port temperature, 250°C; FID temperature 270°C; carrier gas, nitrogen at 30 cm/s average linear velocity; time for splitless injection 1.5 min; chart speed 0.5 cm; and area reject, 10. A Hewlett-Packard model 5995A gas chromatograph/mass spectrometer (GC/MS) was equipped with jet separator, model 5885M disk drive, model 7225B X-Y plotter, automated splitless injection port and 10 m OV-1 fused silica capillary column. Chromatographic conditions were identical for scanning GC/MS and GC-FID analyses. Mass spectrometer conditions for scanning analyses were: lower mass, 45 amu; upper mass, 600 amu; scan speed, 690 amu/s; delay between scans, 0.1 min; electron multiplier voltage, 1400; and MS detection threshold, 10; linear counts. Mass spectrometer conditions for SIM analyses were: electron multiplier voltage, 1800 V; SIM window size, 0.2 amu;

intergrate sensitivity, 0.05; area threshold, 10.00; smoothing factor, 1.000; selected polycyclic and alkylated polycyclic aromatic hydrocarbon with ions chosen for SIM analyses have been given (8). Volatile organic compounds were determined using instrumentation already described in detail (9). Sample volumes in GC and GC/MS analyses were 0.5 to 2 μ l delivered using a model #701N 10 μ l syringe (Hamilton Co., Las Vegas, NV). Conditions other than these will be noted as necessary.

Reagents and Standard Solutions

Dicloromethane (HPLC grade; Fisher Scientific Co., NJ), cyclohexane (pesticide grade; Fisher Scientific Co., NJ), methanol (Burdick and Jackson Laboratories Inc., Muskegon, MI), and nitromethane (Spectrograde; Eastman Kodak Co., Rochester, NY) were used as purchased. Two types of deuterated PAH standards were used at various stages of this research and included: A) a mixture containing acenaphthene (d_{10}), naphthalene (d_8), benz(a)anthracene (d_{12}), chrysene (d_{12}), anthracene (d_{10}), fluorene (d_{10}), and pyrene (d_{10}) in CD_2Cl_2 and C_6D_6 with individual concentrations of 1 mg/mL purchased from MSD Isotopes (Merck Chemical Division, St. Louis, MO) and B) a mixture of naphthalene (d_8), phenanthrene (d_{10}), and anthracene (d_{10}) in methylene chloride at individual concentrations of 0.66 mg/ml was obtained from Supleco, Inc. (Houston, TX). Additionally, 1 ml of 1:50 dilution of saturated solution of benzene (Pesticide grade, Fisher Scientific Co., Fair Lawn, NJ) was used as external standard to estimate the approximate relative concentration of benzene and alkylated benzene in purge and trap analysis of waste samples.

Samples

Grab samples were drawn from waste pits using a 3 meter sampling rod with container attached to end of pole. Attempts were made to collect both aqueous and non-aqueous (surface film) without concern over mass balance of phases.

Exact locations and descriptions of pits with quadrant location and informal names used in this study were: 1) Cuba, 15 miles west of Cuba, NM, Sec. 29 T22N R3W, 5x5 m unlined pit, 5 cm thick black film on surface, water below surface was dark brown; 2) Bloomfield, within 60 feet of San Juan River in flood plain, Sec. 27 T29N R11W, 5x5 m unlined pit with very little liquid wastes but dark stain on sides of pit, waste has slight oil sheen; 3) Archuleta, Sec. 16 T30N R8W, several miles upstream on NW bank of San Juan River from intersection of highways 173 and 511 near Archuleta, pit was 3 to 4 m diameter, fiberglass pit with 5 to 10 cm of thick oil-like phase on surface; 4) Flora Vista 1E, Sec. 23 T30N R12W at SW4/SW4, well located in the community of Flora Vista and within 10 to 20 m of Animas River on a flood plain, fiberglass pit with dark oily brown surface phase and murky brown aqueous phase; 5) Flora Vista 1E(A), same pit sampled four months earlier and stored at 1-2 C; 6) Flora Vista 1, near Flora Vista, NM at Sec. 23 T30N R12W at NW4/NW4, largely solid non-aqueous wastes in fiberglass pit; 7) Aztec, location off highway 173 halfway between Aztec and Archuleta, NM, Sec. 27 T30N R9W at SE4NW4F, 10x10 m unlined pit on mesa above San Juan River, virtually no water with yellow wax contents and dark high water mark near top of pit nearly 1 meter above surface

Procedures

Samples were analyzed for volatile organic compounds using purge and trap method (9). Conditions for purging were: sample size, 1-5 mL; flow rate of purge gas (N_2), 40 mL/min; time of purge, 12 min; and size of Tenax-GC sorbent trap, 100 mg. Contents of traps were then analyzed using pack column GC/MS with direct thermal desorption of Tenax-GC traps. A 2 m long x 2 mm ID borosilicate glass column packed with 3% OV-101 on Chromosorb W was used for analysis. Conditions for desorption were: temperature for desorption, 150°C;

time of desorption, 1.5 min after a 0.5 min period of preheating; and switching valve temperature; 150°C.

A solvent-extraction procedure described by Bartel et al. (19) and modified by Eiceman et al. (8) was used for isolation and concentration of PAH in the samples. Liquid wastes usually but not always had two phases, aqueous and non-aqueous. The non-aqueous phase had viscous properties with distinct petrochemical odor. The aqueous samples were highly colored and also had a petrochemical odor. Samples were separated into aqueous and non-aqueous phases when both were available, however in all cases phases were extracted individually. In each analysis prior to extraction, samples of 50 mL produced water (aqueous phase) and 2 grams of the non-aqueous phase were spiked with 20-30 µL of deuterated PAH standards. In analysis of each aqueous liquid phase, 50 mL of sample were extracted in triplicate with 50 mL of methylene chloride. Extracts were condensed to ca. 3 mL using rotary evaporator (Buchii Brinkmann Co., NY) and further reduced in volume to 1 mL using a gentle stream of nitrogen gas prior to prefractionation procedures. In analysis of non-aqueous phases, 0.45 gram of sample was diluted to 1 mL with methylene chloride and analyzed directly by GC without any preextraction. A procedure blank was used to insure no contamination from solvent or glassware. Extraction efficiency of PAH as well as confirmation of identity using retention indices was possible through comparison of results to those for deuterated PAH standards.

RESULTS AND DISCUSSION

Volatile Constituents of Waste Pits

Although contents of waste pits had been exposed to ambient atmospheres at temperatures as great as 32°C for unknown duration, a discernable odor was detected in aqueous and non-aqueous phases as present in each sample. Results from GC/MS characterization of volatile organic compounds in the aqueous phase are given in Table 1 and in Figure 2A. In Figure 2A, a total ion chromatogram (TIC) is shown from GC/MS analyses of aqueous portion of the Cuba sample for volatile organic compounds. At least 40 resolved or partially resolved components were seen in the TIC and are representative of results found with other water samples. The identities of major components in this and other samples are listed in Table 1 along with abundance values as rough measure of relative concentrations. In the water phase, the range of estimated total concentrations of volatile compounds was 34 to 500 mg/L. These results were reported here only as estimated concentration since matrices were too complex for accurate external standardization and a broad range of deuterated alkylated benzenes was not available for internal standardization. Moreover, large amounts of volatile organic compounds were unexpected since evaporation of volatile compounds to the atmosphere was initially believed to result in trace concentrations of these compounds in all waste pit liquids, particularly aqueous phase. Two major classes of compounds were detected in these samples and were alkane/alkenes and benzene/alkylated benzenes. Such compounds were also major constituents in sample of produced water from the Gulf of Mexico (15). Furthermore, the same compounds have been identified in other wastes generated downstream in natural gas production and in samples of natural gas in consumer distribution lines (8,9).

Composition of the aqueous fraction of liquid wastes in disposal pits was clearly a complex mixture even for the volatile organic compounds alone. Additional evidence for the large complexity is shown in Figure 3B as mass chromatograms from the same scanning GC/MS analysis shown in Figure 2A. Mass chromatograms are shown for benzene, toluene, and alkylated C_2 to C_8 benzenes. Over 20 compounds from this class were resolved as shown in Figure 3B and retention times were consistent with mass spectral results in Table 1. In Table 1, apparent differences in composition amongst samples were sometimes actual differences and not every component was detected in every sample. In contrast, some compounds were present in all samples but not detected due to differences in concentrations of compounds. If concentrations were below a certain threshold, those compounds even though present were not recorded or recognized with the data system of the GC/MS. Nevertheless, since in-field history of samples is unknown, generally few conclusions on fresh produced water composition can be made from these results. Also, particularly striking was the composition of volatile fraction in the non-aqueous wastes in contact with the wastewater described in Figures 2A and 3B. Similarities between the aqueous and non-aqueous (Figures 2B and 3A) phases were strong and patterns were nearly identical in range of molecular weights of compounds and relative composition. However, major differences in relative composition may be seen in Figure 2 at retention times of 3.0, 6.0, 7.8 and 9.8 min. These compounds were present at large relative concentrations in non-aqueous phase but at very low concentrations in the aqueous phase. Thus, description of contents of waste pits in terms of aqueous phase alone will be incomplete and inaccurate particularly since the non-aqueous phase may have comprised as much as 50% or more by volume of contents in pits based on observations of this sampling program. Amount of evaporation of water has been determined as low (< 5%),

even in the arid Southwest and most loss of water was due to seepage perhaps into local groundwater (12).

Extractable Composition of Waste Liquids in Pits

In addition to volatile organic compounds, waste pit samples were analyzed for less-volatile extractable organic compounds with carbon numbers C_{10} to C_{35} . Results from simple direct GC analysis of samples with little or no pre-treatment apart from liquid-liquid extract of aqueous phase and dilution of non-aqueous phase are shown in Figures 4 and 5, respectively. Results are shown as bar plots of chromatographic data as concentration versus retention index. Concentration units were ng/L for aqueous phase (Figure 4) and $\mu\text{g/g}$ for non-aqueous phase (Figure 5) which in some samples had become solid upon storage in the laboratory at 22°C. Total concentrations of organic compounds in samples as determined from integration of GC total peak area with use of an average response factor were: Bloomfield, 200 $\mu\text{g/L}$; Cuba, 11,000 $\mu\text{g/L}$; Flora Vista 1E, 10,400 $\mu\text{g/L}$; Archuleta, 11,7000 $\mu\text{g/L}$; and Flora Vista 1E(A), 23,500 $\mu\text{g/L}$. Total organic carbon estimated from GC data for the non-aqueous phase were (in g/kg): Flora Vista 1E, 39; Archuleta, 15; Flora Vista 1E(A), 11; Flora Vista 1, 44, and Aztec, 402. Results for both phases for all samples were not reported here since both phases were not always found in all pits. In certain pits (Bloomfield, Cuba) only an aqueous phase was found while in others (Aztec, Flora Vista 1) only a non-aqueous phase was present and collected.

Although organic compounds were present in non-aqueous wastes at concentrations greater than 1000x those for the aqueous phase, both patterns of bar plots and range of molecular weights in general were very similar. Such results are evidence that when phases are present together, movement of compounds between two phases may be expected. Nearly all samples were complex

mixtures with 20 to 130+ compounds as has been found in discharge water from hydrostatic testing and in pipeline condensate with carbon number range between C_{10} to C_{30}^+ with a maximum relative abundance seen at C_{14} to C_{18} .

Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons have been found throughout natural gas consumer distribution lines and in natural gas supplied to consumers (20). This class of compounds has also been found in discharge water from hydrostatic testing of natural gas pipelines (8). Therefore, the presence of PAH in waste disposal pits may reasonably be expected since natural gas was believed the source of PAH in these earlier studies. Results from SIM analyses of aqueous and non-aqueous wastes in disposal pits for PAH are shown in Figure 6 and Tables 2 and 3. In Figure 6, SIM plots are given for 12 molecular ions for PAH and alkylated PAH in both phases for a single waste pit. The presence of each PAH was measured against deuterated internal PAH for qualitative identification and quantitative content. Patterns in composition of PAH in both phases, as shown in Figures 6A and 6B for the Cuba sample, were similar and consistent with the concept of equilibrium between phases. In those pits in which both phases exist and the aqueous phase is covered or protected from ambient atmosphere by the non-aqueous (hydrocarbon) phase, major changes may not occur rapidly in compositions from weathering leading to evaporation or decomposition. However, this is speculation and further study is needed on weathering of disposal pits at high altitude in hot dry climates such as is found in the US Southwest.

Environmental Conclusions

The concentrations of PAH in either phase is sufficiently large for concern should these wastes reach groundwater destined for human consumption. While movement of PAH in certain soils is relatively slow, additional study on PAH transport is necessary with sand-like soils in parts of New Mexico and perhaps elsewhere. Results from these analyses show caution is necessary in extrapolating results from waste pits in a small geographical area insomuch that major differences were seen in composition of aqueous and non-aqueous phases in these samples. The origin for differences is presently unknown. However, considerable amounts of a large number of EPA regulated priority pollutants were found in these waste disposal pits and warrant further investigations on movement and fate of toxic and hazardous organic compounds which are generated from production of natural gas.

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TABLE 1: Summary of Volatile Organic Compounds in Aqueous Phase of Waste Pits from Natural Gas Production

Retention Index	Compound	Cuba	Archuleta	Bloomfield	Flora Vista 1E(A)
Absolute MS Abundances					
693	C ₄ H ₈ (alkene)	1431	ND	-	ND
715	C ₆ H ₁₂ (alkene)	1190	-	1762	-
727	C ₇ H ₁₆ branched alkane	681	-	-	-
729	Benzene	-	3117	-	-
733	C ₇ H ₁₄ isomer	1159	-	1679	-
756	C ₇ H ₁₆ branched alkane	1249	-	2243	-
766	C ₇ H ₁₄ isomer	3945	-	3920	-
805	Toluene	730	3729	-	-
822	C ₈ H ₁₆ alkene	3984	-	-	-
820	C ₈ H ₁₆ alkene isomer	5589	-	6767	-
844	C ₈ H ₁₈ branched alkane	2843	-	-	-
849	Alkene (U)	-	287	-	-
851	C ₈ H ₁₈ branched alkane	-	-	5618	-
868	C ₈ H ₁₆ alkene	3599	351	-	-
873	C ₈ H ₁₆ alkene	-	-	3721	-
895	Xylene	13911	2848	26834	-
900	n-C ₉ H ₂₀	2040	-	-	-
905	Branched alkane/alkene	-	-	-	3789
912	Xylene isomer	6025	758	14604	-
917	C ₉ H ₁₈ alkene	-	-	-	9448
932	Branched alkane C ₉ H ₂₂	6114	806	7916	-
946	C ₉ H ₁₈ isomer	2073	1672	1735	-

*Abundance for external benzene standard = 39460. Abundance Units for 14 mg/L.

TABLE 1 (continued)

Retention Index	Compound	Cuba	Archuleta	Bloomfield	Flora Vista 1E(A)
954	C ₁₀ H ₂₂ isomer	1266	-	-	-
959	C ₁₀ H ₂₀ alkene	1439	-	-	1837
971	C ₃ -benzene	5995	425	6989	-
976	C ₁₀ H ₂₀ alkene	-	-	-	1315
993	C ₃ benzene isomer	6283	395	8713	-
998	C ₁₀ H ₂₀ alkene isomer	-	-	-	3630
1000	n-C ₁₀ H ₂₂	7506	743	1345	-
1030	C ₁₀ H ₂₀ isomer	2313	-	1615	-
1040	C ₄ -benzene	1955	-	1071	-
1067	Mixture C ₄ -benzene with unidentified alkane	2909	458	-	-
1070	C ₄ -benzene	-	-	1513	-
1089	C ₅ -benzene	952	-	393	-
1100	n-C ₁₁ H ₂₂	7781	814	6063	-
1114	Branched alkane	544	-	428	-
1159	Naphthalene	2169	-	789	-
1200	n-C ₁₂ H ₂₆	7555	-	2252	-
1231	C ₁₂ H ₂₄ alkene	887	-	-	-
1300	n-C ₁₃ H ₂₈	7528	1124	1376	-
1337	C ₁₃ H ₂₆	5439	-	-	-
1353	Saturated alkane	5033	-	-	-
1373	Branched alkene	-	-	541	-

TABLE 2: Concentrations of PAH in Aqueous Phase of Waste Pits from Natural Gas Production

	Cuba	Archuleta	Flora Vista 1E	Bloomfield	Flora Vista 1E(A)
	Concentration (µg/L)				
Naphthalene	850	480	ND	ND	500
C ₁ -Naphthalene	770	390	"	"	1900
C ₂ -Naphthalene	1300	2500	"	"	4200
C ₃ -Naphthalene	1400	2400	"	"	3600
Biphenyl	680	480	"	"	450
C ₁ -Biphenyl	850	720	"	"	1400
C ₂ -Biphenyl	1000	1700	"	"	1400
C ₃ -Biphenyl	1100	920	"	"	960
Anthracene	200	430	3.5	130	530
C ₁ -Anthracene	290	560	5.2	ND	1900
C ₂ -Anthracene	260	380	ND	"	2200
C ₃ -Anthracene	180	170	"	"	1700
Fluorene	82	140	ND	ND	320
C ₁ -Fluorene	180	360	"	"	650
C ₂ -Fluorene	140	390	"	"	870
C ₃ -Fluorene	78	430	"	"	650
Pyrene	13	200	300	ND	410
C ₁ -Pyrene	65	130	1400	"	260
C ₂ -Pyrene	46	100	ND	"	280
C ₃ -Pyrene	33	160	"	"	280
Benzopyrene	ND	ND	ND	ND	ND
C ₁ -Benzopyrene	"	"	"	"	"
C ₂ -Benzopyrene	"	"	"	"	"
C ₃ -Benzopyrene	"	"	"	"	"
TOTAL	9,517	14,740	1,709	130	24,460

ND - Not detected.

TABLE 3: Concentrations of PAH in Non-Aqueous Phase of Waste Pits from Natural Gas Production

	Concentration (mg/kg)					
	Cuba	Archuleta	Flora Vista 1E	Flora Vista 1E(A)	Flora Vista	Aztec
Naphthalene	160	23	240	80	375	ND
C ₁ -Naphthalene	110	22	290	410	250	"
C ₂ -Naphthalene	1500	190	4700	1000	2600	1100
C ₃ -Naphthalene	1600	170	3400	590	1200	360
Biphenyl	54	23	390	72	230	ND
C ₁ -Biphenyl	230	86	1200	250	450	33
C ₂ -Biphenyl	420	120	1100	280	300	160
C ₃ -Biphenyl	320	85	650	270	45	130
Anthracene	130	52	220	17	150	26
C ₁ -Anthracene	240	66	400	120	280	33
C ₂ -Anthracene	140	34	290	130	200	15
C ₃ -Anthracene	99	23	190	79	99	14
Fluorene	27	11	66	30	38	8
C ₁ -Fluorene	39	27	130	61	56	10
C ₂ -Fluorene	36	54	84	86	41	10
C ₃ -Fluorene	30	56	19	92	32	10
Pyrene	24	10	26	13	13	6
C ₁ -Pyrene	24	8.6	24	28	13	5
C ₂ -Pyrene	10	8.6	19	30	12	ND
C ₃ -Pyrene	9	11	11	33	11	"
Benzopyrene	ND	ND	ND	ND	ND	ND
C ₁ -Benzopyrene	"	"	"	"	"	"
C ₂ -Benzopyrene	"	"	"	"	"	"
C ₃ -Benzopyrene	"	"	"	"	"	"
TOTAL	5,202	1,055	13,449	3,541	11,895	1,920

ND - Not detected.

LIST OF FIGURES

1. Map of Locations of Waste Pits. Locations on map designated by letter is referenced to text according to: a) Cuba, b) Bloomfield, c) Archuleta, d) Aztec, e) Flora Vista 1E and f) Flora Vista 1. Attempt was made to locate letter in general vicinity of associated waste pit.
2. Total Ion Chromatogram from GC/MS Analysis of A) Aqueous Wastes from Cuba sample and B) Non-Aqueous Wastes for same sample for Volatile Organic Compounds.
3. Mass Chromatograms for Benzene and Alkylated Benzenes from Scanning GC/MS Analysis of Non-Aqueous (A) and Aqueous (B) Phases from Cuba sample.
4. Bar Plots from GC/FID Analyses of Aqueous Phase from Waste Pits for Extractable Compounds. Samples were: A) Cuba, B) Flora Vista 1E, C) Flora Vista 1, D) Procedure Blank, E) Archuleta and F) Bloomfield.
5. Bar Plots from GC/FID Analyses of Non-Aqueous Phase from Waste Pits for Extractable Compounds. Samples were: A) Cuba, B) Flora Vista 1E(A), C) Flora Vista, D) Flora Vista 1E, E) Archuleta and F) Aztec.
6. SIM Plots from GC/MS Analyses of Non-Aqueous (A) and Aqueous (B) Phases from Waste Pits from Cuba sample for Polycyclic Aromatic Hydrocarbons.

Figure 1. Davani et al

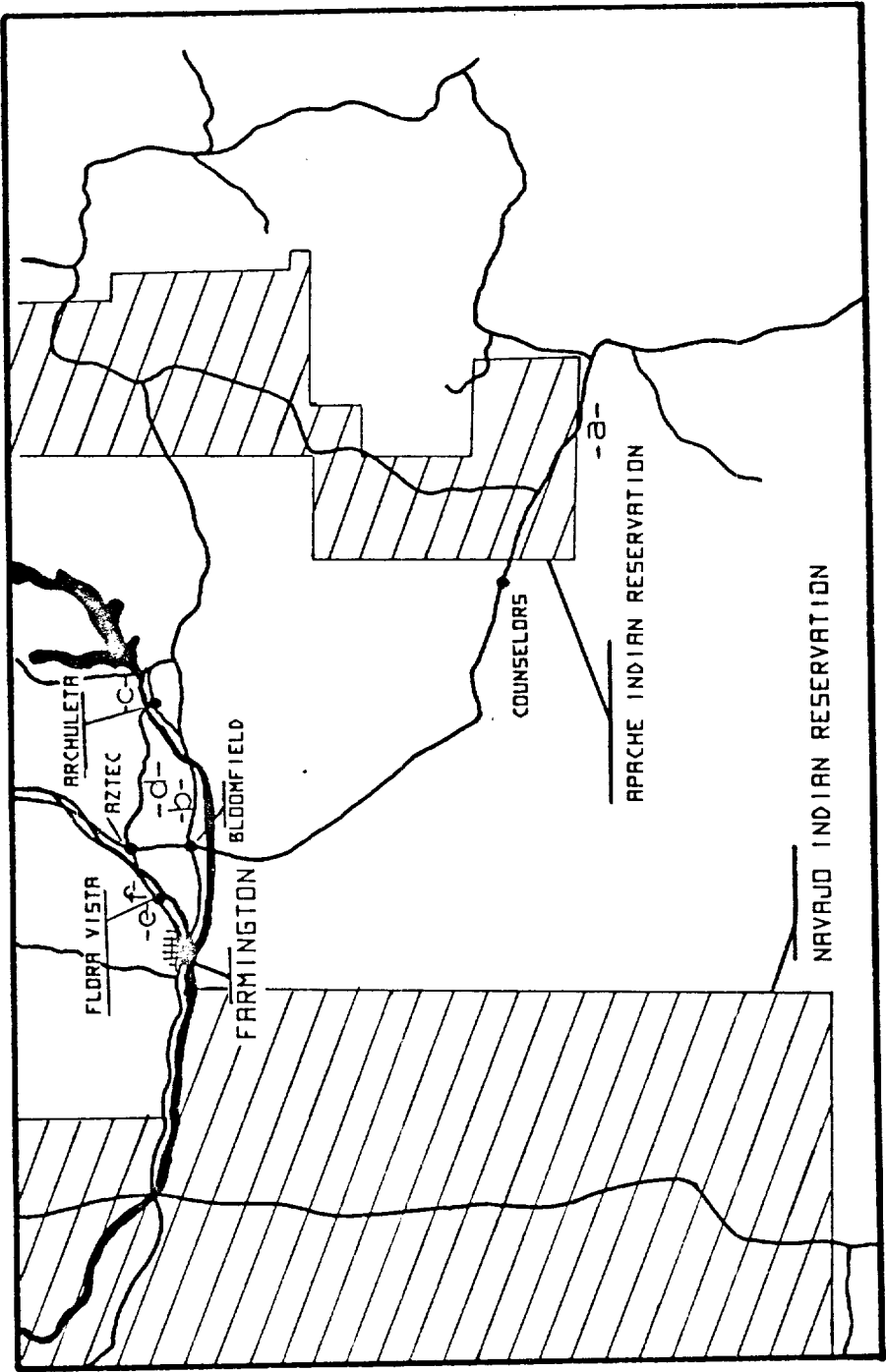
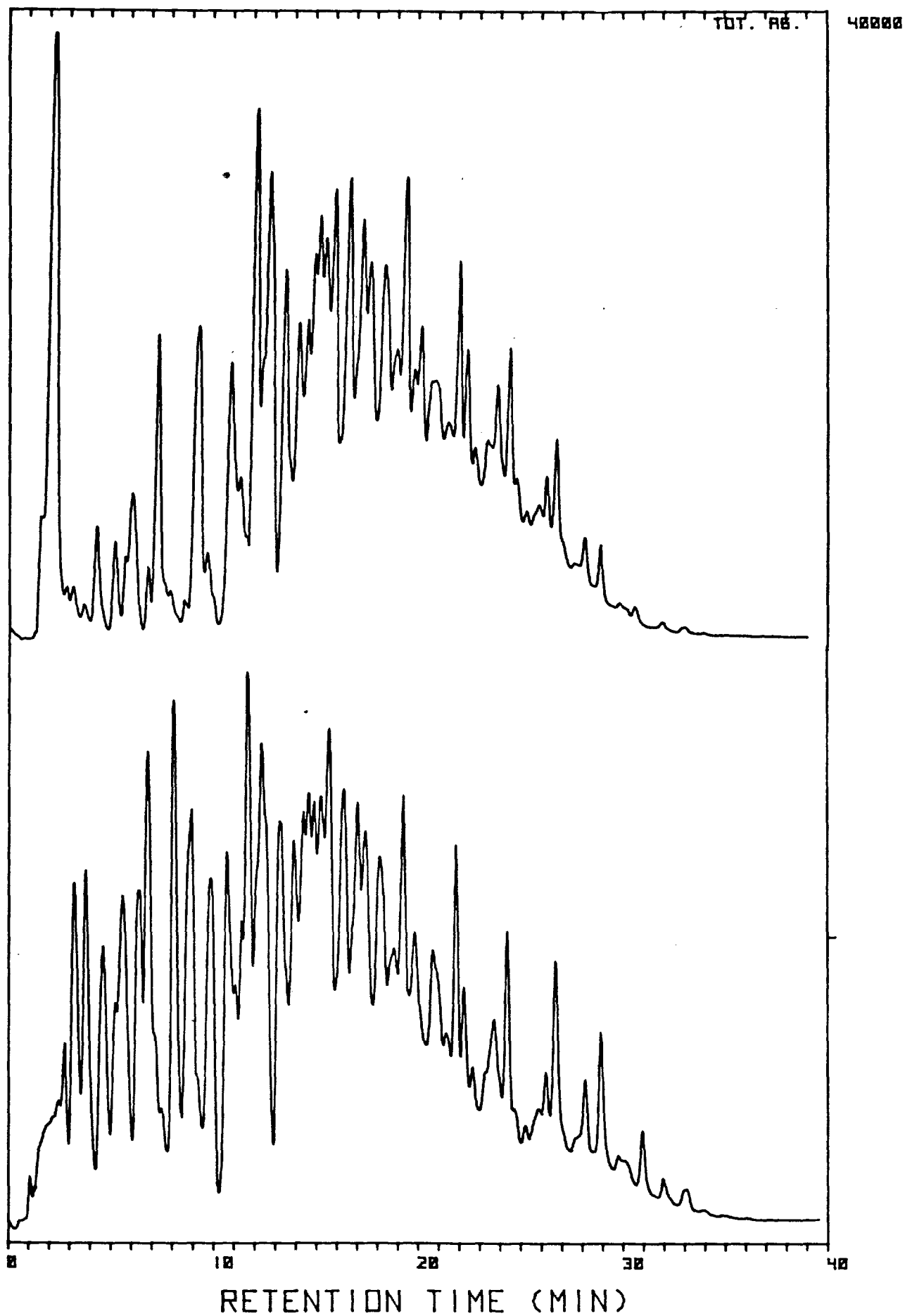
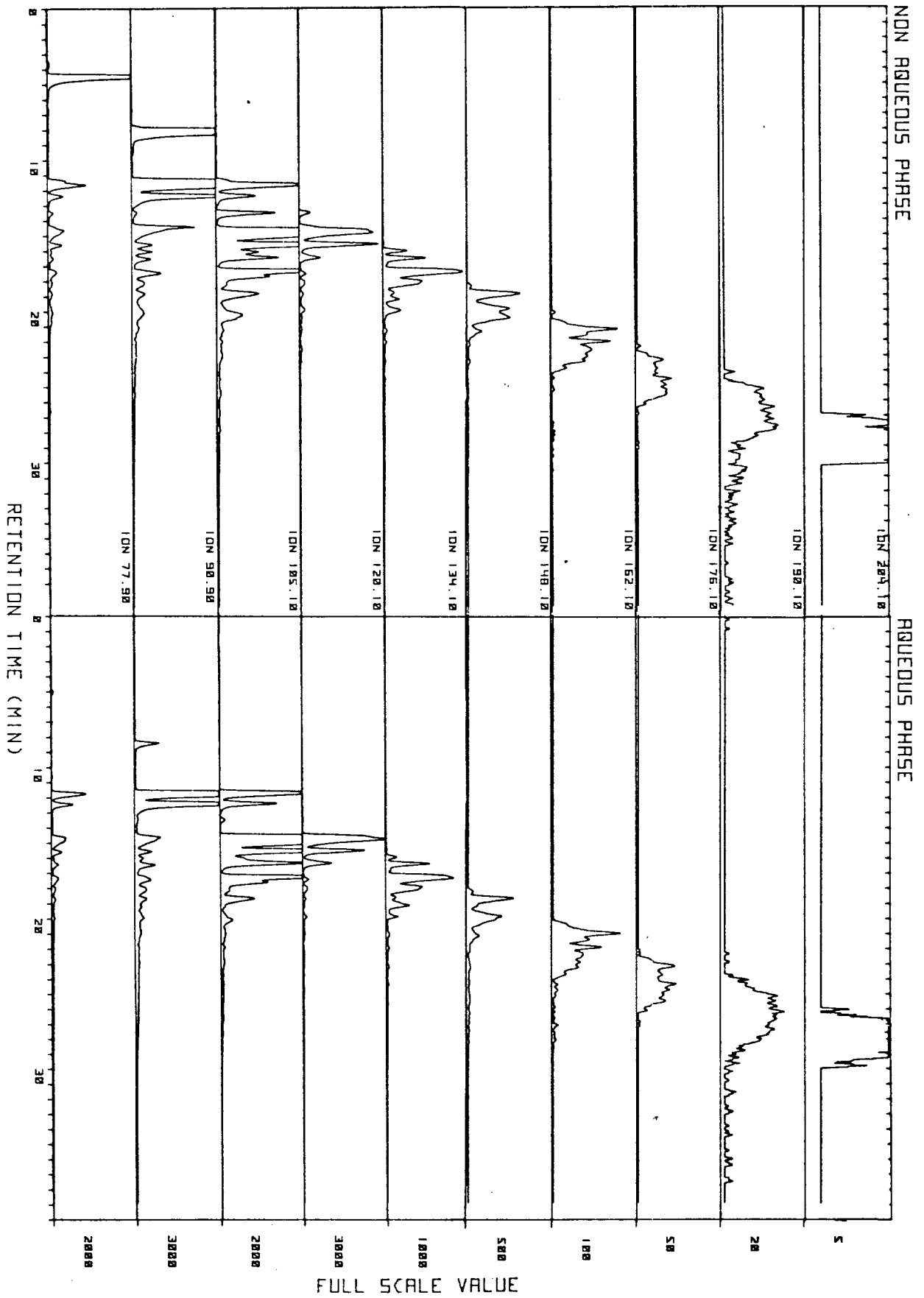


Figure 2. Davani et al.

TOTAL ION ABUNDANCE



ION ABUNDANCE



CONCENTRATION FULL SCALE = (2000 NG/ML)

RETENTION INDEX

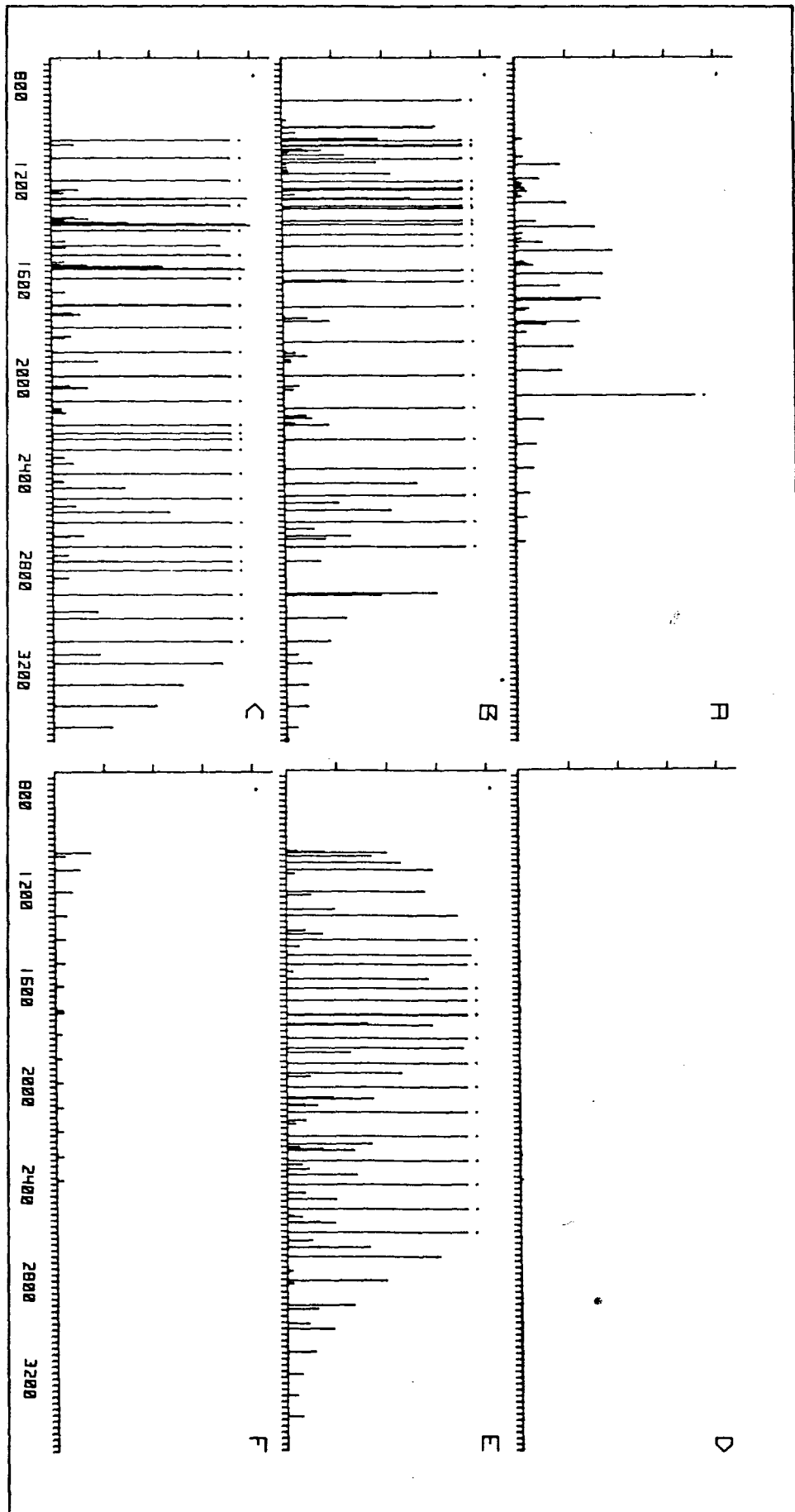


Figure 5. Davani et al

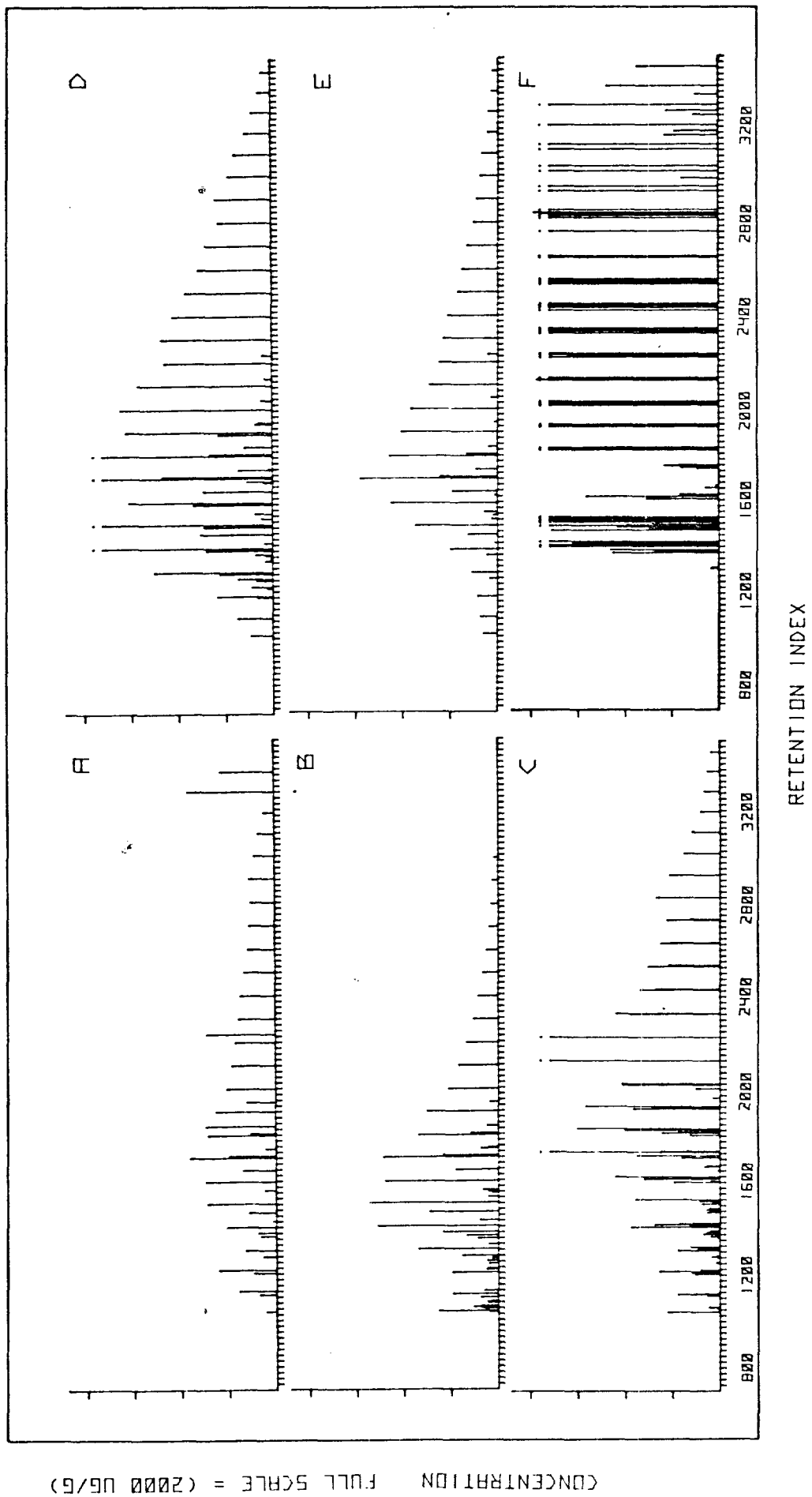
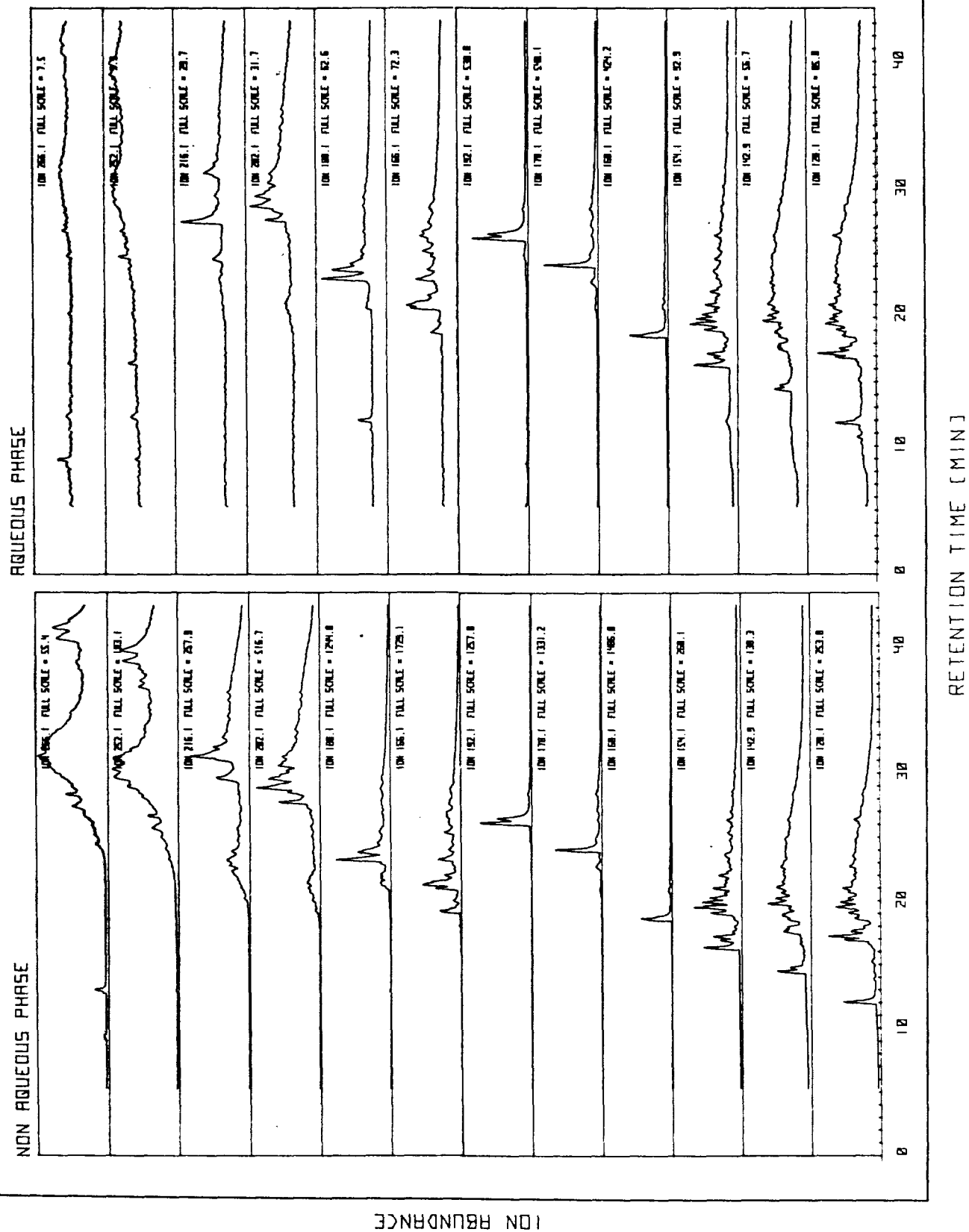
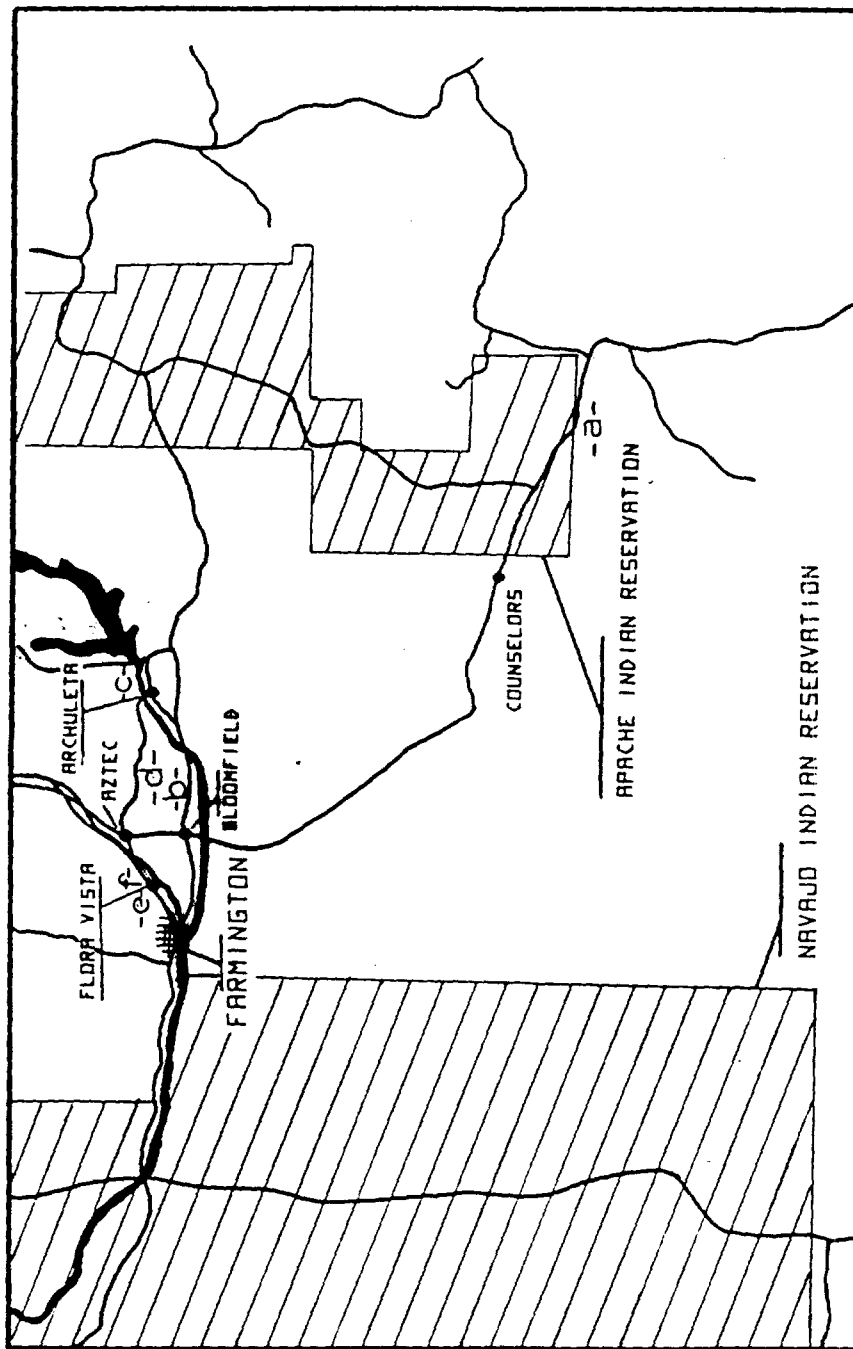


Figure 6. Davani et al

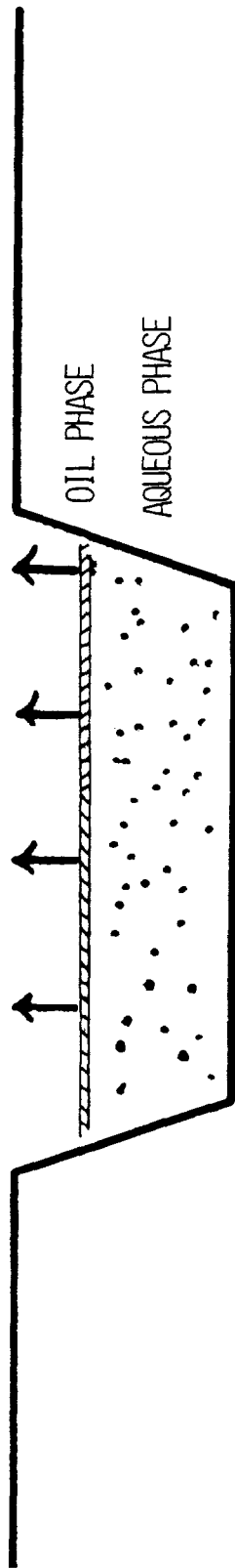


8



3

1. BAKER AND BRENDKE, GROUNDWATER 1983, 21, 317-324

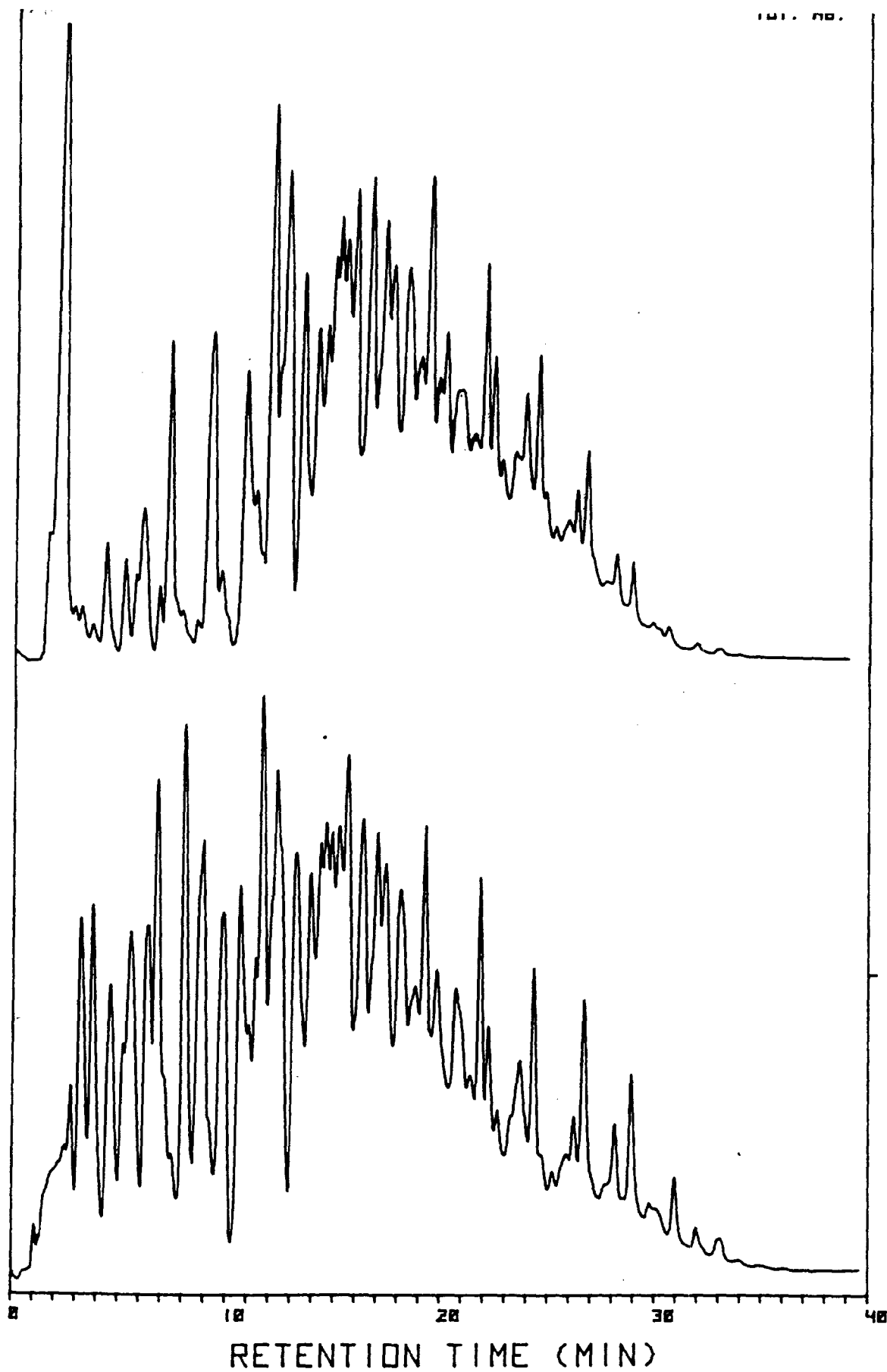


WASTE DISPOSAL PITS IN NEW MEXICO

1. AGRICULTURE	138
2. INDUSTRIAL	317
3. MINING	838
4. MUNICIPAL	703
5. OIL AND GAS	15,761

1. REPORT TO API BY DAVES AND MOORE, OCT 1982
2. SEEPAGE FROM OILFIELD BRINE DISPOSAL PONDS IN UTAH, GROUNDWATER 1983, 21, 317-324.
3. INVESTIGATION AND REHABILITATION OF A BRINE-CONTAMINATED AQUIFER, GROUNDWATER 1975, 15, 155
4. OIL-FIELD POLLUTION...AND WHATS BEING DONE ABOUT IT. OGJ JUNE 1963, 76-86...2.25 BILLION BBL OF BRINE IN TX IN 1961.

TOTAL ION ABUNDANCE



4

TABLE 1: Summary of Volatile Organic Compounds in Aqueous Phase of Waste Pits
from Natural Gas Production

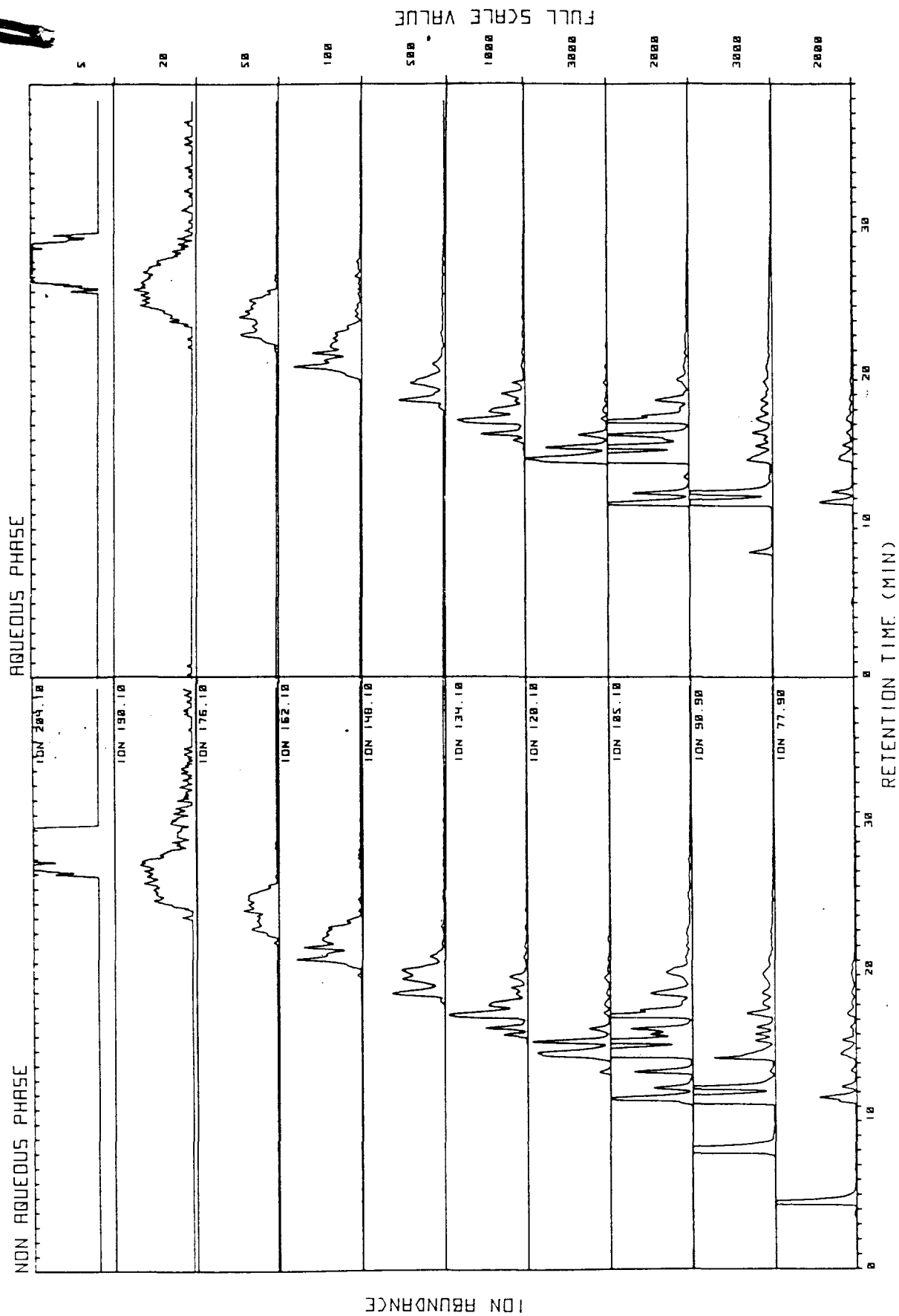
Retention Index	Compound	Cuba	Archuleta	Bloomfield	Flora Vista	IE(A)
Absolute MS Abundances						
693	C ₄ H ₈ (alkene)	1431	ND	-	ND	
715	C ₆ H ₁₂ (alkene)	1190	-	1762	-	
727	C ₇ H ₁₆ branched alkane	681	-	-	-	
729	Benzene	-	3117	-	-	
733	C ₇ H ₁₄ isomer	1159	-	1679	-	
756	C ₇ H ₁₆ branched alkane	1249	-	2243	-	
766	C ₇ H ₁₄ isomer	3945	-	3920	-	
805	Toluene	730	3729	-	-	
822	C ₈ H ₁₆ alkene	3984	-	-	-	
820	C ₉ H ₁₆ alkene isomer	5589	-	6767	-	
844	C ₈ H ₁₈ branched alkane	2843	-	-	-	
849	Alkene (U)	-	287	-	-	
851	C ₈ H ₁₈ branched alkane	-	-	5618	-	
868	C ₈ H ₁₆ alkene	3599	351	-	-	
873	C ₈ H ₁₆ alkene	-	-	3721	-	
895	Xylene	13911	2848	26834	-	
900	n-C ₉ H ₂₀	2040	-	-	-	
905	Branched alkane/alkene	-	-	-	3789	
912	Xylene isomer	6025	758	14604	-	
917	C ₉ H ₁₈ alkene	-	-	-	9448	
932	Branched alkane C ₉ H ₂₂	6114	806	7916	-	
946	C ₉ H ₁₈ isomer	2073	1672	1735	-	

*Abundance for external benzene standard = 39460. Abundance Units for 14 mg/L.

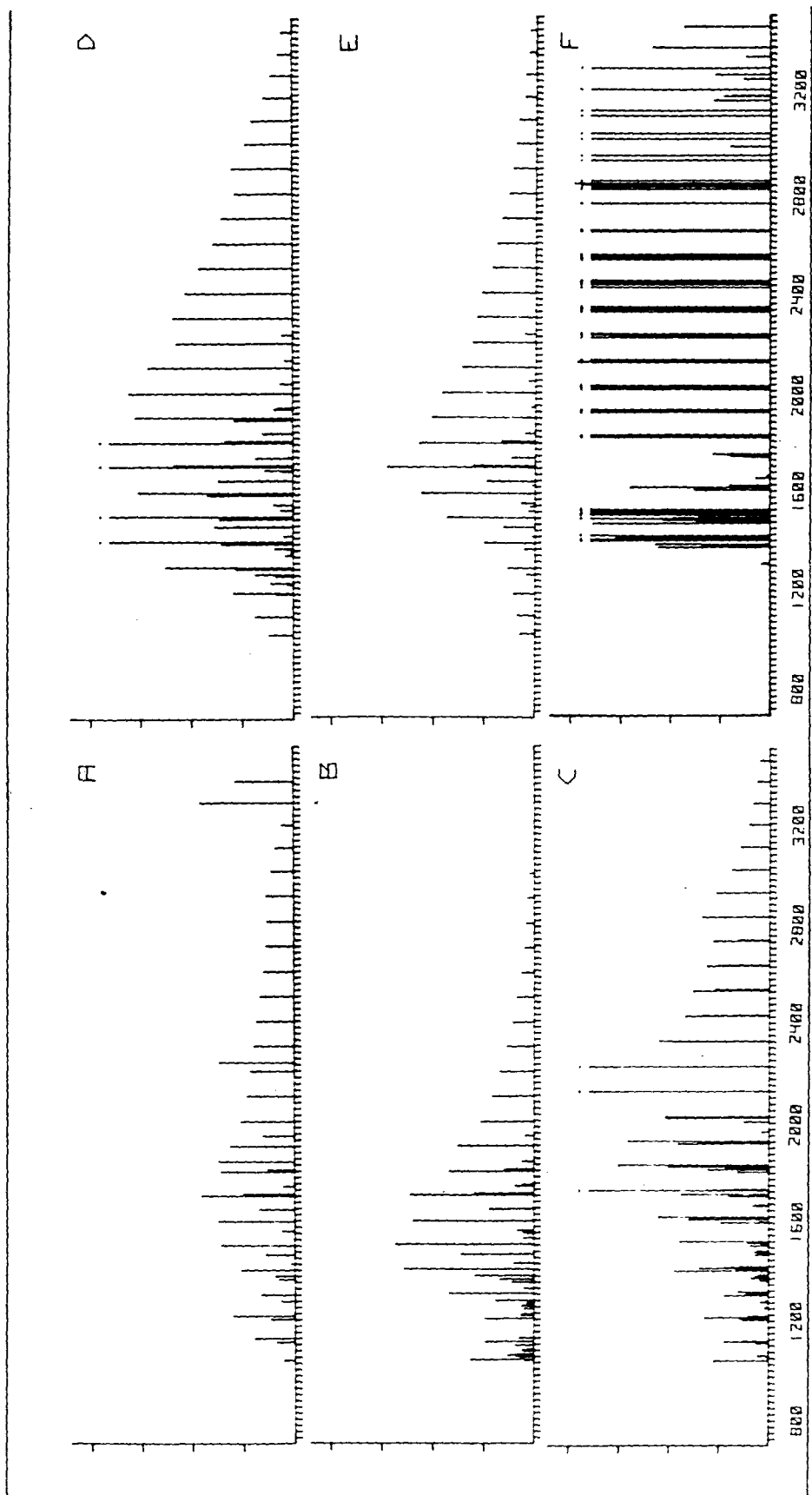
TABLE 1 (continued)

Retention Index	Compound	Cuba	Archuleta	Bloomfield	Flora Vista 1E(A)
954	$C_{10}H_{22}$ isomer	1266	-	-	-
959	$C_{10}H_{20}$ alkene	1439	-	-	1837
971	C_3 -benzene	5995	425	6989	-
976	$C_{10}H_{20}$ alkene	-	-	-	1315
993	C_3 benzene isomer	6283	395	8713	-
998	$C_{10}H_{20}$ alkene isomer	-	-	-	3630
1000	n- $C_{10}H_{22}$	7506	743	1345	-
1030	$C_{10}H_{20}$ isomer	2313	-	1615	-
1040	C_4 -benzene	1955	-	1071	-
1067	Mixture C_4 -benzene with unidentified alkane	2909	458	-	-
1070	C_4 -benzene	-	-	1513	-
1089	C_5 -benzene	952	-	393	-
1100	n- $C_{11}H_{22}$	7781	814	6063	-
1114	Branched alkane	544	-	428	-
1159	Naphthalene	2169	-	789	-
1200	n- $C_{12}H_{26}$	7555	-	2252	-
1231	$C_{12}H_{24}$ alkene	887	-	-	-
1300	n- $C_{13}H_{28}$	7528	1124	1376	-
1337	$C_{13}H_{26}$	5439	-	-	-
1353	Saturated alkane	5033	-	-	-
1373	Branched alkene	-	-	541	-

7



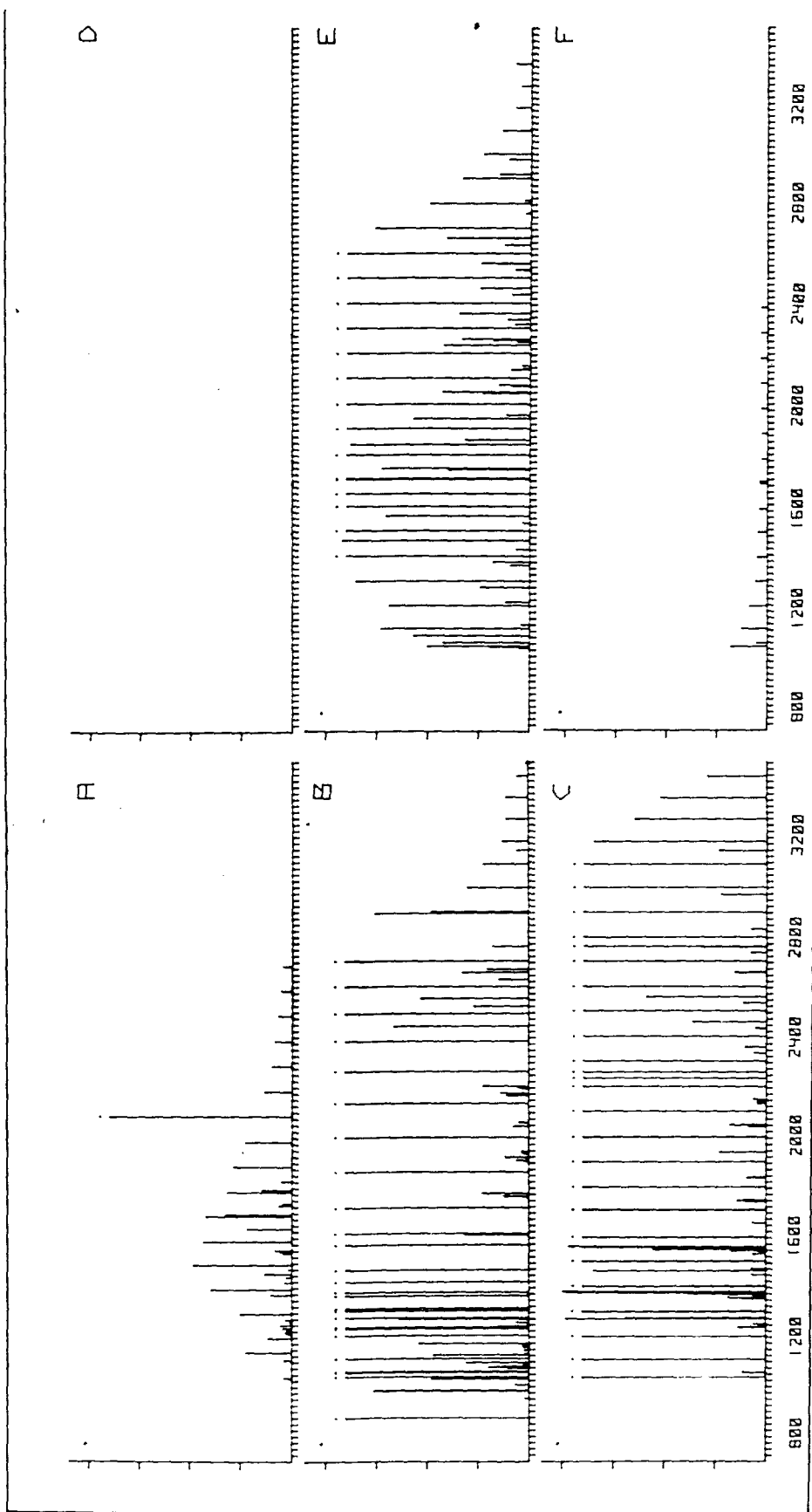
(CONCENTRATION FULL SCALE = (2000 UG/G)



RETENTION INDEX

3

CONCENTRATION FULL SCALE = (2000 NG/ML)



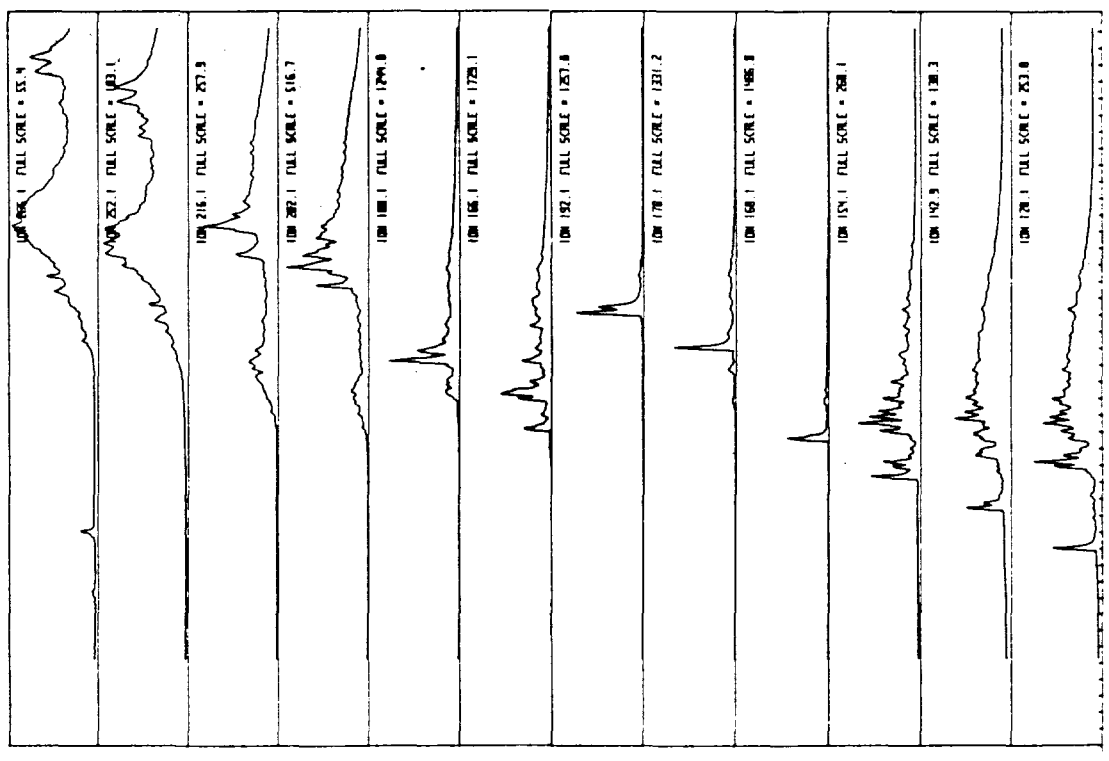
RETENTION INDEX

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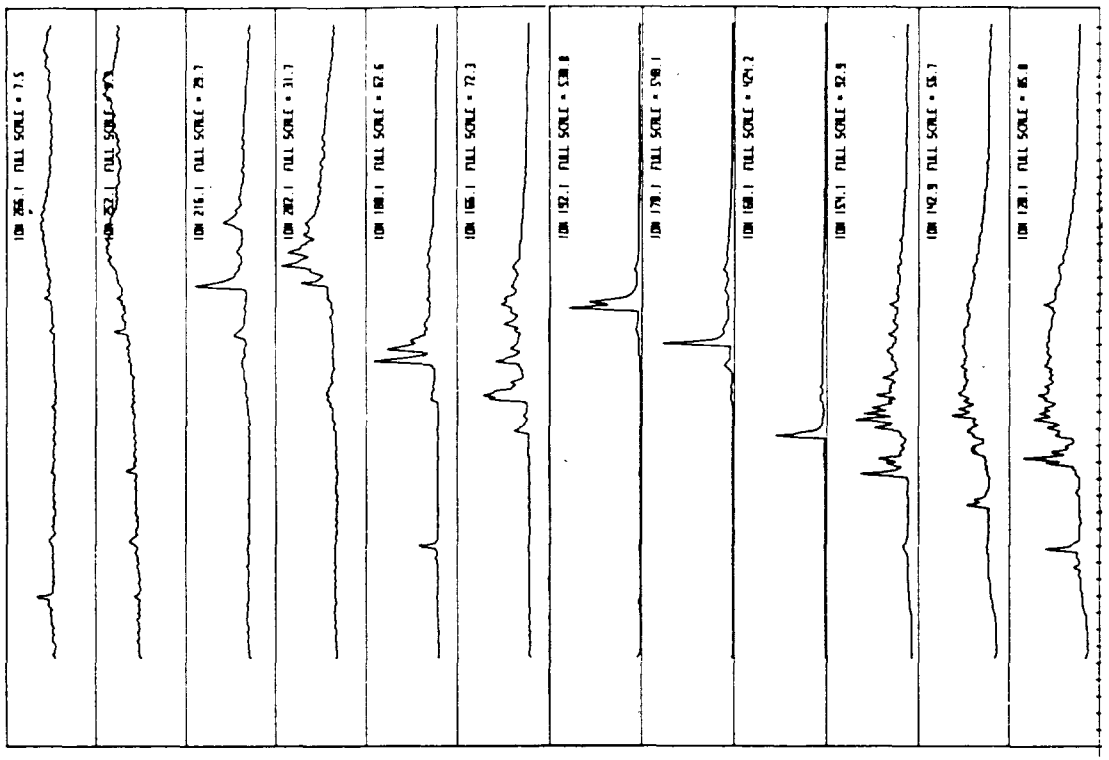
110

ION ABUNDANCE

NON AQUEOUS PHASE



AQUEOUS PHASE



RETENTION TIME [MIN]

TABLE 2: Concentrations of PAH in Aqueous Phase of Waste Pits from Natural Gas Production

	Cuba	Archuleta	Flora Vista 1E	Bloomfield	Flora Vista 1E(A)
	Concentration (µg/L)				
Naphthalene	850	480	ND	ND	500
C ₁ -Naphthalene	770	390	"	"	1900
C ₂ -Naphthalene	1300	2500	"	"	4200
C ₃ -Naphthalene	1400	2400	"	"	3600
Biphenyl	680	480	"	"	450
C ₁ -Biphenyl	850	720	"	"	1400
C ₂ -Biphenyl	1000	1700	"	"	1400
C ₃ -Biphenyl	1100	920	"	"	960
Anthracene	200	430	3.5	130	530
C ₁ -Anthracene	290	560	5.2	ND	1900
C ₂ -Anthracene	260	380	ND	"	2200
C ₃ -Anthracene	180	170	"	"	1700
Fluorene	82	140	ND	ND	320
C ₁ -Fluorene	180	360	"	"	650
C ₂ -Fluorene	140	390	"	"	870
C ₃ -Fluorene	78	430	"	"	650
Pyrene	13	200	300	ND	410
C ₁ -Pyrene	65	130	1400	"	260
C ₂ -Pyrene	46	100	ND	"	280
C ₃ -Pyrene	33	160	"	"	280
Benzopyrene	ND	ND	ND	ND	ND
C ₁ -Benzopyrene	"	"	"	"	"
C ₂ -Benzopyrene	"	"	"	"	"
C ₃ -Benzopyrene	"	"	"	"	"
TOTAL	9,517	14,740	1,709	130	24,460

ND - Not detected.

TABLE 3: Concentrations of PAH in Non-Aqueous Phase of Waste Pits from Natural Gas Production

Concentration (mg/kg)

	Cuba	Archuleta	Flora Vista 1E	Flora Vista 1E(A)	Flora Vista	Aztec
Naphthalene	160	23	240	80	375	ND
C ₁ -Naphthalene	110	22	290	410	250	"
C ₂ -Naphthalene	1500	190	4700	1000	2600	1100
C ₃ -Naphthalene	1600	170	3400	590	1200	360
Biphenyl	54	23	390	72	230	ND
C ₁ -Biphenyl	230	86	1200	250	450	33
C ₂ -Biphenyl	420	120	1100	280	300	160
C ₃ -Biphenyl	320	85	650	270	45	130
Anthracene	130	52	220	17	150	26
C ₁ -Anthracene	240	66	400	120	280	33
C ₂ -Anthracene	140	34	290	130	200	15
C ₃ -Anthracene	99	23	190	79	99	14
Fluorene	27	11	66	30	38	8
C ₁ -Fluorene	39	27	130	61	56	10
C ₂ -Fluorene	36	54	84	86	41	10
C ₃ -Fluorene	30	56	19	92	32	10
Pyrene	24	10	26	13	13	6
C ₁ -Pyrene	24	8.6	24	28	13	5
C ₂ -Pyrene	10	8.6	19	30	12	ND
C ₃ -Pyrene	9	11	11	33	11	"
Benzopyrene	ND	ND	ND	ND	ND	ND
C ₁ -Benzopyrene	"	"	"	"	"	"
C ₂ -Benzopyrene	"	"	"	"	"	"
C ₃ -Benzopyrene	"	"	"	"	"	"
TOTAL	5,202	1,055	13,449	3,541	11,895	1,920

ND - Not detected.

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DETECTOR RESPONSE

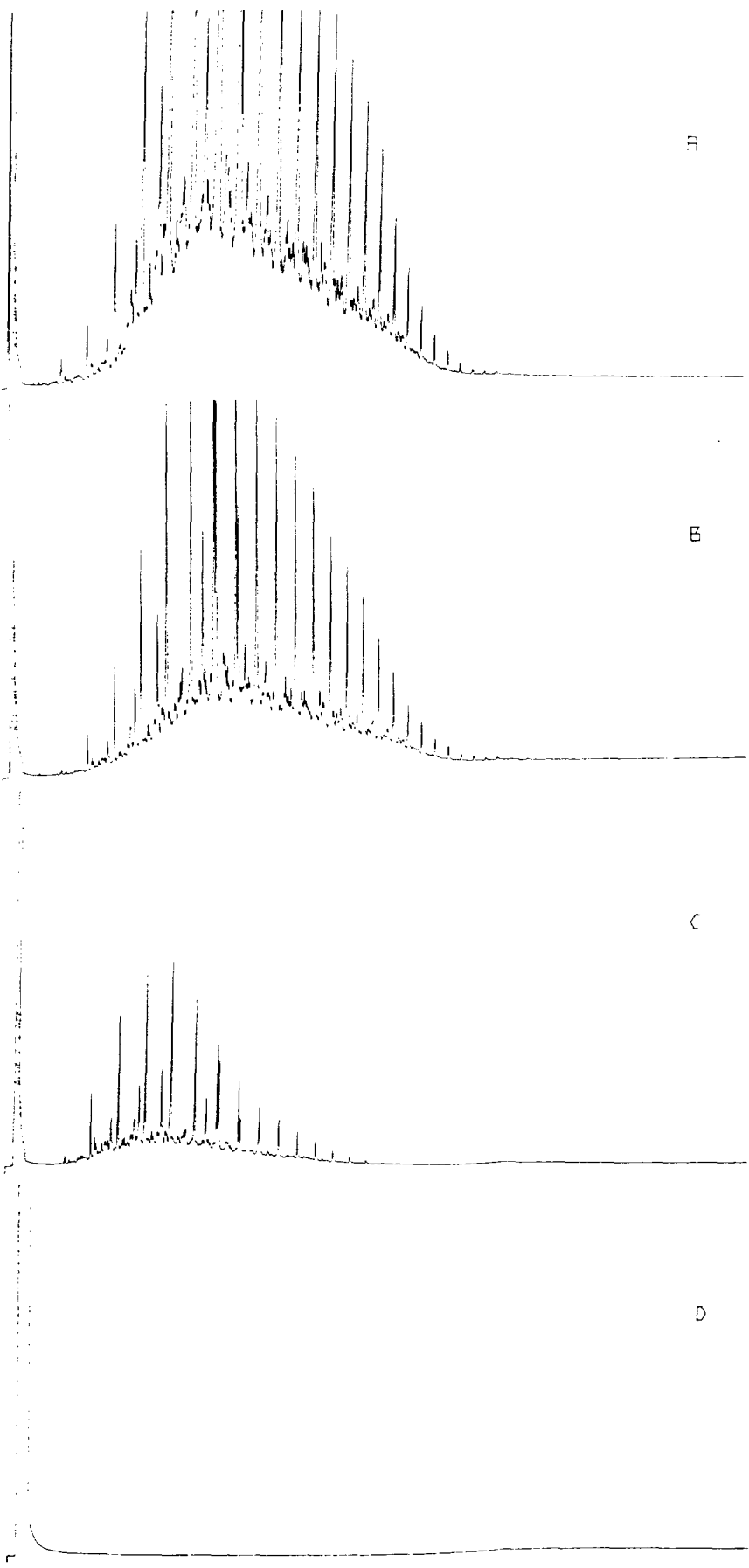


Table III Concentrations of PAH in Soils from Waste Pits

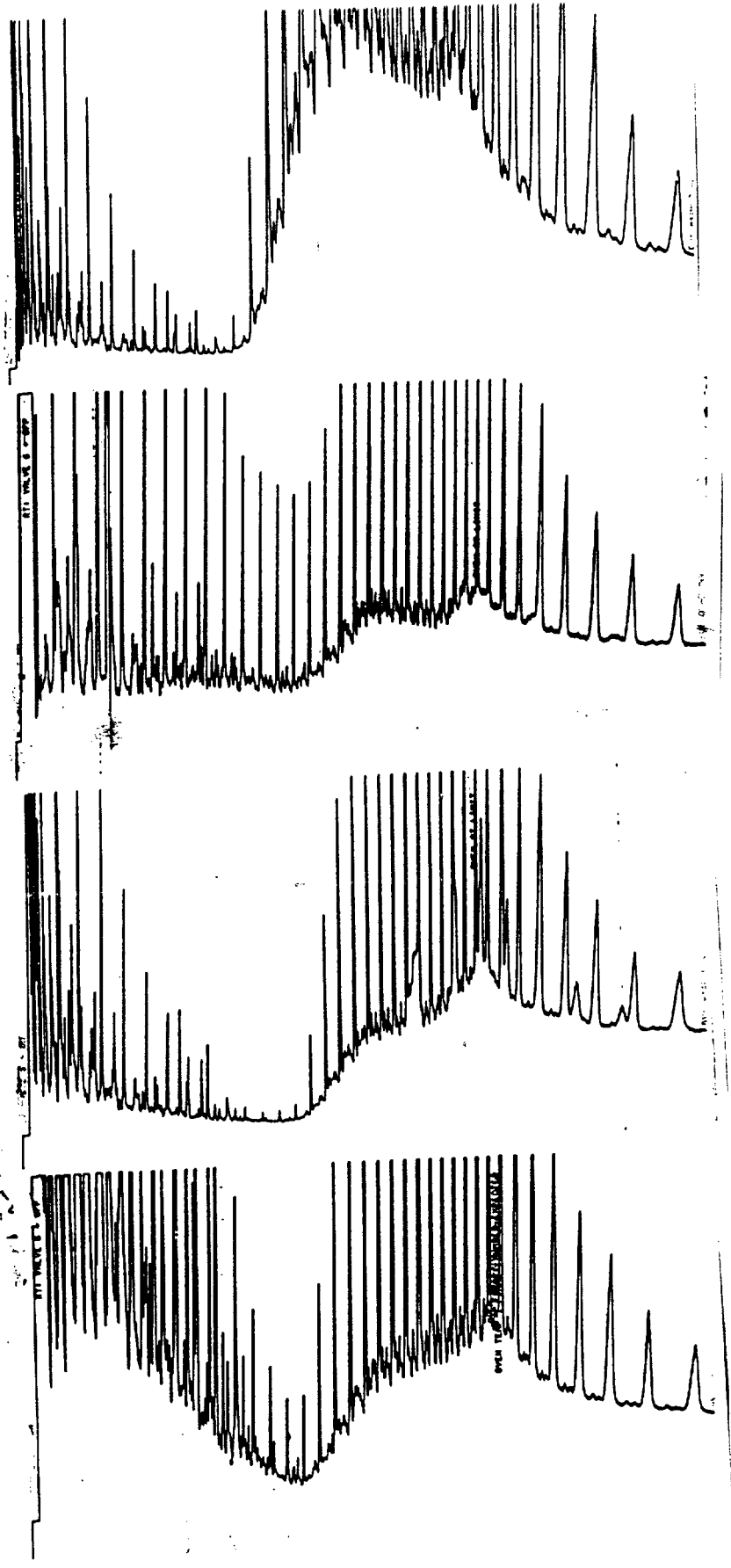


Compound	Concentration (µg/g)		
	Compressor Station Pit #1	Production Pit #1	Production Pit #2
C ₂ -Naphthalenes	53	53	105
C ₂ -Biphenyls	66	42	91
Fluorene	33	18	42
C ₁ -Fluorenes	55	15	48
C ₂ -Fluorenes	52	17	47
Anthracene *	94	36	105
C ₁ -Anthracenes	205	49	276
C ₂ -Anthracenes	178	31	138
Pyrene **	25	5	20

* Including phenanthrene

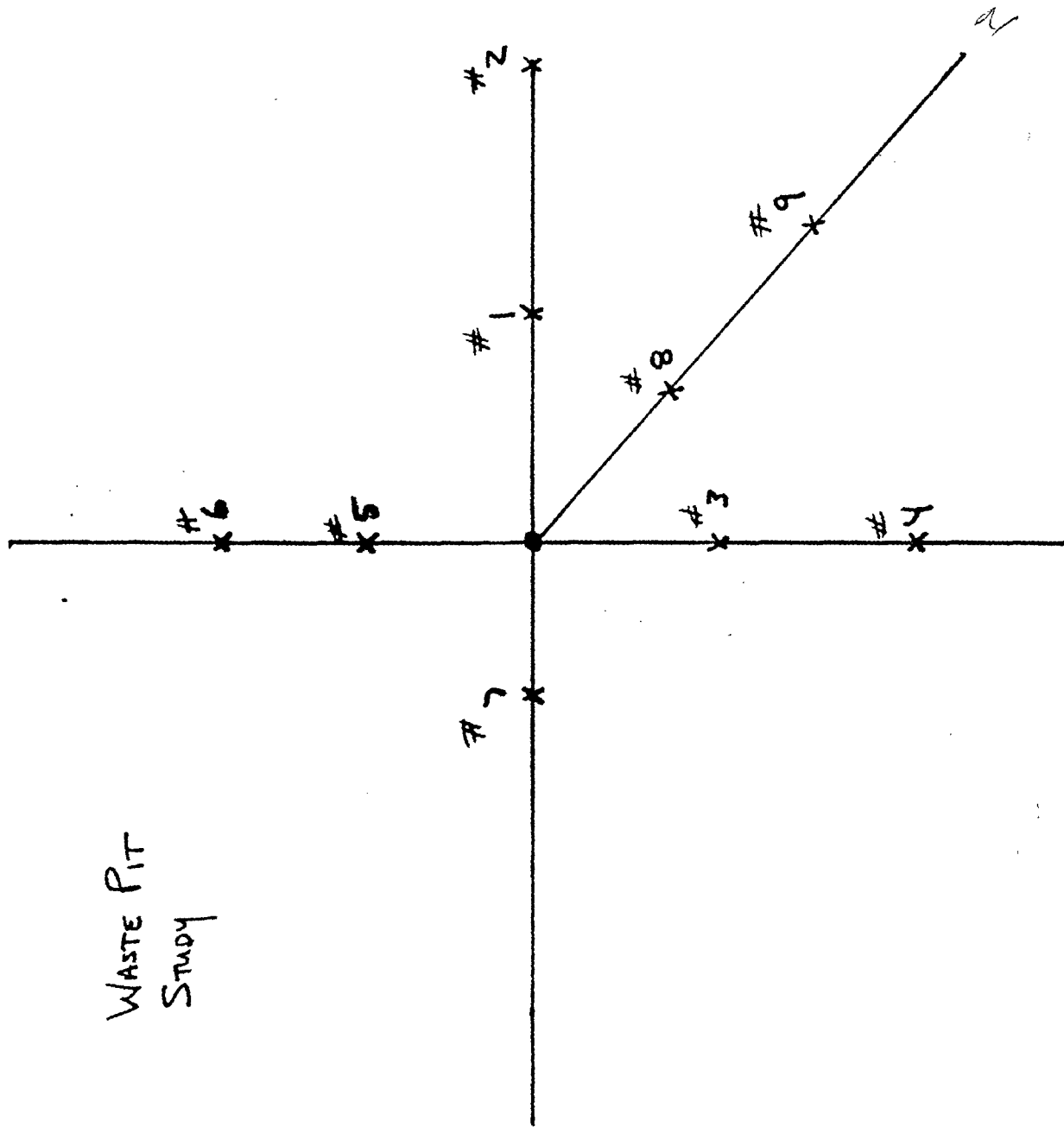
** Including benzanthrane

15

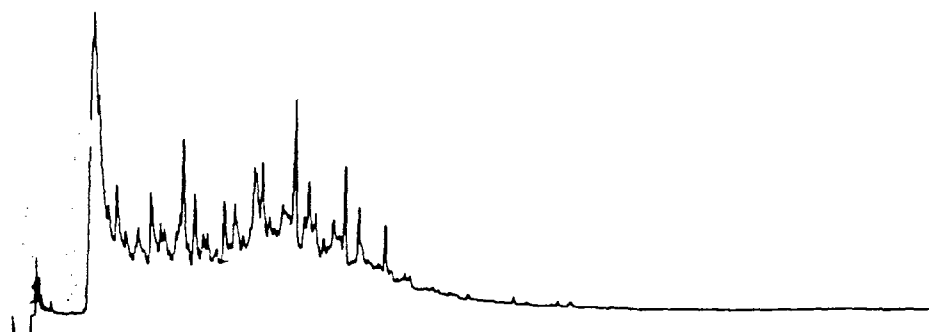
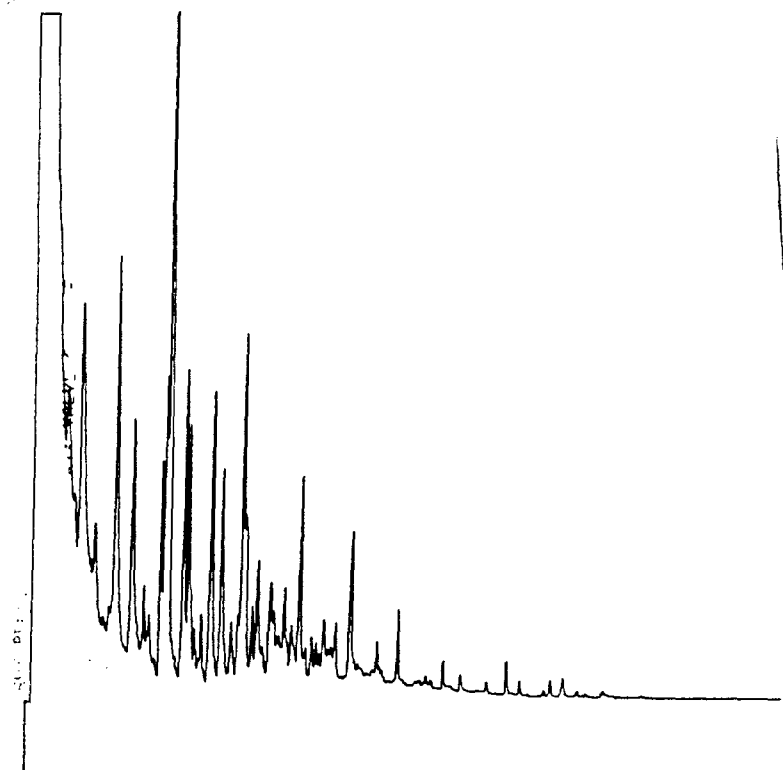
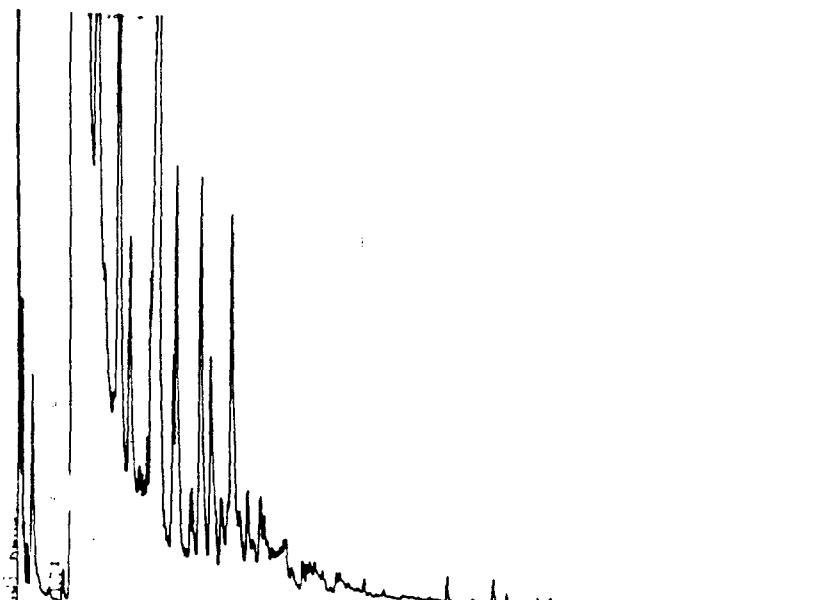


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WASTE PIT Study



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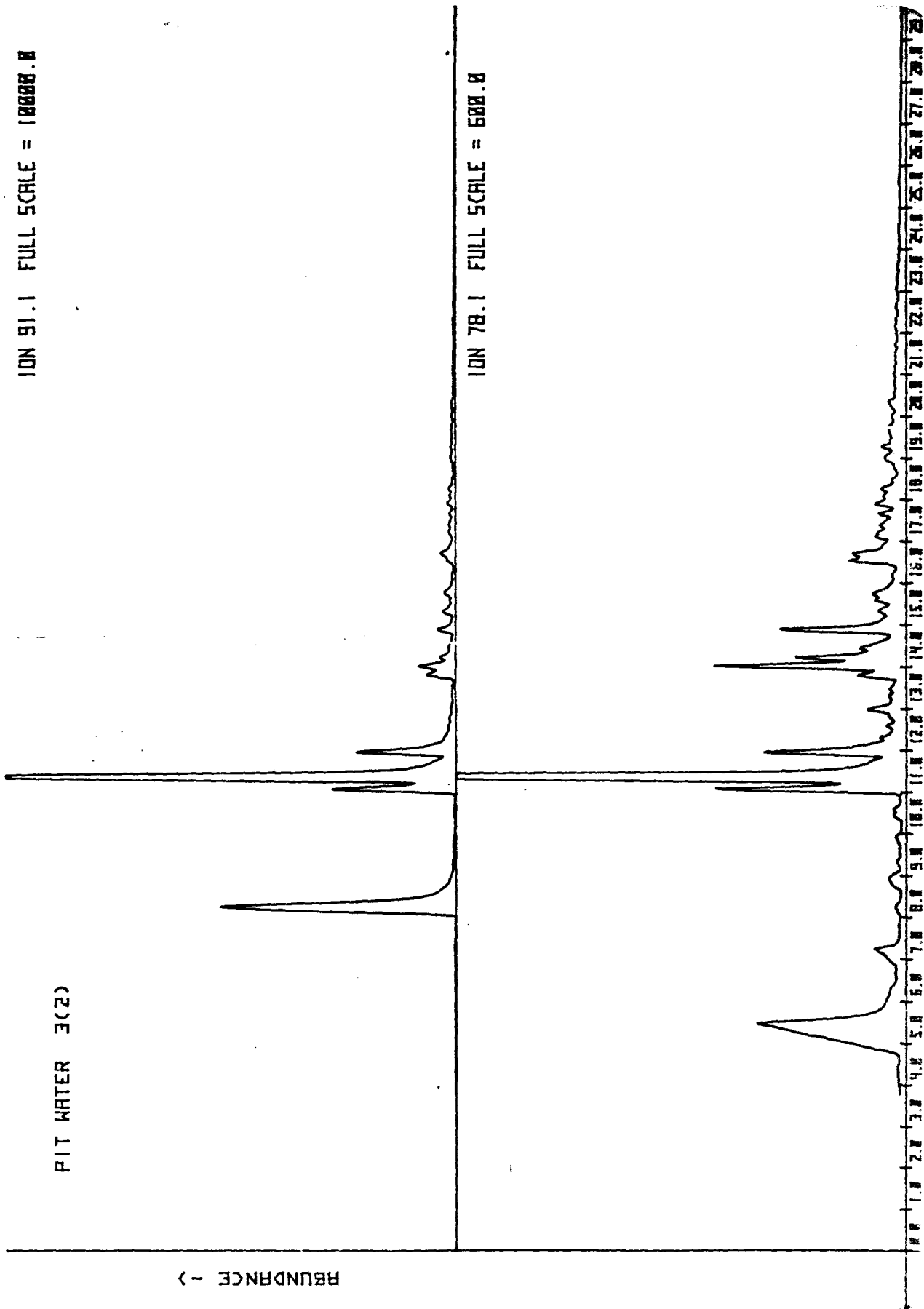
18

ION 91.1 FULL SCALE = 10000.0

PIT WATER 3(2)

ABUNDANCE ->

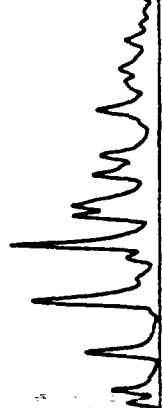
ION 78.1 FULL SCALE = 6000.0



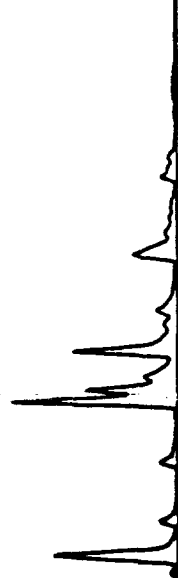
ION 134.1 FULL SCALE = 425.6



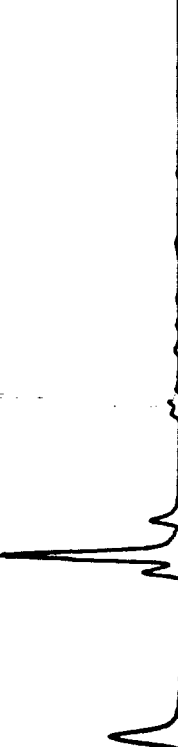
ION 119.1 FULL SCALE = 1072.1



ION 105.1 FULL SCALE = 4624.6



ION 91.1 FULL SCALE = 15072.6



ION 78.1 FULL SCALE = 1301.1



ION 57.0 FULL SCALE = 17176.7

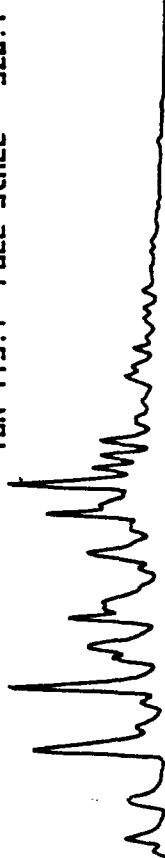


0.0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0 18.0 19.0 20.0 21.0 22.0 23.0 24.0 25.0 26.0 27.0 28.0 29.0
MINUTES ->

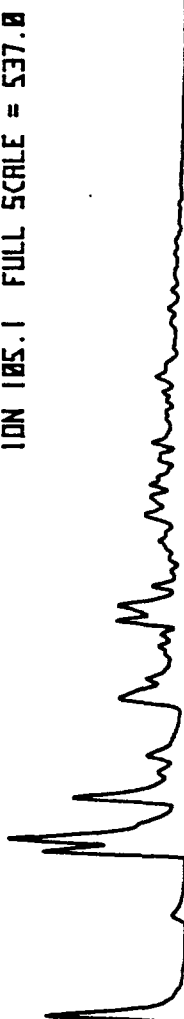
ION 134.1 FULL SCALE = 150.5



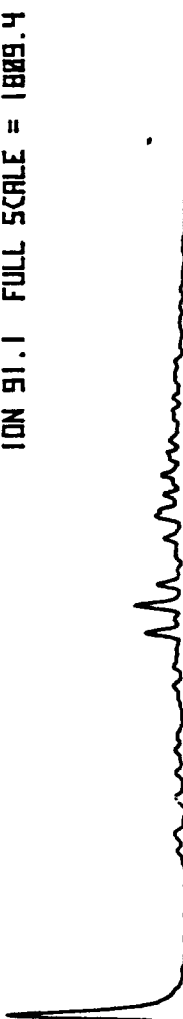
ION 119.1 FULL SCALE = 320.1



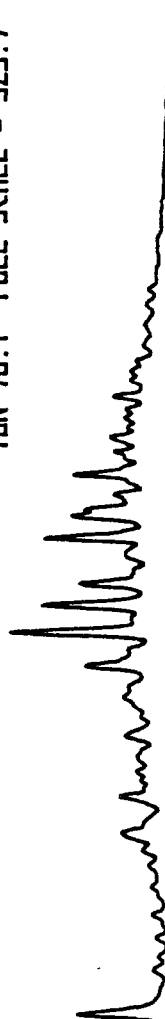
ION 105.1 FULL SCALE = 537.0



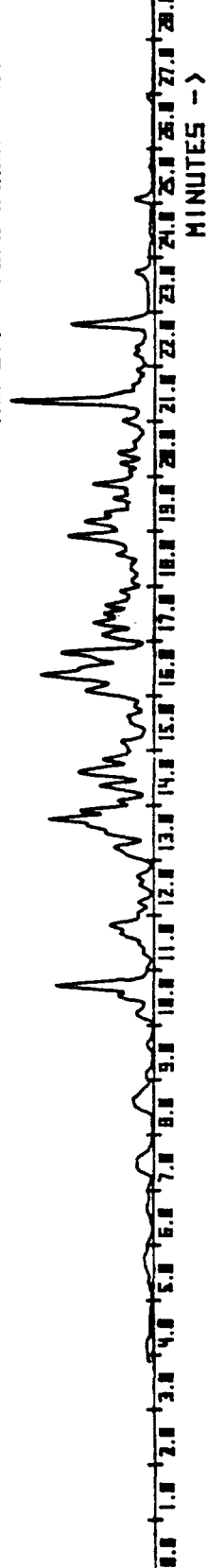
ION 91.1 FULL SCALE = 1809.4



ION 78.1 FULL SCALE = 329.7

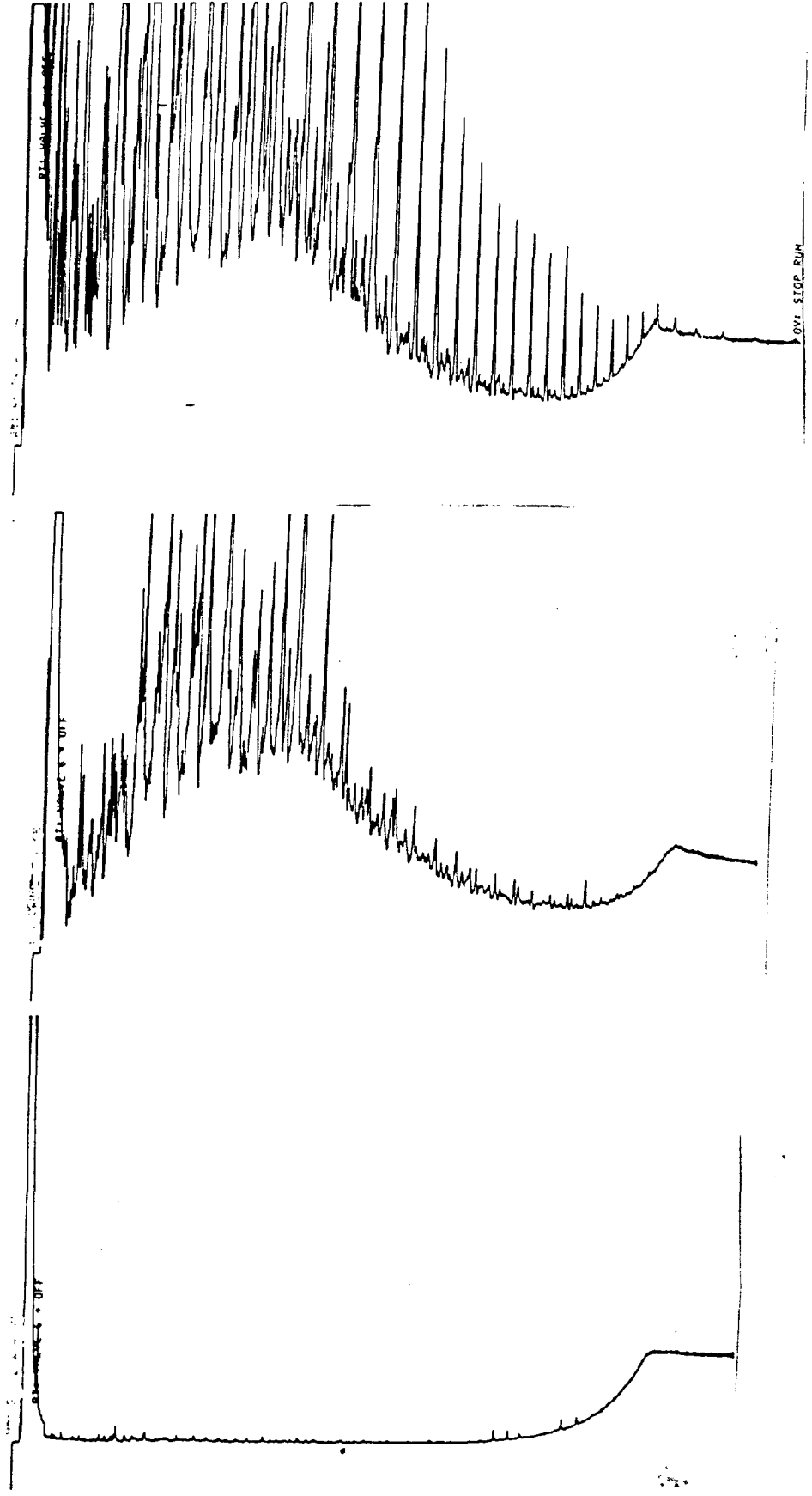


ION 57.0 FULL SCALE = 8230.3



MINUTES -->

ABUNDANCE -->



RAW DATA (MEASUREMENTS) FOR PIT STUDY

	ϕ	ϕCH_3	$\phi (\text{CH}_3)_2$	$\phi (\text{CH}_3)_3$	$\phi (\text{CH}_3)_4$
Pit 1	9.5	12	58 58 ₍₁₀₅₎	1149 15 ₍₁₀₅₎	158 412 ₍₁₁₉₎
2	5.1	3	198 ₍₁₀₅₎	1644 ₍₁₀₅₎	559 ₍₁₁₉₎
3	-	-	114 ₍₁₀₅₎	1083 ₍₁₀₅₎	310 ₍₁₁₉₎
4	-	-	11 ₍₁₀₅₎	36 ₍₁₀₅₎	-
5	ND	ND	ND	ND	ND
6	4	ND	ND	ND	ND
7	4	ND	ND	ND	ND
8	15	10	377 ₍₁₀₅₎	994 ₍₁₀₅₎	296 ₍₁₁₉₎
9	ND	ND	32 ₍₁₀₅₎	96 ₍₁₀₅₎	40 ₍₁₁₉₎
0.7ppb	28				
7ppb	91				
70ppb	549				
Blank					
Pit H ₂ O	190	5244	3254	397	236
Prod H ₂ O	1256	29,670	87,745	2005	1079
$\frac{\text{Ph} \times \text{FSV}}{\text{MAX Scales}} = \text{No.}$					