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ORGANIC CHARACTERIZATION OF AEROSOLS AND VAPOR
PHASE COMPOUNDS IN URBAN ATMOSPHERES

by

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ABSTRACT

Organic pollutants in urban atmospheres were characterized by analyzing particulate and/or vapor-phase samples collected by EPA in St. Louis, Missouri; Miami, Florida; Denver, Colorado; Houston, Texas; and at the General Motors Test Track in Milford, Michigan. The particulate samples were extracted with solvents and the extractable materials analyzed by elemental combustion analysis and infrared spectroscopic analysis. To evaluate more than one solvent extraction technique, the particulate samples were aliquoted and analyzed by several extraction procedures. Some of the problems encountered with these procedures are discussed. Vapor-phase samples were collected on Chromosorb 102 chromatographic traps and analyzed using qualitative gas chromatography-mass spectrometry analysis. Individual species tentatively identified are shown on reconstructed gas chromatograms and individual mass spectra for all chromatographic peaks are included in the appendix.

Ames Tests for mutagenicity on model aerosol products were also conducted. Products tested were from toluene/ NO_x , 1-heptene/ NO_x , and α -pinene/ NO_x systems. None of the aerosol products from these systems showed mutagenic properties.

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SECTION 1

INTRODUCTION

Urban particulate and vapor-phase samples were collected by EPA during a series of sampling and monitoring programs, and given to Battelle-Columbus Laboratories for analysis. The Particulate and vapor-phase samples, collected in certain urban atmospheres, were analyzed by solvent extraction followed by elemental combustion analysis and infrared spectroscopic analysis. The vapor-phase samples, collected from the ambient atmosphere over St. Louis and in Milford, Michigan, adjacent to the General Motors (GM) test track were analyzed by electron impact (EI) and methane chemical ionization (CI) gas chromatography-mass spectrometry (GC-MS).

In addition to ambient sample analyses, several model aerosol samples were investigated for mutagenic properties. The results of the AMES mutagenicity tests on model aerosols derived from toluene, α -pinene, and 1-heptene are presented.

SECTION 2

METHODS AND PROCEDURES

SOLVENT EXTRACTION OF PARTICULATE MATTER

Urban particulate and vapor-phase samples were collected by EPA during a series of sampling and monitoring programs, and submitted to Battelle-Columbus Laboratories for analysis. Sample sites and collection dates are shown in Table 1. The samples have been numbered to permit convenient reference in the discussion to follow. Samples 1 through 6 represent particles less than 1.1 μm ; and were collected on treated quartz filters, preceded by an Andersen-2000 High Volume Sampling Head. The particulate and vapor-phase samples were analyzed by solvent extraction followed by elemental combustion analysis and infrared spectroscopic analysis. The procedures of analysis and results of the analysis are discussed in the following sections.

In this project, the filters used in the sampling were extracted with a solvent to remove the organic particulate for analysis. Solvent extraction of particulate matter was directed toward both the acquisition of data and the evaluation of various extraction techniques and solvents. The most frequently used technique was Soxhlet extraction. During this program, as well as during the study "Haze Formation-Its Nature and Origin" (1), methylene chloride was generally used in place of benzene. Methylene chloride (b.p. 40°C) is considerably more volatile than benzene (b.p. 80°C) and hence can be removed with less risk of losing volatile sample compounds. Particularly in cases where detailed analysis of extractable matter is to be conducted, maintenance of sample integrity has dictated the use of the more volatile solvent. Nevertheless, in view of the previous widespread use of benzene as an extraction solvent, we undertook a comparison of the two solvents by dually extracting samples 13, 14, 15, and 16. The 8-inch x 10-inch filters were divided in half. One half was extracted first with benzene and then with diethyl ether. The second half was extracted first with methylene chloride and then with diethyl ether. Data for weight-percent solvent extractable are shown in Table 2. For three of the four samples comparability between benzene and methylene chloride extractions is extremely close.

Diethyl ether was also used as a solvent so that it could be evaluated for extraction of the relatively polar organic constituents of particulate matter. Methanol has been used for this purpose, but is less than ideal in that inorganic salts may be additionally extracted. Higher alcohols are insufficiently volatile to permit their facile removal. During the haze formation study (1) dioxane was evaluated for use as a polar solvent, and proved unsatisfactory because of a high and variable solvent blank (residue). This was observed even with re-distilled solvent, and was attributed to the

TABLE 1. URBAN ATMOSPHERE SAMPLES

Sample No.	Site	Date	Type
1	St. Louis, Missouri, Site BH (Q-049)	July 25, 1975	Particulate
2	St. Louis, Missouri, Site MC (Q-050)	July 25, 1975	Particulate
3	St. Louis, Missouri, Site BH (Q-044)	July 23, 1975	Particulate
4	St. Louis, Missouri, Site MC (Q-046)	July 23, 1975	Particulate
5	Miami, Florida, Site #10 (Q-009)	June 11, 1975	Particulate
6	Miami, Florida, Site #10 (Q-003)	July 4, 1975	Particulate
7	St. Louis, Missouri	March 2, 1974	Particulate
8	St. Louis, Missouri	February 26, 1974	Particulate
9	St. Louis, Missouri	October 4, 1973	Particulate
10	St. Louis, Missouri	October 3, 1973	Particulate
11	Denver, Colorado	November, 1973	Particulate
13	St. Louis, Missouri	March 2, 1974	Particulate
14	St. Louis, Missouri	February 26, 1974	Particulate
15	St. Louis, Missouri	October 4, 1973	Particulate
16	St. Louis, Missouri	October 3, 1973	Particulate
HN1	Houston, Texas	July 23-24, 1974	Vapor-phase
HN2	Houston, Texas	July 24, 1974	Vapor-phase
HN3	Houston, Texas	July 24-25, 1974	Vapor-phase
HN4	Houston, Texas	July 25-26, 1974	Vapor-phase
S1	St. Louis, Missouri	July 30, 1975	Vapor-phase
S2	St. Louis, Missouri	August 5, 1975	Vapor-phase
S3	St. Louis, Missouri	August 5, 1975	Vapor-phase
S4	St. Louis, Missouri	August 5, 1975	Vapor-phase
S5	St. Louis, Missouri	July 28, 1975	Vapor-phase
S6	St. Louis, Missouri	July 30, 1975	Vapor-phase
S7	St. Louis, Missouri	July 28, 1975	Vapor-phase
S8	St. Louis, Missouri	August 8, 1975	Vapor-phase
S9	St. Louis, Missouri	August 8, 1975	Vapor-phase
S10	St. Louis, Missouri	October, 1975	Vapor-phase
M1	Milford, Michigan	October, 1975	Vapor-phase
M2	Milford, Michigan	October, 1975	Vapor-phase
M3	Milford, Michigan	October, 1975	Vapor-phase

TABLE 2. SOXHLET EXTRACTION OF ATMOSPHERIC PARTICULATE MATTER

Sample	Site	Date	Weight-Percent Solvent Extractable(a)			
			First Extraction, Methylene Chloride	Second Extraction, Diethyl Ether	First Extraction, Benzene	Second Extraction, Diethyl Ether
16	St. Louis	October 3, 1973	26.1	4.9	25.6	5.6
15	St. Louis	October 4, 1973	37.9	2.4	46.3	2.4
14	St. Louis	February 26, 1974	5.5	0.4	5.5	1.5
13	St. Louis	March 2, 1974	3.1	0.2	3.2	0.6

(a) Corrected for blank.

formation of peroxides. In view of various disadvantages associated with the use of other solvents, the use of diethyl ether was evaluated. The data indicates that only a small additional increment of material is obtained during the second extraction with diethyl ether. These data may be compared with data from the haze formation study (1) in which extraction was conducted first with methylene chloride and then with dioxane. For seven urban particulate samples from New York City, Columbus, Ohio, and Pomona, California, the data averaged 13 weight-percent methylene chloride extractable and 19 weight-percent dioxane extractable. The data suggest that diethyl ether is not suitable for extraction of the desired polar organics.

More fundamental than selection of extraction solvents is the question of suitability of Soxhlet extraction for obtaining the organic constituents of particulate matter. The technique has been criticized as leading to incomplete extraction, irregular data, and the decomposition of some sensitive organics (i.e. polynuclear aromatic hydrocarbons) during extended periods of solvent refluxing.

In an alternative procedure devised by Sawicki and Golden (2), particulate organics are extracted by ultrasonic agitation with solvent using a horn-type sonicator. The authors describe the procedure as leading to fine shielding of filter material and breakdown of cohesive clumps of particulate matter, with improved overall extraction efficiency. Moreover, the method is conducted entirely at room temperature or below. In the published procedure 16 cm² portions of filter material are extracted with 60 ml of solvent. However, an 8-inch x 10-inch filter has an area of 645 cm². Private communication with Dr. Sawicki revealed that scale up of the procedure has not proven feasible. Dr. Sawicki described an alternative approach under investigation in his laboratory in which a high-frequency mechanical disruption apparatus is substituted for a horn-type sonicator. Such devices (3) combine high-frequency cavitation with efficient mechanical disruption. In order to evaluate and gain experience with this technique, we have utilized it in place of Soxhlet extraction for samples 1 through 6. The instrument used in Dr. Sawicki's laboratory is the Polytron-45 (Brinkman Industries). The instrument used at Battelle was the closely comparable Super Dispax-45 (Tekmar Company, Cincinnati, Ohio).

For the mechanical extraction procedure, the 8-inch x 10-inch filters were divided in half. One half was extracted first with benzene, and then with methanol. The second half was extracted with distilled water only. The volumes required for the mechanical extraction procedure were relatively large compared with those employed during Soxhlet extraction. Even after filtration and centrifugation, the mechanical extracts contained quantities of apparently colloidal material. Concentration of the extracts led to agglomeration of most of the remaining colloidal material in a form that could be filtered or removed after centrifugation.

Data for weight-percent solvent extractable are shown in Table 3. Despite significantly lower mass-loading, the Miami samples average approximately 19-percent greater content of benzene extractable matter than the St. Louis samples. Among the St. Louis samples, those collected

TABLE 3. HIGH-FREQUENCY DISPERSIVE EXTRACTION OF ATMOSPHERIC PARTICULATE MATTER(a)

Sample	Site	Date	Weight-Percent Solvent Extractable			
			First Extraction, Benzene(b)	Second Extraction, Methanol(c)	Filter Loading	Water Extraction(c) (only)
Q003	Miami, Site #10	6/4/75	16.55	15.94%	20.1 mg	9.7 mg x 2 = 19.4 mg
Q009	Miami, Site #10	6/11/75	14.63	6.36%	21.3 mg	6.9 mg x 2 = 13.8 mg
Q044	St. Louis, Site BH	7/23/75	13.62	26.32	34 mg	14.4 mg x 2 = 28.8 mg
Q046	St. Louis, Site MC	7/23/75	10.15	28.42	34 mg	17.1 mg x 2 = 34.2 mg
Q049	St. Louis, Site BH	7/25/75	15.32	34.04	40 mg	14.2 mg x 2 = 28.4 mg
Q050	St. Louis, Site MC	7/25/75	13.05	36.90	30 mg	24.2 mg x 2 = 48.4 mg
Blank	--	--	--	--	--	14.2 mg x 2 = 28.4 mg

(a) For the above described extractions, the filter was divided in half. One half was used for benzene and methanol extractions, the second half was used for water extraction.

(b) Blank subtracted.

(c) Blank not subtracted.

at the industrial BH site show significantly higher content of benzene extractable matter. Finally, the blank value for benzene extractable matter obtained using the mechanical disruption technique is approximately 100-fold greater than the corresponding value obtained when pre-extracted quartz filter material is subjected to Soxhlet extraction.

ELEMENTAL ANALYSIS OF EXTRACTABLE PARTICULATE MATTER

Benzene and methanol extractable matter were subjected to elemental combustion analysis for carbon, hydrogen, and nitrogen. Values shown for weight-percent oxygen were calculated by difference from the CHN (carbon, hydrogen, and nitrogen) data. Water extracts were analyzed for total organic carbon and for nitrate, sulfate, and ammonium. The data are shown in Tables 4 and 5.

The analysis in these tables show several irregularities that are probably due to systematic errors resulting from the small sample sizes. Three of the hydrogen percentages in Table 5, for instance, are over 100 percent, probably because of water absorbed onto the filter. The carbon analyses in Table 4 from the water extracts show an exceptionally wide variation, again leading one to suspect analytical problems.

INFRARED ANALYSIS OF PARTICULATE MATTER

Infrared spectra were obtained on the benzene extractables of three samples: two collected in St. Louis, Missouri (Q049 and Q050) and one collected in Miami, Florida (Q003). These samples were chosen because they represent an industrial and a metropolitan site in St. Louis, and for comparison, the entirely different Miami site.

Sample Q003 contained large amounts of a phthalate ester (assumed to be introduced in handling) which effectively prevented the measurement of the absorption bands of interest (carbonyl peak at 1710 cm^{-1} , percarbonyl peak at 1770 cm^{-1} , and the organic nitrate peak at 1630 cm^{-1}). Therefore, no data are presented for this sample.

Sample Q049 contained large amounts of a silicon grease (again assumed to be introduced in handling), but the absorption bands of the silicon grease do not obscure the sample absorption bands of interest. Table 6 lists the relative intensities for the carbonyl peak, the percarbonyl band, and the organic nitrate absorption of Q049 and Q050. Relative intensity is defined as:

$$\text{R.I.} = \frac{\text{O.D. at specified frequency}}{\text{O.D. at } 2920\text{ cm}^{-1}}$$

where O.D. = optical density or peak absorption.

The infrared spectra of the benzene extractables are much like the spectra of the methylene chloride extractables presented in the report "Haze Formation-Its Nature and Origin" (1). The haze formation report also explains the nature of the absorption bands observed.

TABLE 4. WEIGHT PERCENT CARBON, HYDROGEN, NITROGEN, AND OXYGEN IN EXTRACTABLE MATTER OBTAINED BY HIGH-FREQUENCY MECHANICAL DISPERSION WITH SOLVENT

Sample	Site	Date	Benzene				Methanol				Water	
			Extractable Matter				Extractable Matter				Extractable Matter	
			weight percent				weight percent				weight percent	
			C	H	N	[O]	C	H	N	[O]	C (total organic carbon)	
Q003	Miami #10	6/4/75	77.8	11.1	0.7	10.4	31.3	4.4	2.0	62.3		1.2
Q009	Miami #10	6/11/75	78.7	11.3	0.5	9.5	23.9	0	1.9	71.2		0.7
Q044	St. Louis BH	7/23/75	75.7	10.8	0.8	12.7	18.1	4.7	8.5	68.7		3.0
Q046	St. Louis MC	7/23/75	76.0	10.8	0.8	12.4	15.4	4.8	10.0	69.8		3.1
Q049	St. Louis BH	7/25/75	72.9	10.6	1.0	15.5	23.1	5.2	9.0	62.7		73.3
Q050	St. Louis MC	7/25/75	74.6	10.3	0.4	14.7	19.2	4.8	9.2	66.8		51.19

TABLE 5. CONSTITUENTS OF ATMOSPHERIC PARTICULATE, EXPRESSED
AS WEIGHT-PERCENT OF TOTAL PARTICULATE

Sample	Site	Date	Weight Percent					
			Carbon(a)	Hydrogen(a)	Nitrogen(a)	Nitrate(b)	Sulfate(b)	Ammonium(b)
Q003	Miami, Site #10	6/4/75	37.9	114.1	11.0	0.50	9.95	<0.001
Q009	Miami, Site #10	6/11/75	29.1	102.4	6.7	0.11	4.54	<0.001
Q044	St. Louis, Site BH	7/23/75	54.1	106.5	19.1	0.95	25.88	4.12
Q046	St. Louis, Site MC	7/23/75	32.3	70.0	13.2	0.02	25.00	4.17
Q049	St. Louis, Site BH	7/25/75	41.5	59.1	14.6	0.75	28.3	4.98
Q050	St. Louis, Site MC	7/25/75	38.0	72.2	16.4	1.28	18.27	5.43

(a) From combustion analysis of particulate on quartz fiber filter, unextracted.

(b) From analysis of water extracts of collected particulate. Blank subtracted.

The infrared absorption data observed for the St. Louis samples (Q049 and Q050) are lower than most of the data given in the haze formation report (with the exception of the Denver, Colorado samples). This indicates smaller amounts of carbonyl, percarbonyl, and nitrate in the St. Louis sample. It is not known how benzene extractables compare to methylene chloride extractables except that the infrared spectra appear to be qualitatively similar.

TABLE 6. INFRARED SPECTROSCOPIC DATA ON BENZENE EXTRACTS OF ST. LOUIS PARTICULATE

Sample	Site	Carbonyl Band (1710 cm^{-1})	Percarbonyl Band (1780 cm^{-1})	Nitrate Band (1300 cm^{-1})
		Relative Intensity	Relative Intensity	Relative Intensity
Q049	St. Louis	0.26	0.04	0.03
Q050	Louis	0.25	0.02	0.03

SECTION 3

CHARACTERIZATION OF URBAN ATMOSPHERES

ANALYSIS OF AMBIENT HOUSTON ORGANIC VAPOR

Four ambient organic vapor samples were obtained from a sampling location on May Drive, Jacinto City, Houston, during July 1974. The samples were obtained sequentially using Chromosorb 102 chromatographic traps. The available details pertaining to these samples may be summarized as follows:

Sample Number	HN1	HN2	HN3	HN4
Starting date/hour	23/1700	24/0925	24/2050	25/1650
Ending date/hour	24/0900	24/2030	25/1636	26/1050
Sample Volume CF	480	300	600	540
Weather	Haze	Clear	Clear	Clear

Qualitative methane ionization GC-MS analysis was carried out in the manner described in the next section. No analytical data was obtained for Sample HN2; it appears that an unforeseen error occurred either during sampling or analysis of the corresponding chromatographic trap. Similarities are evident between all three samples which were successfully analyzed, although sample HN1 which was collected under hazy conditions shows a greater number of detectable organic species. While the nature of these survey analyses precludes accurate assessments of specie concentrations, it appears that the materials tentatively identified in Sample HN1 are at somewhat higher concentrations than Samples HN3 and HN4, despite the higher sample volumes of the latter two samples. Hydrocarbons appear to be particularly abundant in all three Houston samples; the oxygen-containing species present could presumably be formed by the combustion or photooxidation of hydrocarbons. The individual species tentatively identified in Samples HN1, HN3, and HN4 are shown on the reconstructed gas chromatograms, Figures 1, 2, and 3, respectively. The individual mass spectra for all chromatographic peaks in Sample HN1 (Figure 2) are included in Appendix G.

ANALYSIS OF AMBIENT ATMOSPHERE OVER GREATER ST. LOUIS

Airborne sample collection of ambient atmosphere over St. Louis was conducted using Chromosorb 102 chromatographic traps without the use of filters. Approximately 300 liters of gas per sample were collected over a period of about 20 minutes. Samples were collected on four different days at four different sites near St. Louis.

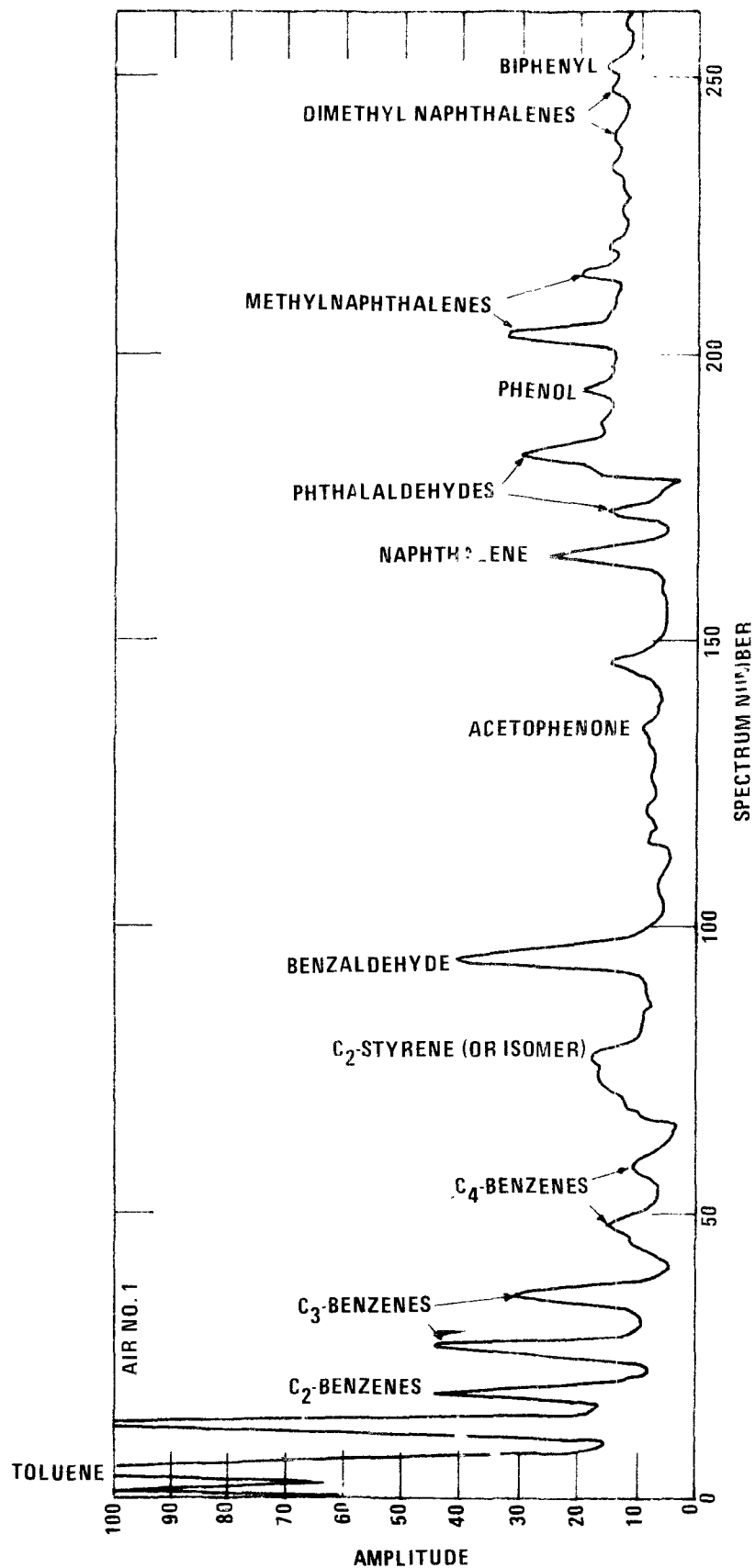


Figure 1. Methane ionization GC-MS analysis of ambient Houston organic vapors, sample HN1.

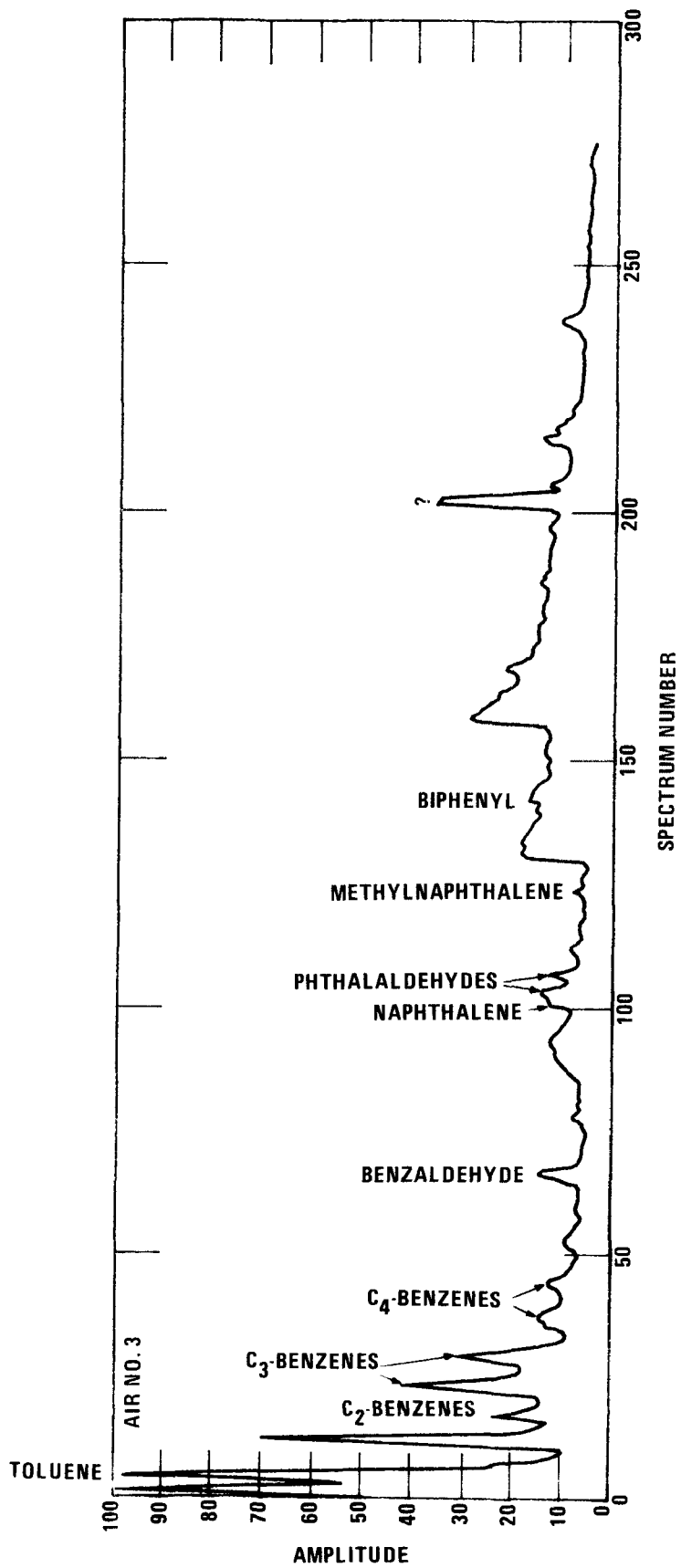


Figure 2. Methane ionization GC-MS analysis of ambient Houston organic vapors, sample HN3.

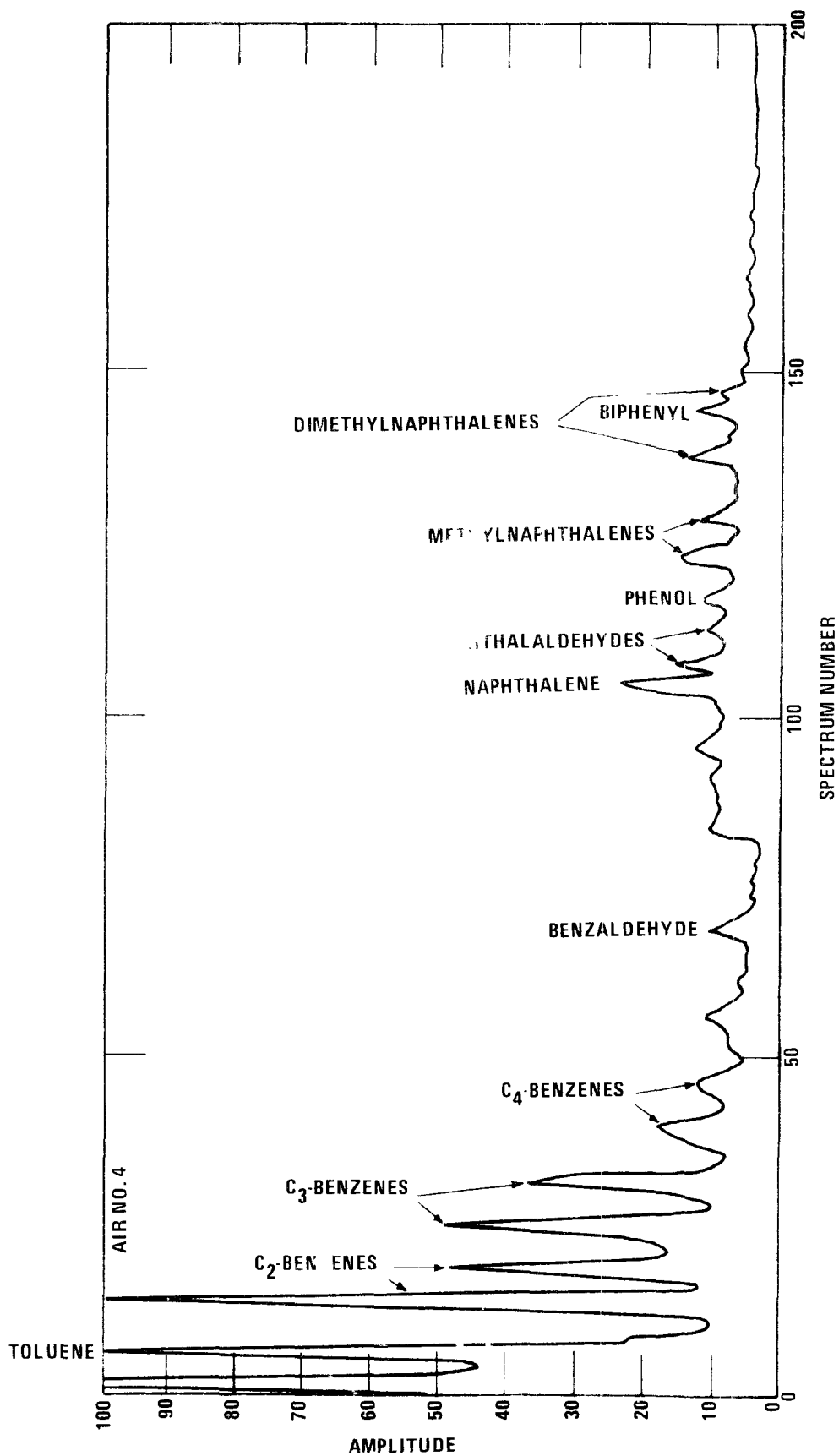


Figure 3. Methane ionization GC-MS analysis of ambient Houston organic vapors, sample HN4.

The collected samples were recovered by thermal desorption, followed by freeze-out and then thermal injection onto a gas chromatographic column similar to that described for analysis of model aerosols in Section 3. Gas chromatographic separation was achieved using a Silar 5CP chromatographic column. Gas chromatographic-mass spectrometry analysis was carried out by methane chemical ionization.

Wood River

Two samples, S7 and S5, were collected on July 28, 1975, 1/4 miles upwind and downwind of Wood River, respectively. Each sample was analyzed using GC-MS and the reconstructed gas chromatograms (RGC) are given in Figures 4 and 5. Gas chromatographic peaks with the corresponding molecular weights as determined from the mass spectra are indicated on the RGC; tentative identification for some of these various compounds are listed in Table 7. Compounds unique to each sample are indicated by a "U" on the RGC and their mass spectra are included in Appendix A, referenced by the spectrum number of the compound.

As indicated by Table 7, the only material that could be tentatively identified in Sample S5 which was not found in Sample S7 was biphenyl. Nevertheless, a compound having a molecular weight of 154 was indicated in Sample S7. However, its GC retention time does not correspond to that of biphenyl. It is interesting to note that both S5 and S7 contain a large number of unique materials with S5 having the larger number of the two. Since sampling site S5 is downwind from S7 this is not surprising and indicates a major source of pollution upwind of both of these sites.

Baldwin and Hardin

Sample S6 was collected 1 mile southeast of Baldwin on the morning of July 30, 1975 while Sample S1 was collected 1 mile east of Hardin on the afternoon of July 30, 1975. The RGCs of these two samples are given in Figures 6 and 7. Table 7 indicates the compounds which were tentatively identified in these samples and Appendix B includes the spectra found to be unique.

Sample S1 was chosen to illustrate the major types of materials collected in Samples S1 through S10. The mass spectra of these materials are presented in Appendix C.

St. Louis

Sample 3 was collected 22 miles upwind from the edge of St. Louis while Sample S4 was collected 20 miles downwind from the edge of St. Louis. Sample S2 was obtained through the Labadie Plume 5 miles downwind from the stack. Unfortunately, due to an error in our data acquisition system while analyzing Sample S2, all data from Sample S2 was lost, and because thermal desorption is a once-only technique, S2 could not be reanalyzed.

The RGCs for Samples S3 and S4 are given in Figures 8 and 9. These two samples are surprisingly similar with each sample containing only one

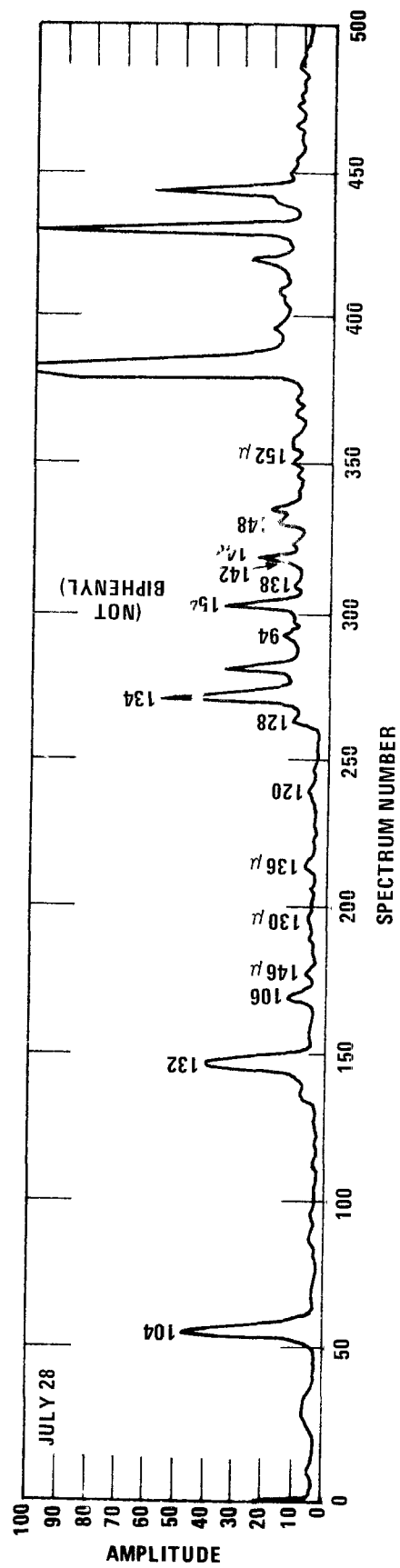


Figure 4. RGC of methane ionization GC-MS of St. Louis sample S7.

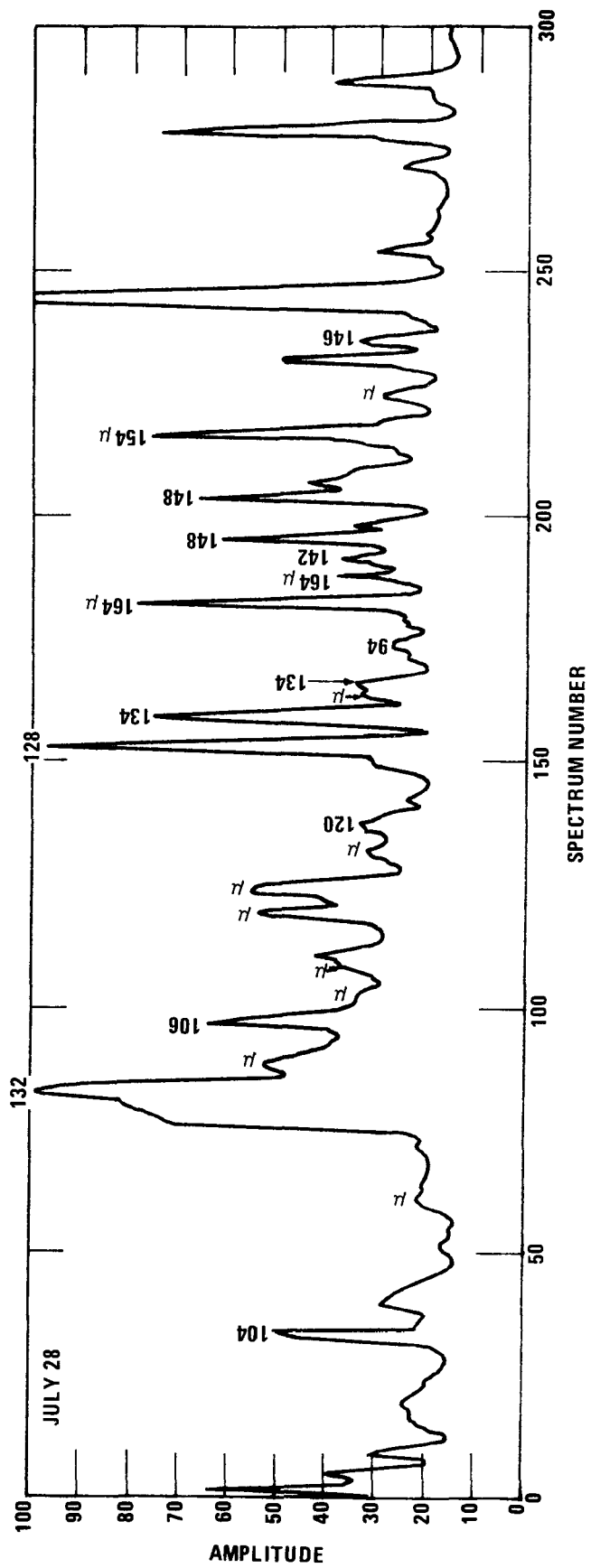


Figure 5. RGC of methane ionization GC-MS of St. Louis sample S5.

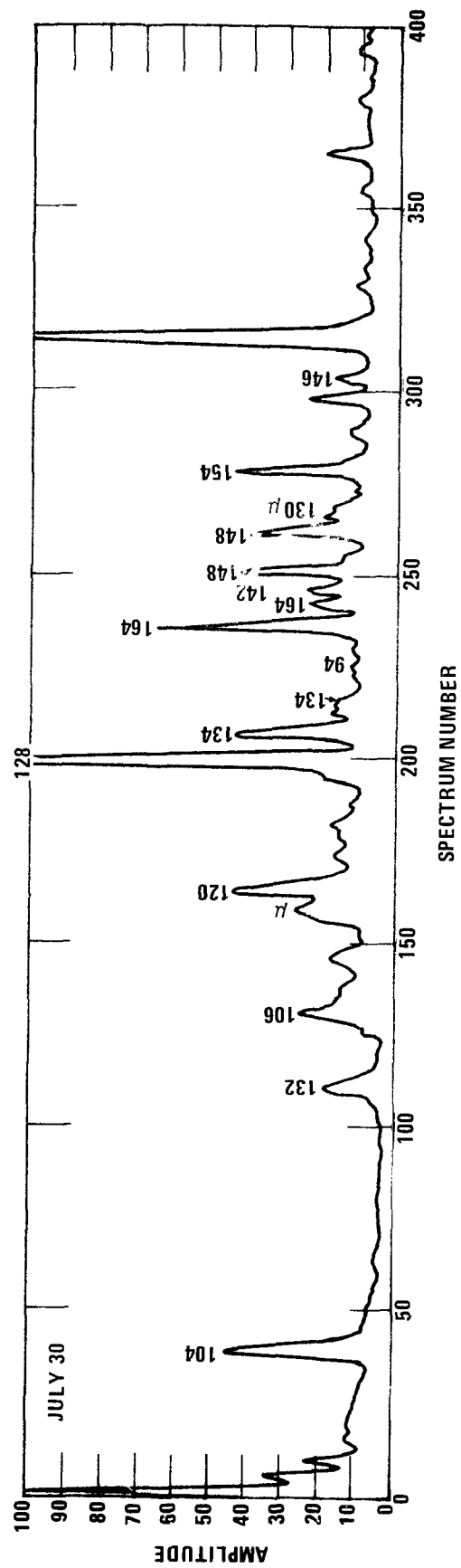


Figure 6. RGC of methane ionization GC-MS of St. Louis sample S6.

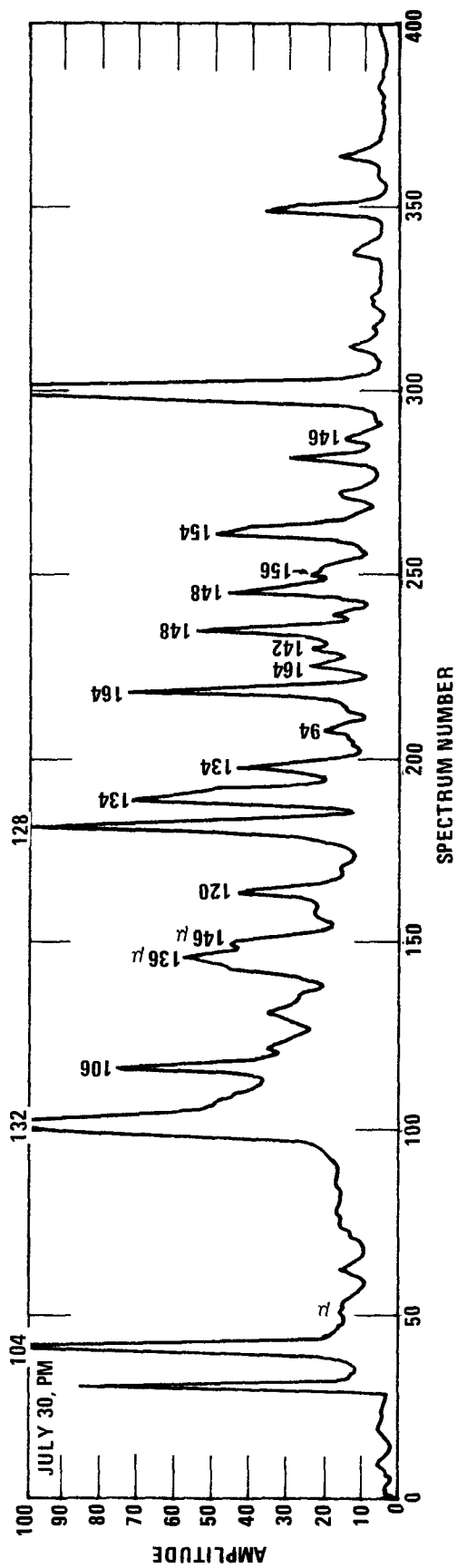


Figure 7. RGC of methane ionization GC-MS of St. Louis sample S1.

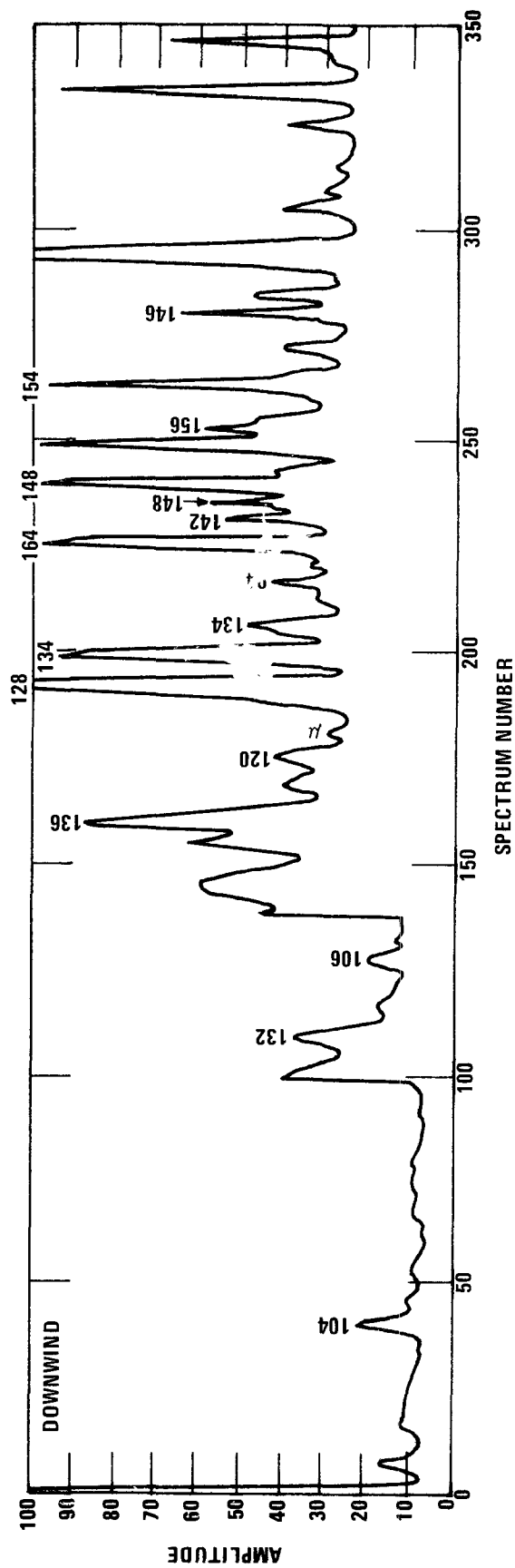


Figure 8. RGC of methane ionization GC/MS of St. Louis sample S3.

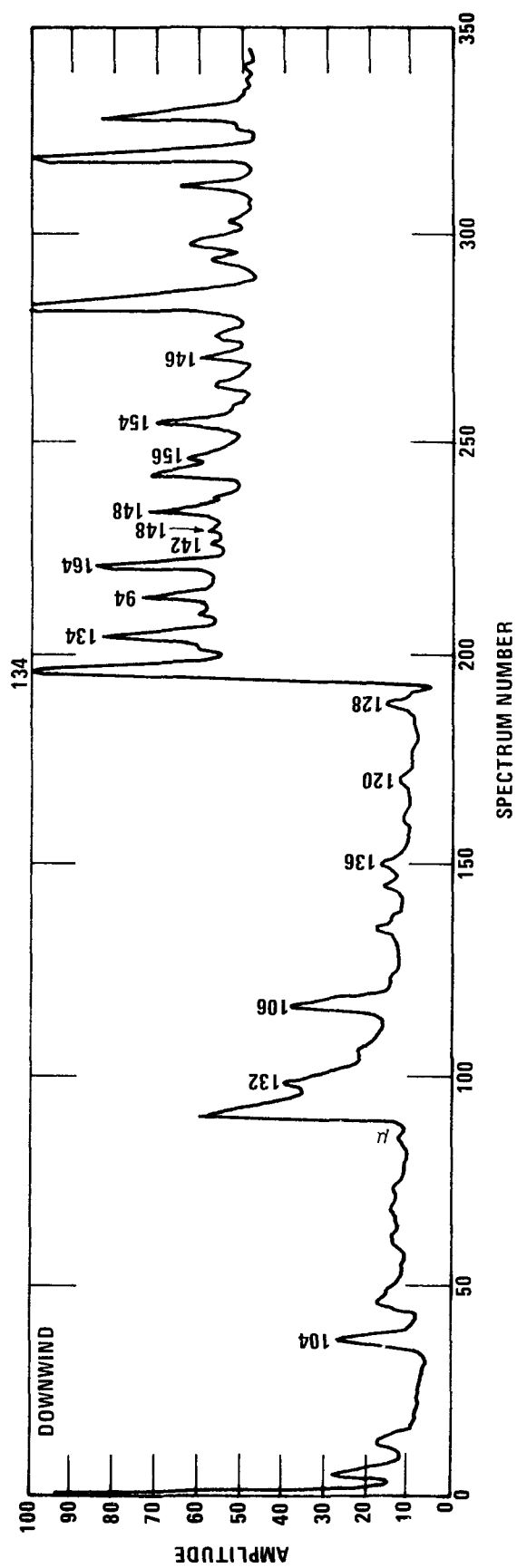


Figure 9 RGC of methane ionization GC-MS of St. Louis sample S4.

TABLE 7. COMPOUNDS TENTATIVELY IDENTIFIED FROM METHANE
IONIZATION GC-MS ANALYSIS OF AMBIENT ST. LOUIS
VAPOR SAMPLES

Compound	MW	S7	S5	S6	S1	S3	S4	S8	S9	S10
Styrene	104	X	X	X	X	X	X	X	X	X
Allylbenzaldehyde	132	X	X	X	X	X	X	X	X	X
Benzaldehyde	106	X	X	X	X	X	X	X	X	X
Phenylacetate	136				X	X	X	X	X	X
Acetophenone	120		X	X	X	X	X	X	X	X
Naphthalene	128	X	X	X	X	X	X	X	X	X
Terephthaldehyde	134	X	X	X	X	X	X	X	X	X
Phenol	94	X	X	X	X	X	X	X	X	X
Methylnaphthalene	142	X	X	X	X	X	X			
C5-benzene	148	X	X	X	X	X	X	X	X	X
C2-naphthalene	156				X	X	X			
Biphenyl	154		X	X	X	X	X	X	X	X

unique compound, neither of which could be identified. The mass spectra of these materials are included in Appendix D. It is also of interest to note the relatively large amount of naphthalene found upwind of St. Louis as compared to that found downwind. It appears that sampling site S3 is adjacent to a localized source for this material.

Baldwin Power Plant, Granite City

Sample S8 was collected over Granite City along Interstate 64, S9 was collected just south of Baldwin Power Plant, and S10 was collected on a 13-minute flight from Granite City to Smartt Field. The RGCs for these samples are given in Figures 10, 11, and 12, and Table 7 lists the tentatively identified compounds for these samples. Appendix E gives the mass spectra of compounds unique to each sample or common to only two samples. None of these unique materials have been identified except for MW 137, tentatively identified as phenyl acetate, which was absent in sample S10.

Summary

The qualitative survey analysis illustrated, not surprisingly, that a large number of organic vapor species are common to most of the sampling locations in St. Louis. However, it is possible to ascertain the presence of species unique to specific areas, and thus it may be possible to establish that a localized source for these specific compounds exists. A more detailed sampling survey of locations such as those examined in this study could facilitate both detection and location of the source of airborne organic pollutants.

ANALYSIS OF ORGANIC VAPORS ADJACENT TO THE GM TEST TRACK

During road tests of catalytic converter equipped motor vehicles at the Milford (Michigan) GM test track during October, 1975, a disagreeable odor was noted. The vehicles were being operated with fuel containing several organic sulfur compounds, and the preliminary reaction of EPA personnel present was that organo sulfur compounds could be responsible for the odor. Three samples of ambient organic vapors were subsequently collected adjacent to the GM test tract (M1, M2, M3) during the automobile test runs using Chromosorb 102 adsorbent traps (5). The collected vapor samples were thermally desorbed (5) and subjected to both EI and methane CI GC-MS.

It was not possible to determine why the relative concentrations of oxygenated species in the automobile exhaust were so abnormally high in this GM test track experiment on the basis of our analyses; it is however tempting to speculate that the catalytic converters fitted to the test vehicles were not operating efficiently. In our opinion, the high relative concentrations of oxygenated species, particularly benzaldehyde and phenol, could have been responsible for the unpleasant exhaust odor noted.

Following EI and CI GC-MS analyses, the individual components in the collected vapor samples were assigned structures on the basis of CI molecular weight determinations and fragmentation patterns and on the basis of EI

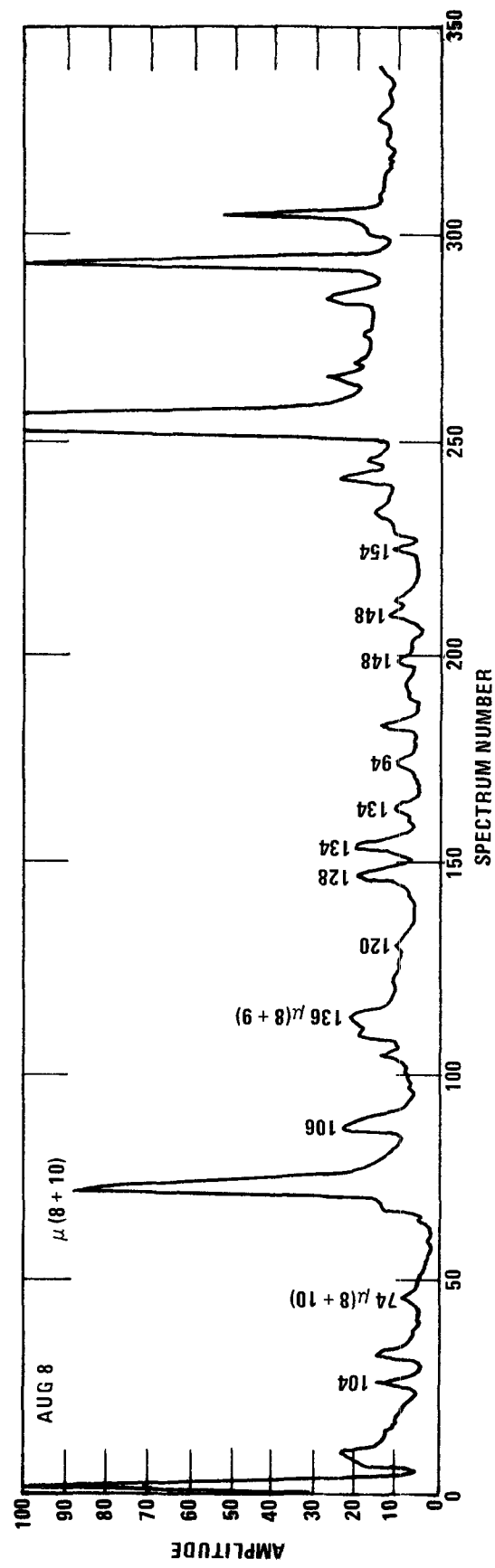


Figure 10. RGC methane ionization GC-MS of St. Louis sample S8.

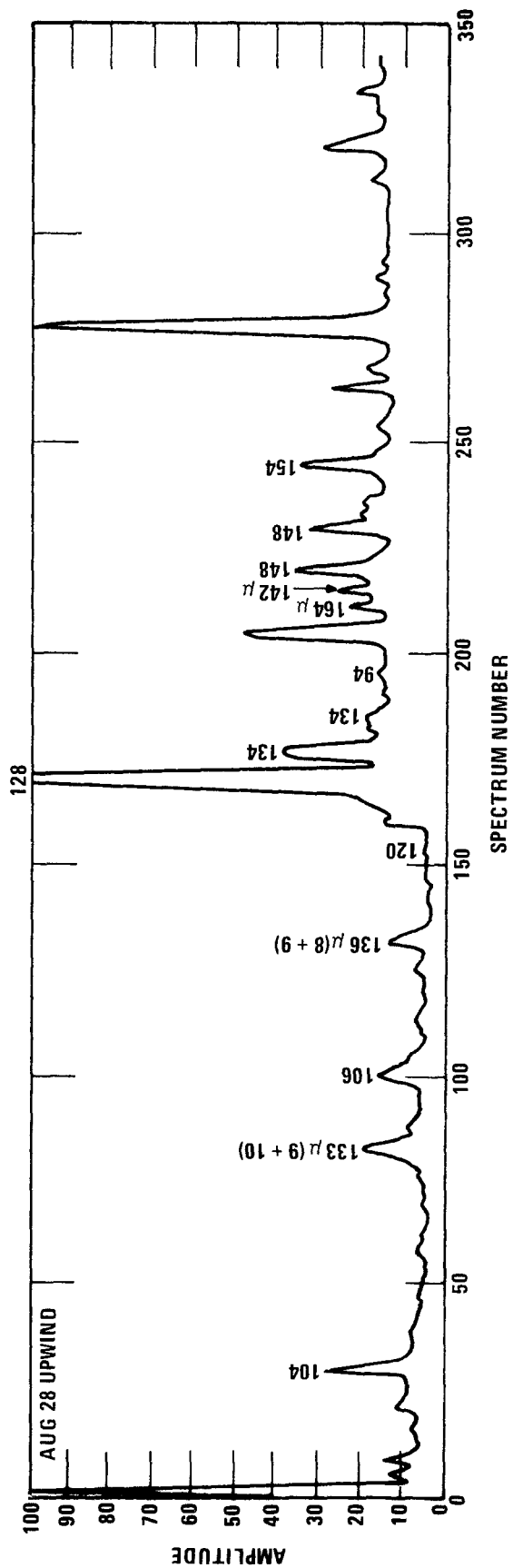


Figure 11. RGC methane ionization GC-MS of St. Louis sample S9.

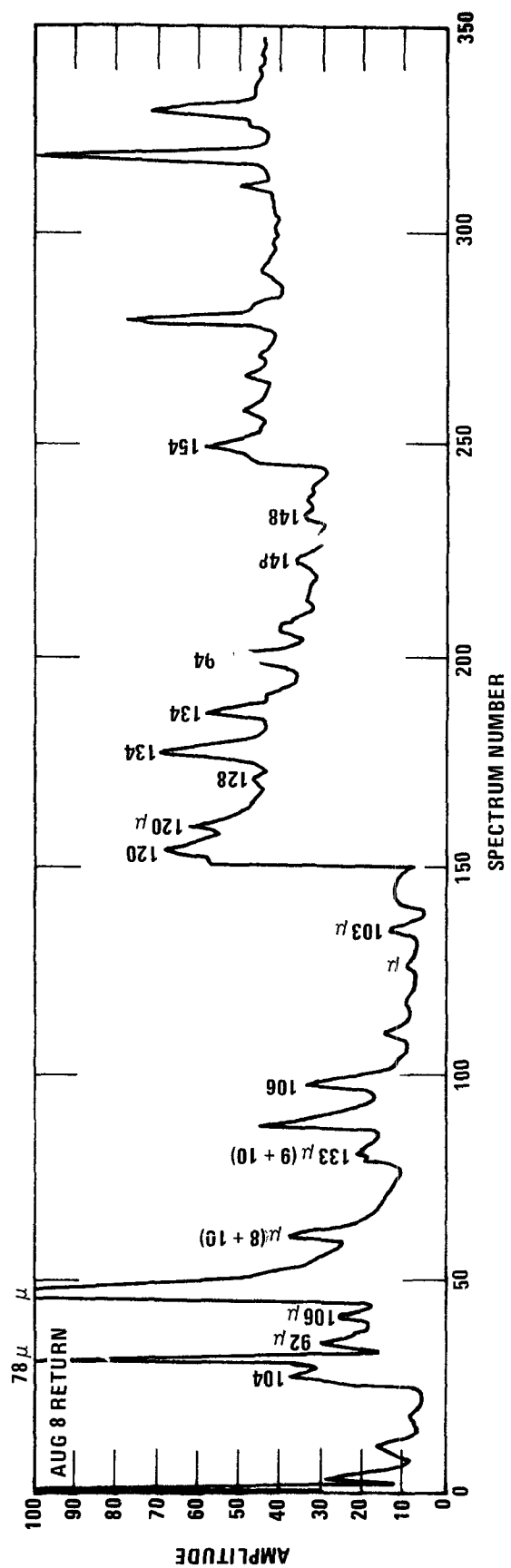


Figure 12. RGC of methane ionization GC-MS of St. Louis sample S10.

spectral matching with the Battelle data bank of approximately 27,000 reference spectra. Where several structural isomers were possible, no attempt was made to identify each isomer since this was believed to be beyond the scope of this experiment. Samples were analyzed by both CI and EI GC-MS; since all three samples were very similar, only data for M1 is shown on Figures 13 and 14.

The major ambient species determined in the above manner are shown on the EI and CI reconstructed gas chromatograms (Figures 13 and 14, respectively) and are listed below; the more abundant species are marked with an asterisk. Individual mass spectra for the CI GC-MS analysis are given in Appendix F.

*Xylenes	*Acetophenone
*C ₂ -Benzenes	*Naphthalene
*C ₄ -Benzenes	*Vinylbenzylalcohol (or isomer)
Methylstyrene (or isomer)	*C ₂ -Benzaldehyde
Allyltoluenes (or isomer)	*Phenol
*Benzaldehyde	C ₂ -Acetophenones
Tetralin	Di-t-butylbenzoquinone
*Methylbenzoate	*Dimethylphenol

No sulfur compounds were observed, although these species were specifically sought.

It is noteworthy that the estimated relative concentrations of oxygenated species appear to be abnormally high, particularly that of benzaldehyde, for example. The concentration of benzaldehyde in automobile exhaust is typically of the order of 0.5 percent of the concentration of the aromatic hydrocarbons (6,7). Within the constraints prevailing in this qualitative GC-MS analysis, it appears that the concentration of benzaldehyde may be approximately comparable with that of the total alkyl benzenes, and that the total of oxygenated species observed may in fact exceed the total concentration of alkyl benzenes. Thus, the ratio of benzaldehyde to alkyl benzenes, for instance, was found to be approximately 200 times greater than that observed in "normal" vehicle exhaust.

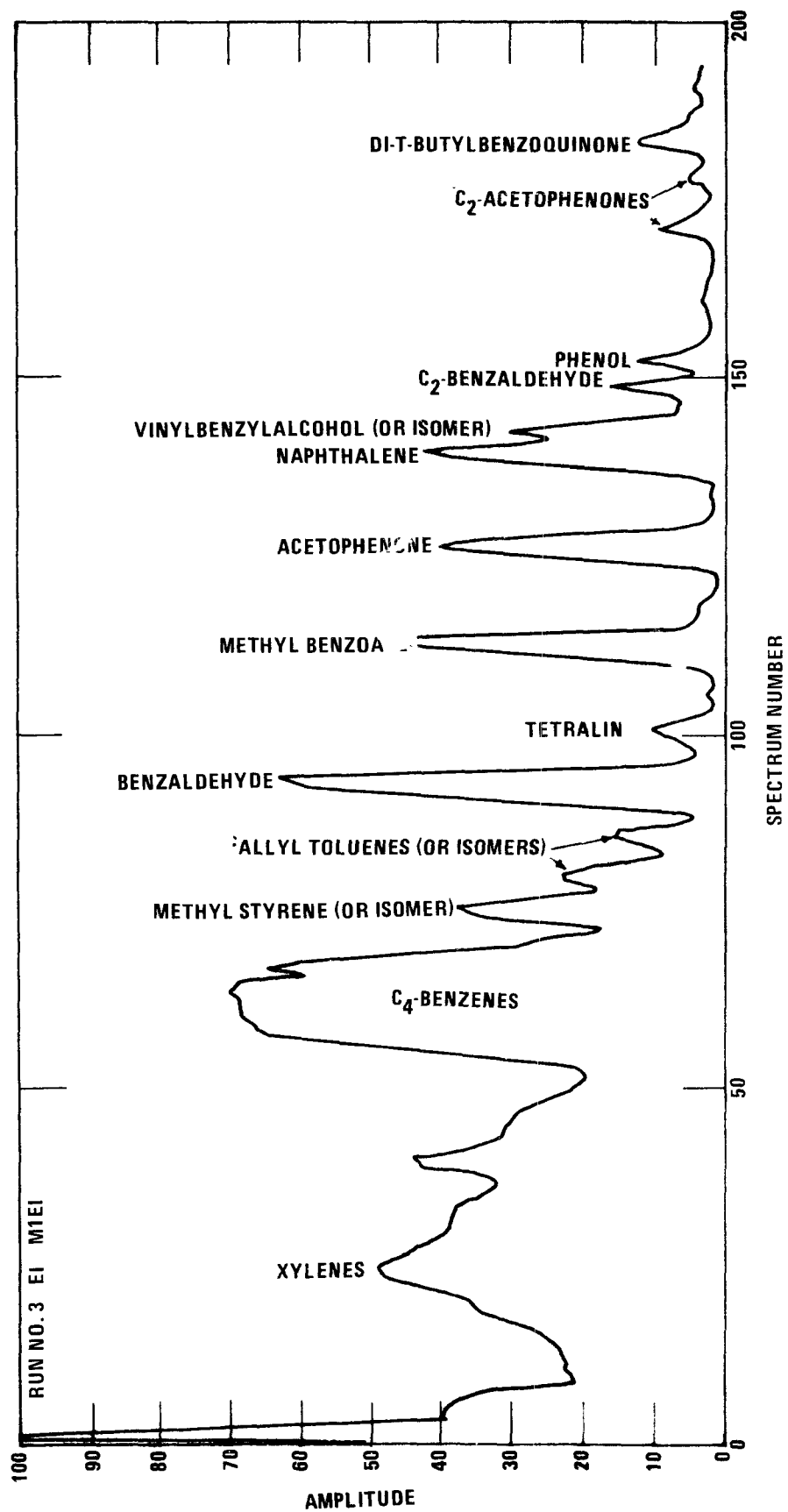


Figure 13. Electron impact GC-MS analysis of ambient vapors at Milford, Michigan, GM Test Track.

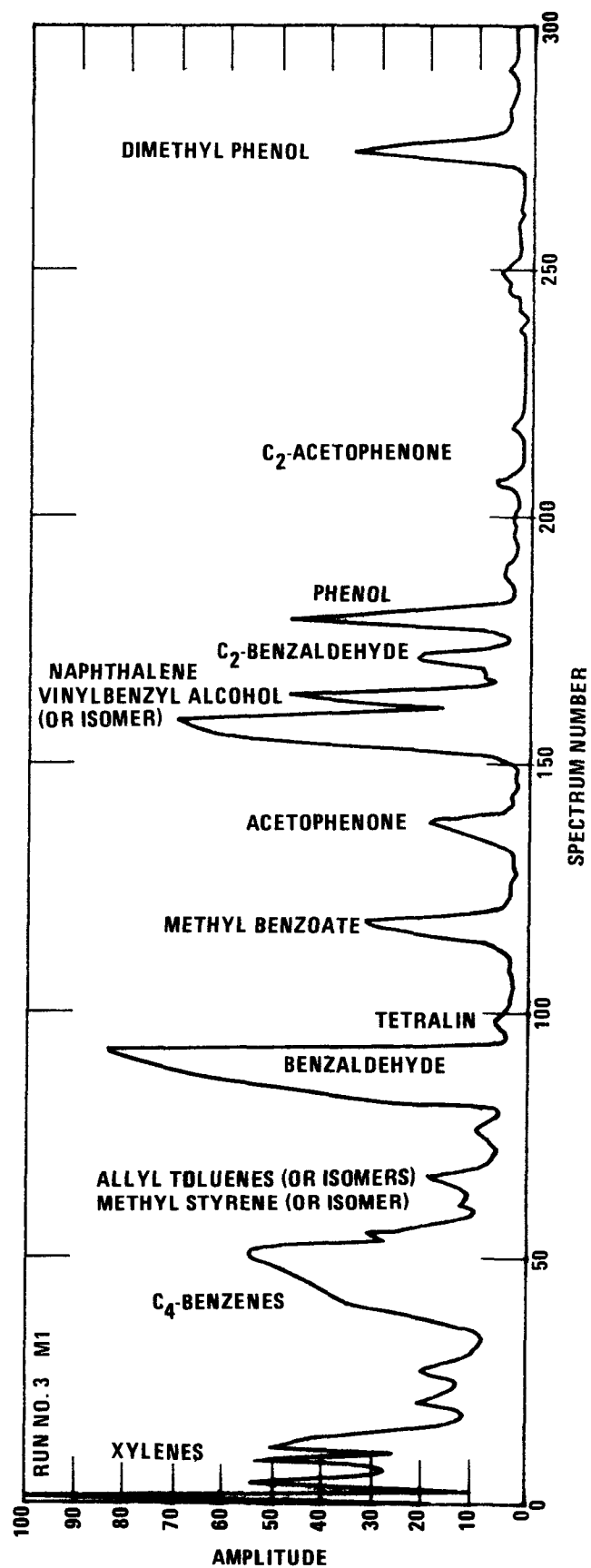


Figure 14. Methane ionization GC-MS analysis of ambient vapor at Milford, Michigan, GM Test Track.

SECTION 3

TEST OF MODEL ATMOSPHERIC AEROSOLS FOR MUTAGENICITY

Several previous studies at Battelle-Columbus were concerned with the composition of organic aerosols formed under simulated atmospheric conditions. The amount of material in model atmospheric aerosols derived from several hydrocarbons and NO_x to which we could assign a structure was a small fraction of the total aerosol collected. Since it was reasonable to suspect that potential carcinogens, in particular hydroperoxides and eposides, may have been present among the unidentified components, we investigated several aerosol samples for mutagenic properties. A test was performed that involves the use of special bacteria that under certain conditions will multiply only after undergoing mutation in the presence of chemicals or other agents.

The potential mutagens contained within each of the samples were detected by means of a special set of Salmonella strains obtained from Dr. Bruce Ames (Biochemistry Department, University of California, Berkeley, California). The tester strains are histidine deficient and are used for the purpose of detecting frameshift and base pair substitution mutations as indicated by reversion to prototrophy. These systems were selected for their sensitivity and specificity to be reverted back to the wild type by particular mutagens (8).

The assay has been adapted for use in detecting compounds which may be potential mutagens. Potential mutagens are compounds which are not in themselves carcinogenic or mutagenic but are converted to active mutagens by mammalian metabolism, especially by the TPNH dependent microsomal enzymes of the liver. Since these specific bacteria do not have the mammalian liver, homogenates are added to the system to activate the non-mutagenic parental compounds to possible mutagens. This activation system is derived from the rat liver microsome.

The experimental procedure used for detecting mutagens is as follows. Into 2 ml of molten agar is added 0.1 ml of the bacterial tester strain, a quantity of the potential mutagen (100, 50, 20, 10, and 5 μl of the solution supplied), and the liver microsome solution (when used). The agar is then poured over the surface of a minimal agar plate and permitted to solidify. Controls are included at all times, consisting of a sample to measure the spontaneous reversion rate for each tester strain where the mutagen is omitted, a sterility check of the mutagen solution and liver microsome solution (5-9), and positive controls consisting of compounds which do and do not require metabolic activation.

The plates were incubated for 48 hours and observed. The number of revertant colonies for each bacterial strain were counted and reported as the number of revertants detected. A sample was considered negative if the number of induced revertants obtained with the 100 percent sample analyzed compared to the spontaneous revertants was less than twofold.

It is apparent from the results in Table 8 that none of the model aerosols show mutagenic properties when the incidence of spontaneous mutations is taken into account. This result, while reassuring, was obtained with aerosols derived from simple hydrocarbons. Urban atmospheric aerosols, on the other hand, are expected to contain organics derived from a wide variety of hydrocarbon precursors, and may show very different properties than those obtained in these experiments. Moreover, mutagenic effects are not the only effects that aerosol components may have on cellular components, as we have pointed out earlier (4).

TABLE 8. AMES TEST FOR MUTAGENICITY
OF ATMOSPHERIC AEROSOLS
(Plate incorporation using induced S-9)

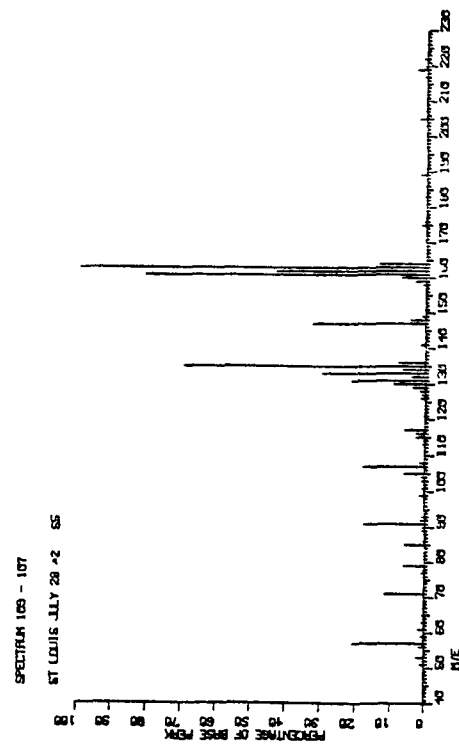
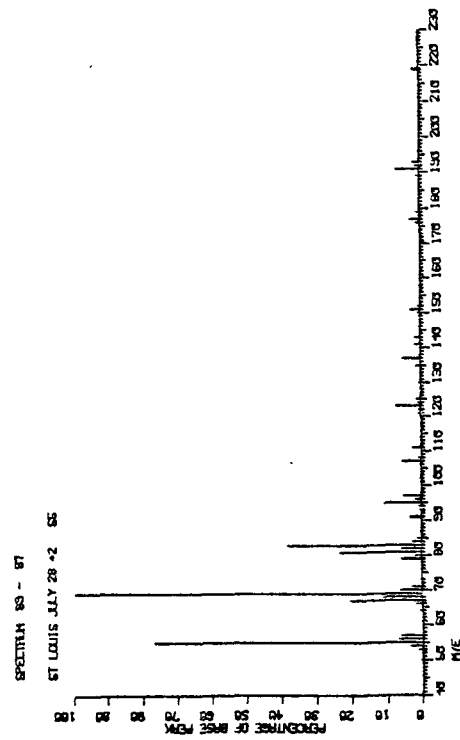
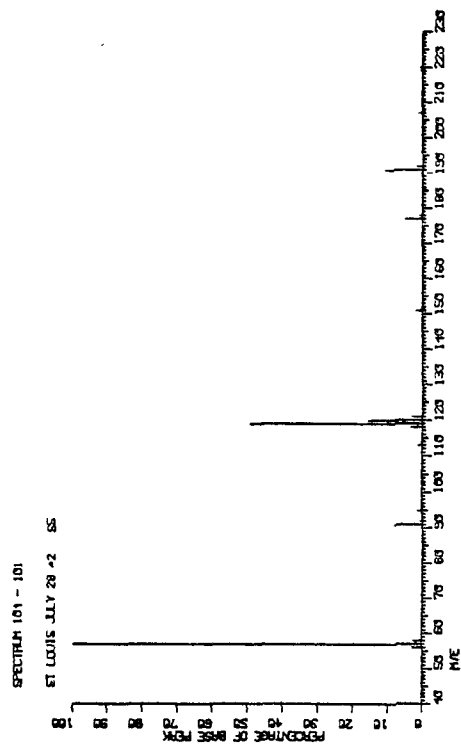
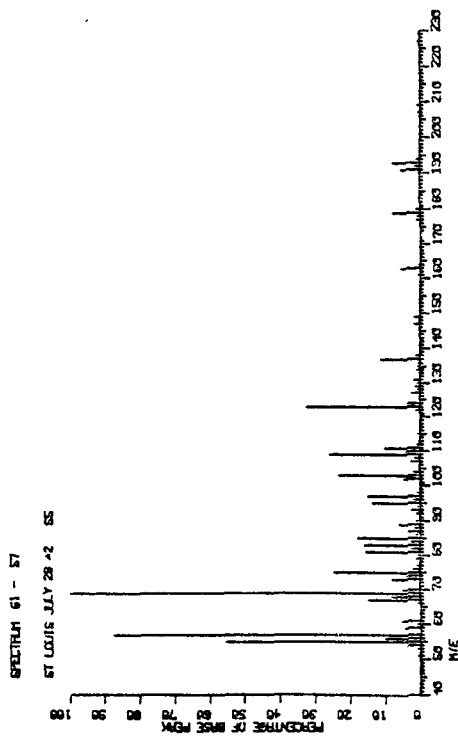
Aerosol sample tested	Tester strain	Concentration of Chemical in ul.					
		100	50	50-S-9	20	10	5
1 (Toluene/NO _x)	TA-100	364	382	334	309	323	291
M-400	TA-98	43	59	52	54	38	55
Methanol extract	TA-1538	19	19	10	12	12	16
2 (Toluene/NO _x)	TA-100	391	358	331	334	302	295
M-400	TA-98	89	70	85	45	45	39
CH ₂ Cl ₂ extract	TA-1538	21	17	11	8	10	9
3 (1-Heptene/NO _x)	TA-100	300	342	280	318	302	310
M-500	TA-98	43	42	40	46	40	38
Methanol extract	TA-1538	14	15	9	12	16	8
4 (1-Heptene/NO _x)	TA-100	330	366	295	345	300	289
M-500	TA-98	43	39	43	30	47	55
CH ₂ Cl ₂ extract	TA-1538	15	12	13	7	7	5
5 (α-Pinene/NO _x)	TA-100	340	311	315	322	313	277
M-200	TA-98	63	46	27	39	33	44
Methanol	TA-1538	11	11	11	6	14	13
6 (α-Pinene/NO _x)	TA-100	371	333	333	311	347	355
M-200	TA-98	56	50	24	40	42	43
CH ₂ Cl ₂	TA-1538	11	13	10	12	5	10
Control Spontaneous Revertants							
		TA-100	TA-98	TA-1538			
	+S-9	300-317	45-45	14-8			
	-S-9	279-234	40-43	9-9			
S-9 sterility = No colonies x2							
compound sterility (100 ul tested):							
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	
	NC	NC	NC	NC	NC	NC	

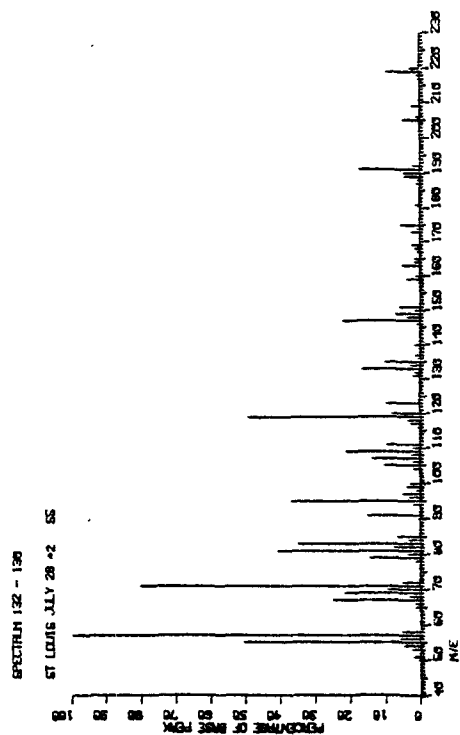
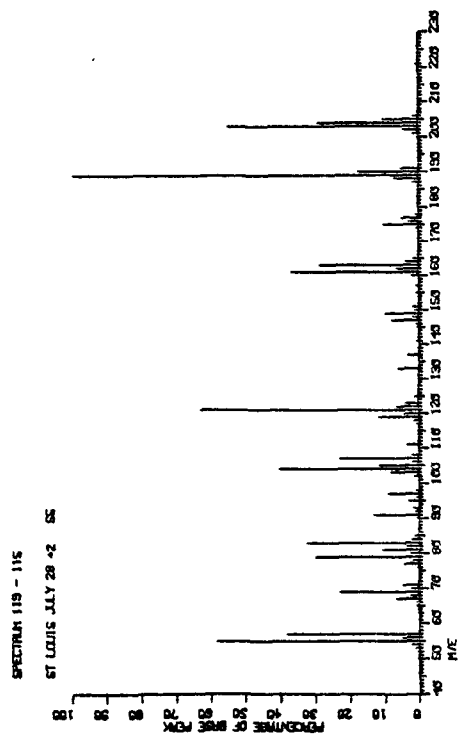
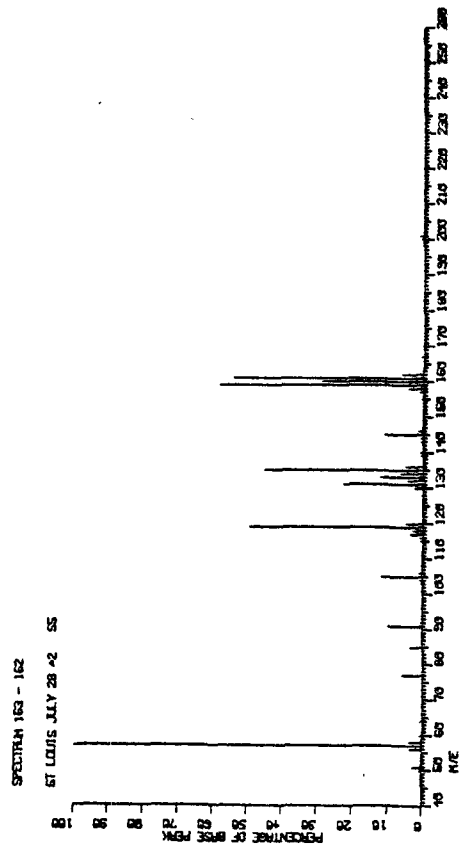
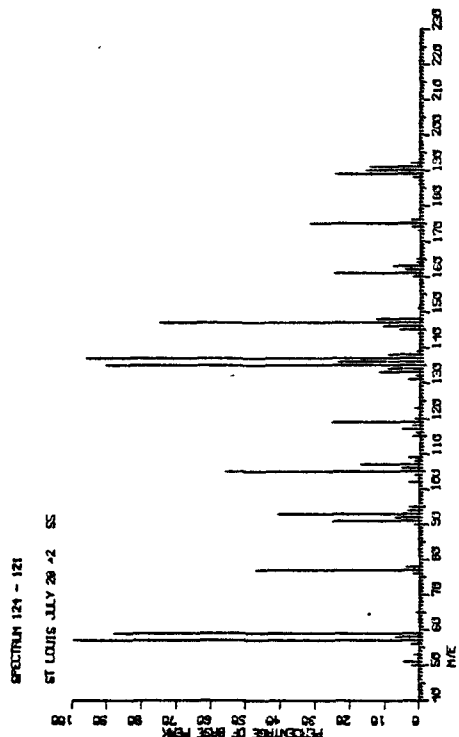
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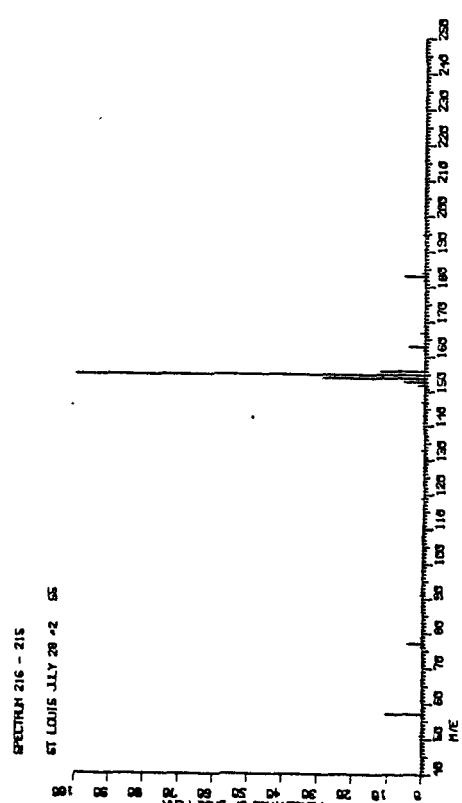
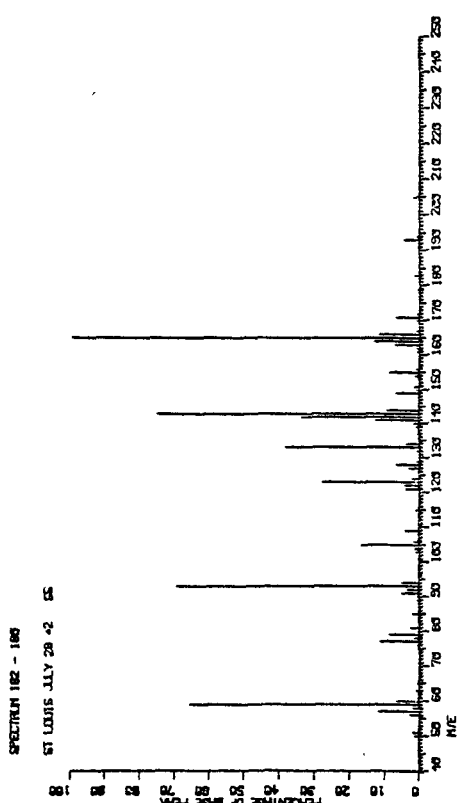
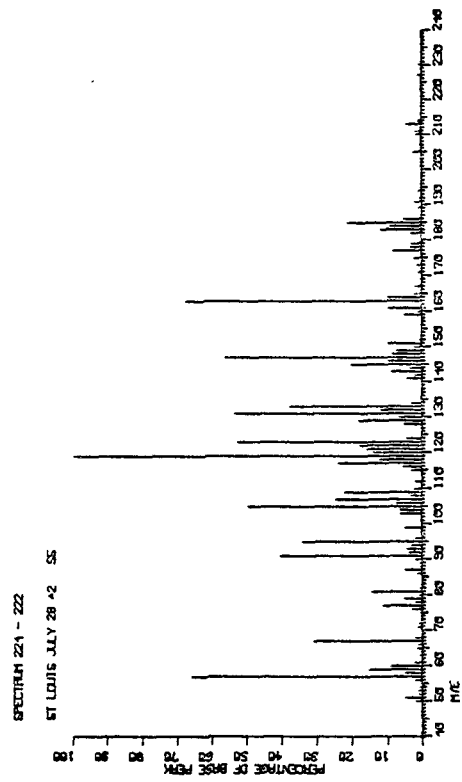
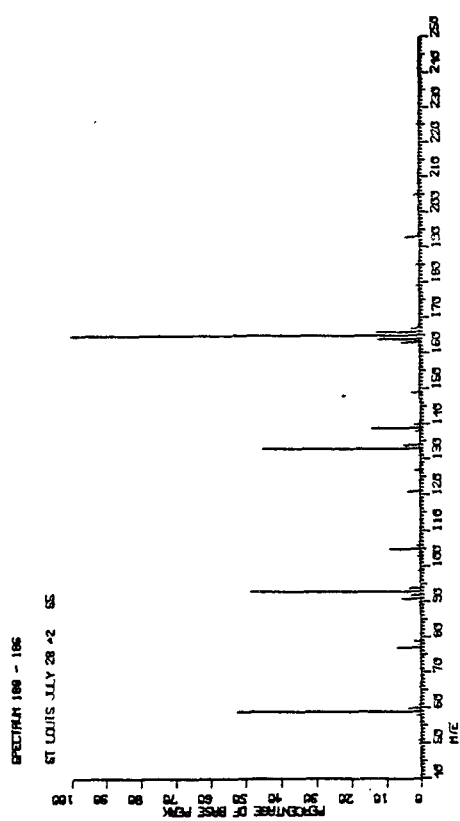
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APPENDIX A

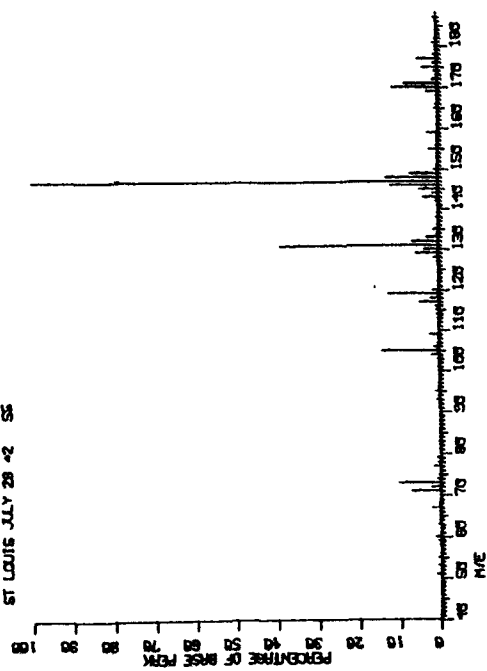
METHANE IONIZATION MASS SPECTRA OF AMBIENT ST. LOUIS ORGANIC VAPORS UNIQUE TO SAMPLES S5 AND S7



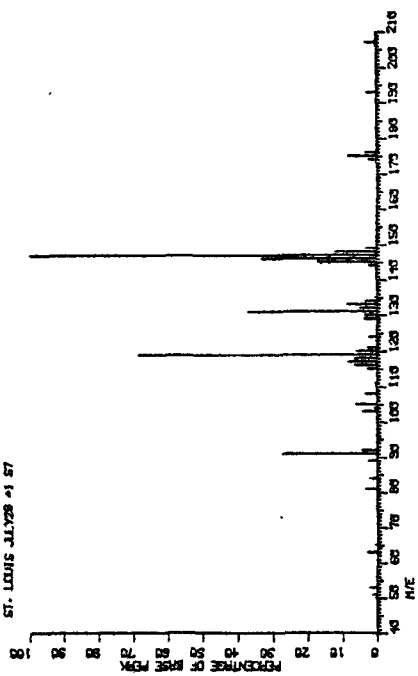




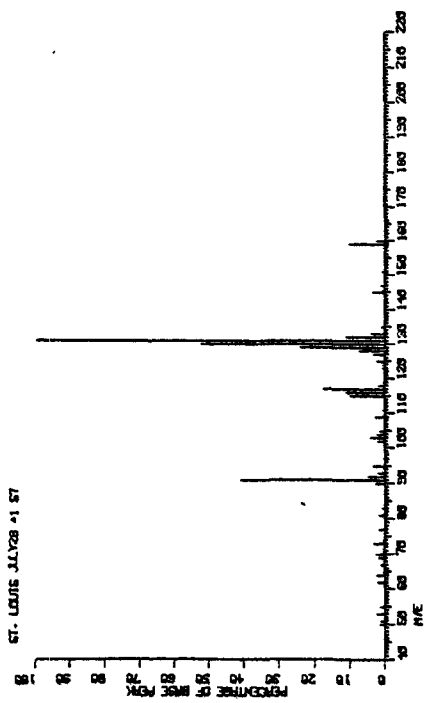
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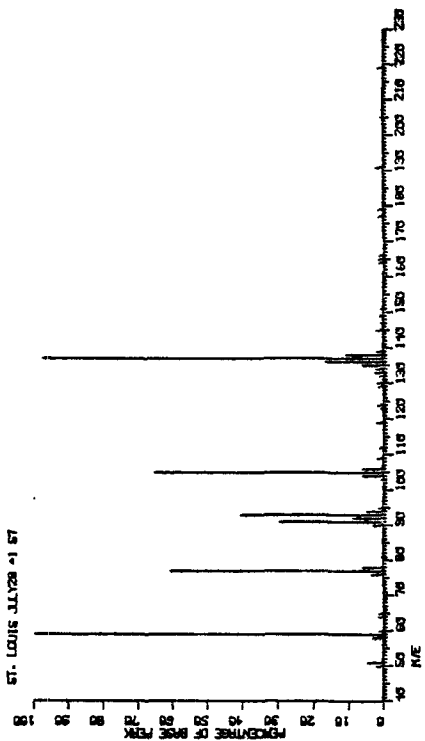
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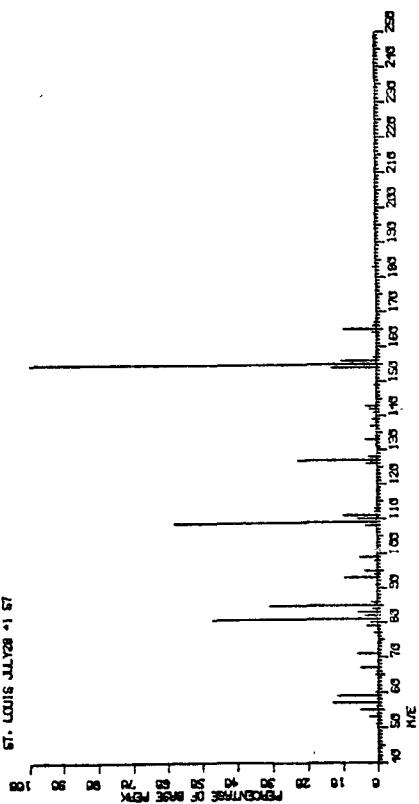
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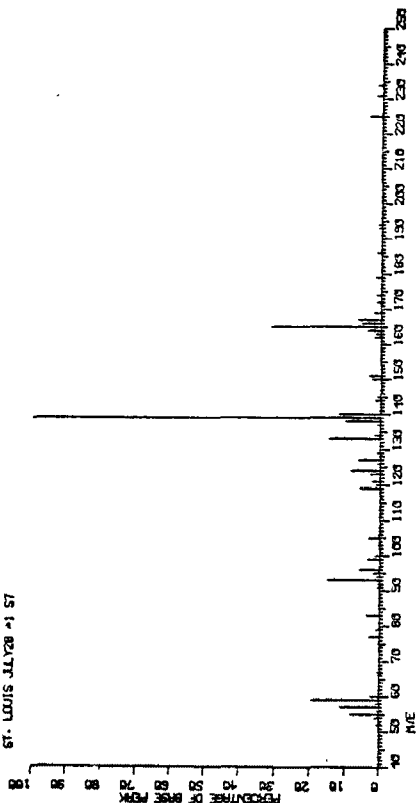
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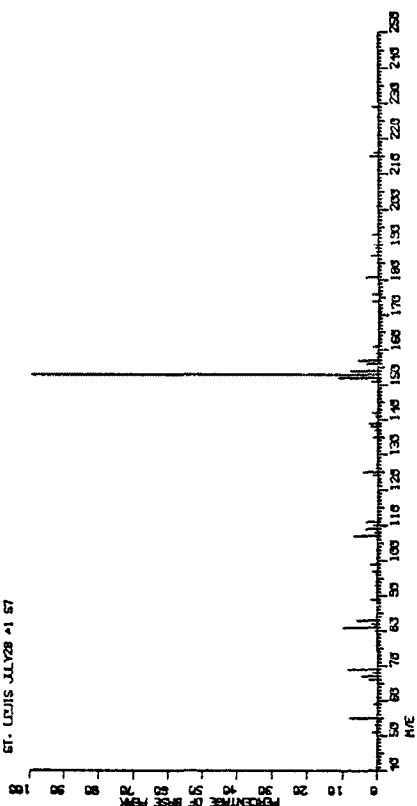
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ST. LOUIS JULY28 *1 57



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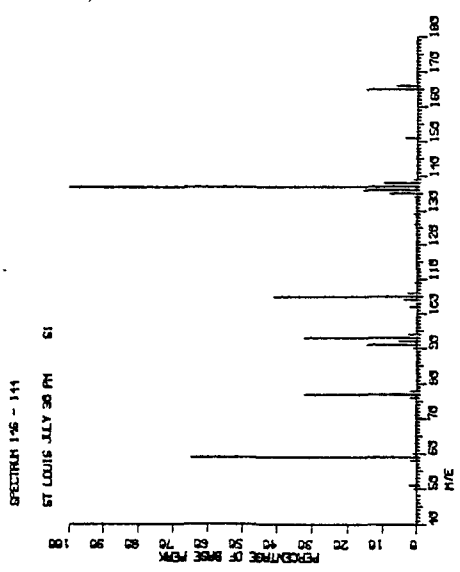
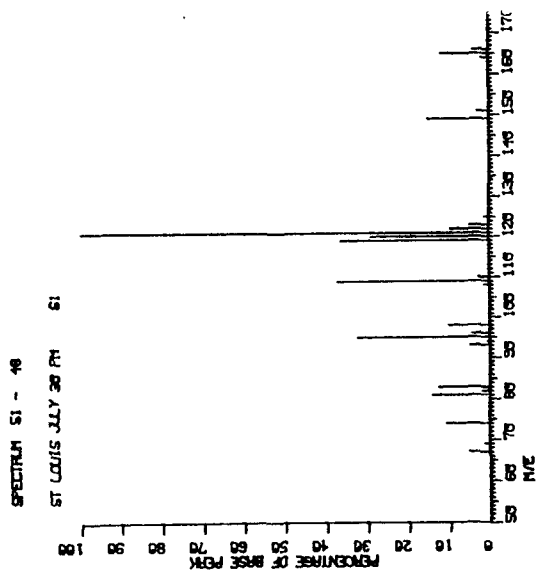
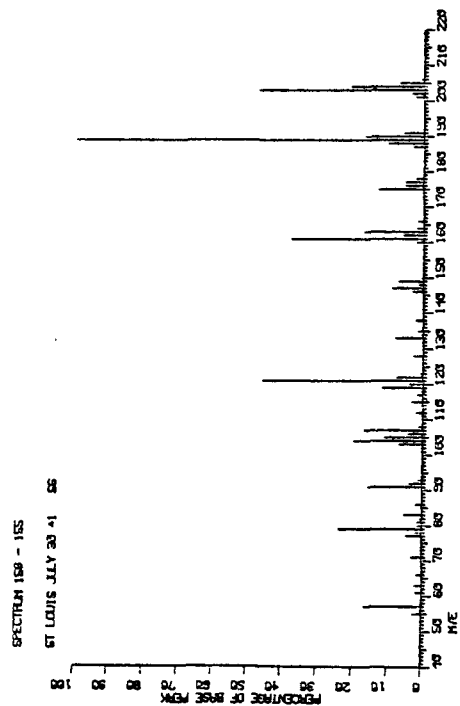
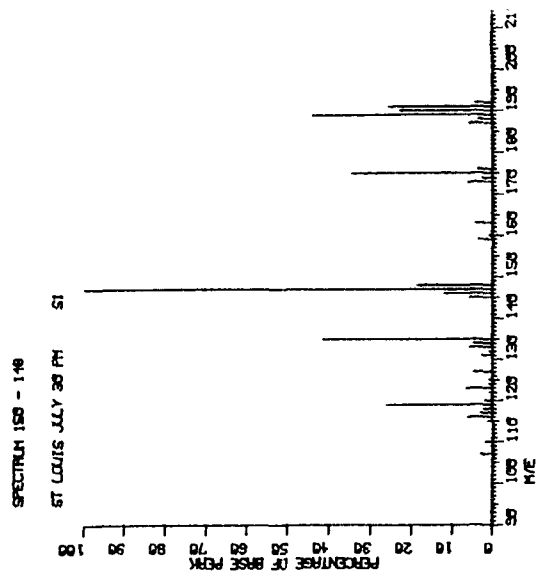


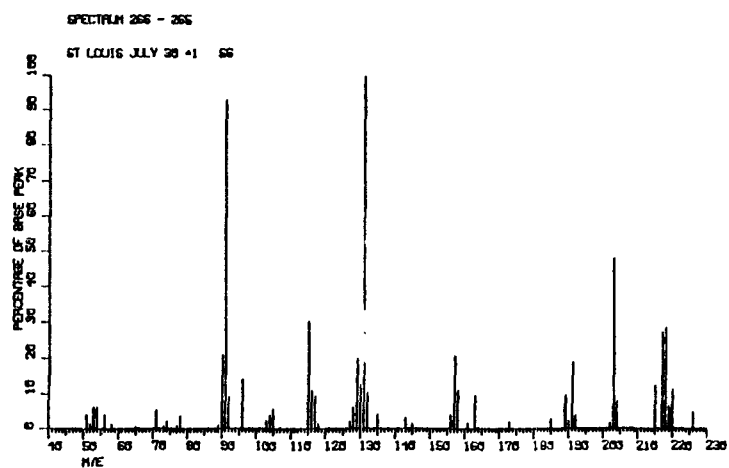
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APPENDIX B

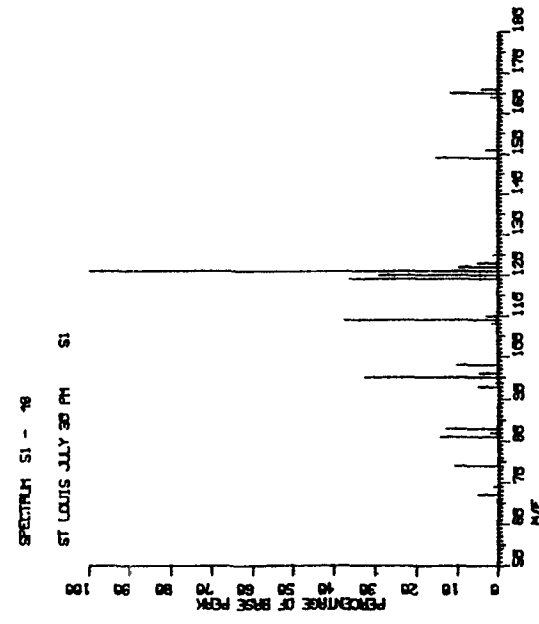
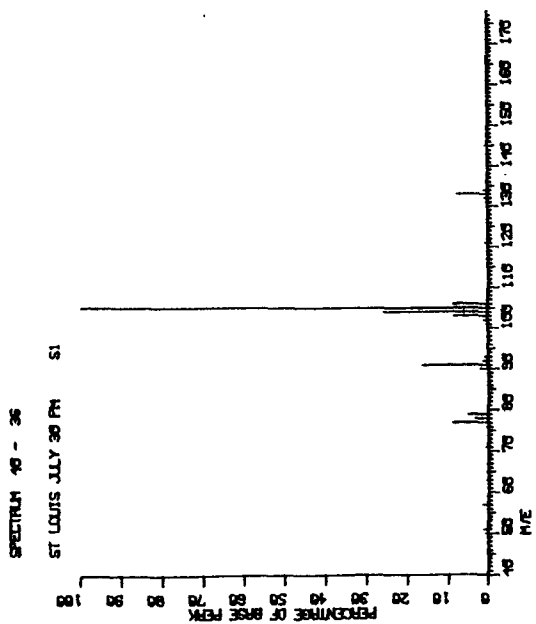
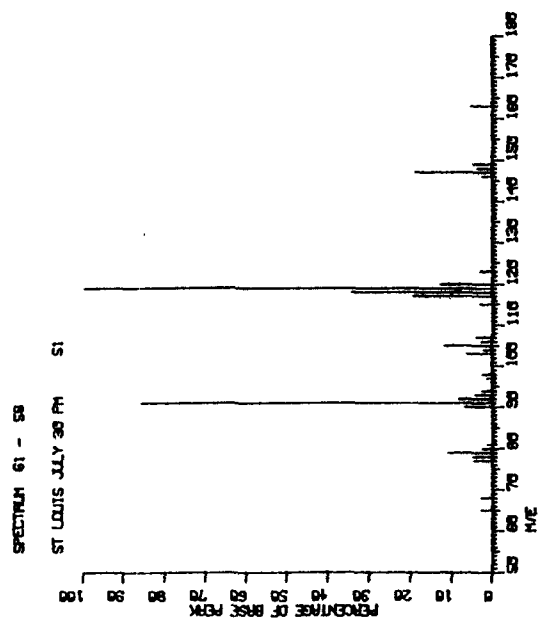
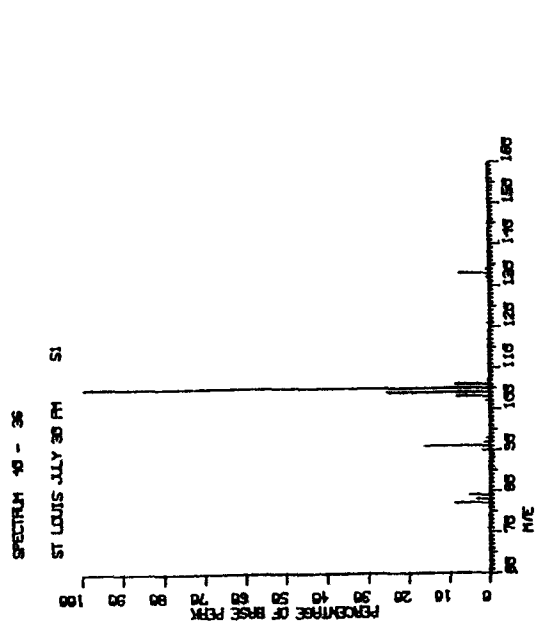
METHANE IONIZATION MASS SPECTRA OF
AMBIENT ST. LOUIS ORGANIC VAPORS
UNIQUE TO SAMPLES S1 AND S6



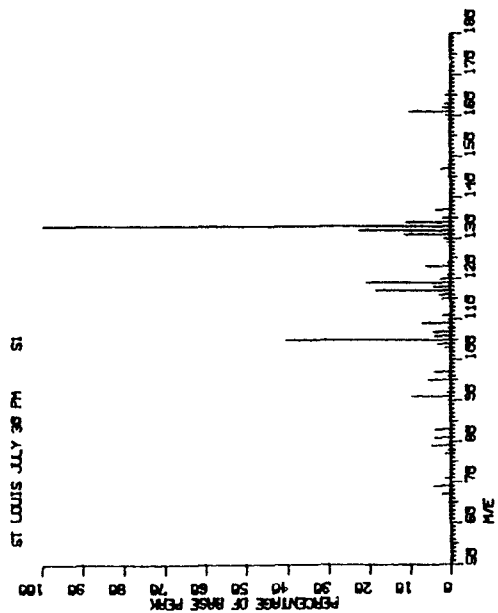


APPENDIX C

METHANE IONIZATION MASS SPECTRA OF
AMBIENT ST. LOUIS ORGANIC VAPORS
OF SAMPLE S1

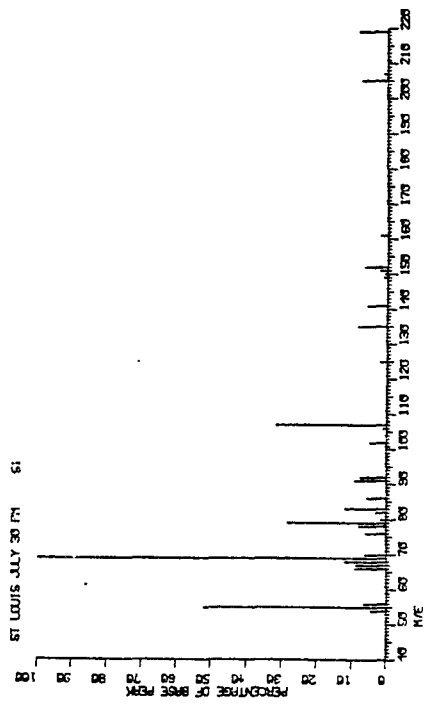


SPECTRUM 101 - 97



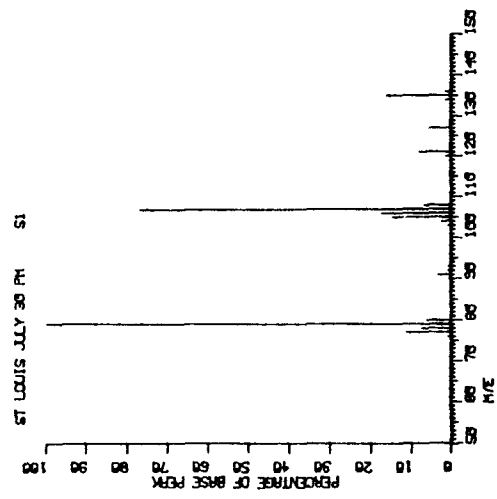
ST LOUIS JULY 30 PM S1

SPECTRUM 107 - 105



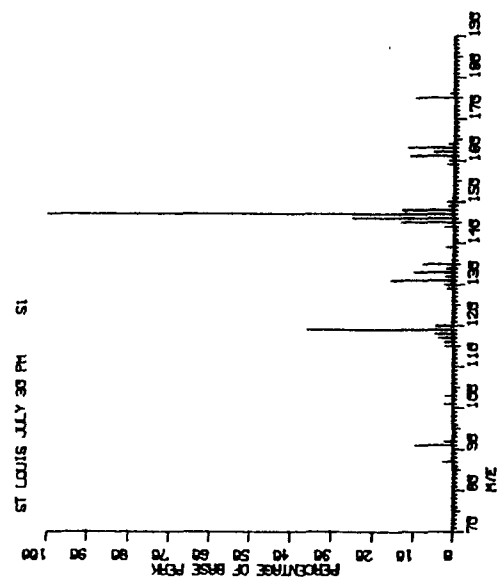
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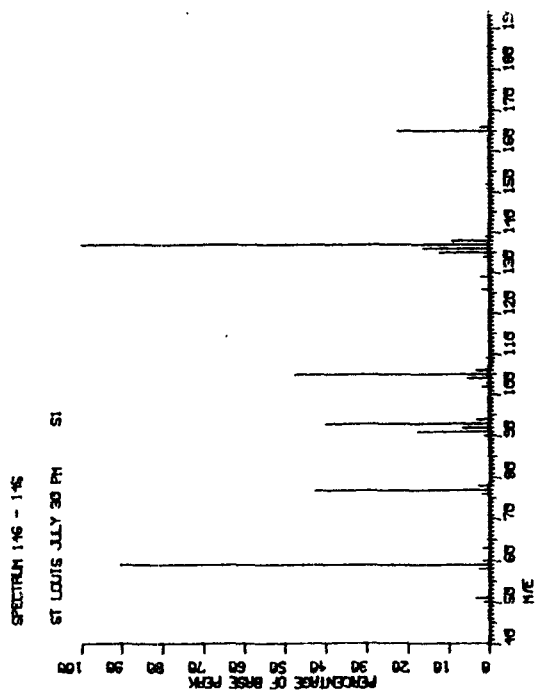
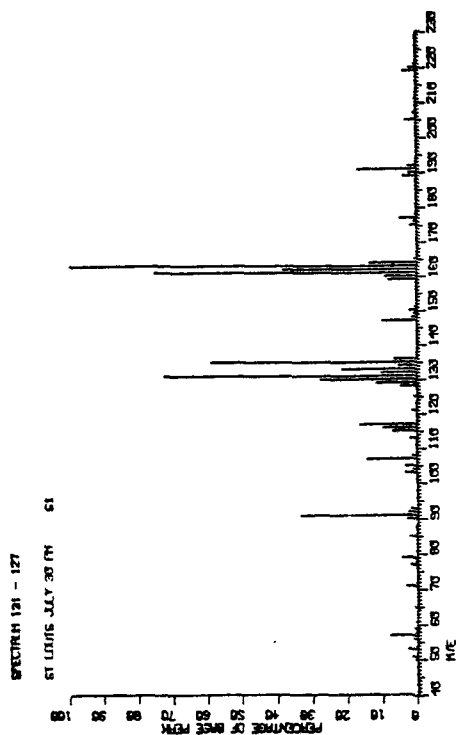
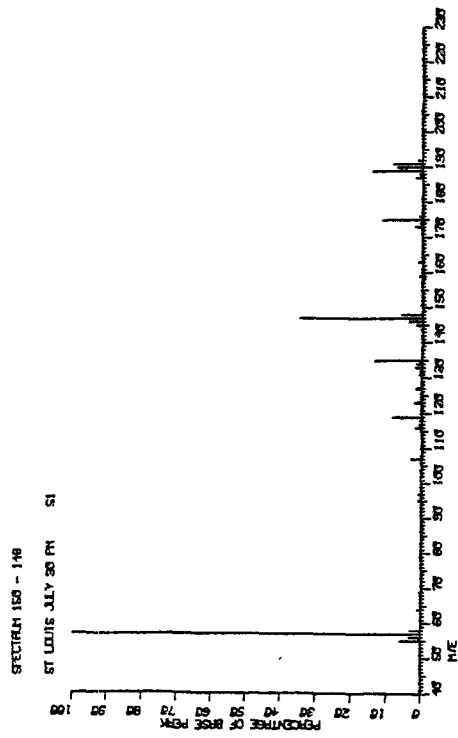
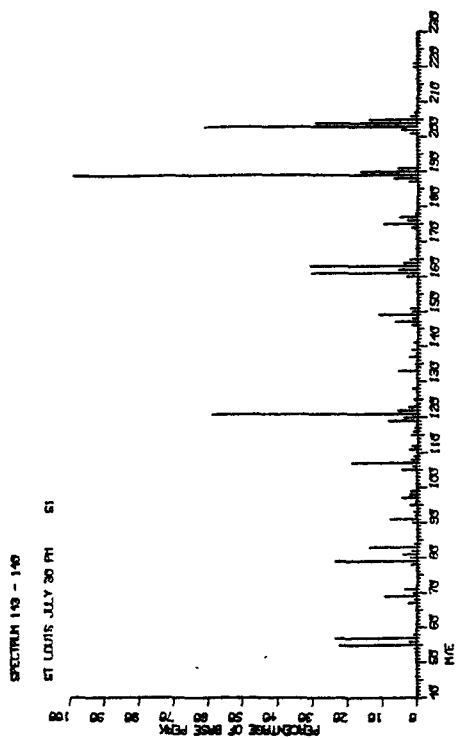


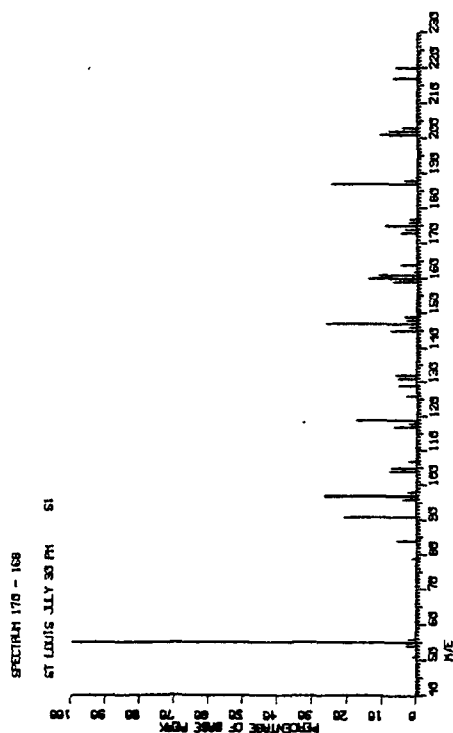
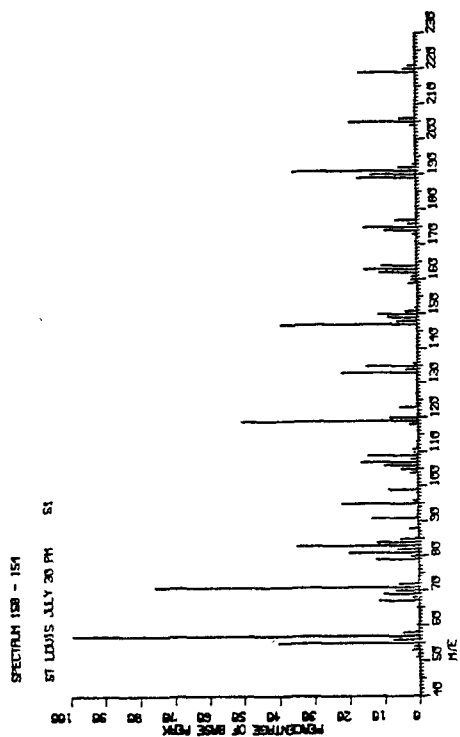
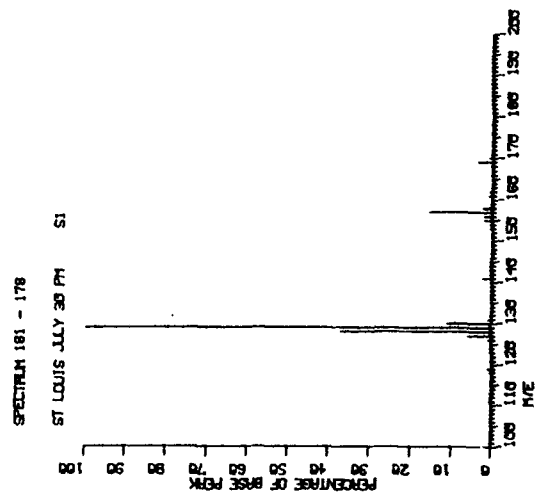
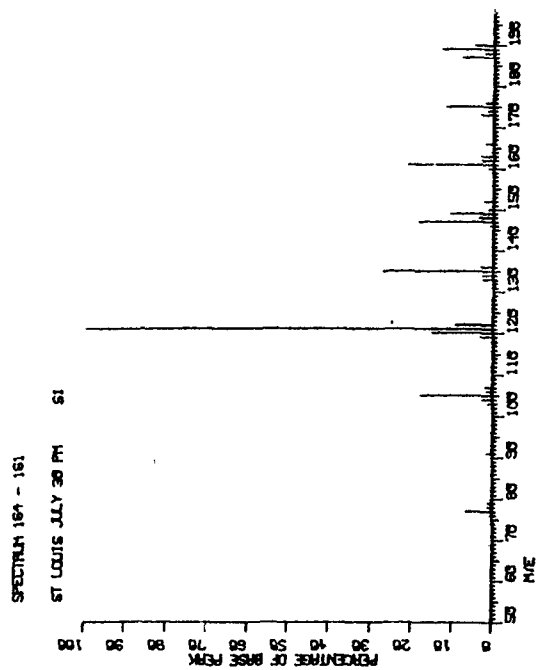
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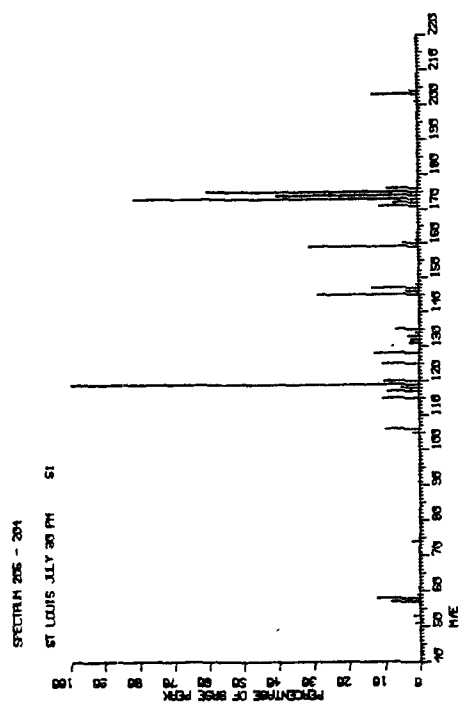
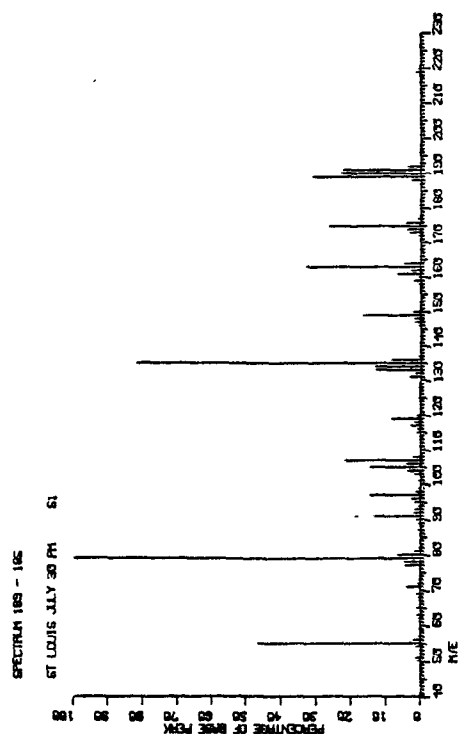
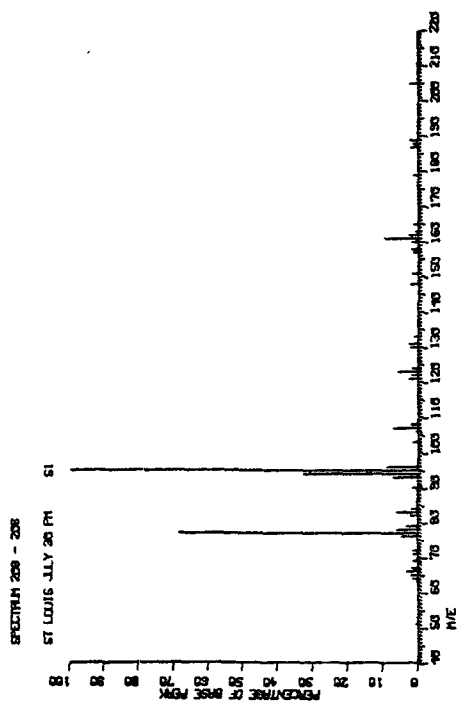
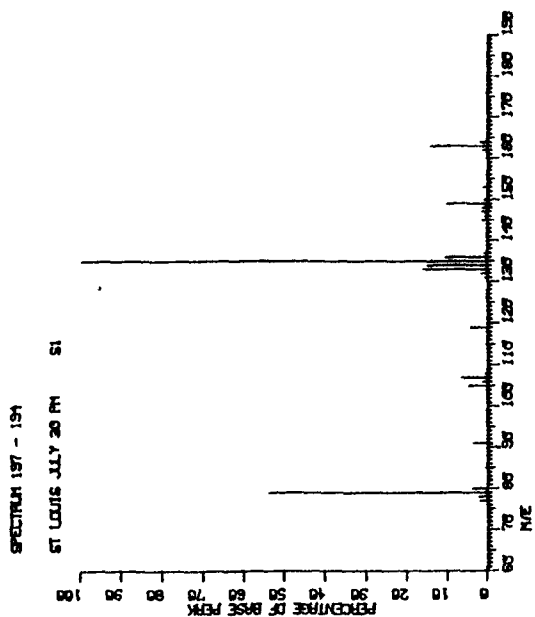
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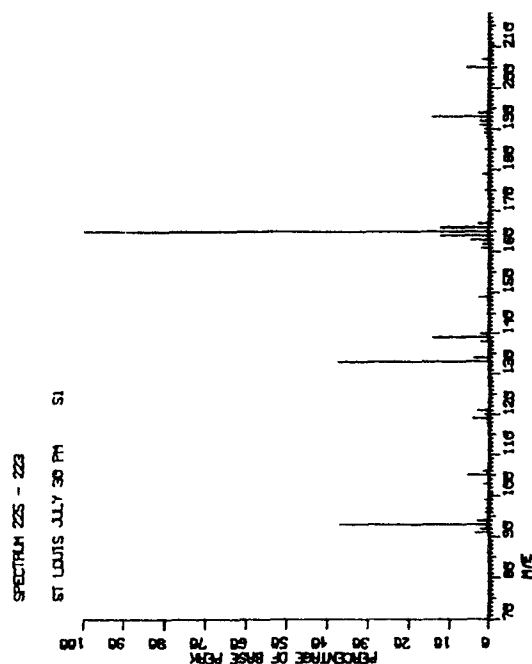
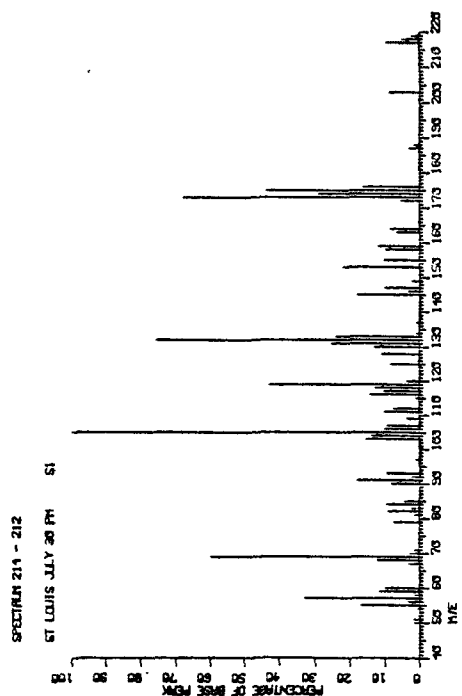
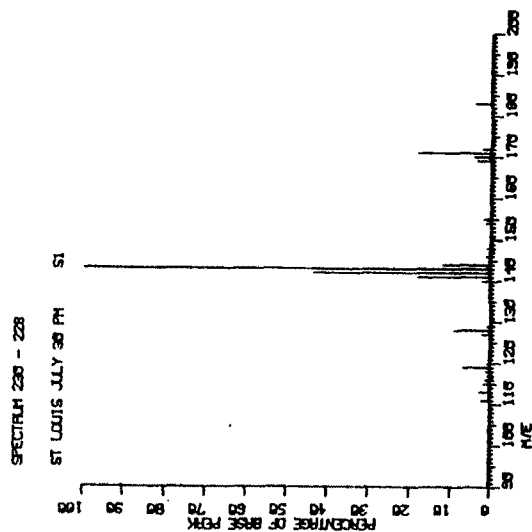
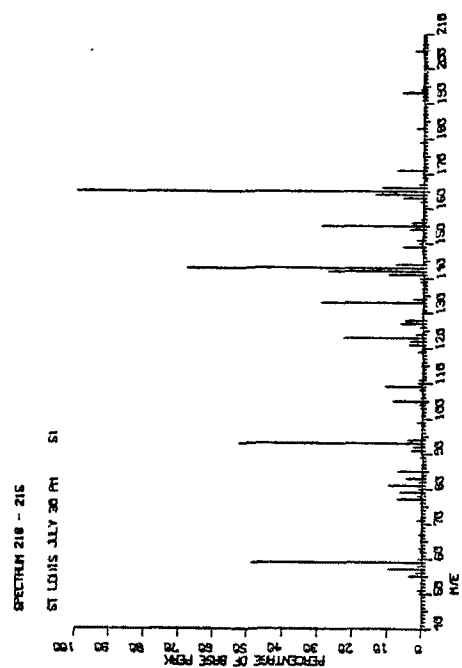


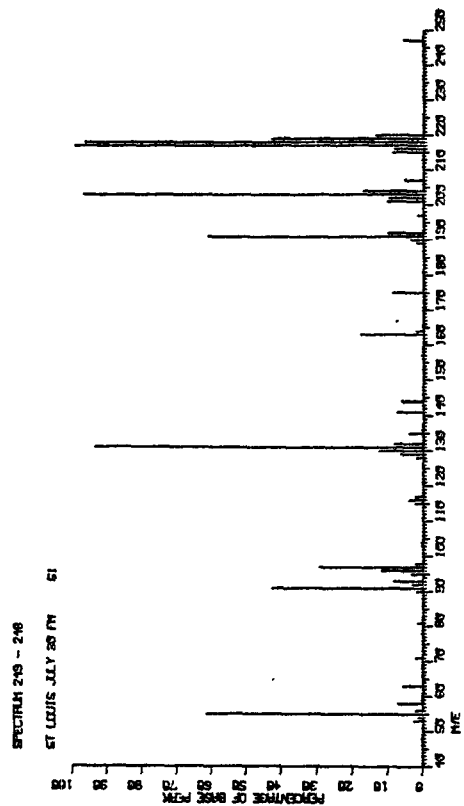
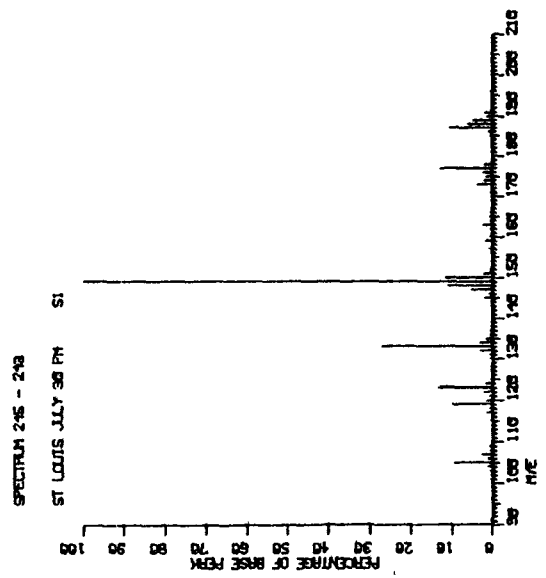
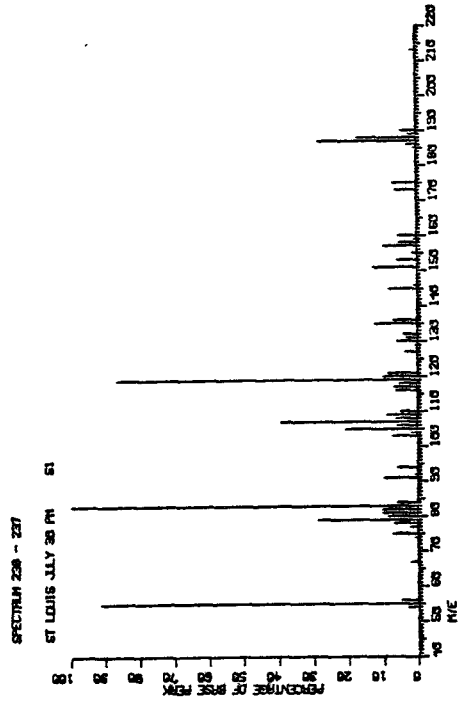
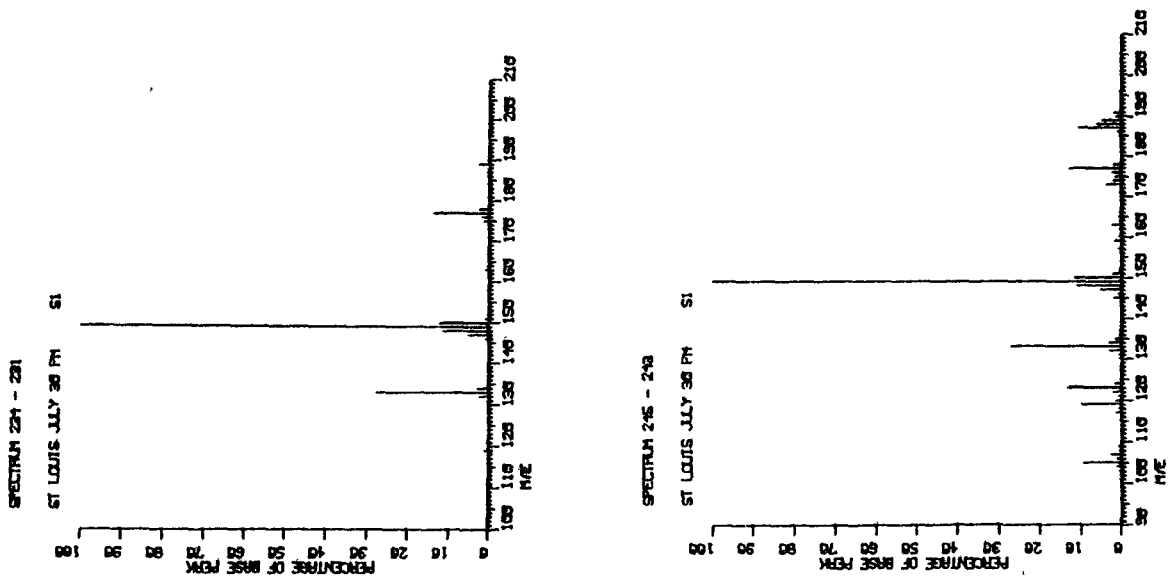
ST LOUIS JULY 30 PM S1

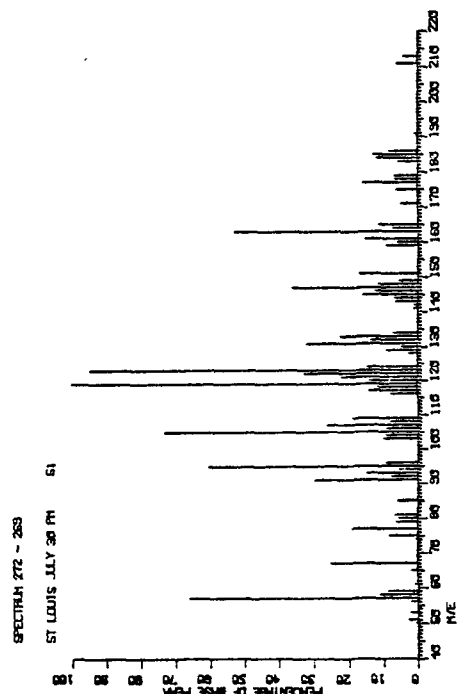
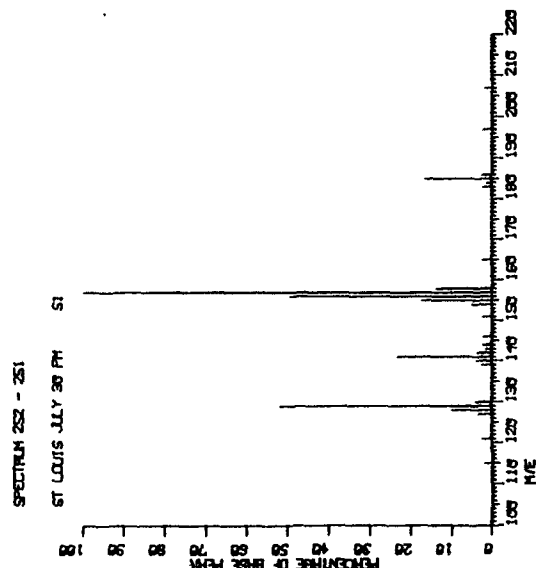
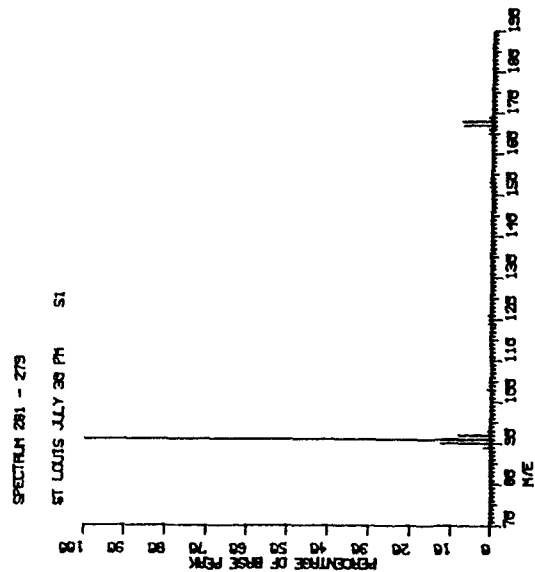
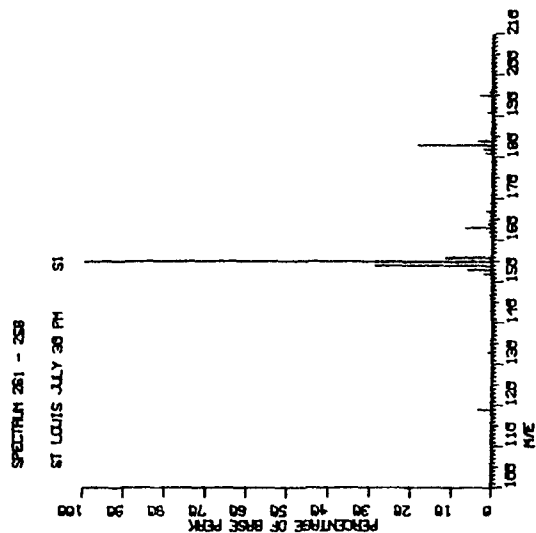


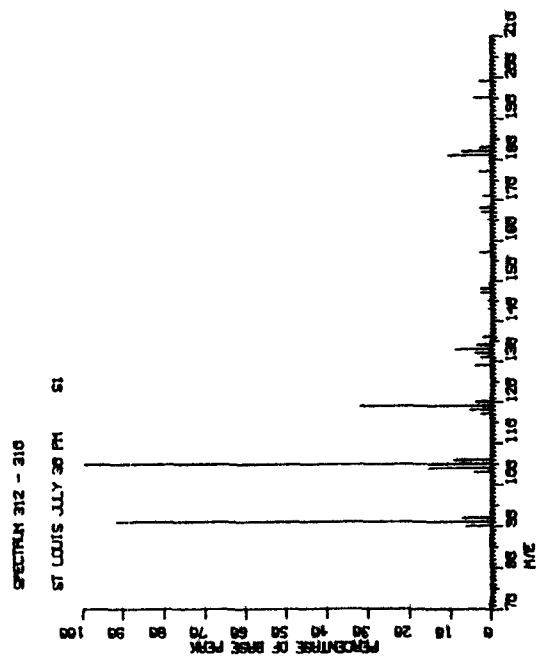
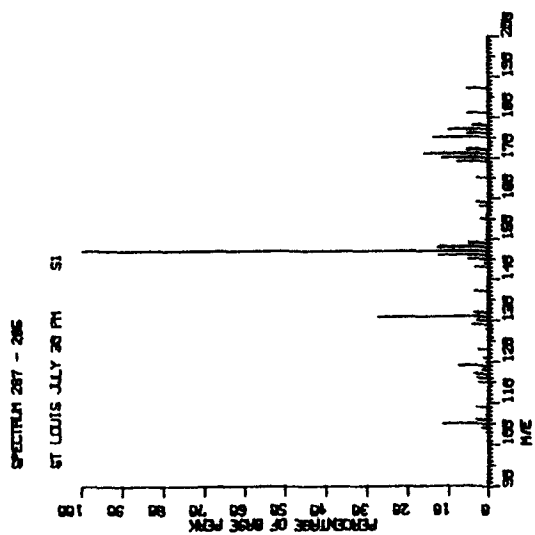
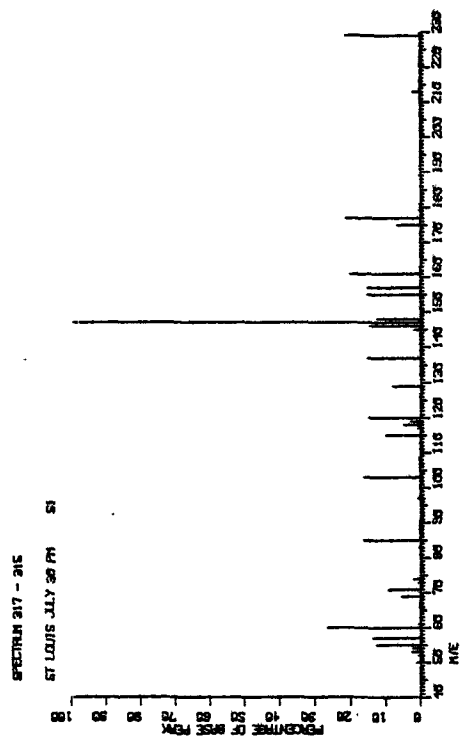
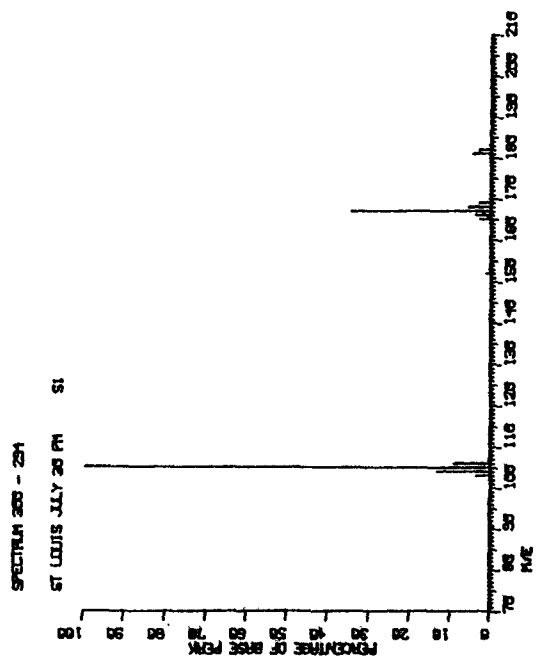


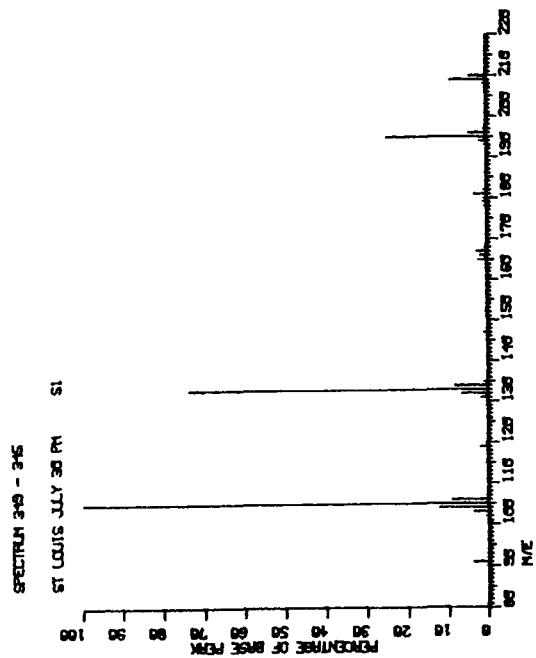
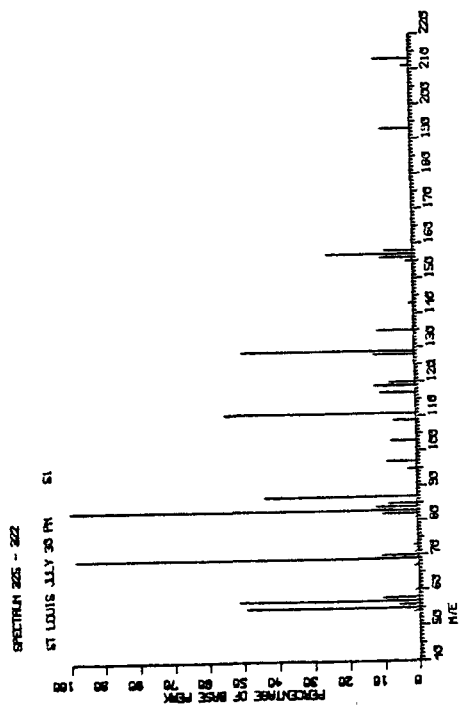
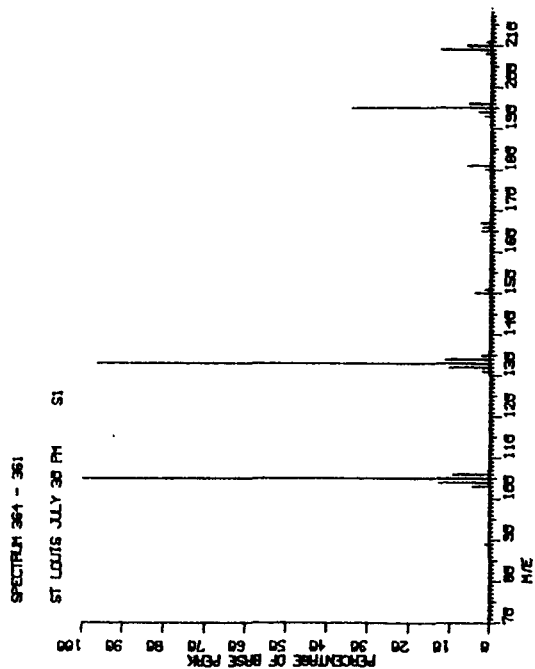
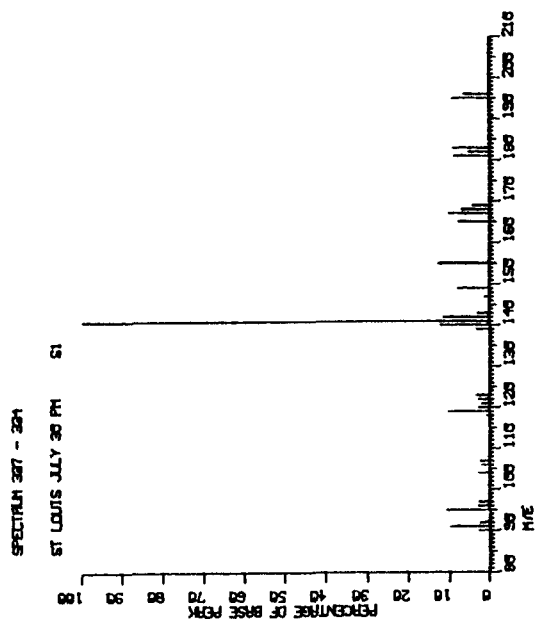






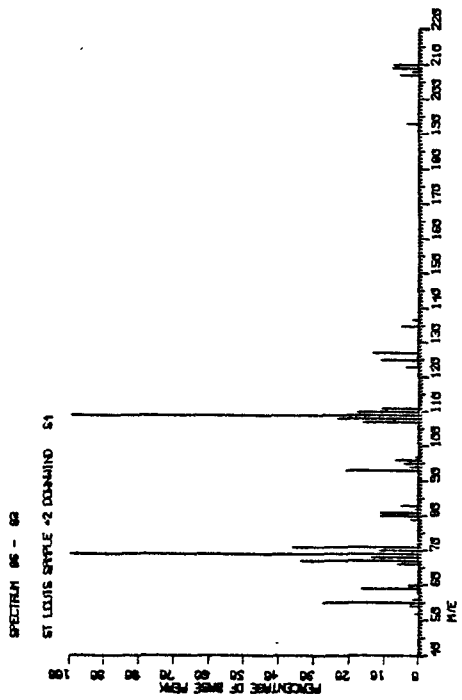
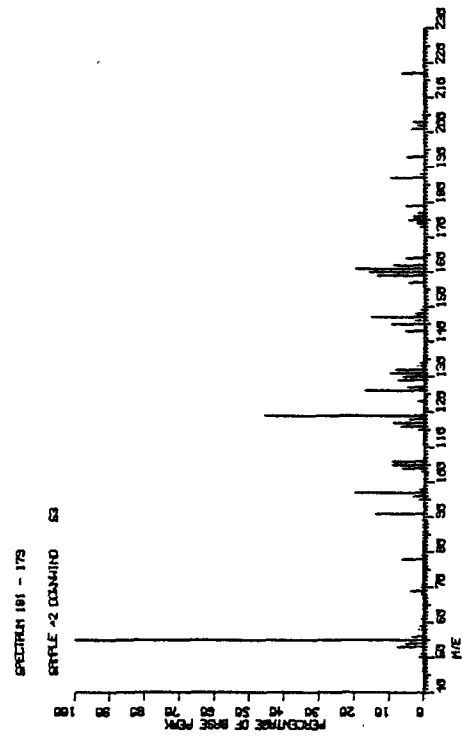






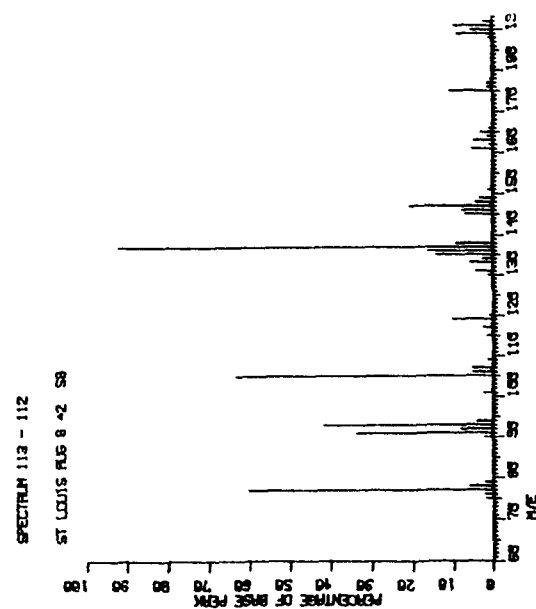
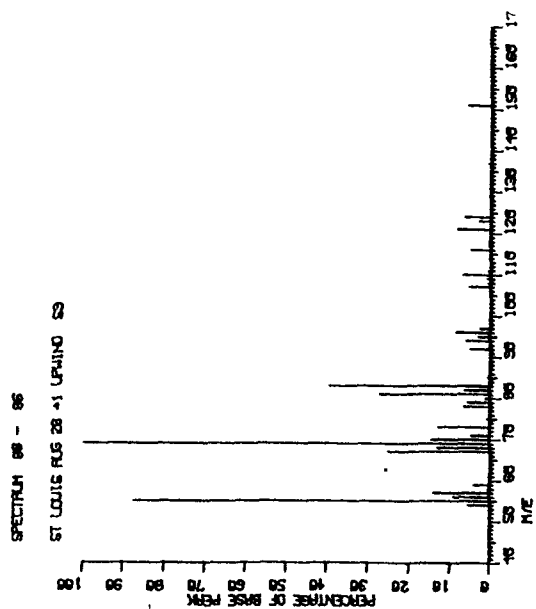
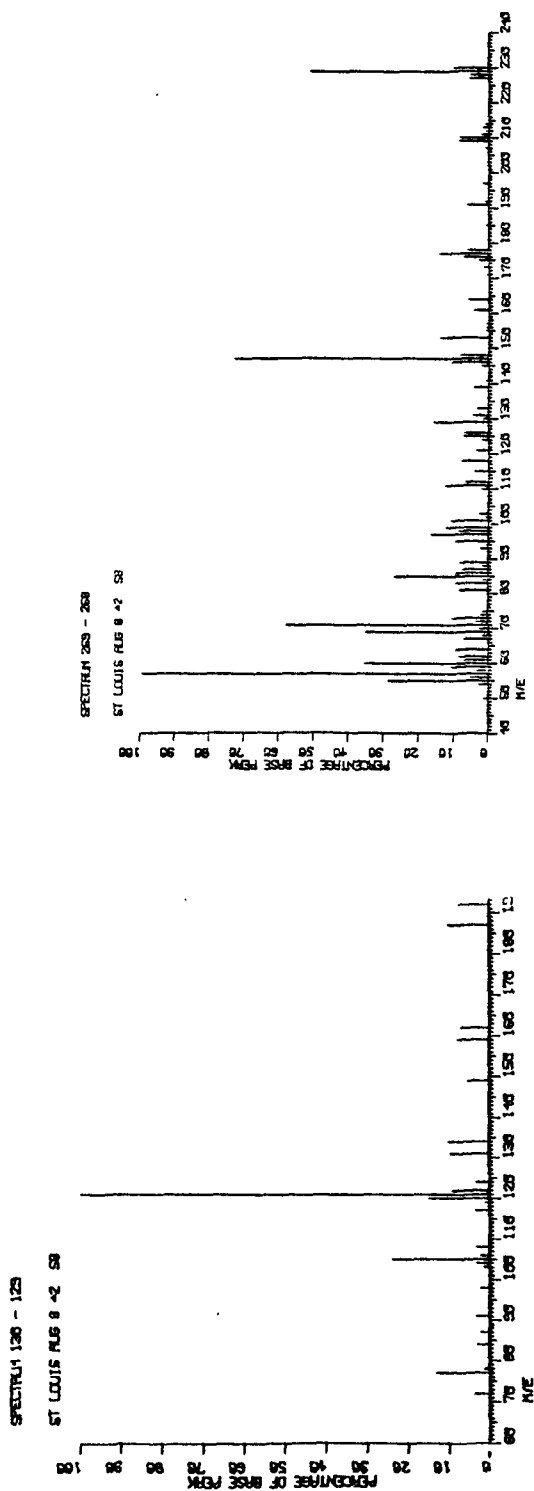
APPENDIX D

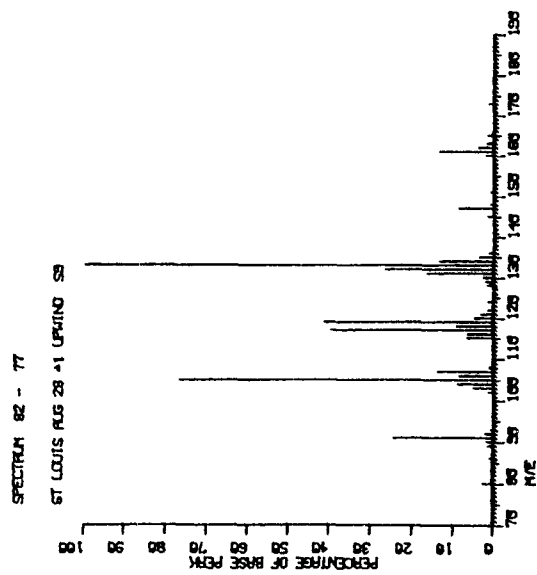
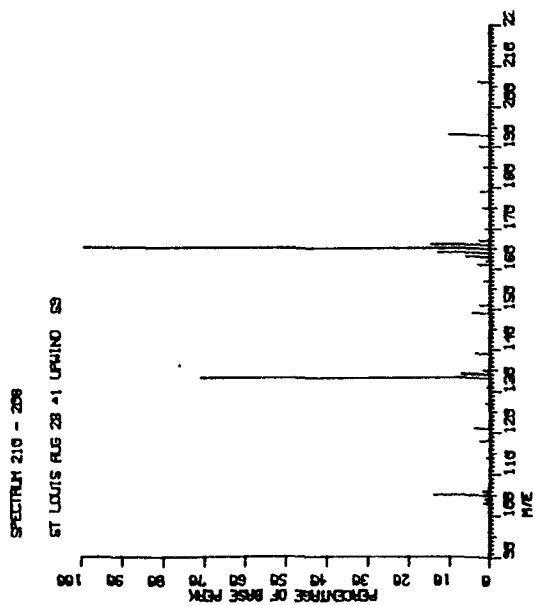
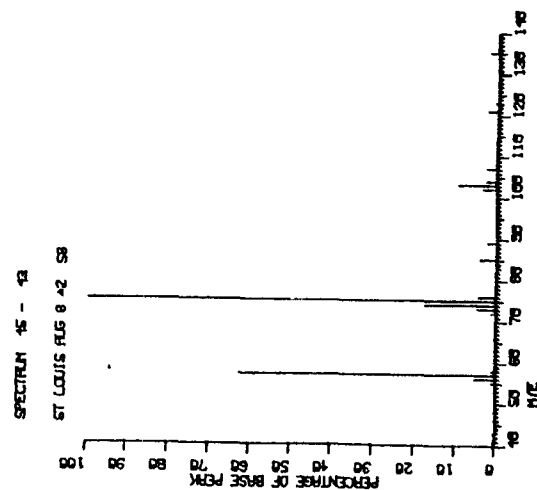
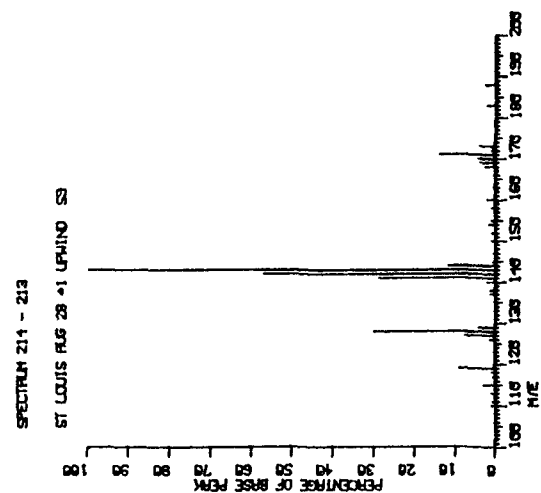
METHANE IONIZATION MASS SPECTRA
OF AMBIENT ST. LOUIS ORGANIC VAPORS
UNIQUE TO SAMPLES S3 AND S4

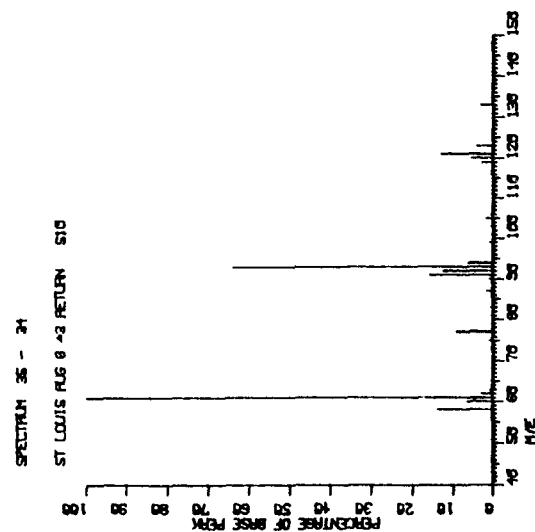
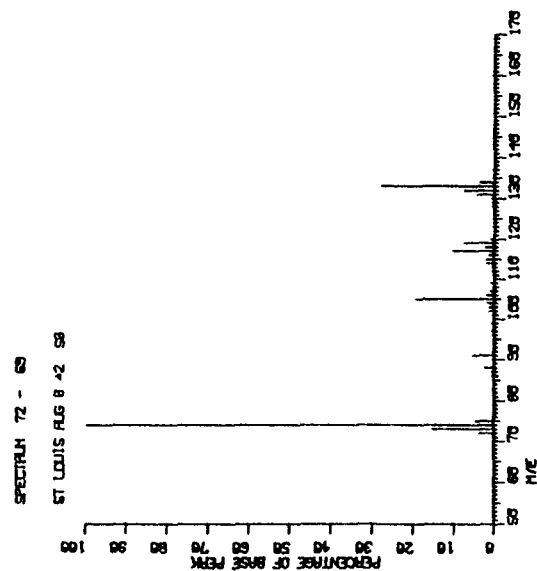
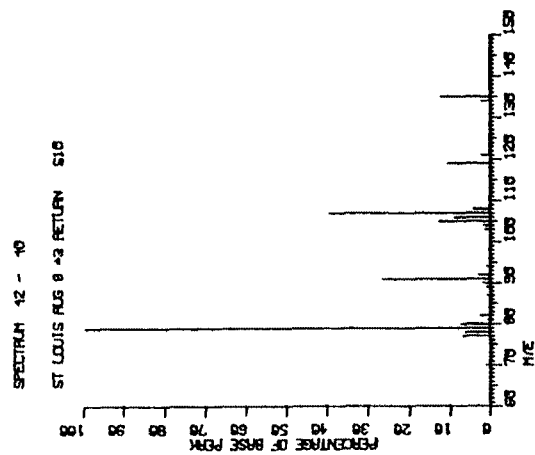
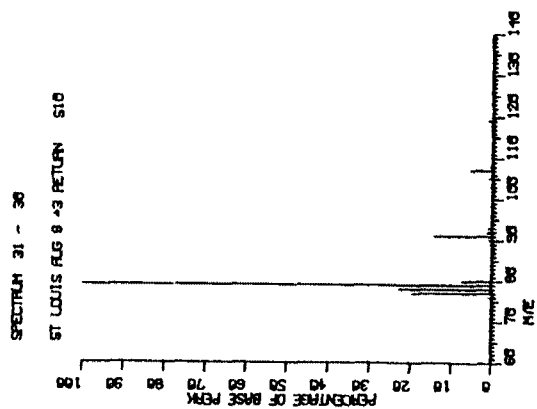


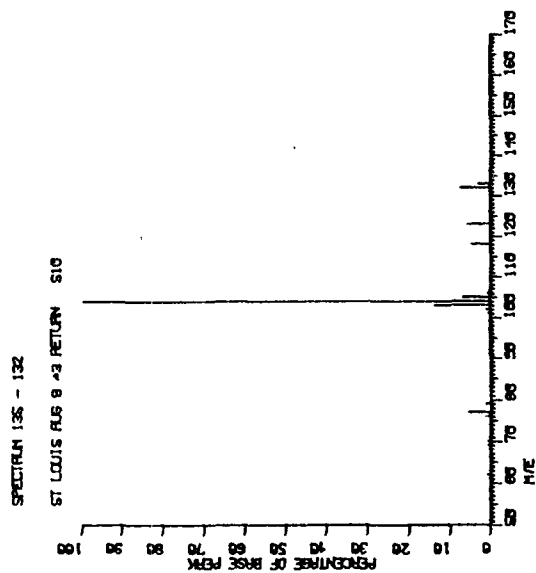
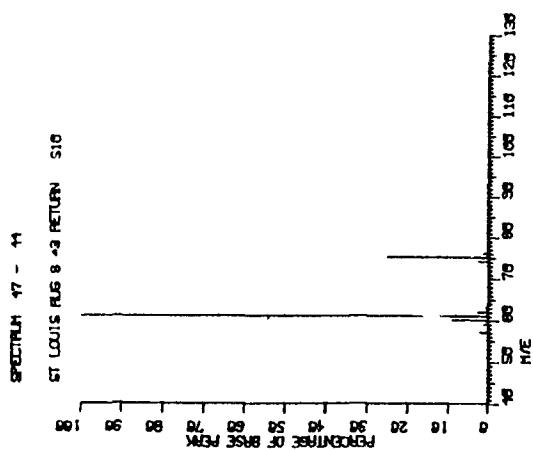
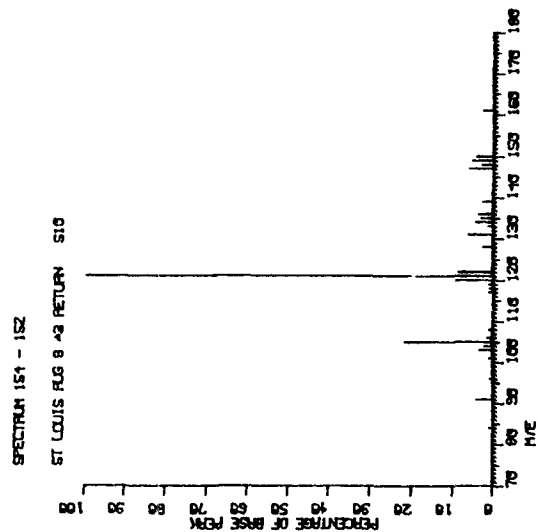
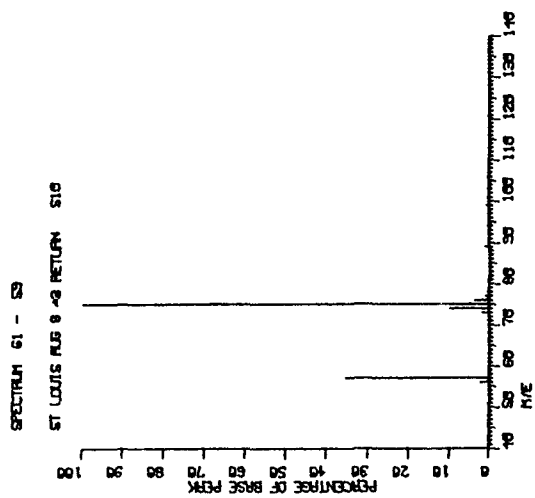
APPENDIX E

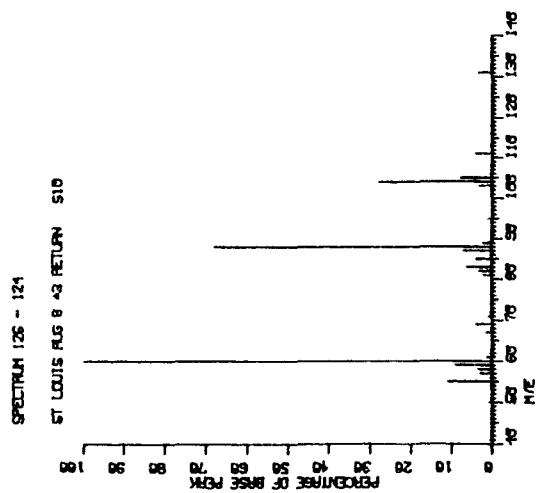
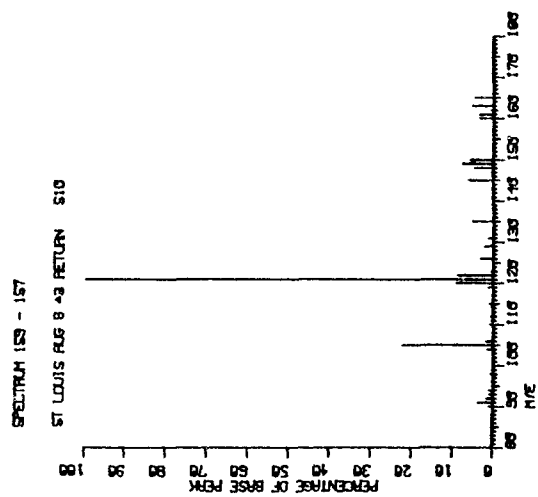
METHANE IONIZATION MASS SPECTRA OF
AMBIENT ST. LOUIS ORGANIC VAPORS
UNIQUE TO SAMPLES S8, S9, AND S10





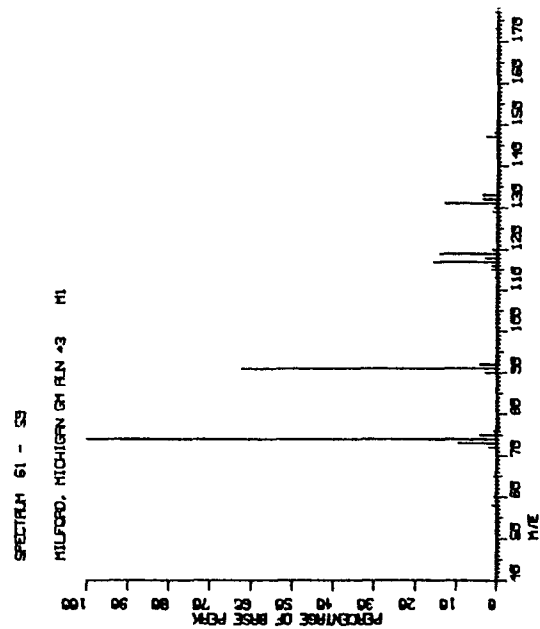
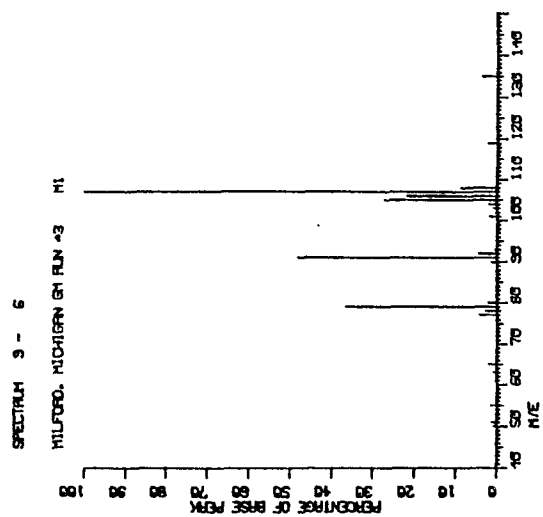
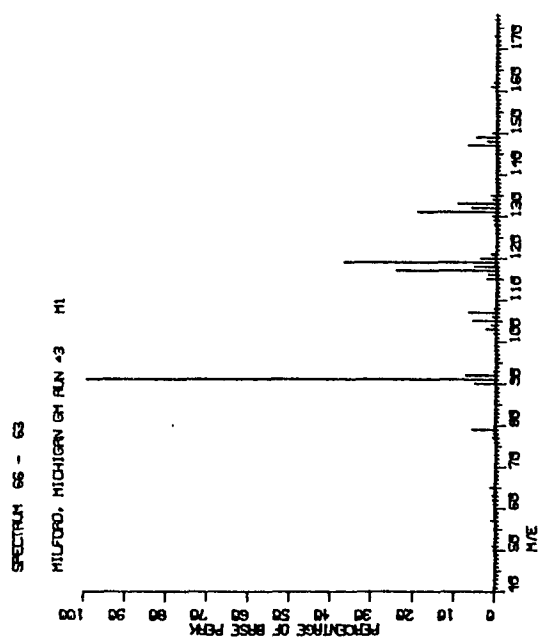
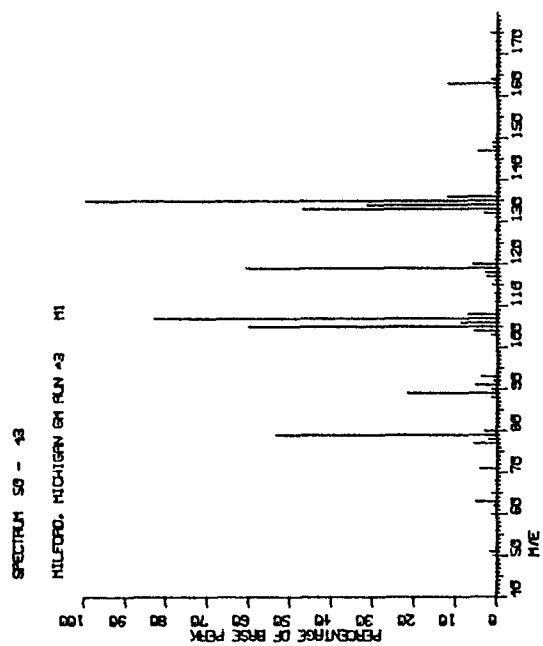


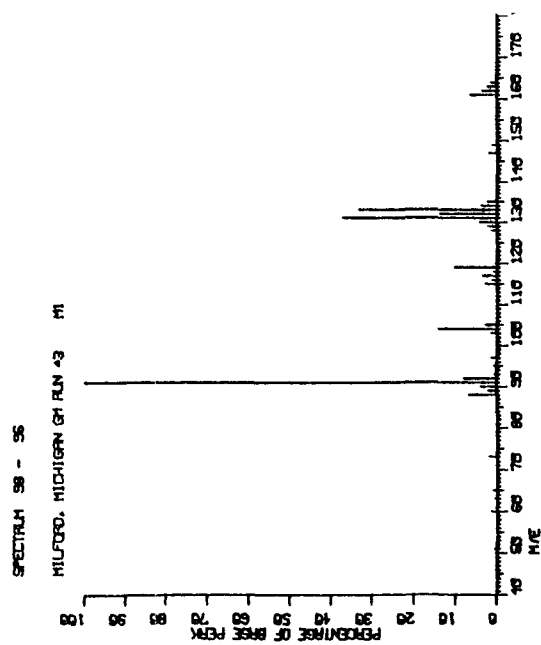
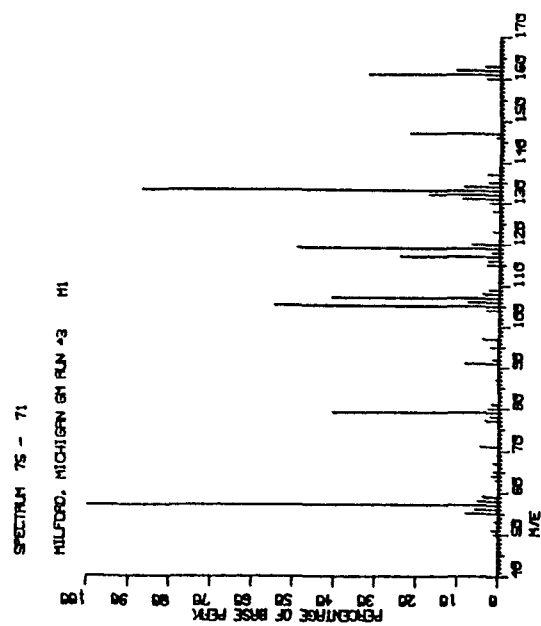
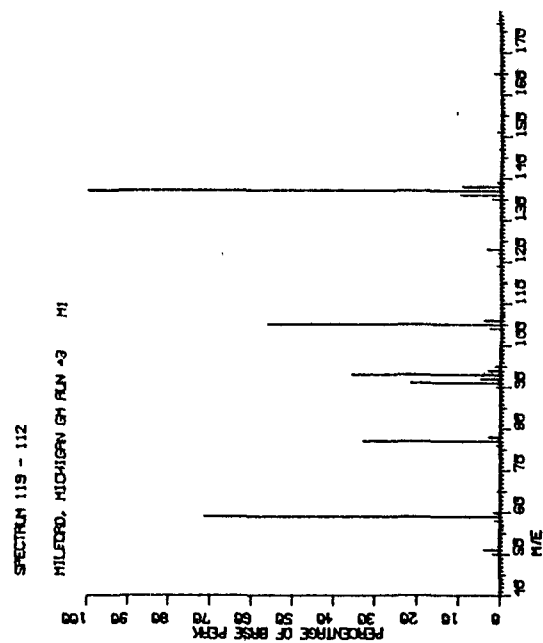
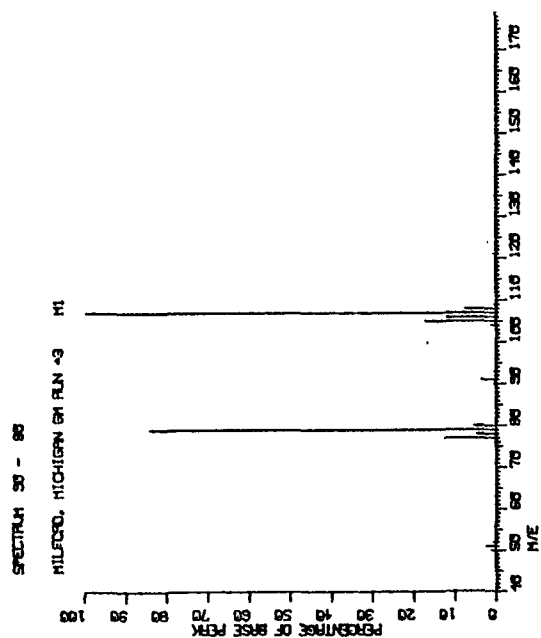




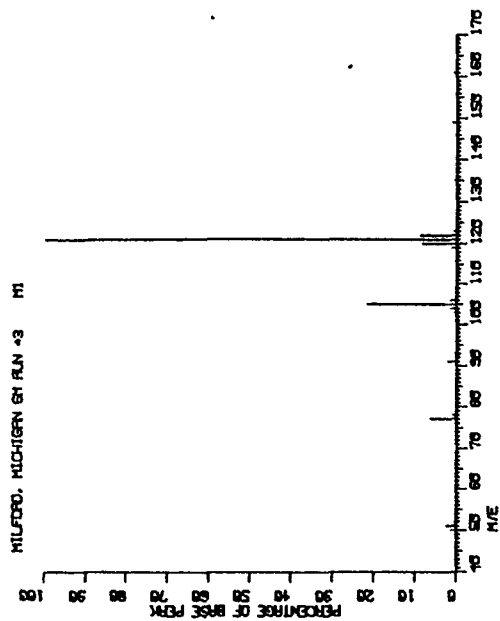
APPENDIX F

CHEMICAL IONIZATION MASS SPECTRA FOR
COMPOUNDS TENTATIVELY IDENTIFIED ON THE
GC-MS ANALYSIS (FIGURE 11) OF AMBIENT ORGANIC
VAPORS ADJACENT TO THE MILFORD, MICHIGAN,
GM TEST TRACK

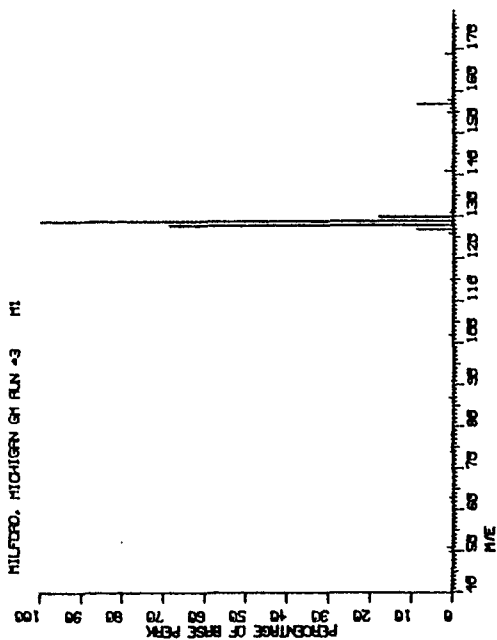




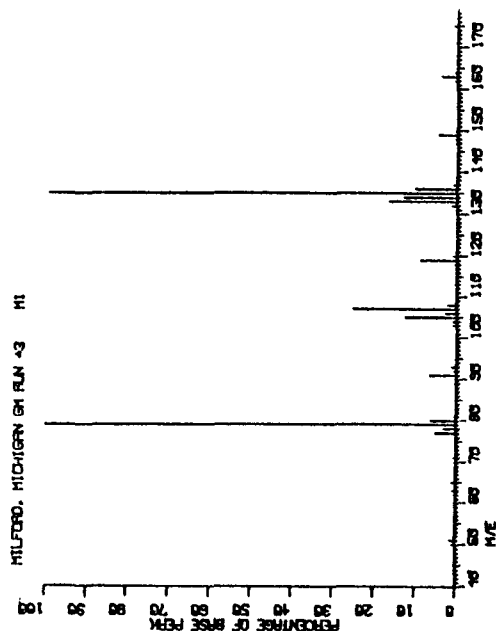
SPECTRUM 128 - 122



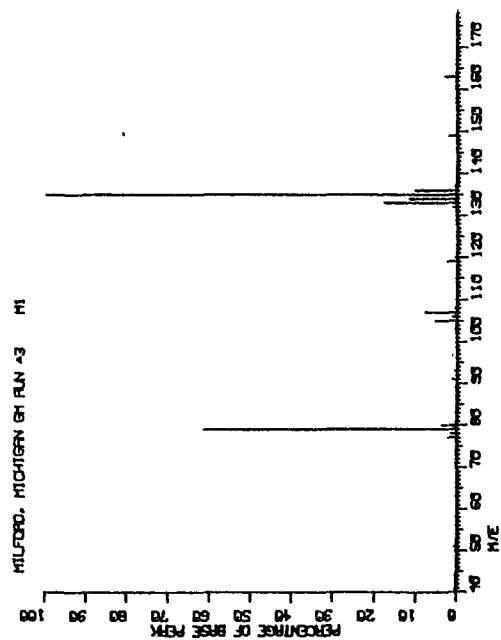
SPECTRUM 129 - 119

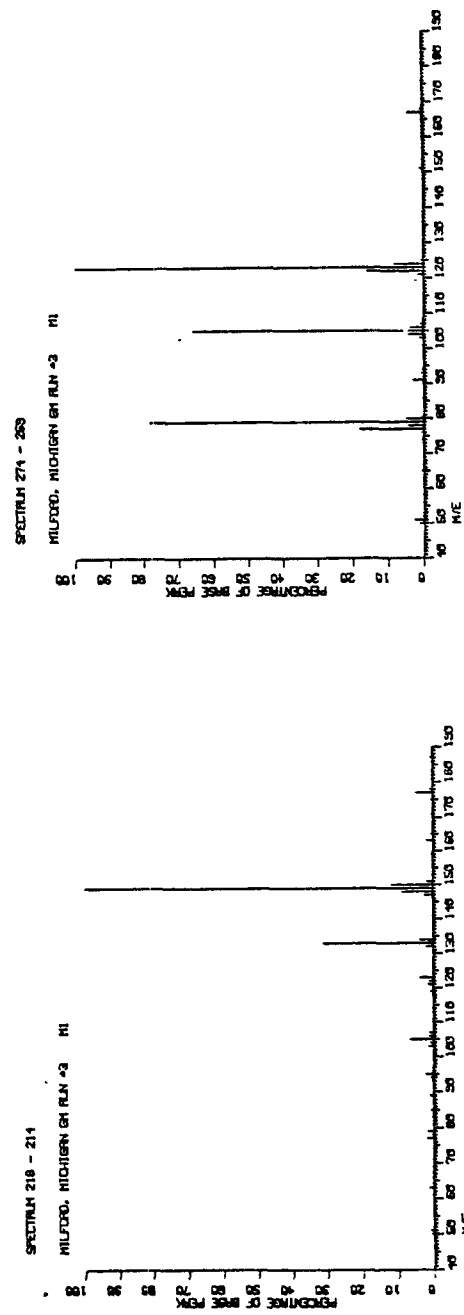
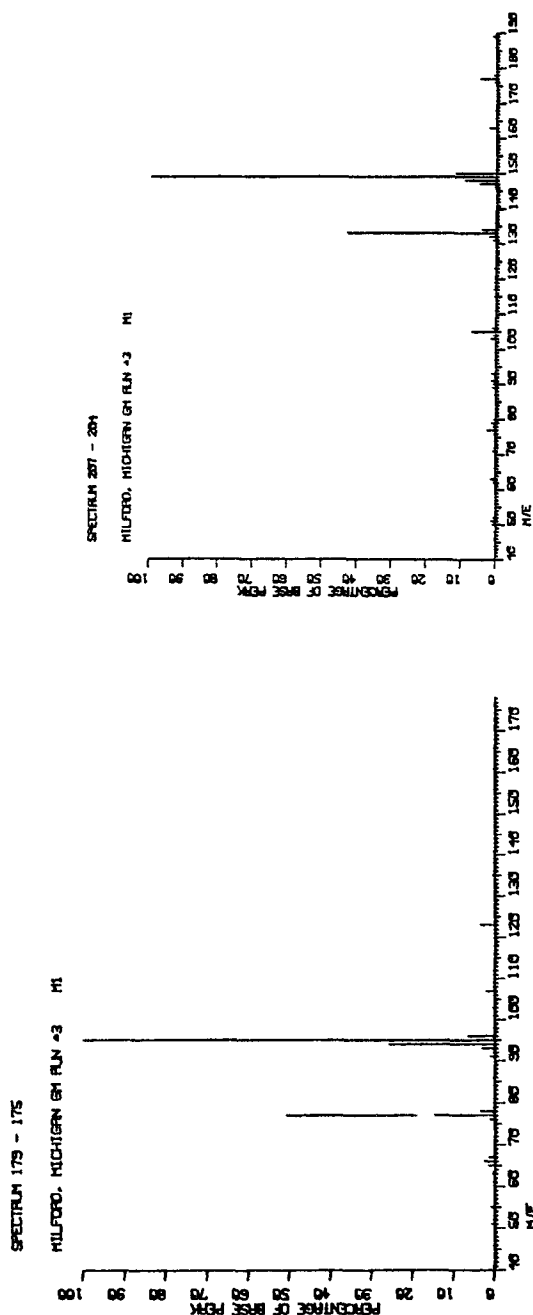


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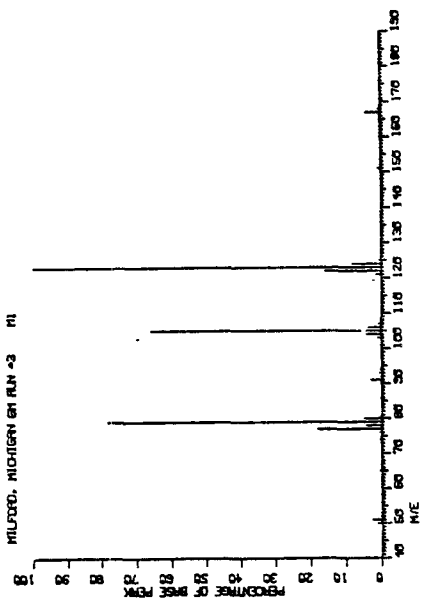


SPECTRUM 171 - 169



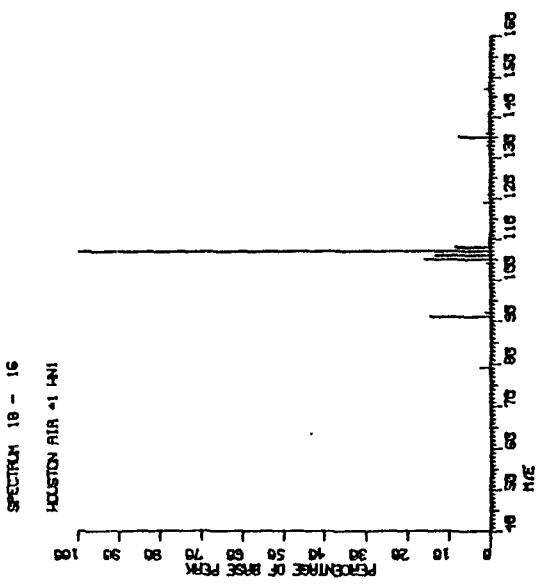
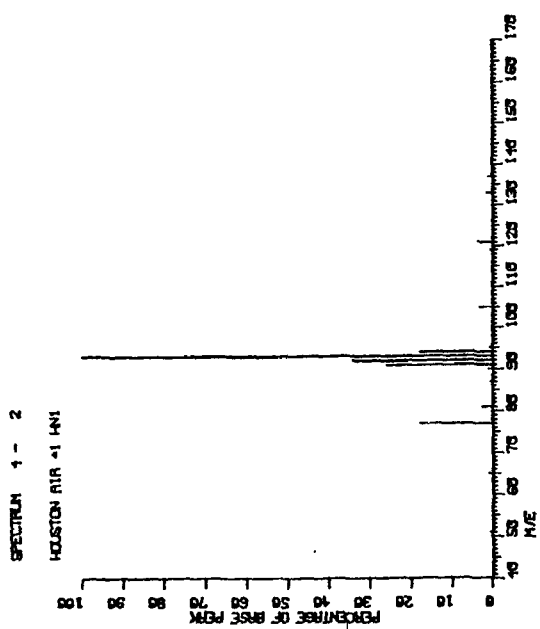
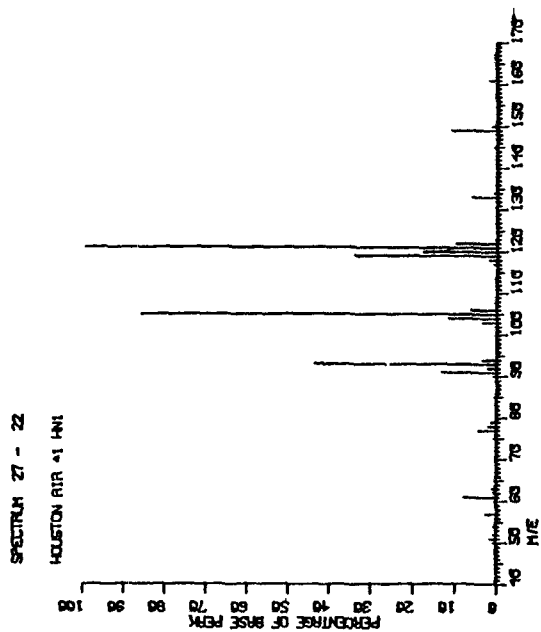
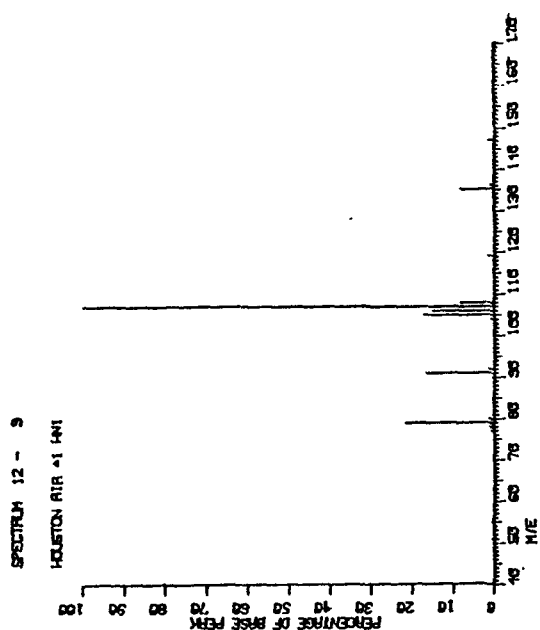


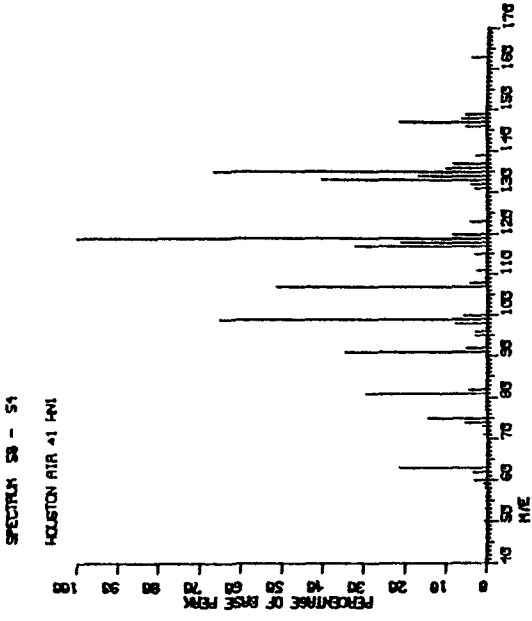
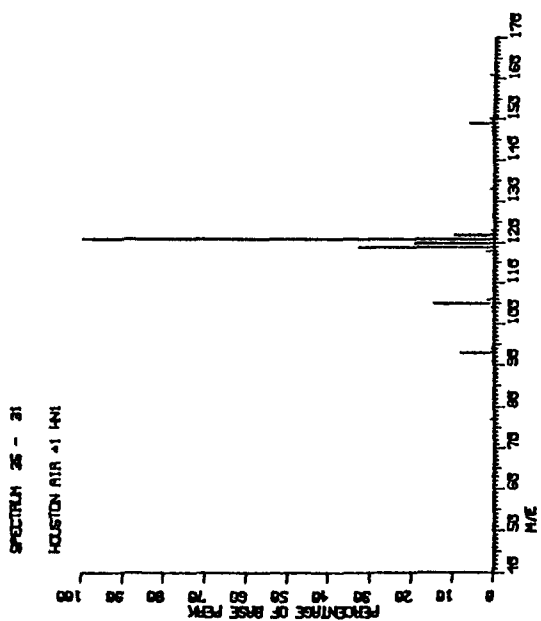
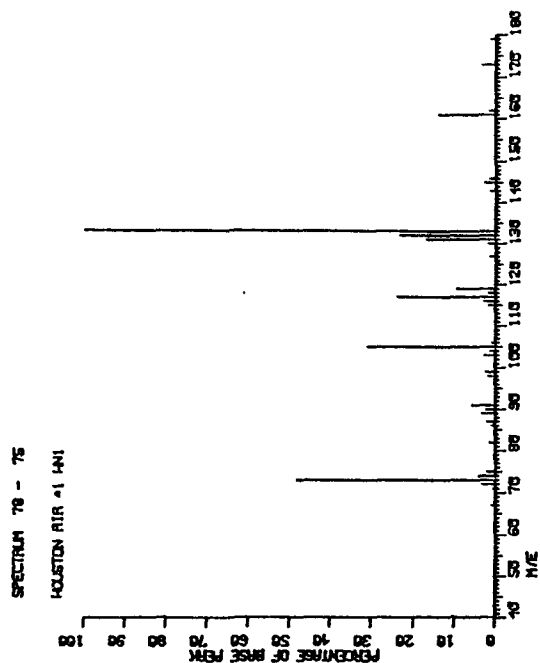
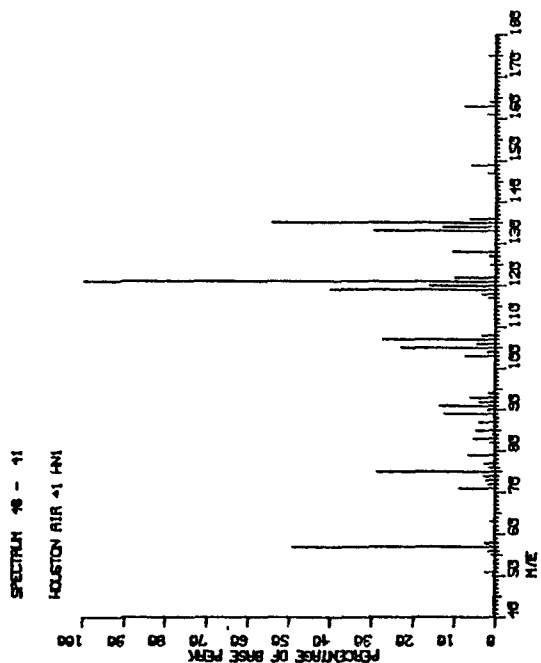
SPECTRUM 271 - 269
MILFORD, MICHIGEN GR RUN #3 MI

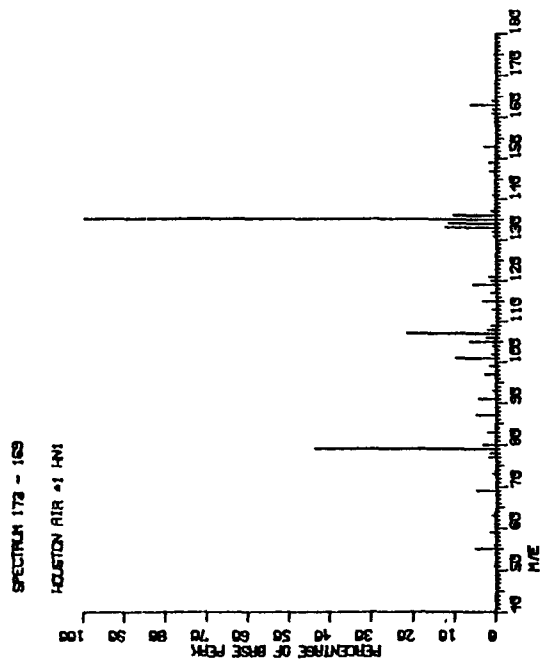
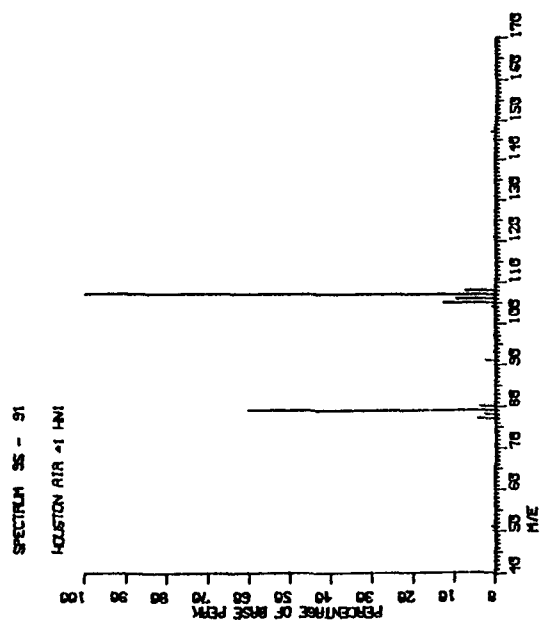
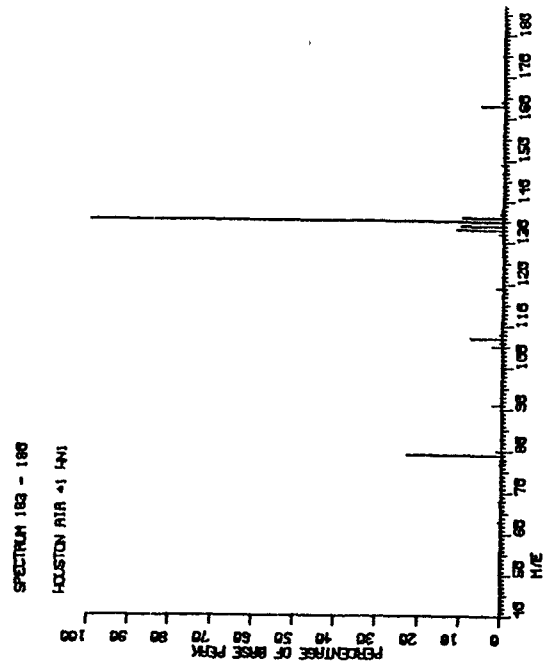
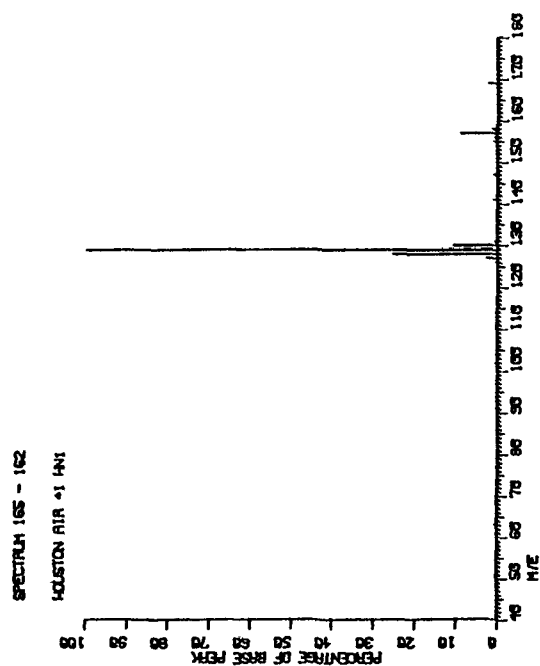


APPENDIX G

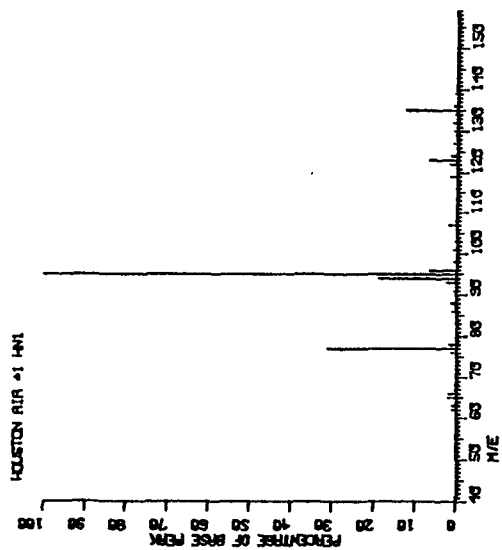
METHANE IONIZATION MASS SPECTRA OF
AMBIENT HOUSTON ORGANIC VAPORS,
CORRESPONDING TO GC-MS
ANALYSIS OF SAMPLES HN1 (FIGURE 12)



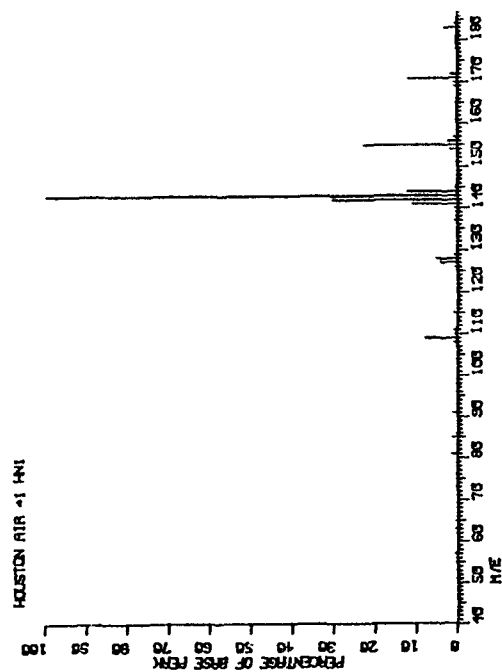




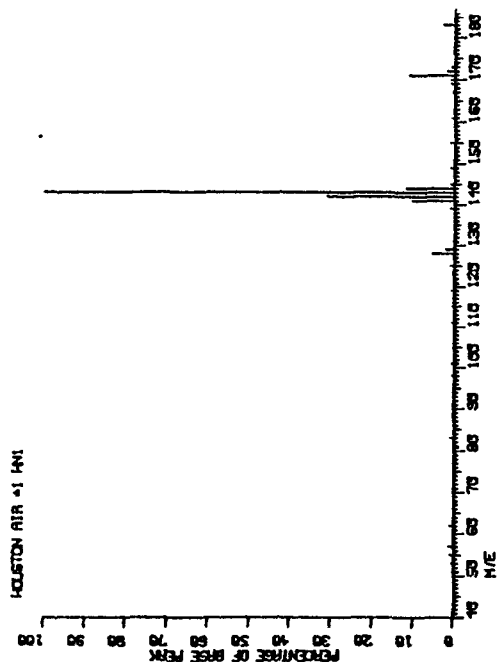
SPECTRUM 191 - 192



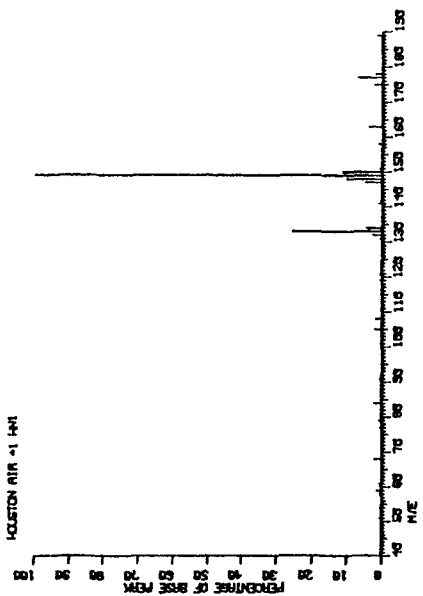
SPECTRUM 203 - 209

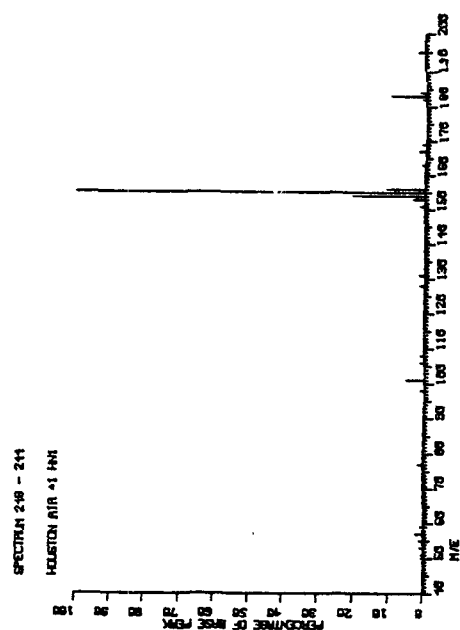
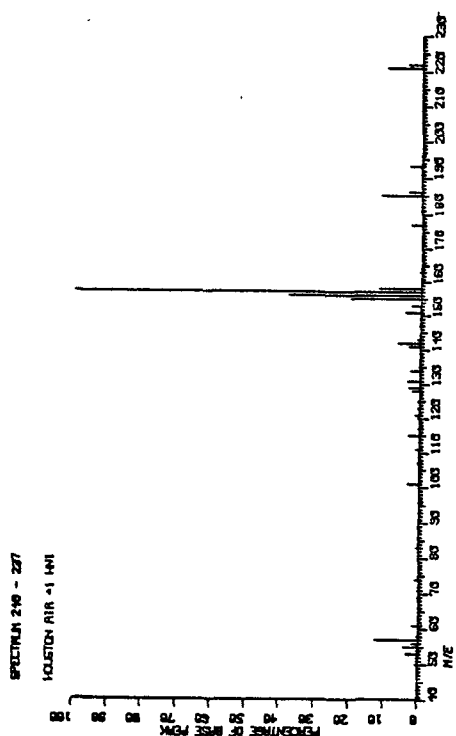
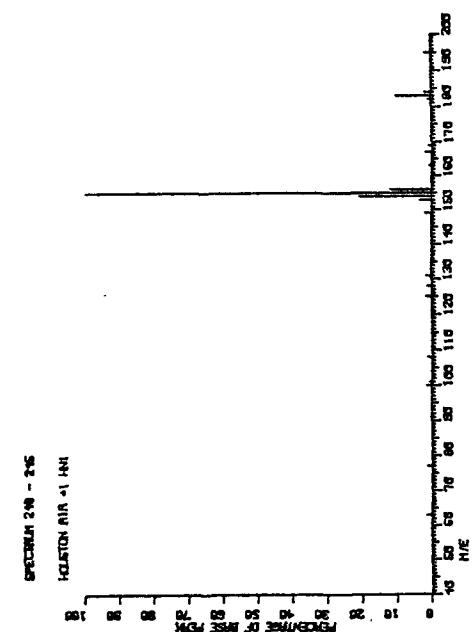


SPECTRUM 215 - 212



SPECTRUM 219 - 217





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4. TITLE AND SUBTITLE ORGANIC CHARACTERIZATION OF AEROSOLS AND VAPOR PHASE COMPOUNDS IN URBAN ATMOSPHERES	5. REPORT DATE March 1978	6. PERFORMING ORGANIZATION CODE
	8. PERFORMING ORGANIZATION REPORT NO.	
7. AUTHOR(S) G.D. Mendenhall, P.W. Jones, P.E. Strup and W.L. Margard	10. PROGRAM ELEMENT NO. 1AD712 BD-21 (FY-77)	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Battelle Columbus Laboratories 505 King Avenue Columbus, Ohio 43201	11. CONTRACT/GRANT NO. 68-02-1409	
	13. TYPE OF REPORT AND PERIOD COVERED Final	
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Sciences Research Laboratory - RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711	14. SPONSORING AGENCY CODE EPA/600/09	
	15. SUPPLEMENTARY NOTES	
16. ABSTRACT Organic pollutants in urban atmospheres were characterized by analyzing particulate and/or vapor-phase samples collected by EPA in St. Louis, Missouri; Miami, Florida; Denver, Colorado; Houston, Texas; and at the General Motors Test Track in Milford, Michigan. The particulate samples were extracted with solvents and the extractable materials analyzed by elemental combustion analysis and infrared spectroscopic analysis. To evaluate more than one solvent extraction technique, the particulate samples were aliquoted and analyzed by several extraction procedures. Some of the problems encountered with these procedures are discussed. Vapor-phase samples were collected on Chromosorb 102 chromatographic traps and analyzed using qualitative gas chromatography-mass spectrometry analysis. Individual species tentatively identified are shown on reconstructed gas chromatograms and individual mass spectra for all chromatographic peaks are included in the appendix. Ames Tests for mutagenicity on model aerosol products were also conducted. Products tested were from toluene/NO _x , 1-heptene/NO _x , and α-pinene/NO _x systems. None of the aerosol products from these systems showed mutagenic properties.		
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*Air pollution *Aerosols *Vapors *Organic compounds *Chemical analysis		13B 07D 07C
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