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Informal Report

CARBONACEOUS AEROSOL PARTICLES FROM COMMON VEGETATION IN THE GRAND CANYON

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MASTER

Abstract

The problem of visibility reduction in the Grand Canyon due to fine organic aerosol particles in the atmosphere has become an area of increased environmental concern. Aerosol particles can be derived from many emission sources. In this report, we focus on identifying organic aerosols derived from common vegetation in the Grand Canyon. These aerosols are expected to be significant contributors to the total atmospheric organic aerosol content.

Aerosol samples from living vegetation were collected by resuspension of surface wax and resin components liberated from the leaves of vegetation common to areas of the Grand Canyon. The samples were analyzed using high-resolution gas chromatography/mass spectrometry (GC/MS). Probable identification of compounds was made by comparison of sample spectra with National Institute of Standards and Technology (NIST) mass spectral references and positive identification of compounds was made when possible by comparison with authentic standards as well as NIST references. Using these references, we have been able to positively identify the presence of n-alkane and n-alkanoic acid homolog series in the surface waxes of the vegetation sampled. Several monoterpenes, sesquiterpenes, and diterpenes were identified also as possible biogenic aerosols which may contribute to the total organic aerosol abundance leading to visibility reduction in the Grand Canyon.

Carbonaceous Aerosol Particles from Common Vegetation in the Grand Canyon

Introduction

Aerosol particles in desert regions has become an area of increasing environmental research. One desert region which has been affected by the presence of aerosol particles is the Grand Canyon. The scenic view of the canyon is at times obscured greatly due to the haze produced by the presence of fine particulate matter suspended in the troposphere. The visibility reduction results from the ability of these particles to both scatter and absorb solar radiation. [1]

Aerosol particles are released into the atmosphere by many sources both natural and anthropogenic. Recent studies have shown that carbonaceous aerosol is the largest contributor to the total fine particulate mass at many desert sites. [2-6] In this report, we focus on identifying carbonaceous aerosols from live vegetation sampled at Hopi Point, AZ (southern rim of the Grand Canyon). These fine particle aerosols (size $< 2.0\ \mu m$) are derived from epicuticular plant waxes, resinous exudates, and the lipid fraction of airborne microorganisms. [7] Samples of dead vegetation were also collected at Hopi Point as well as live and dead vegetation from Indian Gardens, AZ. However, extensive data reduction has not been performed for these samples as of yet.

Experimental Section

Sample Collection. A grab sampling technique was used to collect samples of live vegetation common to Hopi Point, AZ. These samples included vegetation from the Ponderosa Pine Forest and Pinyon-Juniper Woodlands on the southern rim of the Grand Canyon. Elevational belts, called life zones, have been established in which the dominant vegetation of the area reflects ecosystem ecology as a function of elevation. The Pinyon-Juniper Woodland is part of the Upper Sonoran Zone having an elevation of approximately

3500 to 7000 feet and the Ponderosa Pine Forest is part of the Transition Zone having an elevation of approximately 7000 to 8250 feet. [8] Figure 1 gives a pictorial summary of the life zones and plant communities of the Grand Canyon and Table 1 represents the vegetation collected for sampling.

To simulate the abrasion of leaf surfaces by wind, the leaves of the vegetation collected were placed in a clean Teflon bag and agitated to liberate and suspend surface waxes and resins. The contents of the Teflon bag was withdrawn through 2 μm size cut cyclone separators and collected on quartz fiber filters. (9)

Each filter was spiked with a known amount of perdeuterated tetracosane (n-$C_{24}D_{50}$) to serve as an internal recovery standard in GC/MS analysis. (10-12) Samples were extracted from the quartz fiber filters by the addition of three 15 ml portions of hexane, followed by three 15 ml portions of a 2:1 mixture of benzene/isopropanol.(13) Details of the extraction procedure and volume reduction procedure have been outlined in an earlier report (13). Once sample volume reduction was completed, the concentrated extract was divided into two aliquots. One aliquot was reacted with diazomethane to convert organic acids to their methyl esters and acidic hydroxy compounds to their methoxy analogues.(13)

GC/MS Analysis. Samples were analyzed using a Varian 4600 high-resolution gas chromatograph (HRGC). A Grob injector was used and the injector temperature was kept at 300°C. A 30 meter fused silica column was employed for compound separation. The gas chromatograph was connected to a flame ionization detector, which operated at a detector sensitivity of 10^{-12} m volts/amp (at attenuation = 1).. Mass spectrometric analysis was performed using a Finnigan 4000 quadrupole gas chromatograph/mass spectrometer interfaced with an INCOS data aquisition system. Ionization was produced by electon impact with an electron energy of 70eV. The scanning frequency was set at 0.5 sec^{-1}, ranging from 50 to 550 Daltons.(13) 1-phenyldodecane was used as a coinjection standard.

Results and Discussion

Compounds were identified by comparison of their mass fragmentation patterns to the NIST mass spectral reference library contained in the Finnigan INCOS data system. Additional searching was performed using the IBM-AT, version 3, 1990, NIST library.

When standards were available, compound identification was confirmed by comparison of mass fragmentation patterns and retention times of the sample with authentic standards analyzed using the same GC/MS system.(13)

The following key was used to denote the accuracy of compound identification: (a) positive, when the sample spectrum, standard spectrum, and NIST library spectrum were identical and also the retention time of the authentic standard and the sample were comparable; (b) probable, same as above except no authentic standard was available, but the NIST library spectrum agreed well with the sample spectrum; (c) possible, same as above, except that the sample mass fragmentation pattern contained additional ions from other compounds having minor peak coelution; (d) tentative, when the sample spectrum revealed additional mass fragments from one or more coeluting compounds with substantial overlap.

Figure 2 shows a typical gas chromatograph for vegetation samples. This chromatograph is for the live vegetation component collected as fine aerosol at Hopi Point, AZ. Compound identification for this sample is listed in Table 2.

Members of the n-alkane homolog series, n-C_{16} to n-C_{36}, have been identified in this sample with C_{23} to C_{36} being the most prevalent range. The n-alkanes exibit very similar mass fragmentation patterns. The key fragment ions displayed in the mass spectra of n-alkanes include masses 57, 71, 85, 99, 113, 129 etc.(7) Because the fragmentation patterns of n-alkanes are so similar, identification was based on the molecular ion and comparison of retention times with authentic standards. A typical mass fragmentation pattern for n-alkanes is shown in Figure 3.

High molecular weight n-alkanes (C_{12} to C_{40}) are produced by biosynthetic processes which occur in vegetation.(14-16) These n-alkanes are derived from epicuticular plant waxes.(17-22) The n-alkane homologs show strong odd carbon number predominance providing evidence that n-alkanes having an odd number of carbon atoms are more abundant in plant waxes.(13) A selected ion plot of mass m/z 57 for the isolation of n-alkane homologs is shown in Figure 4. This figure clearly demonstrates the existance of odd carbon number predominance. Table 3 lists the n-alkane homologs identified in the selected ion plot.

Along with the n-alkanes, the n-alkanoic acids prove to be major contributors to the organic aerosol content from the vegetation sampled. With the exception of C_{29}, the n-alkanoic acids, C_6 to C_{30}, have been identified successfully in the Hopi Point, live vegetation sample. The n-fatty acids are derived from epicuticular plant waxes and microbial lipid deposits on leaf surfaces.(7,15,23-33) The n-alkanes have a characteristic fragment of mass 74.(7) Figure 5 shows a selected ion plot of mass m/z 74 and Table 4 lists the n-alkanoic acid homologs identified in the selected ion plot. Unlike the n-alkanes, the n-alkanoic acids display strong even carbon number predominance.(27,32,34)

1-Octacosanol and the n-alkan-2-ones are derived from the same sources as the n-alkanes and n-alkanoic acids. The n-alkan-2-ones were classified as such due to their fragmention patterns, however, compound names could not be specified.

Several monoterpenoids (C_{10}), sesquiterpenoids (C_{15}), and diterpenoids (C_{20}) have been tentatively identified as aerosols derived from the vegetation sampled. These compounds are constituents of resins from the conifer vegetation.(35) Although the identification of these compounds is only tentative, they are logical possibilities due to the type of vegetation sampled, i.e. Ponderosa pine, pinyon, and juniper. Several unknown sesquiterpenoids and diterpenoids have been classified as such due to their fragmentation patterns and molecular formulas.

The phthalate esters and organosilanes detected are sample contaminants derived from the silicone greases, plastics, and rubber components which are contributed from the sampling equipment and analytical procedures. (7) Several aromatic hydrocarbons (e.g. 1,1'-biphenyl) are also contaminants and originate from the organic extraction solvents.

Conclusions

The n-alkanes and n-alkanoic acid series appear to be prominent contributors to the total organic aerosol particulate matter traceable to plant waxes and resins. Identification of terpenoids emitted directly into the environment by vegetation provides insight into the possible terpenoid chemical compounds which undergo photochemical reactions in the atmosphere.

Although the concentrations of these aerosols have not yet been determined, the identification of the aerosols produced by vegetation is an important first step towards understanding the organic aerosol composition which contributes to visibility reduction in the Grand Canyon. Knowing the types of organic compounds present as aerosols and their origins helps in determining a natural background for the total organic aerosol content.

Acknowledgements

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Table 1. Dominant Vegetation Collected at Hopi Point, AZ.

Life Zone	Community	Vegetation Common Name	Vegetation Scientific Name	Plant Family
Transition	Ponderosa Pine Forest	Native grass		
Transition	Ponderosa Pine Forest	Ponderosa Pine	Pinus ponderosa	Pinaceae
Transition Upper Sonoran	Ponderosa Pine Forest Pinyon-Juniper Woodland	Sagebrush	Artemisia tridentata	Compositae
Upper Sonoran	Pinyon-Juniper Woodland	Utah Juniper	Juniperus osteosperma	Cupressaceae
Upper Sonoran	Pinyon-Juniper Woodland	Banana Yucca	Yucca baccata	Liliaceae
Upper Sonoran	Pinyon-Juniper Woodland	Pinyon	Pinus edulis	Pinaceae

Table 2.

GC/MS Injection F7217 -- Live Vegetation, Hopi Point, Fine Aerosol

Peak Number	File.Scan Number	Compound Name	Formula	Compound Identification*
Standard Compounds				
31	F7217.0735	1-Phenyldodecane	$C_{18}H_{30}$	a
42	F7217.0851	Perdeutero tetracosane	$C_{24}D_{50}$	a
n-Alkanes				
	F7217.	n-Decane	$C_{10}H_{22}$	nd
	F7217.	n-Dodecane	$C_{12}H_{26}$	nd
	F7217.	n-Tridecane	$C_{13}H_{28}$	nd
	F7217.	n-Tetradecane	$C_{14}H_{30}$	nd
	F7217.	n-Pentadecane	$C_{15}H_{32}$	nd
	F7217.0618	n-Hexadecane	$C_{16}H_{34}$	a
	F7217.	n-Heptadecane	$C_{17}H_{36}$	nd
	F7217.	n-Octadecane	$C_{18}H_{38}$	nd
30	F7217.0721	n-Nonadecane	$C_{19}H_{40}$	b
33	F7217.0750	n-Cosane	$C_{20}H_{42}$	a
	F7217.	n-Heneicosane	$C_{21}H_{44}$	nd
	F7217.	n-Docosane	$C_{22}H_{46}$	nd
40	F7217.0836	n-Tricosane	$C_{23}H_{48}$	b
	F7217.	n-Tetracosane	$C_{24}H_{50}$	nd
45	F7217.0887	n-Pentacosane	$C_{25}H_{52}$	b
	F7217.	n-Hexacosane	$C_{26}H_{54}$	nd
49	F7217.0934	n-Heptacosane	$C_{27}H_{56}$	b
	F7217.	n-Octacosane	$C_{28}H_{58}$	nd
53	F7217.0987	n-Nonacosane	$C_{29}H_{60}$	b
55	F7217.1020	n-Triacontane	$C_{30}H_{62}$	a
57	F7217.1062	n-Heneitriacontane	$C_{31}H_{64}$	b
	F7217.	n-Dotriacontane	$C_{32}H_{66}$	nd
62	F7217.1172	n-Tritriacontane	$C_{33}H_{68}$	b
63	F7217.1247	n-Tetratriacontane	$C_{34}H_{70}$	a
66	F7217.1358	n-Pentatriacontane	$C_{35}H_{72}$	b
67	F7217.1454	n-Hexatriacontane	$C_{36}H_{74}$	a

Table 2 (continued)

GC/MS Injection F7217 -- Live Vegetation, Hopi Point, Fine Aerosol

Peak Number	File.Scan Number	Compound Name	Formula	Compound identification*
n-Alkanoic Acids (as methyl esters)				
1	F7217.0161	n-Hexanoic acid methyl ester	$C_7H_{14}O_2$ (C6 FA)	a
3	F7217.0281	n-Heptanoic acid methyl ester	$C_8H_{16}O_2$ (C7 FA)	b
5	F7217.0405	n-Octanoic acid methyl ester	$C_9H_{18}O_2$ (C8 FA)	a
10	F7217.0476	n-Nonanoic acid methyl ester	$C_{10}H_{20}O_2$ (C9 FA)	a
13	F7217.0530	n-Decanoic acid methyl ester	$C_{11}H_{22}O_2$ (C10 FA)	a
15	F7217.0575	n-Undecanoic acid methyl ester	$C_{12}H_{24}O_2$ (C11 FA)	a
19	F7217.0616	n-Dodecanoic acid methyl ester	$C_{13}H_{26}O_2$ (C12 FA)	a
22	F7217.0653	n-Tridecanoic acid methyl ester	$C_{14}H_{28}O_2$ (C13 FA)	a
28	F7217.0688	n-Tetradecanoic acid methyl ester	$C_{15}H_{30}O_2$ (C14 FA)	a
30	F7217.0721	n-Pentadecanoic acid methyl ester	$C_{16}H_{32}O_2$ (C15 FA)	a
34	F7217.0752	n-Hexadecanoic acid methyl ester	$C_{17}H_{34}O_2$ (C16 FA)	a
	F7217.0782	n-Heptadecanoic acid methyl ester	$C_{18}H_{36}O_2$ (C17 FA)	a
39	F7217.0811	n-Octadecanoic acid methyl ester	$C_{19}H_{38}O_2$ (C18 FA)	a
41	F7217.0839	n-Nonadecanoic acid methyl ester	$C_{20}H_{40}O_2$ (C19 FA)	a
44	F7217.0864	n-Eicosanoic acid methyl ester	$C_{21}H_{42}O_2$ (C20 FA)	a
	F7217.0889	n-Heneicosanoic acid methyl ester	$C_{22}H_{44}O_2$ (C21 FA)	a
	F7217.0913	n-Docosanoic acid methyl ester	$C_{23}H_{46}O_2$ (C22 FA)	a
	F7217.0937	n-Tricosanoic acid methyl ester	$C_{24}H_{48}O_2$ (C23 FA)	a
52	F7217.0963	n-Tetradocosanoic acid methyl ester	$C_{25}H_{50}O_2$ (C24 FA)	a
	F7217.0993	n-Pentadocosanoic acid methyl ester	$C_{26}H_{52}O_2$ (C25 FA)	a
56	F7217.1028	n-Hexacosanoic acid methyl ester	$C_{27}H_{54}O_2$ (C26 FA)	a
	F7217.1071	n-Heptacosanoic acid methyl ester	$C_{28}H_{56}O_2$ (C27 FA)	a
59	F7217.1123	n-Octacosanoic acid methyl ester	$C_{29}H_{58}O_2$ (C28 FA)	a
	F7217.	n-Nonacosanoic acid methyl ester	$C_{30}H_{60}O_2$ (C29 FA)	nd
64	F7217.1268	n-Triacontanoic acid methyl ester	$C_{31}H_{62}O_2$ (C30 FA)	a

Table 2 (continued)

GC/MS Injection F7217 -- Live Vegetation, Hopi Point, Fine Aerosol

Peak Number	File.Scan Number	Compound Name	Formula	Compound Identification*
n-Alkanols				
58	F7217.1113	1-Octacosanol	$C_{28}H_{58}O$	a
n-Alkan-2-ones				
20	F7217.0630	nd	nd	d
61	F7217.1138	nd	nd	d
65	F7217.1292	nd	nd	d
Monoterpenoids (C10 compounds)				
4	F7217.0368	Linalool oxide	$C_{10}H_{18}O_2$	d
7	F7217.0450	Camphor	$C_{10}H_{16}O$	d
8	F7217.0458	4-Terpineol	$C_{10}H_{18}O$	d
9	F7217.0471	Borneol	$C_{10}H_{18}O$	d
11	F7217.0480	α-Terpineol	$C_{10}H_{18}O$	d
12	F7217.0516	Bornyl acetate	$C_{12}H_{20}O_2$	d
16	F7217.0585	Monoterpenoid acid	$C_{12}H_{24}O_3$	d
29	F7217.703	Camphorsulfonic acid	$C_{10}H_{16}O_4S$	d
Sesquiterpenoids (C15 compounds)				
17	F7217.0603	δ-Cadinene	$C_{15}H_{24}$	d
18	F7217.0612	Calamenene	$C_{15}H_{22}$	d
21	F7217.0641	Nerolidol or Farnesol	$C_{15}H_{26}O$	d
23	F7217.0660	Sesquiterpenol	$C_{15}H_{24}O$	d
24	F7217.0666	Ylangene or thujopsene	$C_{15}H_{24}$	d
25	F7217.0670	Sesquiterpenol	$C_{15}H_{24}O$	d
26	F7217.0676	Cadinol	$C_{15}H_{26}O$	d
27	F7217.0679	Cedreanol	$C_{15}H_{26}O$	d
32	F7217.0741	Sesquiterpenol	$C_{15}H_{26}O$	d

Table 2 (continued)

GC/MS Injection F7217 -- Live Vegetation, Hopi Point, Fine Aerosol

Peak Number	File.Scan Number	Compound Name	Formula	Compound Identification*
35	F7217.0756	Sesquiterpenol	$C_{15}H_{22}O$	d
36	F7217.0771	Sesquiterpenol	$C_{15}H_{26}O$	d
<u>Diterpenoids (C20 compounds)</u>				
37	F7217.0779	Manoyl oxide or epimanoyl oxide	$C_{20}H_{34}O$	d
54	F7217.1004	Diterpenoid	nd	d
<u>Aromatic Hydrocarbons</u>				
2	F7217.0168	Methoxybenzene	$C_{7}H_{8}O$	c
6	F7217.0431	Phenol	$C_{6}H_{6}O$	b
14	F7217.0572	1,1'-Biphenyl	$C_{12}H_{10}$	b
<u>Contaminants -- Phthalate Esters</u>				
38	F7217.0799	1,2-Benzenedicarboxylic acid, butyl 2-methylpropyl ester	$C_{16}H_{22}O_{4}$	b
48	F7217.0916	Benzyl butyl phthalate	$C_{19}H_{20}O_{4}$	b
50	F7217.0943	1,2-Benzenedicarboxylic acid, diisooctyl ester	$C_{24}H_{38}O_{4}$	b
<u>Contaminants -- Organosilanes</u>				
43	F7217.0856	Organosilane	nd	d
47	F7217.0909	Organosilane	nd	d
51	F7217.0960	Organosilane	nd	d
56	F7217.1028	Organosilane	nd	d
60	F7217.1128	Organosilane	nd	d

Table 2 (continued)

GC/MS Injection F7217 -- Live Vegetation, Hopi Point, Fine Aerosol

Peak Number	File.Scan Number	Compound Name	Formula	Compound Identification*
Resin Components				
	F7217.0858	Retene	$C_{18}H_{18}$	a
	F7217.(ca 878)	Methyl l-pimarate	$C_{21}H_{32}O_2$	a
	F7217.0876	Methyl isopimarate	$C_{21}H_{32}O_2$	b
46	F7217.0890	Methyl dehydroabietate	$C_{21}H_{30}O_2$	a
	F7217.0891	Methyl 13-isopropyl-5a-podocarpa-	$C_{21}H_{28}O_2$	b
	F7217.(ca 893)	Methyl o-methylpodocarpate	$C_{19}H_{26}O_3$	a
	F7217.(ca 900)	Methyl abietate	$C_{21}H_{32}O_2$	b
	F7217.(ca 951)	Methyl 13-isopropyl-5a-podocarpa- isomer	$C_{21}H_{28}O_2$	c
	F7217.0982	Methyl 7-ketodehydroabietate	$C_{21}H_{28}O_3$	a

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* a = positive, when the sample spectrum, standard spectrum and NIST-library spectrum were identical and also the retention time of the authentic standard and the sample compound were comparable

b = probable, same as above, except no authentic standard was available, but the NIST-library spectrum agreed very well with the sample spectrum and retention time of the standard

c = possible, same as above, except that the sample mass fragmentation pattern contained additional ions from other compounds having minor peak coelution

d = tentative, when the sample spectrum revealed additional mass fragments from one or more coeluting compounds (noise) with substantial overlap

nd = not detected

Table 3.

GC/MS Injection F7217 -- Live Vegetation, Hopi Point, Fine Aerosol
Selected Ion Plot of Mass m/z 57 vs. Scan Time for Isolation of n-Alkane Homologs (n-C19 to -C36).

Peak Number	File.Scan Number	Compound Name	Formula
n-Alkanes			
1	F7217.0721	n-Nonadecane	$C_{19}H_{40}$
2	F7217.0750	n-Cosane	$C_{20}H_{42}$
3	F7217.0809	n-Heneicosane	$C_{21}H_{46}$
4	F7217.0836	n-Tricosane	$C_{23}H_{48}$
5	F7217.0862	n-Tetracosane	$C_{24}H_{50}$
6	F7217.0887	n-Pentacosane	$C_{25}H_{52}$
7	F7217.0911	n-Hexacosane	$C_{26}H_{54}$
8	F7217.0934	n-Heptacosane	$C_{27}H_{56}$
9	F7217.0958	n-Octacosane	$C_{28}H_{58}$
10	F7217.0987	n-Nonacosane	$C_{29}H_{60}$
11	F7217.1021	n-Triacontane	$C_{30}H_{62}$
12	F7217.1062	n-Heneitriacontane	$C_{31}H_{64}$
13	F7217.1172	n-Triatriacontane	$C_{33}H_{68}$
14	F7217.1247	n-Tetratriacontane	$C_{34}H_{70}$
15	F7217.1358	n-Pentatriacontane	$C_{35}H_{72}$
16	F7217.1454	n-Hexatriacontane	$C_{36}H_{74}$

Table 4.

GC/MS Injection F7217 -- Live Vegetation, Hopi Point, Fine Aerosol
Selected Ion Plot of Mass m/z 74 vs. Scan Time for Isolation of n-Alkanoic Acids (as methyl esters)

Peak Number	File.Scan Number	Compound Name	Formula
1	F7217.0161	n-Hexanoic acid methyl ester	$C_7H_{14}O_2$ (C6 FA)
2	F7217.0281	n-Heptanoic acid methyl ester	$C_8H_{16}O_2$ (C7 FA)
3	F7217.0405	n-Octanoic acid methyl ester	$C_9H_{18}O_2$ (C8 FA)
4	F7217.0476	n-Nonanoic acid methyl ester	$C_{10}H_{20}O_2$ (C9 FA)
5	F7217.0530	n-Decanoic acid methyl ester	$C_{11}H_{22}O_2$ (C10 FA)
6	F7217.0575	n-Undecanoic acid methyl ester	$C_{12}H_{24}O_2$ (C11 FA)
7	F7217.0616	n-Dodecanoic acid methyl ester	$C_{13}H_{26}O_2$ (C12 FA)
8	F7217.0653	n-Tridecanoic acid methyl ester	$C_{14}H_{28}O_2$ (C13 FA)
9	F7217.0688	n-Tetradecanoic acid methyl ester	$C_{15}H_{30}O_2$ (C14 FA)
10	F7217.0721	n-Pentadecanoic acid methyl ester	$C_{16}H_{32}O_2$ (C15 FA)
11	F7217.0752	n-Hexadecanoic acid methyl ester	$C_{17}H_{34}O_2$ (C16 FA)
12	F7217.0782	n-Heptadecanoic acid methyl ester	$C_{18}H_{36}O_2$ (C17 FA)
13	F7217.0811	n-Octadecanoic acid methyl ester	$C_{19}H_{38}O_2$ (C18 FA)
14	F7217.0839	n-Nonadecanoic acid methyl ester	$C_{20}H_{40}O_2$ (C19 FA)
15	F7217.0864	n-Eicosanoic acid methyl ester	$C_{21}H_{42}O_2$ (C20 FA)
16	F7217.0889	n-Heneicosanoic acid methyl ester	$C_{22}H_{44}O_2$ (C21 FA)
17	F7217.0909	n-Docosanoic acid methyl ester	$C_{23}H_{46}O_2$ (C22 FA)
18	F7217.0937	n-Tricosanoic acid methyl ester	$C_{24}H_{48}O_2$ (C23 FA)
19	F7217.0963	n-Tetradocosanoic acid methyl ester	$C_{25}H_{50}O_2$ (C24 FA)
20	F7217.0993	n-Pentadocosanoic acid methyl ester	$C_{26}H_{52}O_2$ (C25 FA)
21	F7217.1028	n-Hexacosanoic acid methyl ester	$C_{27}H_{54}O_2$ (C26 FA)
22	F7217.1071	n-Heptacosanoic acid methyl ester	$C_{28}H_{56}O_2$ (C27 FA)
23	F7217.1123	n-Octacosanoic acid methyl ester	$C_{29}H_{58}O_2$ (C28 FA)
24	F7217.1187	n-Nonacosanoic acid methyl ester	$C_{30}H_{60}O_2$ (C29 FA)
25	F7217.1266	n-Triacontanoic acid methyl ester	$C_{31}H_{62}O_2$ (C30 FA)

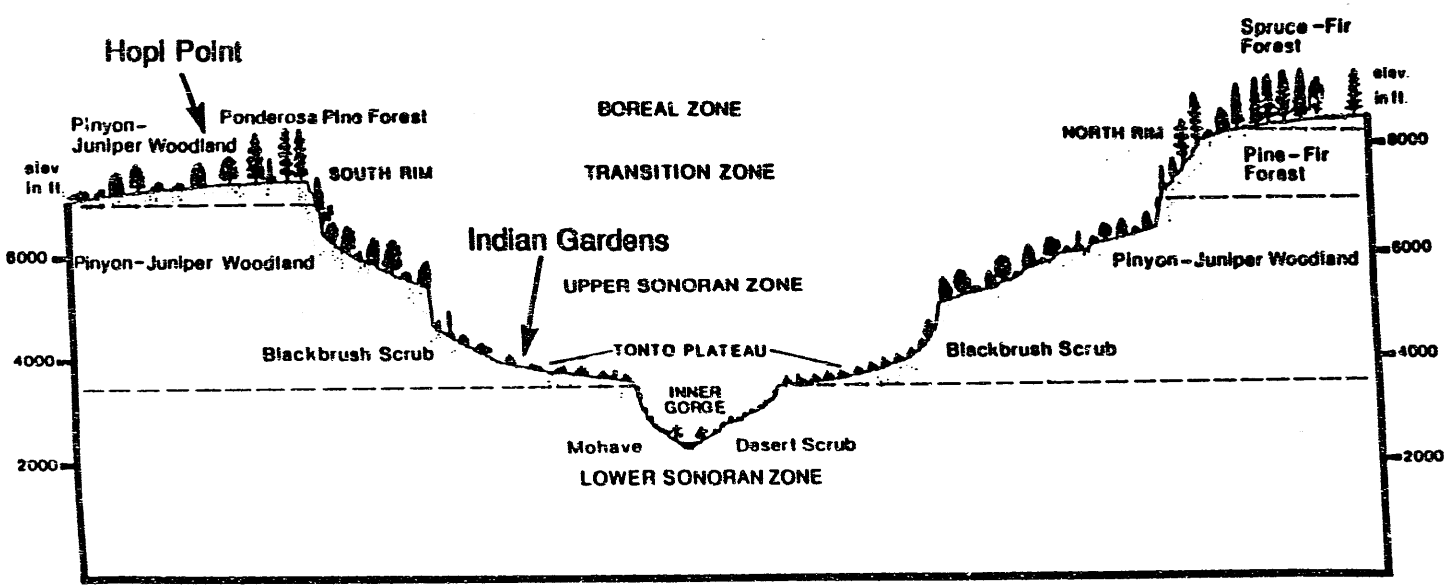

Figure 1. Life zones and plant communities of the Grand Canyon. Approximate location of sampling sites, Indian Gardens and Hopi Point, are indicated.

Source: S. Whitney, 1982. [8].

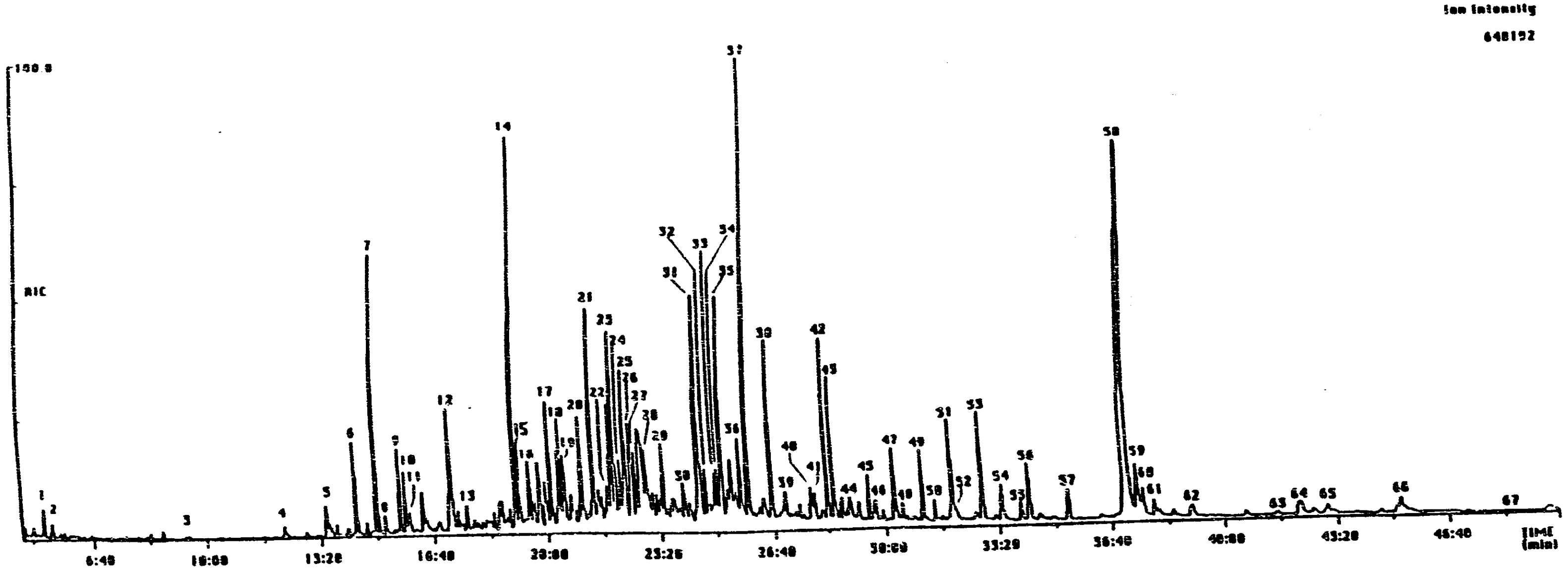

Figure 2. GC/MS plot of reconstructed ion current [RIC] vs. scan time for fine aerosol sample, F7217, derived from live vegetation common to Hopi Point, AZ.

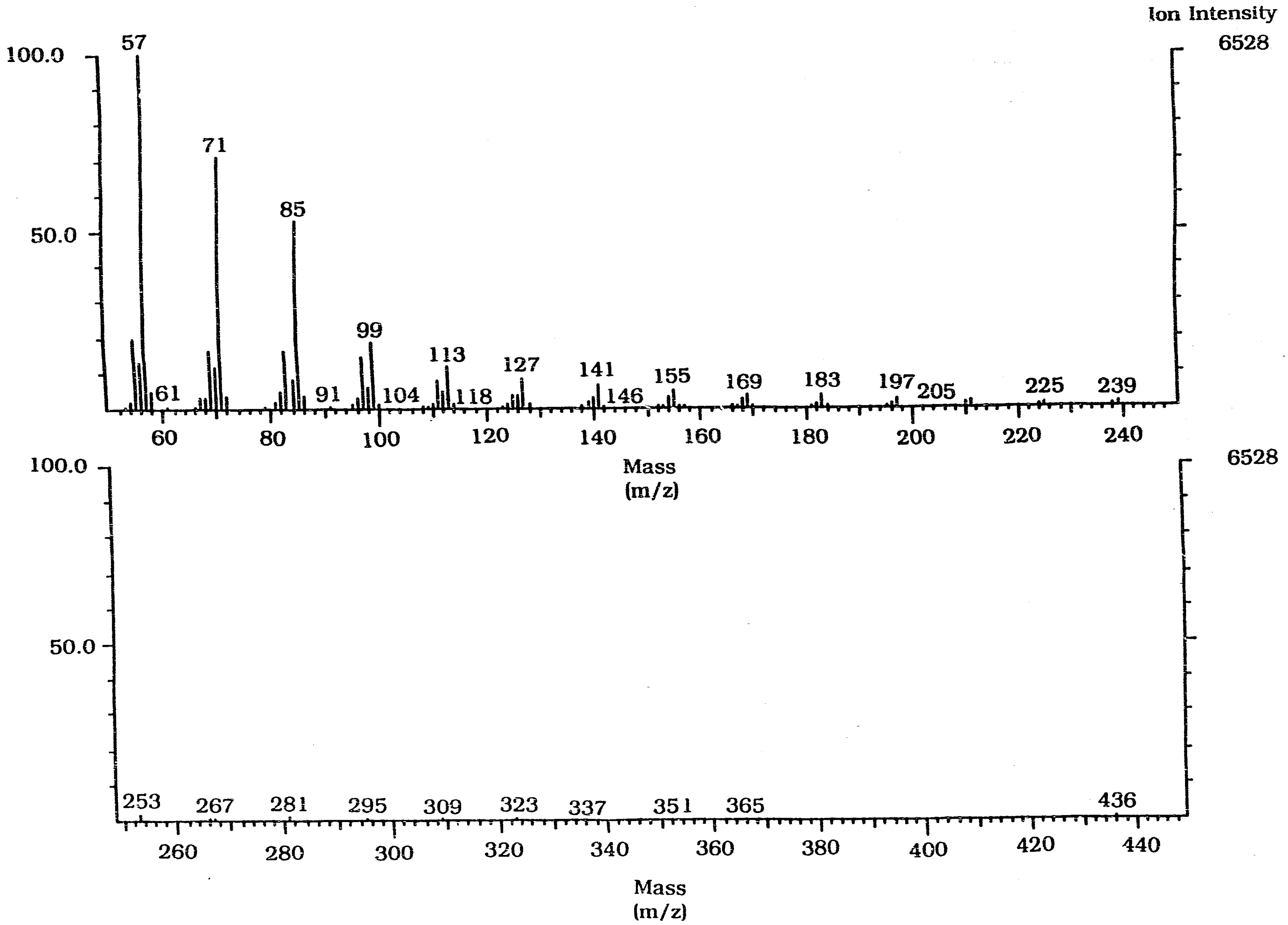

Figure 3. Plot of mass fragmentation pattern vs. relative ion intensity for scan 1062 from live vegetation, fine aerosol sample (F7217). This mass spectrometric plot is for the n-alkane homolog, n-$C_{31}H_{64}$, and shows a very small molecular ion at m/z 436.

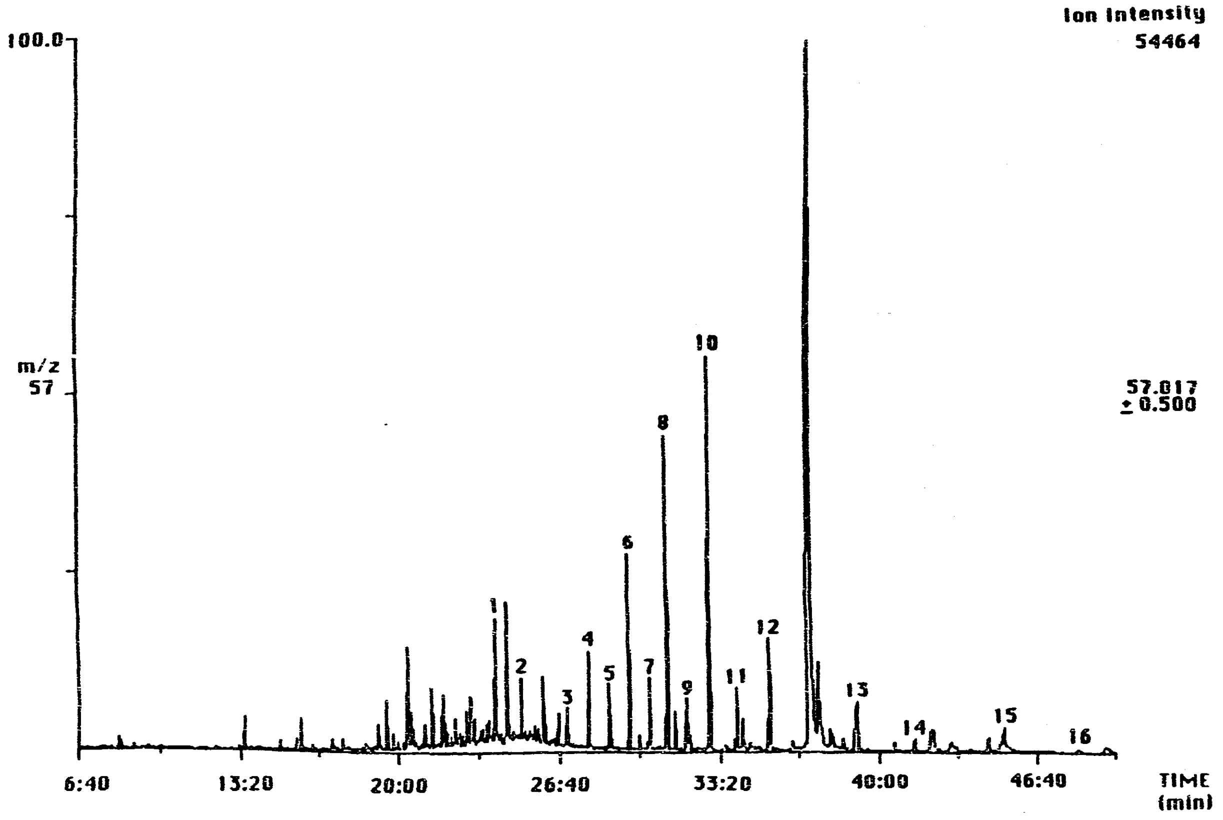

Figure 4. Selected ion plot of mass m/z 57 vs. scan time for isolation of n-alkane homologs (n-C_{19} to -C_{36}) from live vegetation, Hopi Point, fine aerosol sample (F7217).

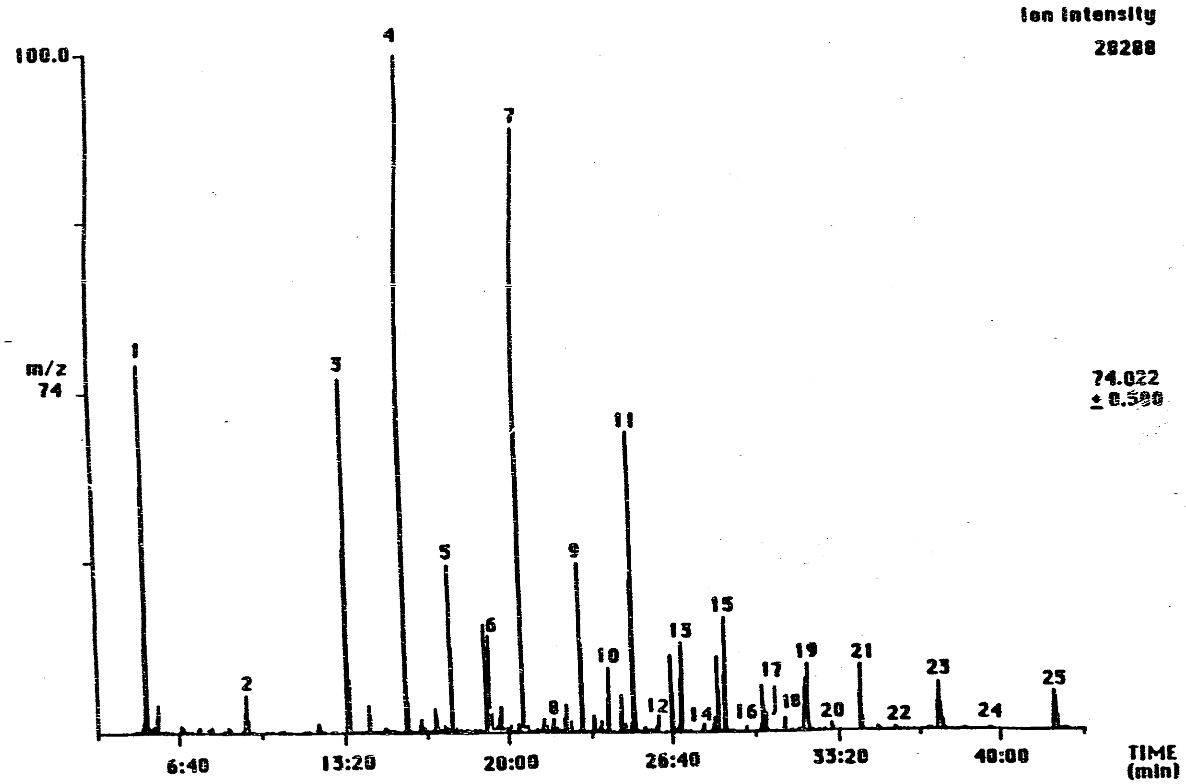

Figure 5. Selected ion plot of mass m/z 74 vs. scan time for isolation of n-alkanoic acids (as methyl esters) from live vegetation, Hopi Point, fine aerosol sample (F7217).

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