VII. PLASTICIZERS IN THE FIRST FRACTION OF THE FILTER EXTRACTS

VII. PLASTICIZERS IN THE FIRST FRACTION OF FILTER EXTRACTS

VII.1. IDENTIFICATION OF THREE DOMINANT NON-HYDROCARBON PEAKS

The hydrocarbon fraction of 29 aerosol sample extracts and four blank filters were analyzed by GC-MS to identify the hydrocarbons (both aliphatics and aromatics) and to assess their concentrations. An aluminum foil and a plastic bag which were used to wrap the filters were also analyzed by GC-MS. The reconstructed mass chromatograms (RIC) of these extracts indicate that three large peaks (marked as compound 1, compound 2 and compound 3) are present in all aerosol samples analyzed except for those collected in Caldecott Tunnel (Figures VII-1 to VII-4). One of the filter blanks (filter #8012) and extracts of the wrapping material (aluminum foil and plastic bag) contained no measurable amount of these peaks.

Compounds 2 and 3 were confirmed to be phthalate esters known as common plasticizers. The estimated concentration of compound 2 in the analyzed samples ranges from 16 ng/m^3 (samples 8053, 8059 and 8060, 8061 from Duarte and Glendora, respectively) to 325 ng/m^3 (sample 8034, 8040, Glendora) and for compound 3 from 19 ng/m^3 (sample 8050, Glendora) to 524 ng/m^3 (sample 8034, 8040, Glendora) (Tables VII-1 and VII-2). Compound 2 was identified as <u>di-n-butyl-phthalate</u> whereas compound 3 is <u>bis(2-ethylhexyl)-phthalate</u>. Because of their widespread use, these phthalates may appear as minor impurities in ambient air, and therefore their presence in almost all aerosol samples should probably be considered as a common atmospheric contaminant. These phthalate compounds are more concentrated in the Glendora samples than those collected in the city of Duarte.

Compound 1 is the single most abundant compound present in the hydrocarbon extract, with a concentration ranging from 121 ng/m^3 (sample 8050,

Glendora) to 1585 ng/m^3 (sample 8007, 8008, Glendora). Again, aerosol samples from the city of Glendora are more concentrated in compound 1 than those from the city of Duarte. The mass spectrum of compound 1 closely resembles that of di-isobutyrate ester, with a formula of $C_{16}H_{30}O_4$. To confirm the chemical structure of compound 1 and investigate its origin, a detailed GC-MS search was performed (Figure VII-1). The mass spectrum of compound 1 (Figure VII-5) was found to most closely match the mass spectra of two structural isomers, A and B (both with compositional formula of $C_{16}H_{30}O_4$), as shown in Figure VII-6.

A) Propanoic acid, 2-methyl-1, (1,1-dimethyl)-2-methyl-1,3-propanediyl-ester

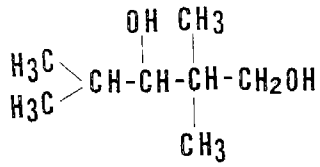
and

B) Propanoic acid, 2-methyl-2-ethyl-1-propyl-1,3-propanediyl-ester.

They all display m/z 159, m/z 111 and m/z 71 dominant fragments and minor m/z fragments at 243, 215, 173, 143, 111, 83 and 56, but lack the molecular ion (MW) 286.

A search of our files for $C_8H_{18}O_2$ diols with m/z fragmentation patterns described above, lead to the conclusions that the isomers A and B are <u>di-isobutyrate</u> esters of $C_8H_{18}O_2$-diols. These diols are commercially manufactured in the production of plasticizers and polymers. Since 1975, higher diols and their esters have become commercially important plasticizers. Two commonly manufactured diols which could fit the scheme are <u>2,2,4-trimethyl-1,3-pentadiol</u> ($C_8H_{18}O_2$, formula C) and <u>1,4, cyclohexane dimethanol</u> ($C_8H_{16}O_2$, formula D). Compound D, however, has a fragmentation pattern different than that observed in the aerosol samples.

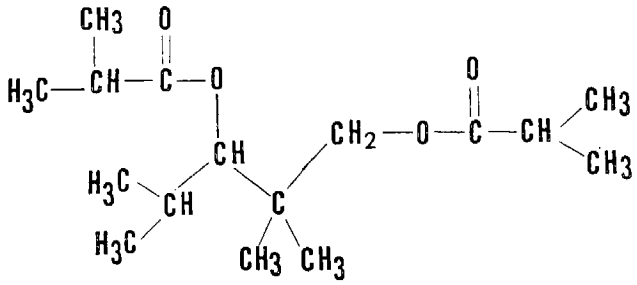
C)



D)

Therefore, our aim to identify the unknown compound 1 was directed at 2,2,4-trimethyl-1,3-pentadiol (formula C) because its di-isobutyrate ester ($C_{16}H_{30}O_4$, formula E) is produced by Eastman Chemical Company under the trade name Kodaflex (TXIB) for use as a plasticizer, primarily in surface coating, vinyl flooring, moldings and other vinyl products and also for use in surfactants, pesticides and resins (Hodgson et al., 1983).

E)



In order to complete the identification of compound 1, we analyzed by GC-MS a purchased Kodaflex (TXIB) sample manufactured by Eastman Chemical Company. The results presented in Figures VII-7 and VII-8 show the excellent match between the mass spectrum of compound 1 detected in aerosol samples

(Figure VII-5) and the purchased sample of TXIB (Figure VII-8).

VII. 2. PRESENCE OF AEROSOL PLASTICIZERS

Phthalate esters, such as di-n-butylphthalate and bis (2-ethylhexyl) phthalate, are plasticizers which have been commonly detected in aerosol and marine sediment samples in both urban and relatively remote locations (Giam et al., 1980).

The occurrence of di-isobutyrate diol ester (TXIB), similar to compound 1, has already been demonstrated in the emissions of volatile organic compounds from architectural materials (Hodgson et al., 1983). Therefore the presence of this compound in all aerosol samples can be interpreted as an atmospheric contaminant.

Tables VII-1 and VII-2 and Figures VII-1 to VII-4 clearly show that TXIB is the dominant plasticizer in the individual and composite samples. On the average, it is two to five times more abundant than bis(2-ethylhexyl)-phthalate and three to sixteen times more abundant than di-n-butylphthalate. The correlation in the concentration of TXIB against the sum of the two phthalates (Figure VII-9) is good ($r = 0.61$) and suggests that these plasticizers were produced from similar sources, otherwise they would display a random correlation.

Surprisingly, these plasticizers were also present in three out of four blank filters analyzed. In two (filter nos. 8016 and 8022) they were in low abundance, however, in filter no. 8030 the concentration was significantly higher. In these filters, TXIB was very dominant and di-n-butylphthalate was second in abundance. We can not explain why blank filter no. 8030 contained such a high concentration of plasticizer.

Because these peaks are so dominant in the filter extract, they should have

a significant influence on the ^{14}C age determination of modern carbon content in the hydrocarbon fraction. However, as shown in Tables XII-7, the TXIB sample measured for $D^{14}C$ contained a very low content of ^{14}C and gave a calculated modern carbon content of 0.5%. Hence, assuming the other plasticizers also contained low or no modern carbon, their combined influence on contaminating the extracts with ^{14}C would be negligible.

Table VII-1. Estimated concentration [(μg/filter) and (ng/m^3)] of plasticizer (compound 1) and two phthalates (compounds 2 and 3) in samples collected at city of Glendora

Order No.#	Filter No.	Sampling Time	Compound 1*		Compound 2*		Compound 3*	
			μg/filter	ng/m^3	μg/filter	ng/m^3	μg/filter	ng/m^3
1	8007,8008	D	631	1585	76	190	50	127
2	8009	D	102	253	17	43	33	81
3	8017,8027	D	229	560	50	123	53	129
4	8019	D	193	530	31	85	44	122
5	9020	D	131	363	21	58	37	102
6	8026,8029	D	240	342	53	75	120	171
7	8033,8036	D	316	522	85	141	262	433
8	8034,8040	D	417	1047	129	325	209	524
9	8043,8044	D	298	493	81	133	155	256
10	8047,8051	D	366	919	103	257	157	395
11	8048,8049	D	304	434	79	113	125	178
12	8054,8055	D	225	365	23	37	47	77
13	8057,8058	D	249	620	35	87	50	124
14	8060,8061	D	163	268	10	16	36	59
15	8013,8014	N	296	248	50	42	133	112
16	8024	N	211	359	51	86	61	104
17	8031	N	120	204	40	67	80	137
18	8037	N	134	238	39	69	71	126
19	8045	N	124	209	30	50	53	90
20	8050	N	72	121	11	18	12	19
21	8056	N	131	226	22	38	34	59
22	3413 (Blank)		ND		Tr		Tr	
23	3459 (Blank)		ND		Tr		Tr	
24	8012 (Blank)		ND		ND		ND	
25	8016 (Blank)		132		2		ND	
26	8022 (Blank)		138		2		ND	
27	8023 (Blank)		ND		Tr		Tr	
28	8028 (Blank)		<50		Tr		<5	
29	8030 (Blank)		205		19		16	
30	8039 (Blank)		ND		Tr		Tr	
31	8052 (Blank)		<20		Tr		Tr	
	Wrapping foil extract		ND		ND		ND	
	Wrapping plastic bag		ND		ND		ND	

D = day
N = night
ND = not detected
Tr = Trace

*1 = TXIB
*2 = Di-n-butylphthalate
*3 = Bis(1-ethylhexyl) phthalate
= Numbers plotted in Figure VII-9

Table VII-2. Estimated concentration [(μg/filter) and (ng/m^3)] of of plasticizer (compound 1) and two phthalates (compounds 2 and 3) in samples collected at city of Duarte.

Order No.#	Filter No.	Sampling Time	Compound 1*		Compound 2*		Compound 3*	
			μg/filter	ng/m^3	μg/filter	ng/m^3	μg/filter	ng/m^3
32	8006,8018	D	383	877	54	123	35	79
33	8010,8025	D	273	384	36	50	202	284
34	8015	N	91	154	14	23	12	20
35	8041	D	114	375	24	79	92	304
36	8053,8059	D	101	164	10	16	22	36

D = day

N = night

*1 = TXIB

*2 = Di-n-butylphthalate

*3 = Bis(2-ethylhexyl) phthalate

= Numbers plotted in Figure VII-9

Figure VII-1

Mass fragmentogram showing Compounds 1, 2 and 3 in Composite #1.

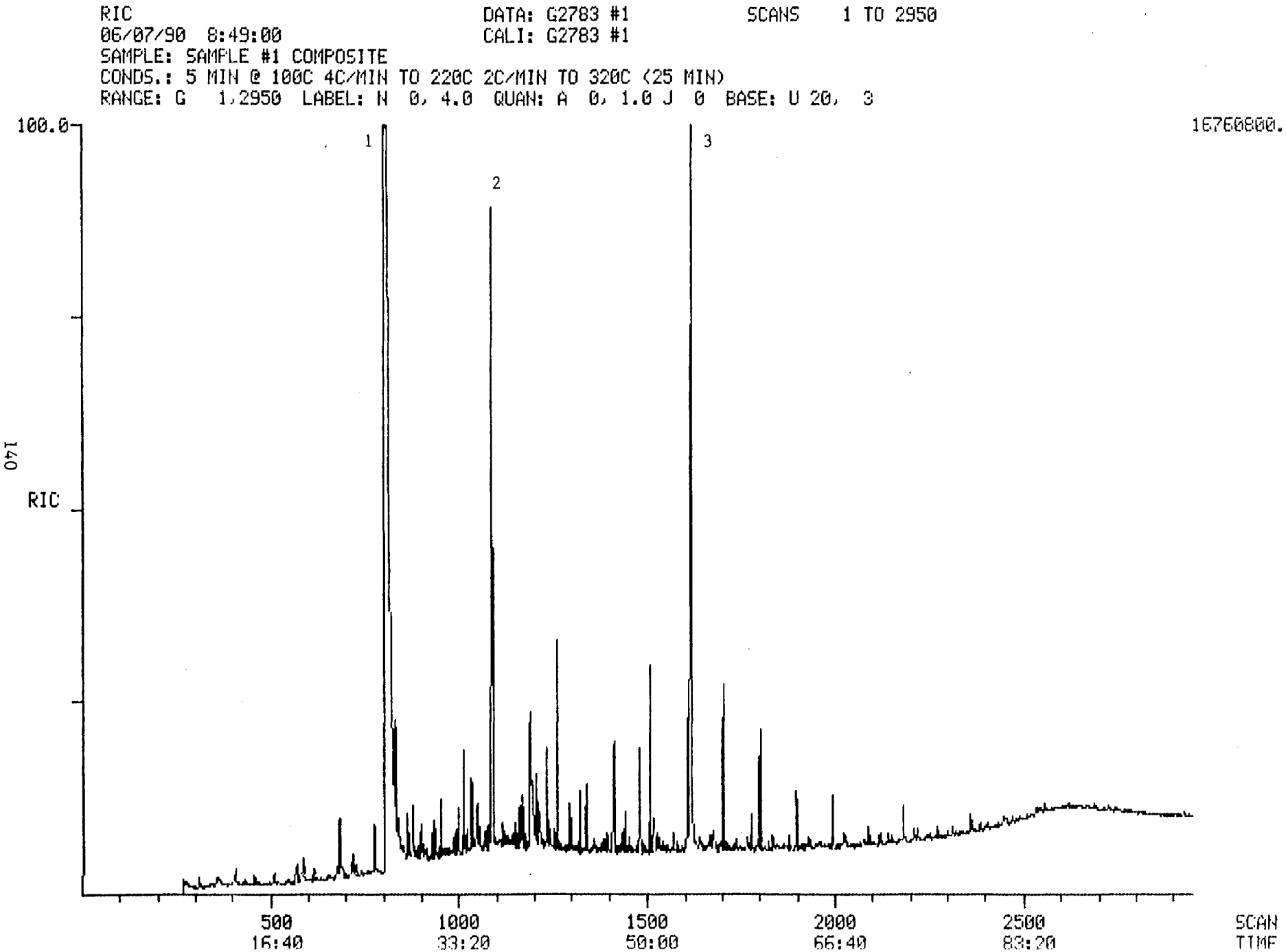


Figure VII-2

Mass fragmentogram showing Compounds 1, 2 and 3 in Composite #2.

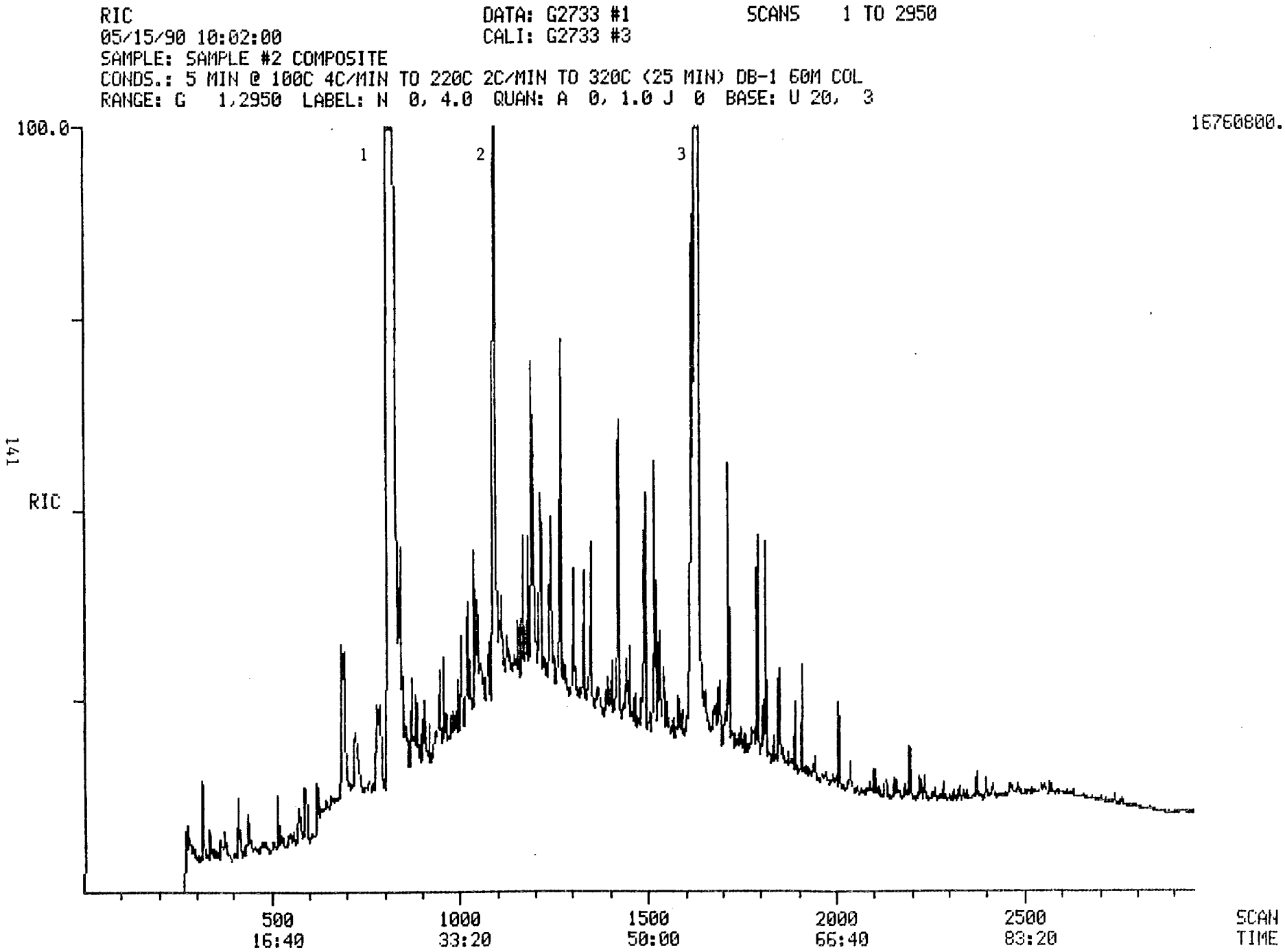


Figure VII-3

Mass fragmentogram showing Compounds 1, 2 and 3 in Composite #3.

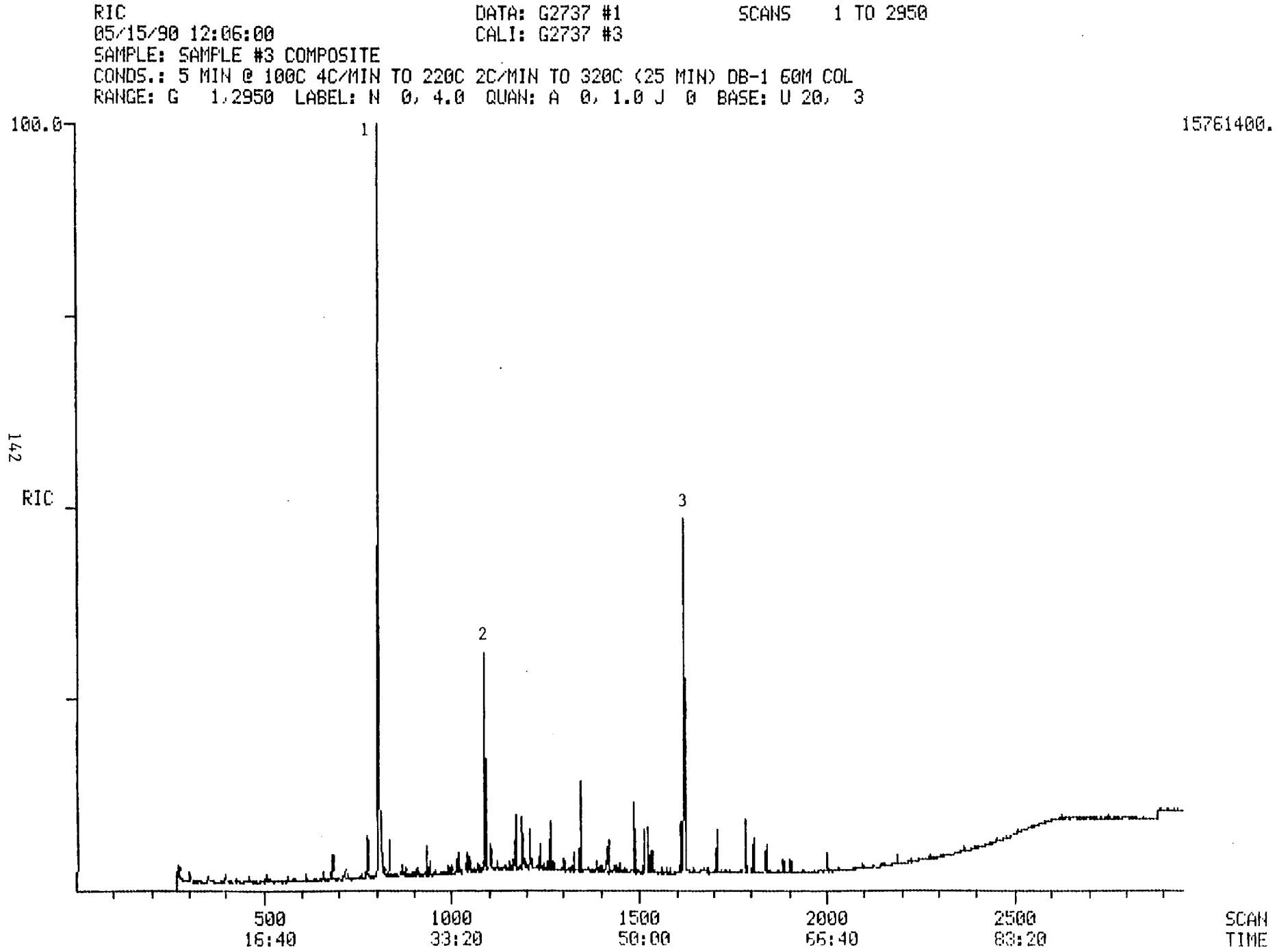


Figure VII-4

Mass fragmentogram showing Compounds 1, 2 and 3 in Composite #4.

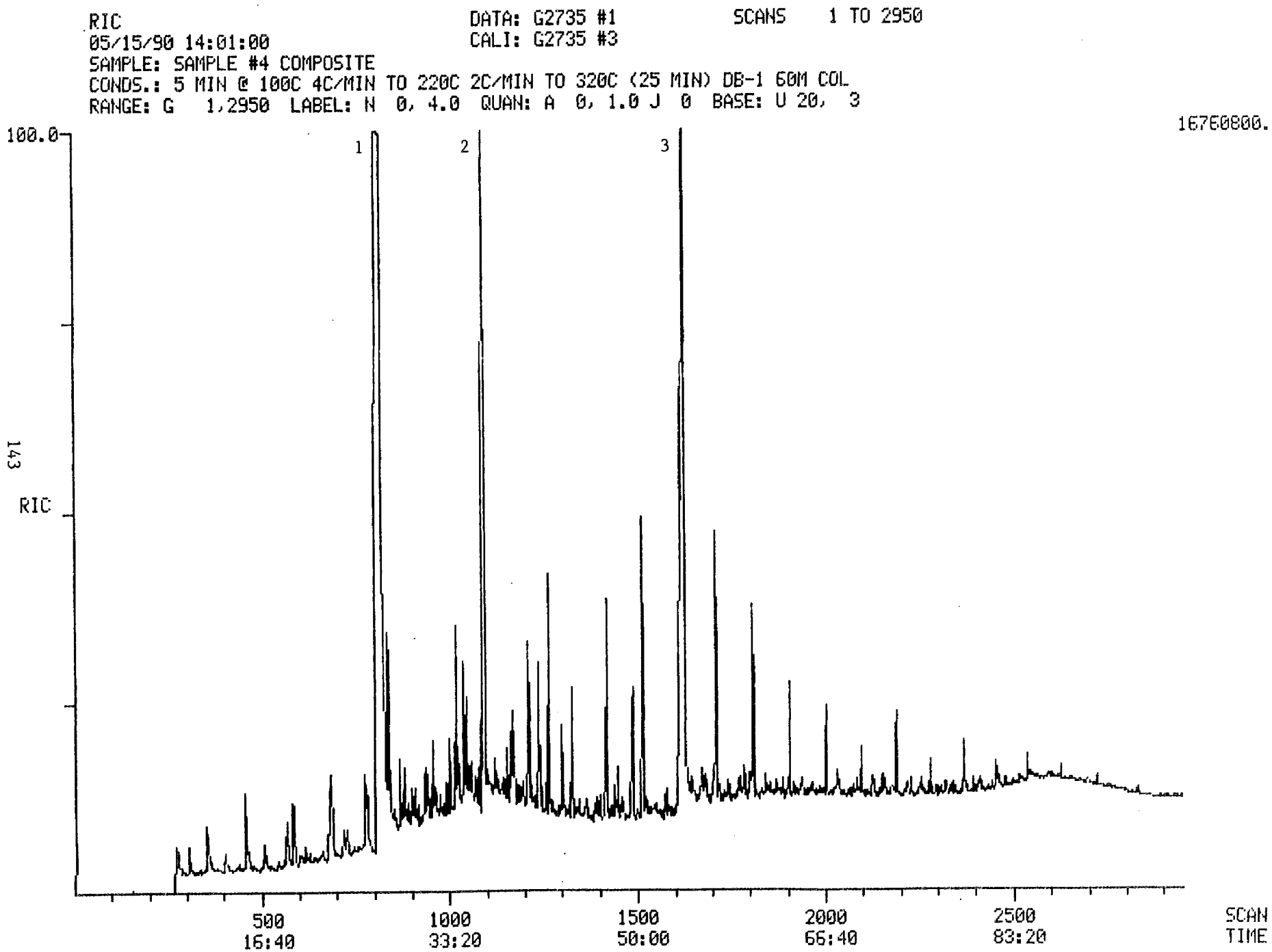


Figure VII-5

Mass spectrum of Compound 1.

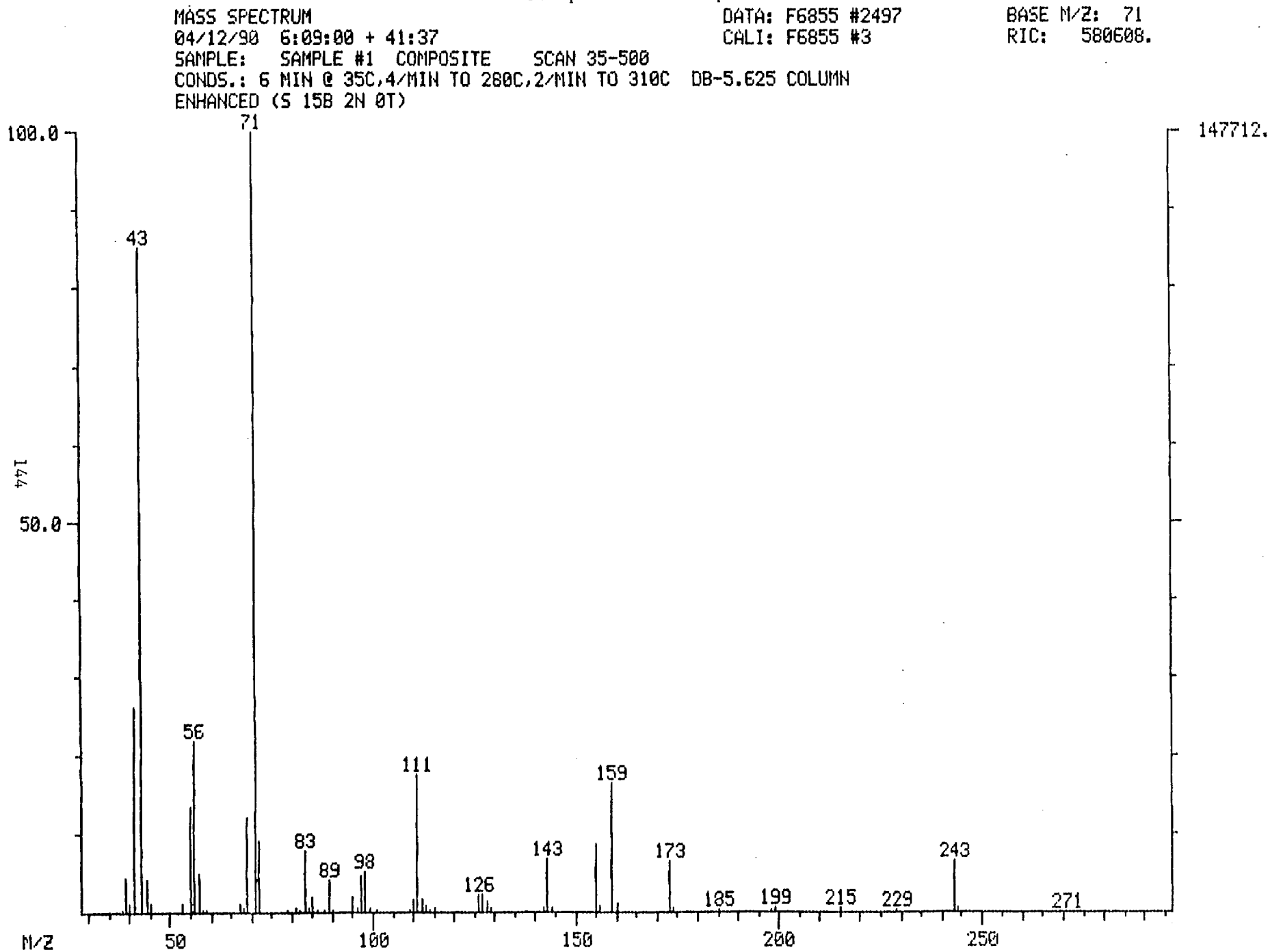


Figure VII-6. Mass spectra for different di-isobutyrate esters.

LIBRARY SEARCH
04/12/90 6:09:00 + 41:37
SAMPLE: SAMPLE #1 COMPOSITE SCAN 35-500
CONDS.: 6 MIN @ 35C,4/MIN TO 280C,2/MIN TO 310C DB-5.625 COLUMN
ENHANCED (S 15B 2N 0T)

DATA: F6855 #2497
CALI: F6855 # 3

BASE M/Z: 71
RIC: 576511.

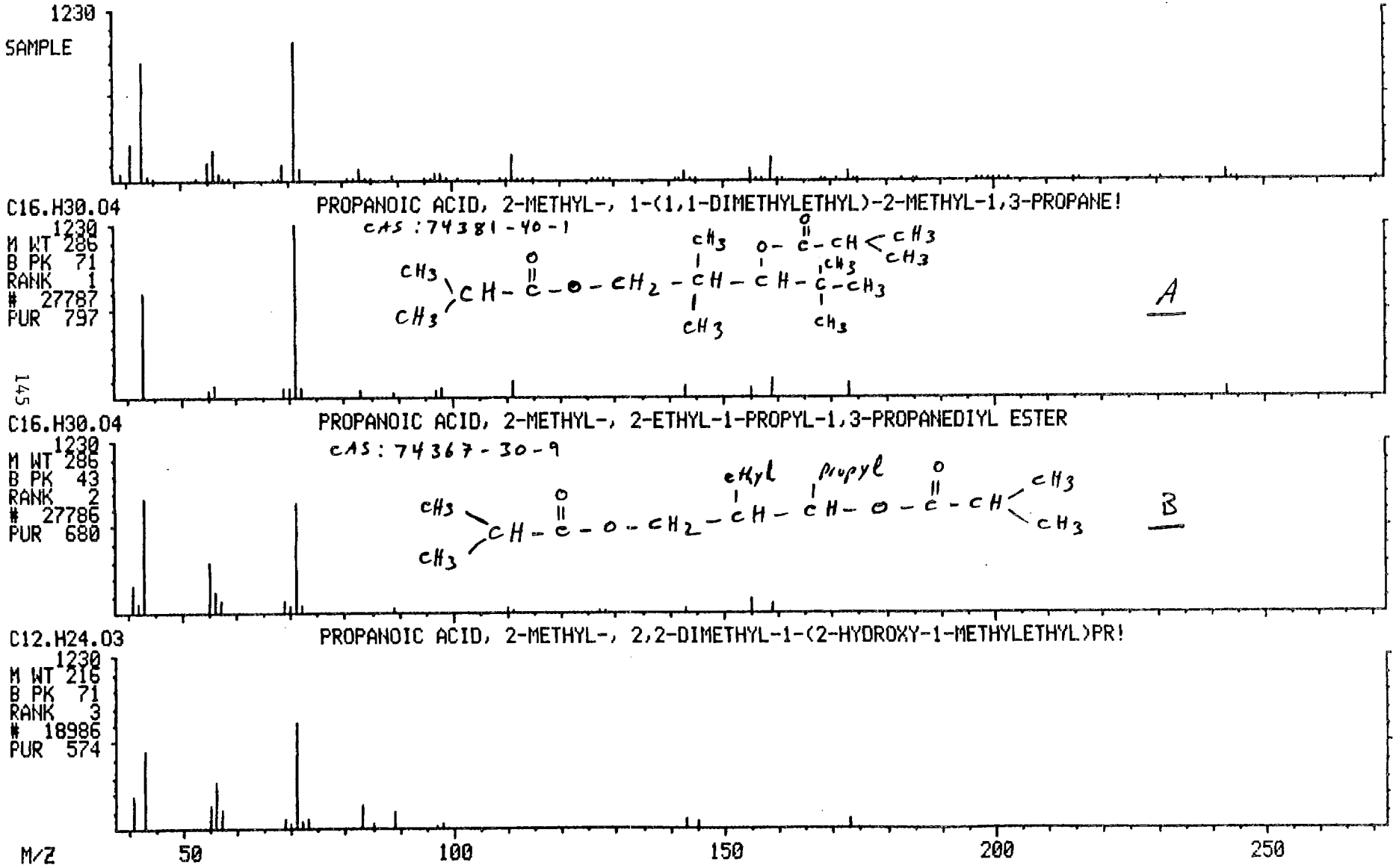


Figure VII-7. Mass fragmentogram of authentic TXIB.

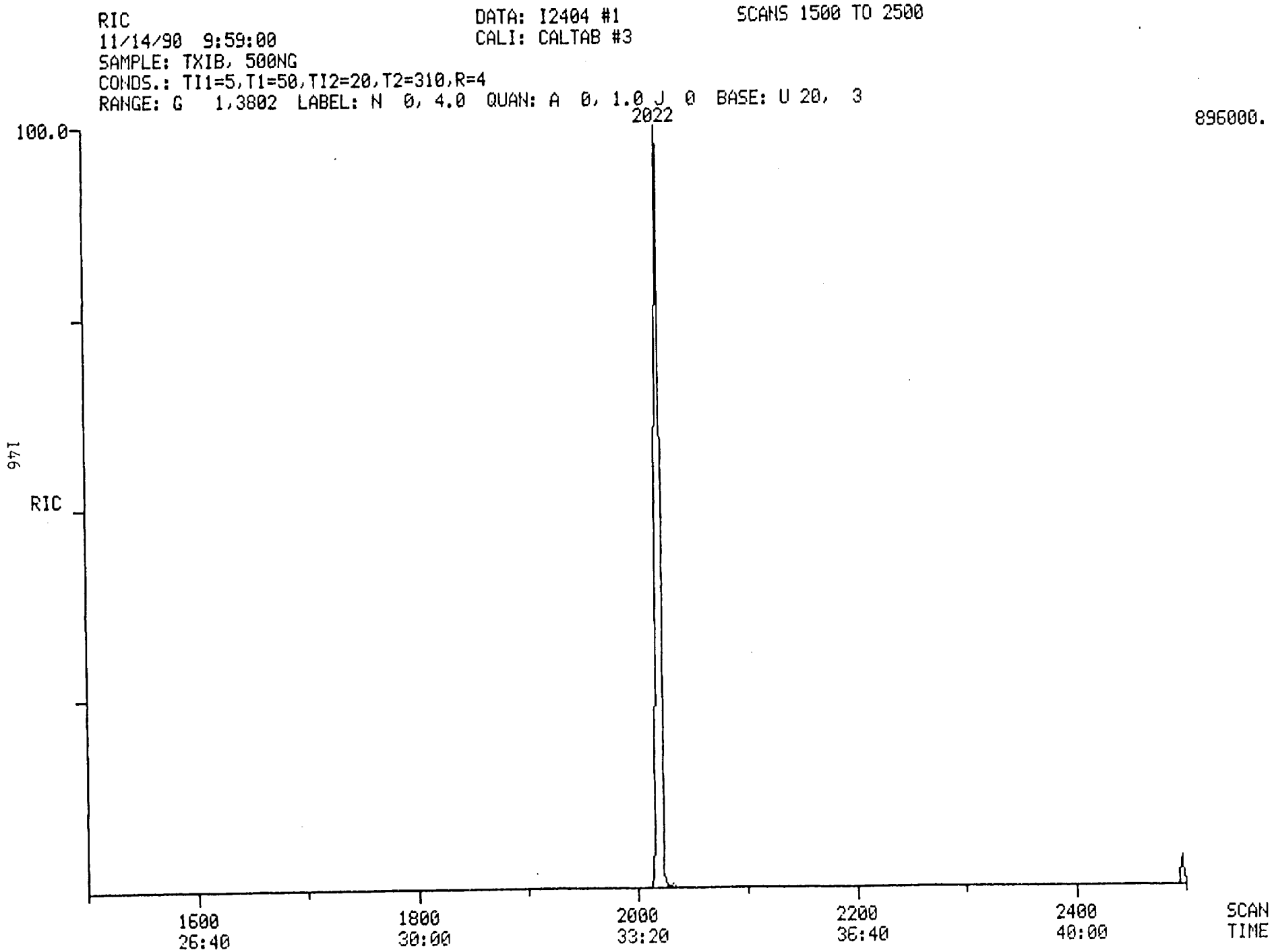


Figure VII-8. Mass spectrum of authentic TXIB.

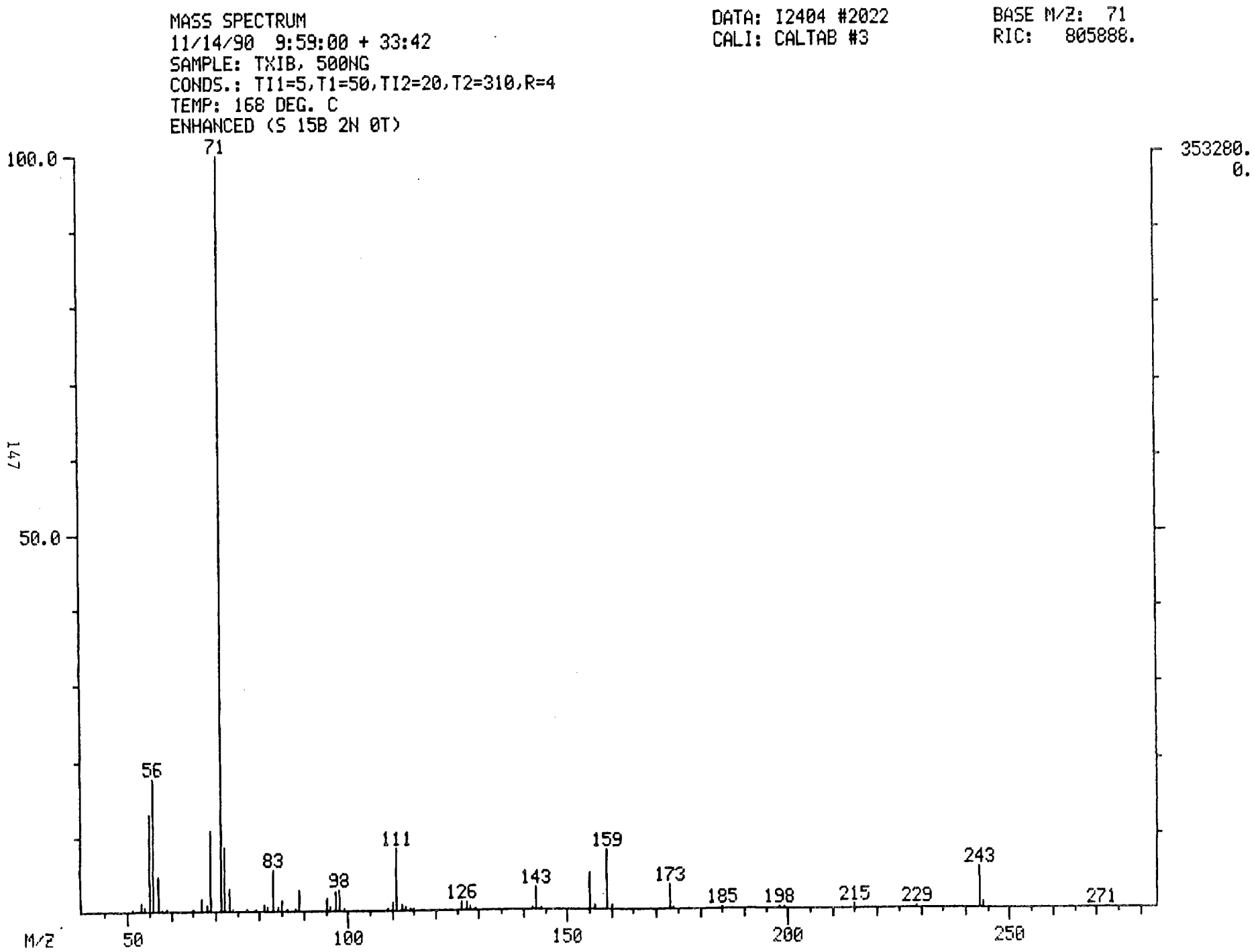
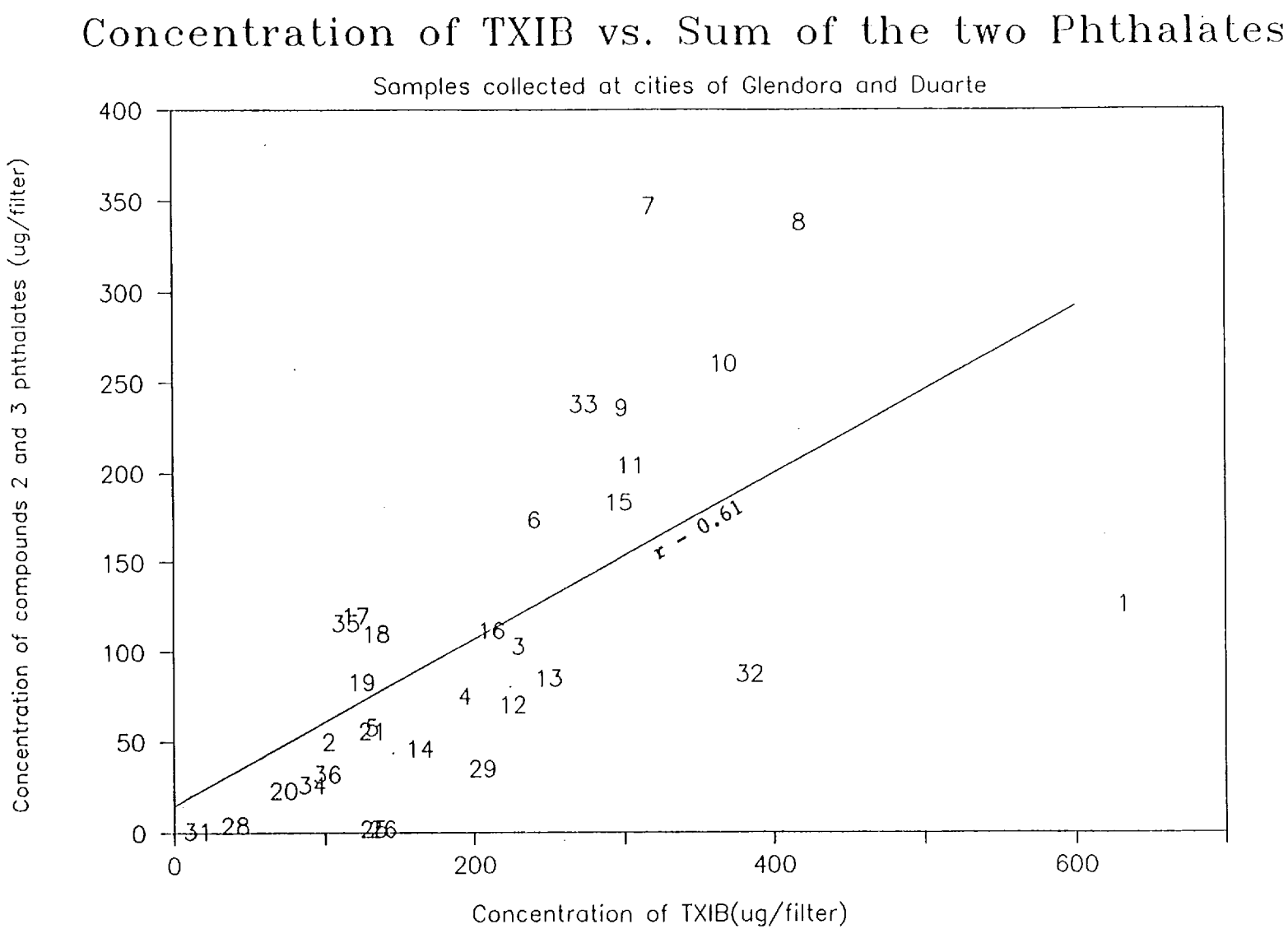


Figure VII-9



(For sample identification, see Tables VII-1 and VII-2)

VIII. FATTY ACIDS IN THE SECOND FRACTION OF THE FILTER EXTRACTS

VIII. FATTY ACIDS

The purpose for conducting analyses on fatty acids in the polar fraction of the filter extract was to attempt to identify recent carbon compounds released from food preparation activity. Because of the reactivity of olefinic unsaturated carbon bonds in a photochemical environment, and because natural biological sources, such as plant waxes, produce only the saturated long chain acids, the presence of unsaturated fatty acids in aerosol particles would be a strong indicator for the recent production and release of fatty acids into the atmosphere. This would be particularly so if the carbon chain length was dominated by the biologically abundant C_{16} and C_{18} acids.

The data shown in Tables VIII-1 to VIII-9 clearly indicate that unsaturated fatty acids with 1 and 2 unsaturated bonds for C16 and C18 fatty acids are present in many of the samples. The fatty acids dominate in the day samples over those at night. Although the singly unsaturated C18:1 was present in all day samples and some night samples and the doubly unsaturated C18:2 and singly unsaturated C16:1 were present in many day samples, no C18:2 fatty acids were detected in any night samples and only one night sample from Glendora contained C16:1 (Tables VIII-1 and VIII-2). The saturated fatty acids generally show a large dominance over the unsaturated fatty acids; however in sample #8019, it is near unity; in sample #8020, it is 1.7 and in three other samples it is <5. One sample from Duarte (Tables VIII-4 and VIII-5) contained C16:1 and none contained C18:2, whereas C18:1 was present in all but one sample. Table VIII-6 shows that one sample, #8041, has a ratio of saturated to unsaturated fatty acids <5, the others are >17. This may further indicate that destruction is rapid and unless generated continually the unsaturated fatty acids would not be present due to rapid destruction.

Surprisingly, the polar extract of tunnel filters, both day and night

contained fatty acids, including unsaturated C16:1, C18:1 and C18:2 (Tables VIII-7 and VIII-8). In this case, the night sample contained more C16:0, C16:1, C18:0 and C18:1, but less C18:2. We believe that these may be entering the Tunnel from recirculation of air.

Whereas biological samples (i.e. beef fat, accumulations on a kitchen filter and wood ash) contain about equal amounts of saturate and unsaturate fatty acids (Table VIII-10, beef has a saturate/unsaturate ratio = 0.5), Glendora and Duarte aerosol samples have ratios varying from ~0.9 to 60. The tunnel samples have a saturate/unsaturate ratio of 1.9 in the day sample to 4.9 in the night sample.

The distribution patterns for the biological samples are shown in Table VIII-10 and in Figure VIII-36 to VIII-38.

Table VIII-1. Individual fatty acid weight per filter (μg) samples collected at city of Glendora.

Collection Date (AUG 1986)	Filter No.	D/N*	C14:0[1]	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	C20:0
13	8007,8008	D	121.3	122.7	nd[2]	82.0	12.7	32.0	nd	nd
13	8009	D	303.6	385.6	29.2	144.0	32.4	98.4	nd	28.0
14/15	8017,8027	D	96.0	76.7	nd	44.7	4.7	nd	nd	nd
14	8019	D	105.2	95.2	20.0	48.8	33.6	101.6	nd	nd
14	8020	D	89.6	123.2	19.2	46.4	9.6	68.4	nd	nd
15	8026,8029	D	82.0	133.3	nd	60.7	8.7	nd	nd	nd
16/17	8034,8040	D	42.0	68.7	nd	18.0	2.7	nd	nd	nd
16	8033,8036	D	144.7	254.0	4.7	144.7	10.0	56.0	nd	59.0
17	8043,8044	D	40.0	69.3	nd	34.0	6.7	nd	nd	nd
18/19	8047,8051	D	56.7	46.0	nd	23.3	2.7	nd	nd	nd
18	8048,8049	D	37.3	64.0	nd	32.7	4.0	9.3	nd	nd
19	8054,8055	D	27.3	40.0	14.0	7.3	4.7	nd	nd	nd
20	8057,8058	D	65.3	62.7	3.3	16.7	3.3	nd	nd	nd
20	8060,8061	D	50.0	84.7	nd	41.3	3.3	nd	nd	nd
13	8013,8014	N	171.3	214.0	nd	106.7	5.3	nd	nd	nd
14	8024	N	77.3	84.0	nd	nd	nd	nd	nd	nd
15	8031	N	42.3	74.2	nd	25.6	nd	nd	nd	nd
16	8037	N	68.0	149.3	nd	44.7	nd	nd	nd	nd
17	8045	N	92.0	155.3	2.7	80.7	7.3	nd	nd	50.0
18	8050	N	81.3	104.7	nd	26.0	5.3	nd	nd	nd
19	8056	N	60.0	78.4	nd	32.8	tr[3]	nd	nd	nd

* D = day; N = night, collection times shown in Table II-1 and page 6

[1] Terminology for extent of unsaturation. 18:0 means totally saturated. 18:1 to 18:3 means from 1 to 3 unsaturated bonds.

[2] nd = not detected

[3] tr = trace

Table VIII-2. Individual fatty acid weight as function of air volume (ng/m3) for samples collected at city of Glendora.

Collection Date (AUG 1986)	Filter No.	D/N*	C14:0[1]	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	C20:0
13	8007,8008	D	262.7	265.7	nd[2]	177.6	27.5	69.3	nd	nd
13	8009	D	657.3	834.8	63.2	311.8	70.1	213.0	nd	60.6
14/15	8017,8027	D	207.9	166.1	nd	96.8	10.2	nd	nd	nd
14	8019	D	248.8	225.1	47.3	115.4	79.5	240.3	nd	nd
14	8020	D	211.9	291.4	45.4	109.7	22.7	161.8	nd	nd
15	8026,8029	D	89.2	145.1	nd	66.1	9.5	nd	nd	nd
16/17	8034,8040	D	90.9	148.8	nd	39.0	5.8	nd	nd	nd
16	8033,8036	D	158.3	277.9	5.1	158.3	10.9	61.3	nd	64.9
17	8043,8044	D	43.5	75.4	nd	37.0	7.3	nd	nd	nd
18/19	8047,8051	D	122.8	99.6	nd	50.5	5.8	nd	nd	nd
18	8048,8049	D	40.4	69.3	nd	35.4	4.3	10.1	nd	nd
19	8054,8055	D	29.1	42.6	14.9	7.8	5.0	nd	nd	nd
20	8057,8058	D	141.4	135.8	7.1	36.2	7.1	nd	nd	nd
20	8060,8061	D	54.1	91.7	nd	44.7	3.6	nd	nd	nd
13	8013,8014	N	123.6	154.4	nd	77.0	3.8	nd	nd	nd
14	8024	N	112.4	122.1	nd	nd	nd	nd	nd	nd
15	8031	N	61.5	107.8	nd	37.2	nd	nd	nd	nd
16	8037	N	103.9	228.2	nd	68.3	nd	nd	nd	nd
17	8045	N	133.7	225.7	3.9	117.3	10.6	nd	nd	73.7
18	8050	N	117.3	151.1	nd	37.5	7.7	nd	nd	nd
19	8056	N	89.1	116.4	nd	48.7	tr[3]	nd	nd	nd

* D = day; N = night

[1] Terminology for extent of unsaturation. 18:0 means totally saturated. 18:1 to 18:3 means from 1 to 3 unsaturated bonds.

[2] nd = not detected

[3] tr = trace

Table VIII-3. Total saturate to unsaturate fatty acid ratio for samples collected at city of Glendora.

Collection Date (AUG 1986)	Filter No.	D/N*	$C_{16} + C_{18}$** Ratio
13	8007,8008	D	4.6
13	8009	D	3.3
14/15	8017,8027	D	25.8
14	8019	D	0.9
14	8020	D	1.7
15	8026,8029	D	22.3
16/17	8034,8040	D	32.1
16	8033,8036	D	5.6
17	8043,8044	D	15.4
18/19	8047,8051	D	25.7
18	8048,8049	D	7.3
19	8054,8055	D	2.5
20	8057,8058	D	12.0
20	8060,8061	D	38.2
13	8013,8014	N	60.5
14	8024	N	***
15	8031	N	***
16	8037	N	***
17	8045	N	23.6
18	8050	N	24.7
19	8056	N	***
	Beef Fat Vapor		0.5
	Fireplace Ash		1.2
	Kitchen Hood Extract		1.2

* D = day; N = night

** $C_{16:0} + C_{18:0} / C_{16:1} + C_{18:1} + C_{18:2} + C_{18:3}$

*** No unsaturated fatty acid

Figure VIII-1

Fatty Acid Distribution,Day

Glendora Sample(Aug.13,89;800−1200hr):Sample No.8007+8008

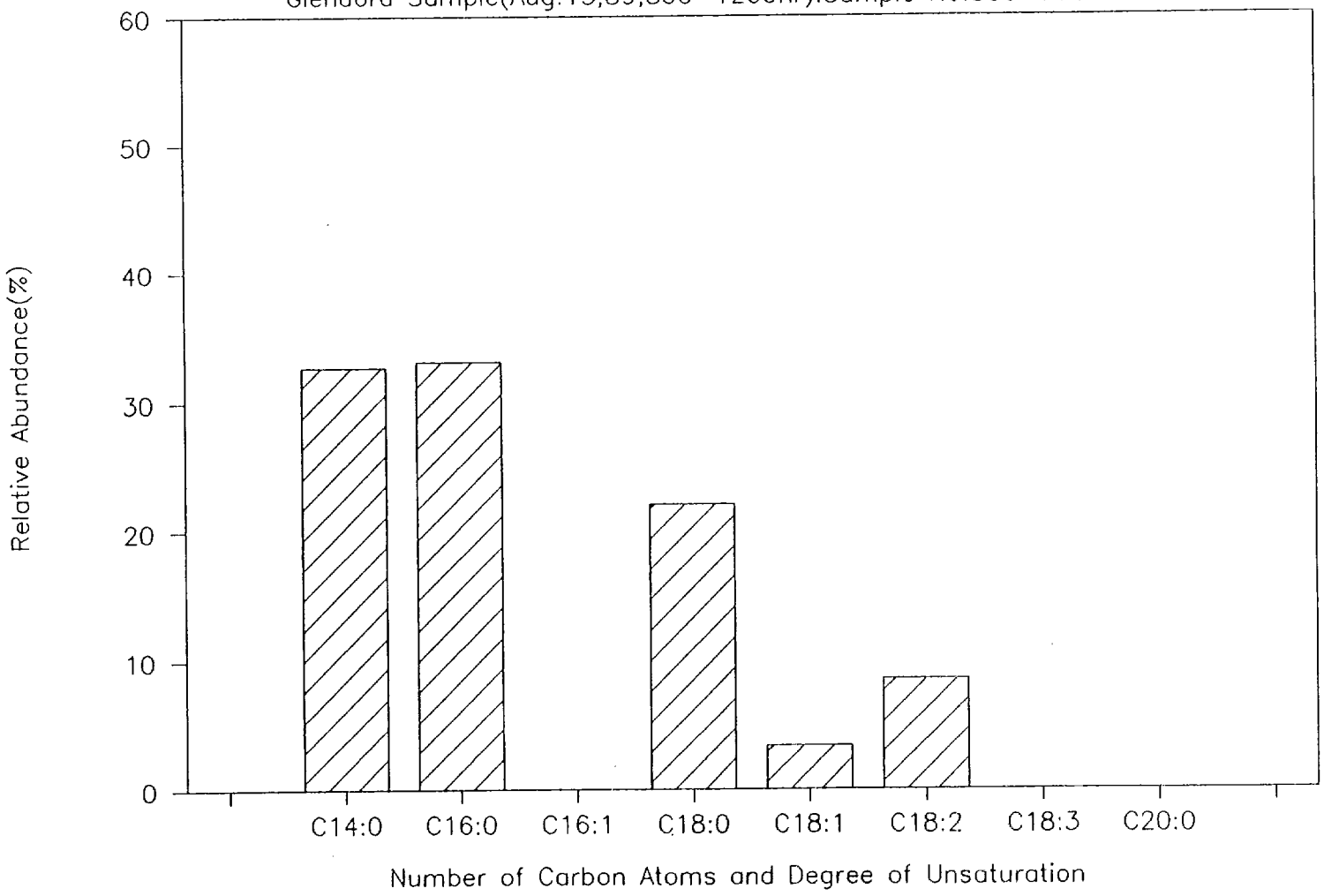


Figure VIII-2

Fatty Acid Distribution,Day

Glendora Sample(Aug.13,89;1200-2000hr):Sample No.8009

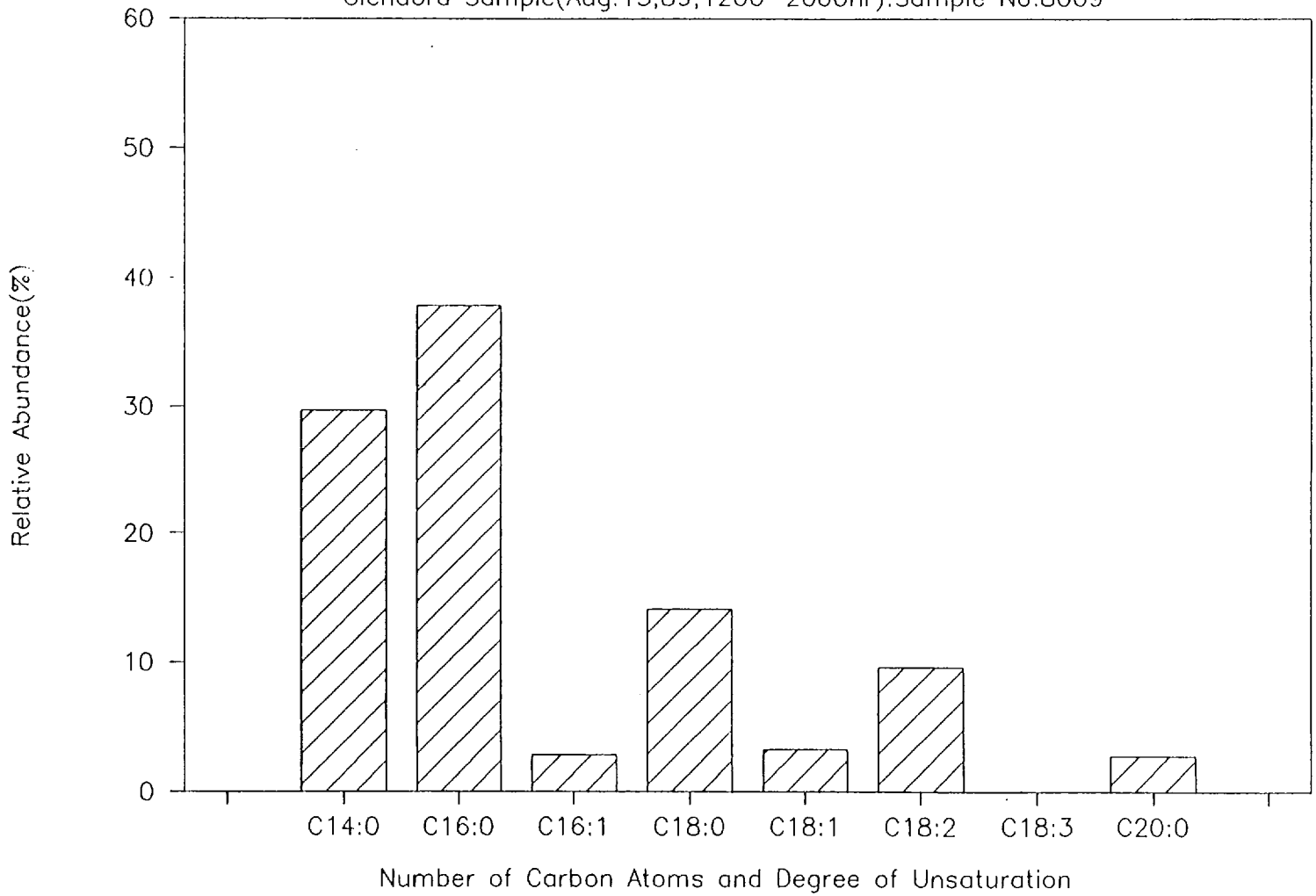


Figure VIII-3

Fatty Acid Distribution,Night

Glendora Sample(Aug.13,86;2000-800hr):Sample No.8013+8014

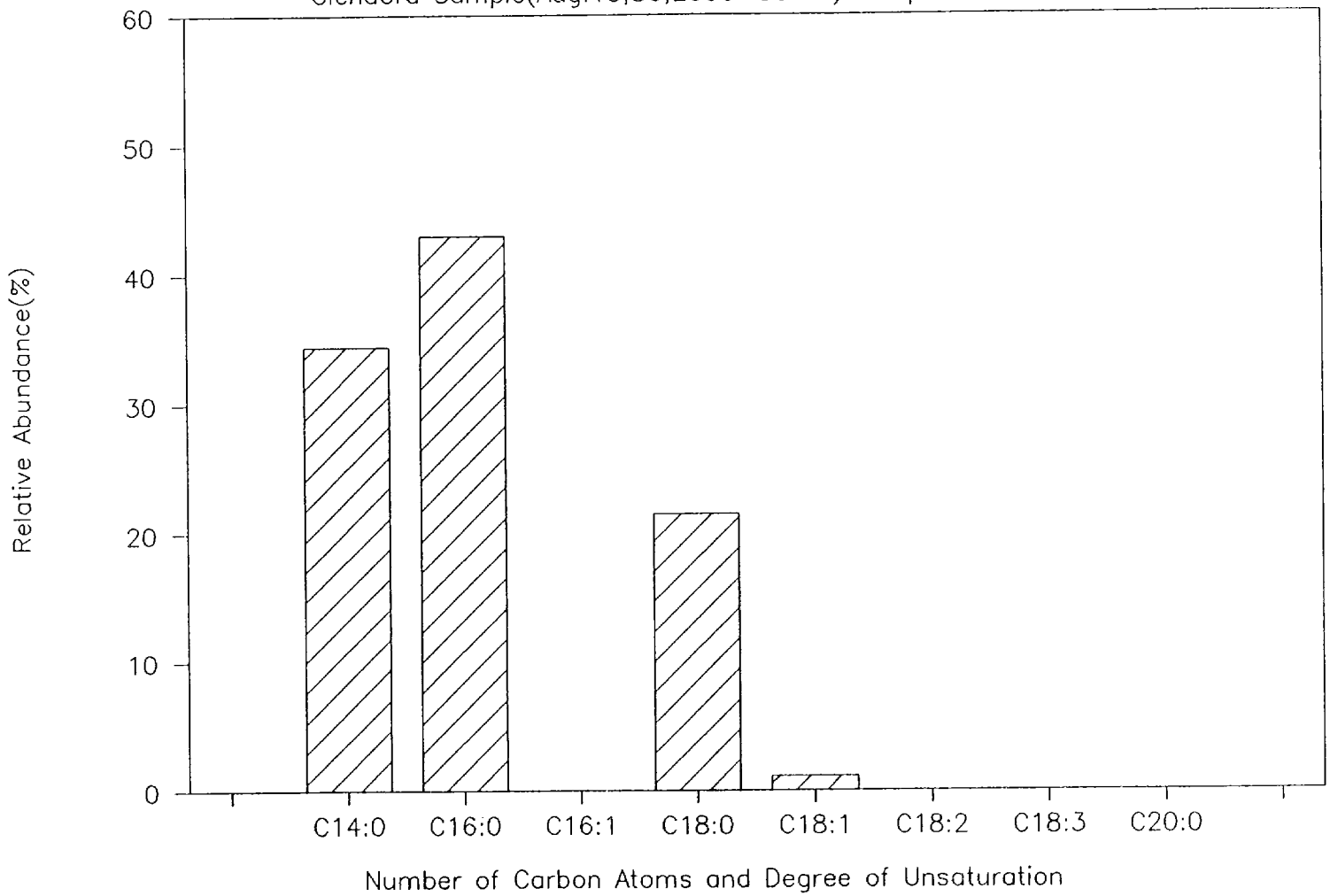


Figure VIII-4

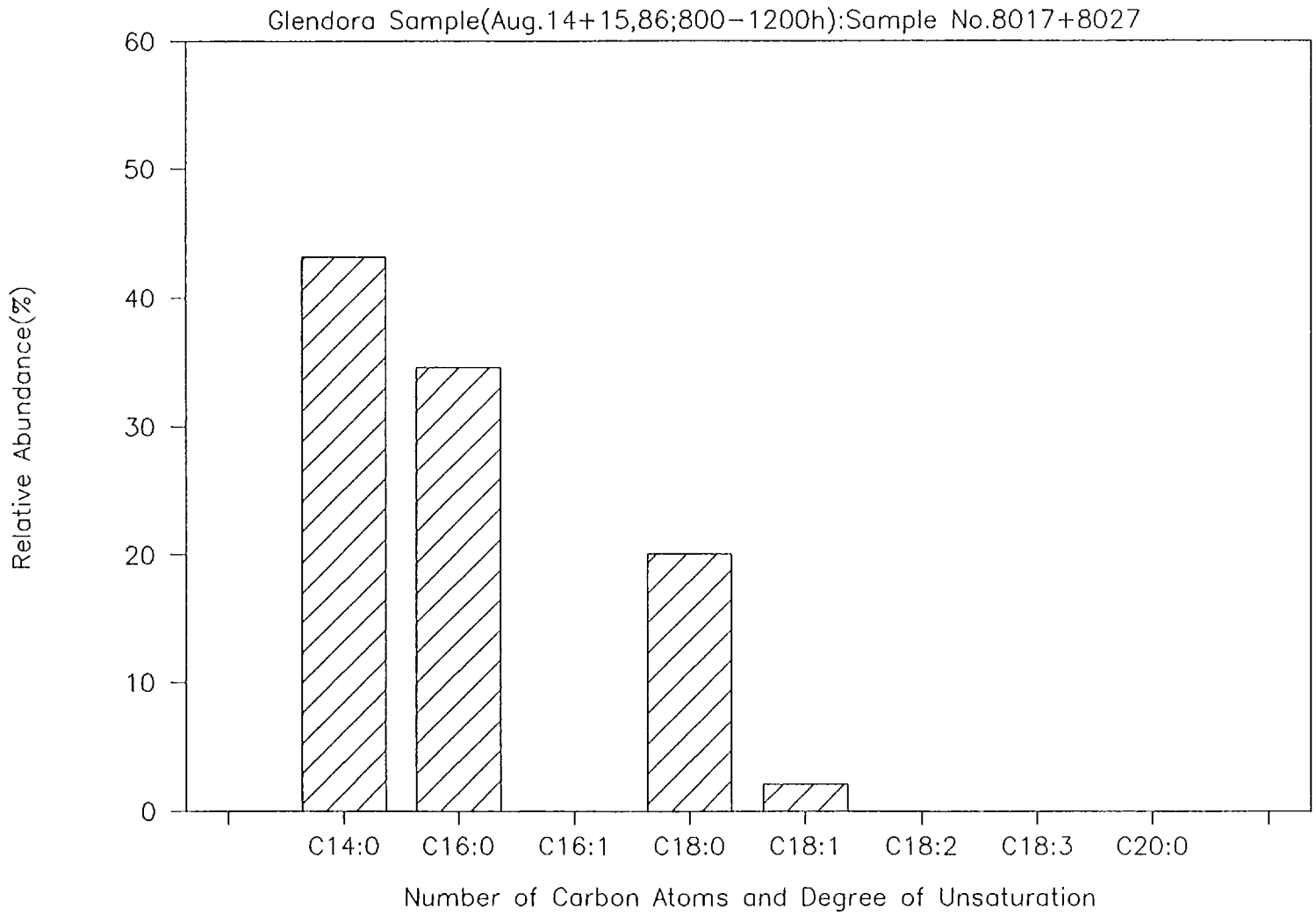


Figure VIII-5

Fatty Acid Distribution,Day

Glendora Sample(Aug.14,86;1210–2000hr):Sample No.8019

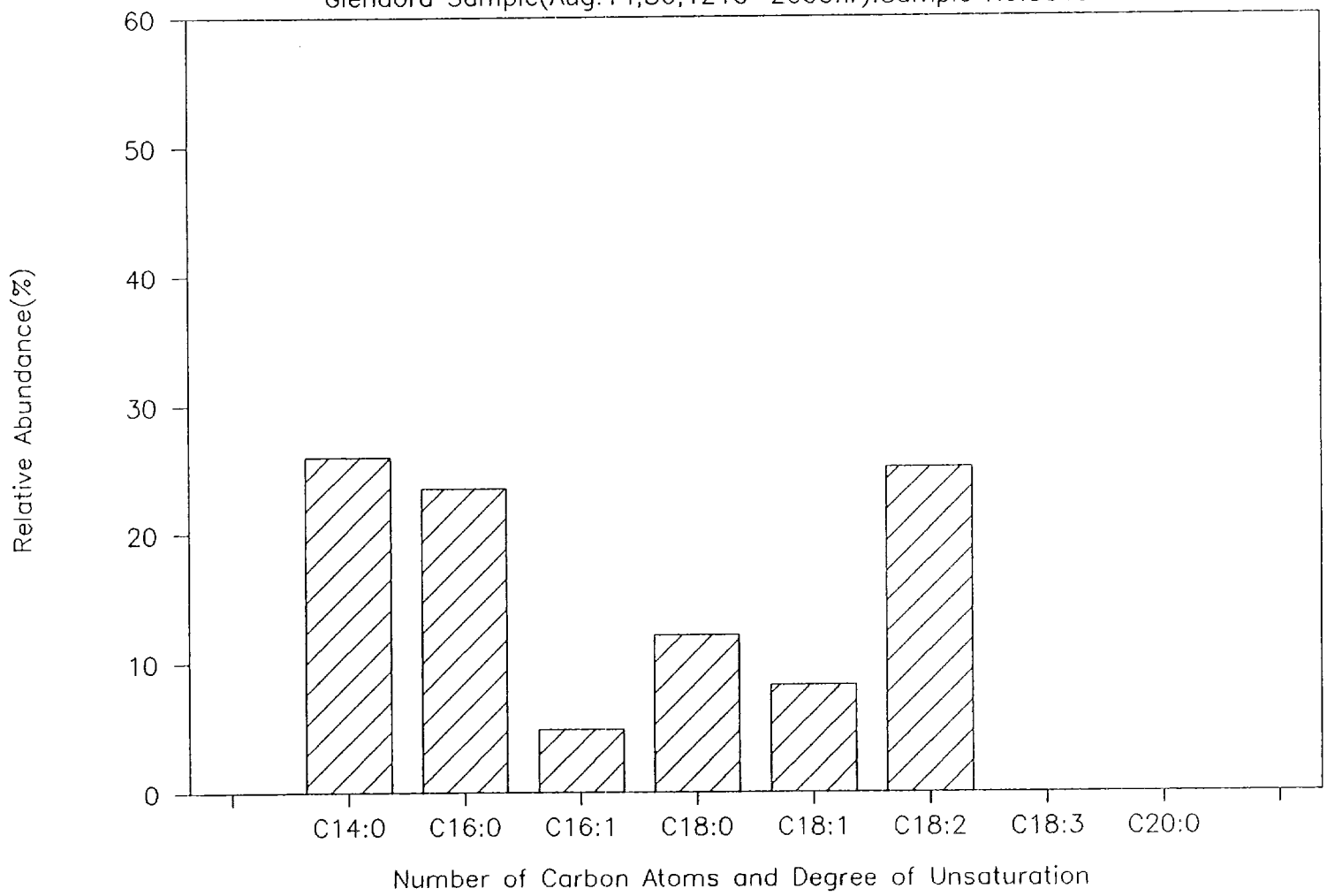


Figure VIII-6

Fatty Acid Distribution,Day#2

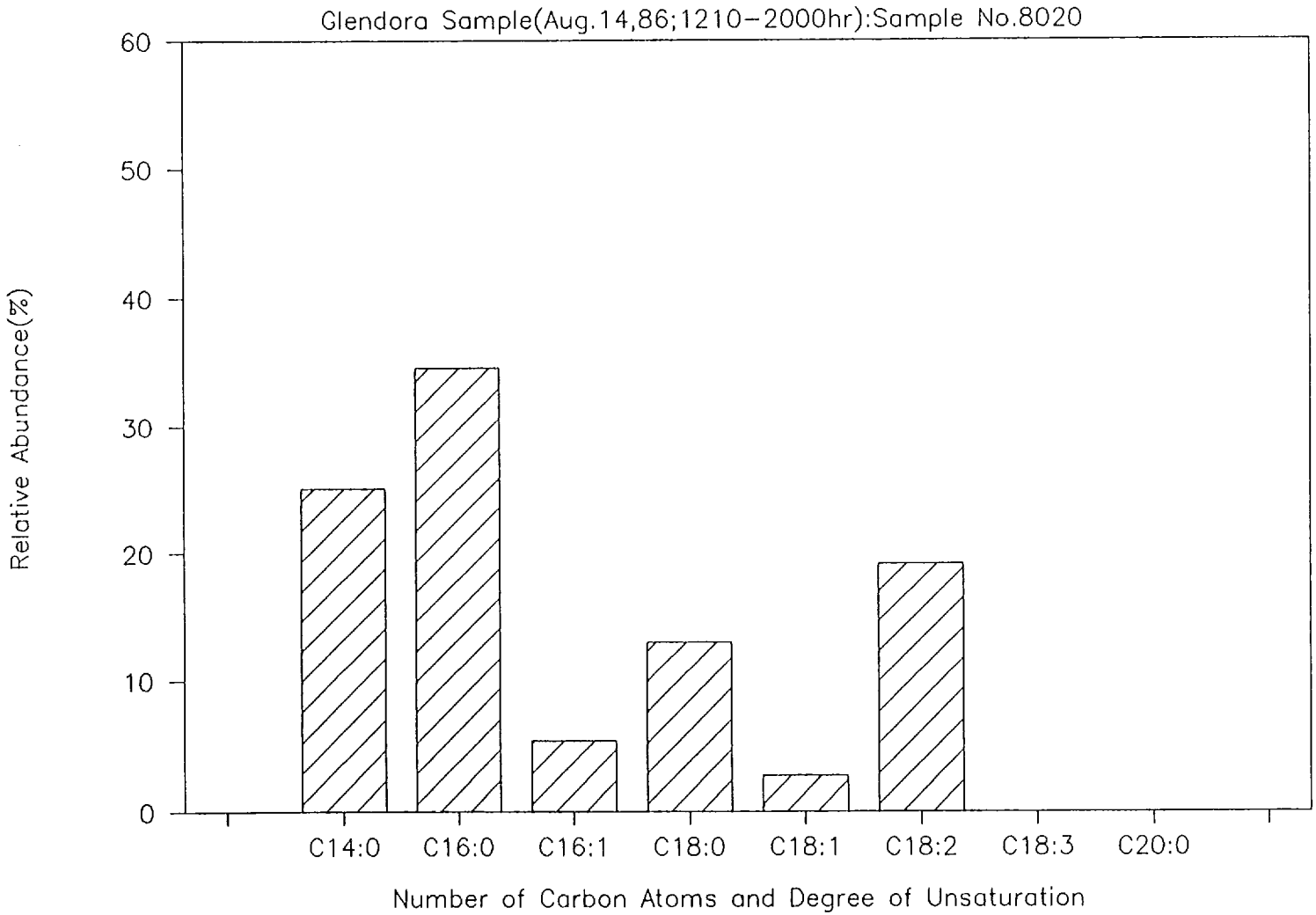


Figure VIII-7

Fatty Acid Distribution,Night

Glendora Sample(Aug.14,86;2005-800hr):Sample No.8024

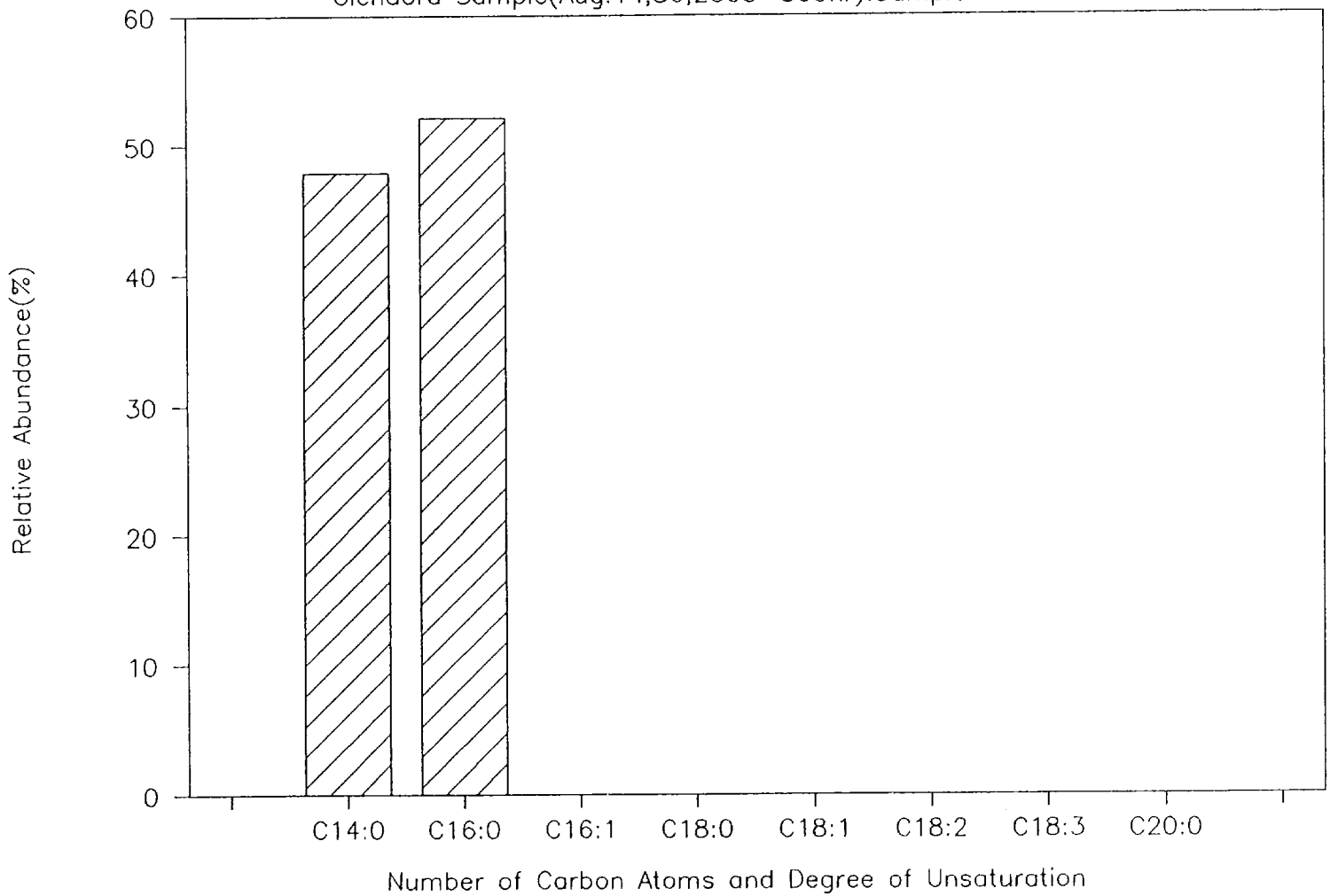


Figure VIII-8

Fatty Acid Distribution,Day

Glendora Sample(Aug.15,86;1200-2000hr):Sample No.8026+8029

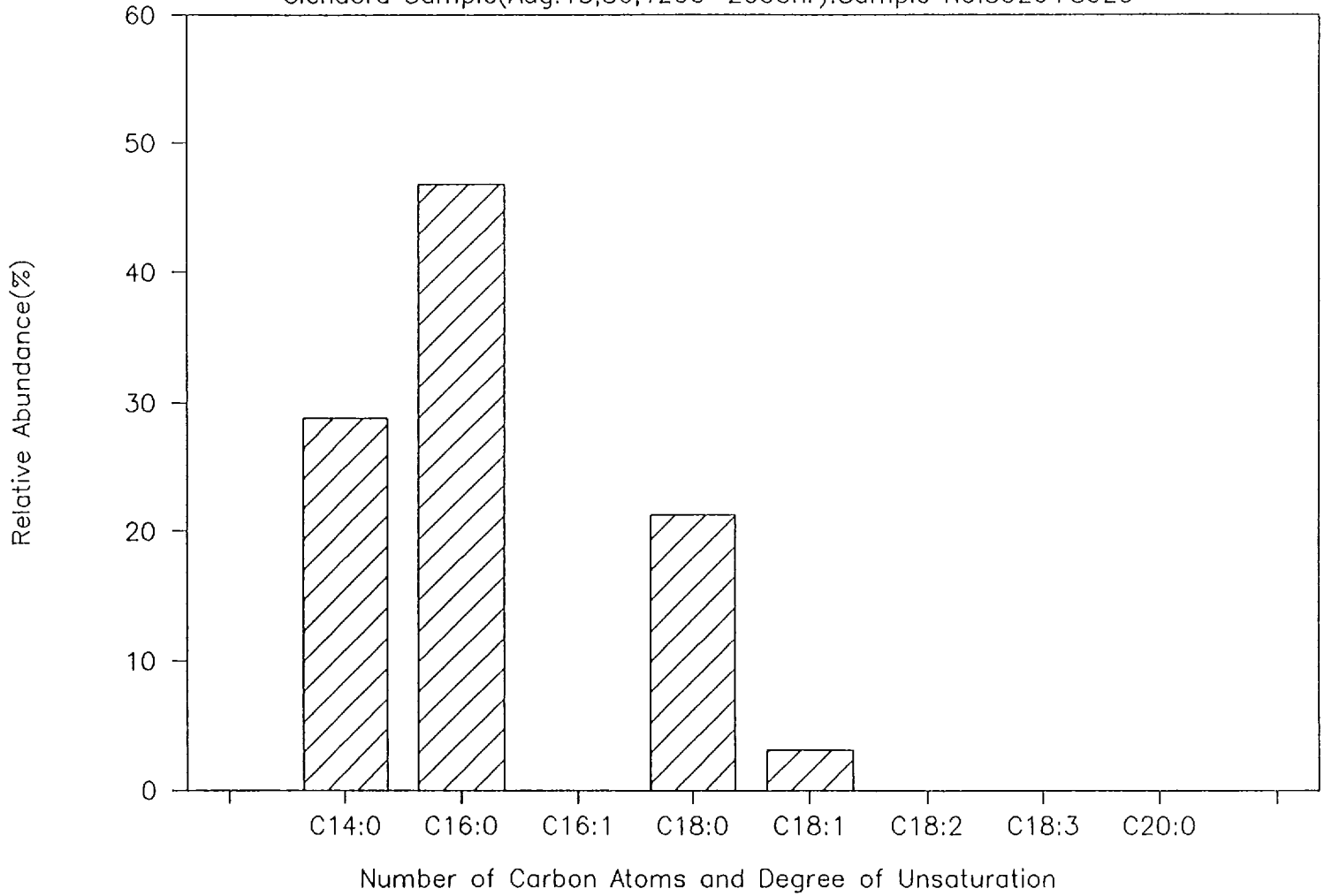


Figure VIII-9

Fatty Acid Distribution,Night

Glendora Sample(Aug.15,86;2005-800hr):Sample No.8031

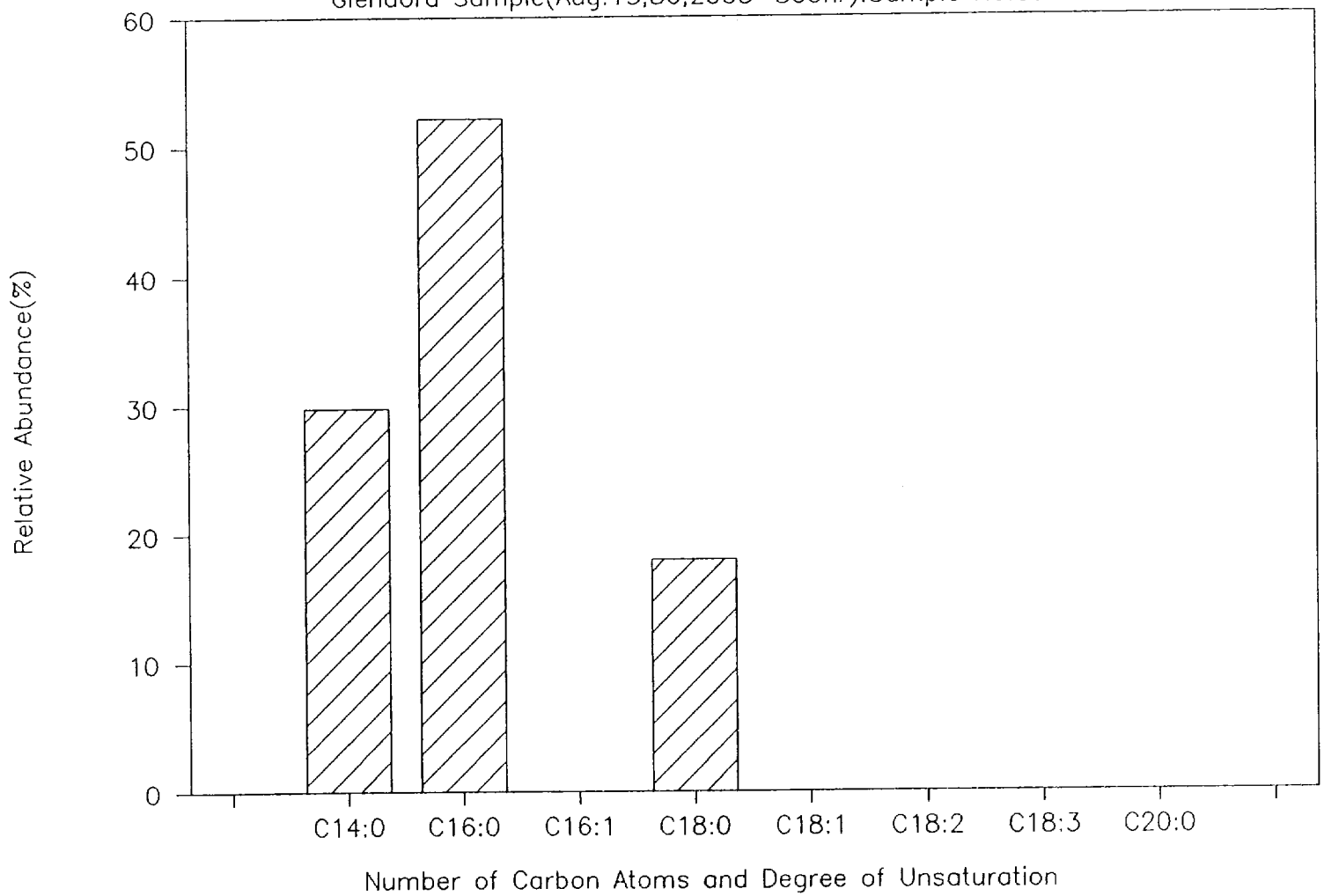


Figure VIII-10

Fatty Acid Distribution,Day

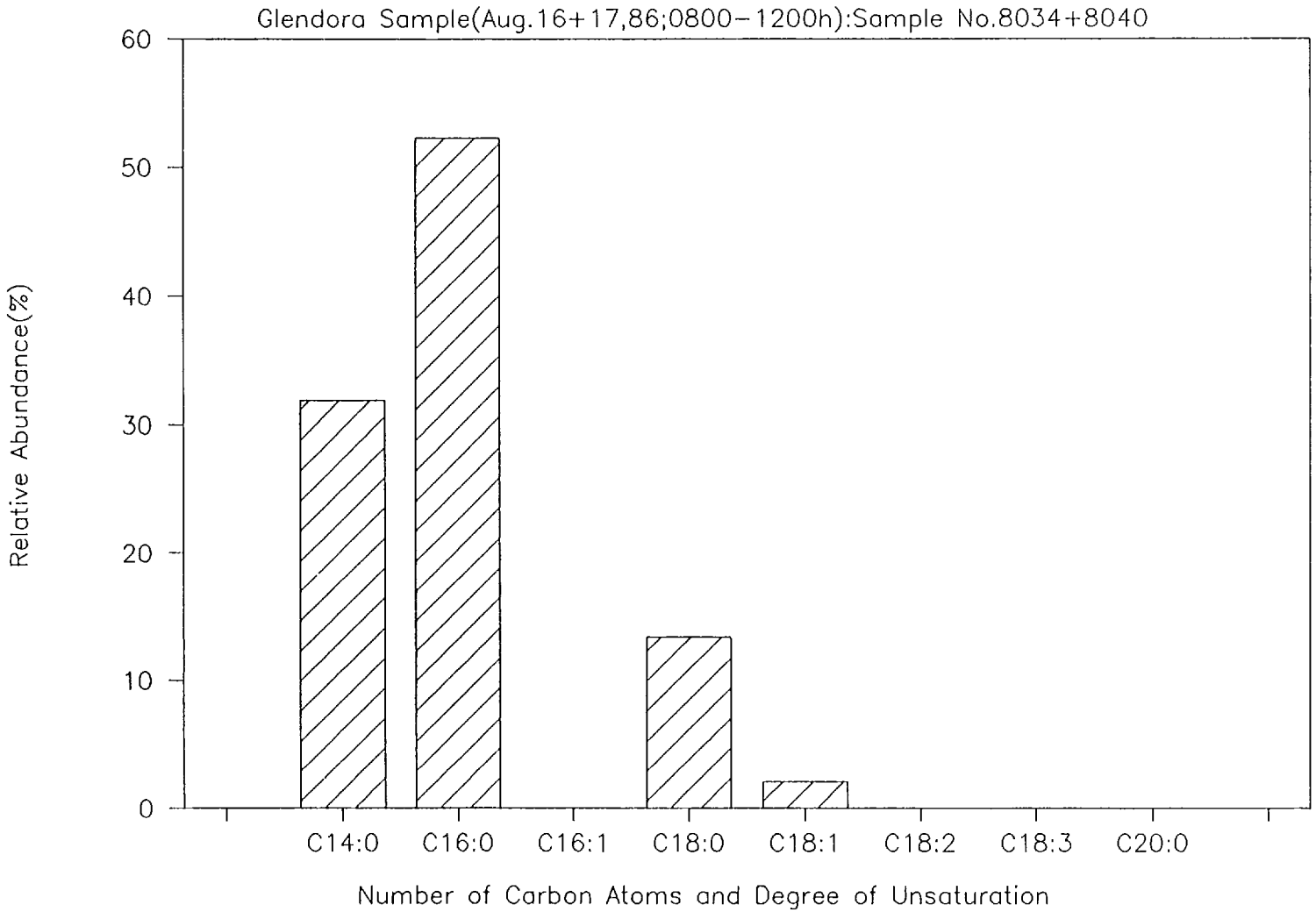


Figure VIII-11

Fatty Acid Distribution,Day

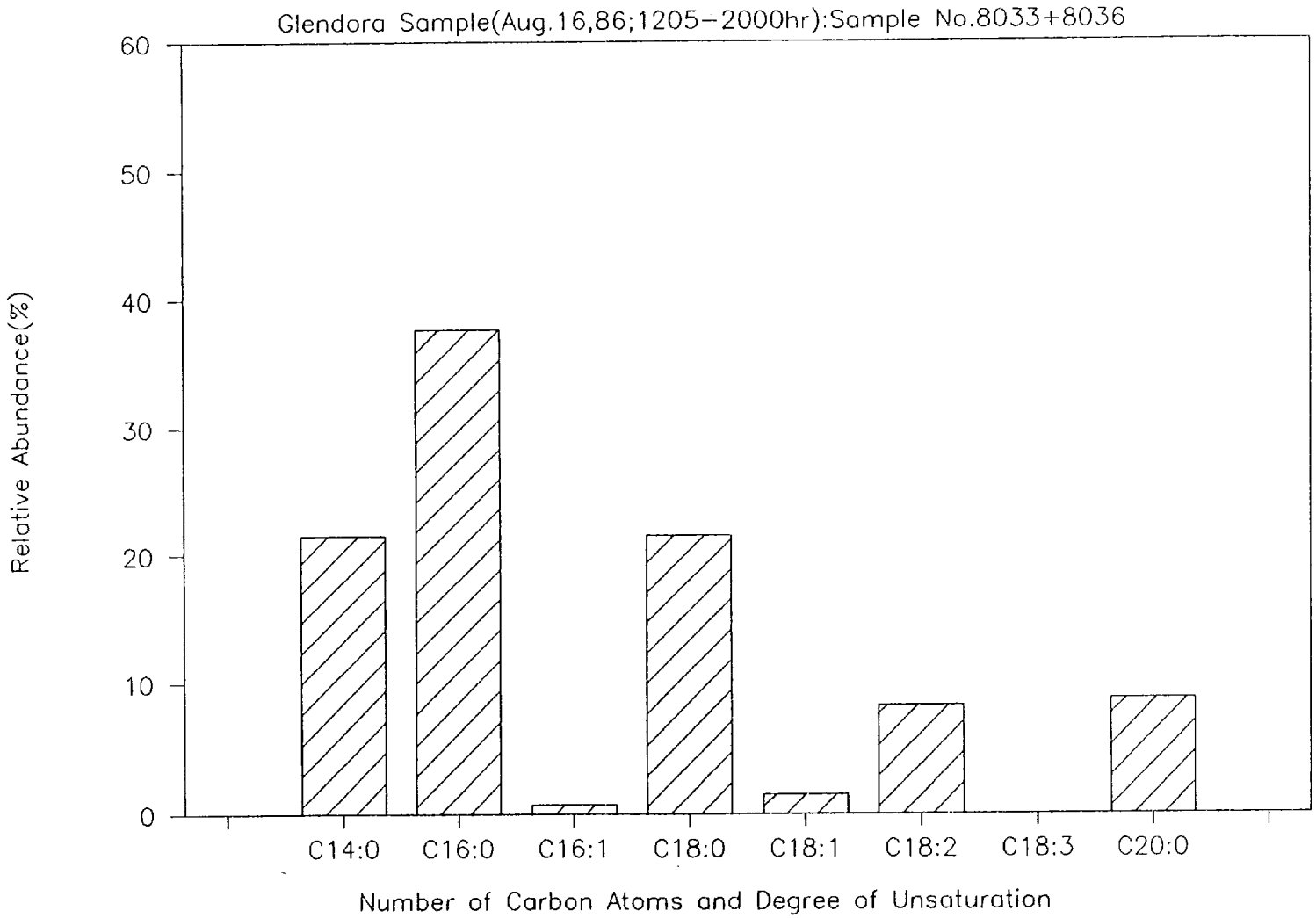


Figure VIII-12

Fatty Acid Distribution,Night

Glendora Sample(Aug.16,86;2000-720hr):Sample No.8037

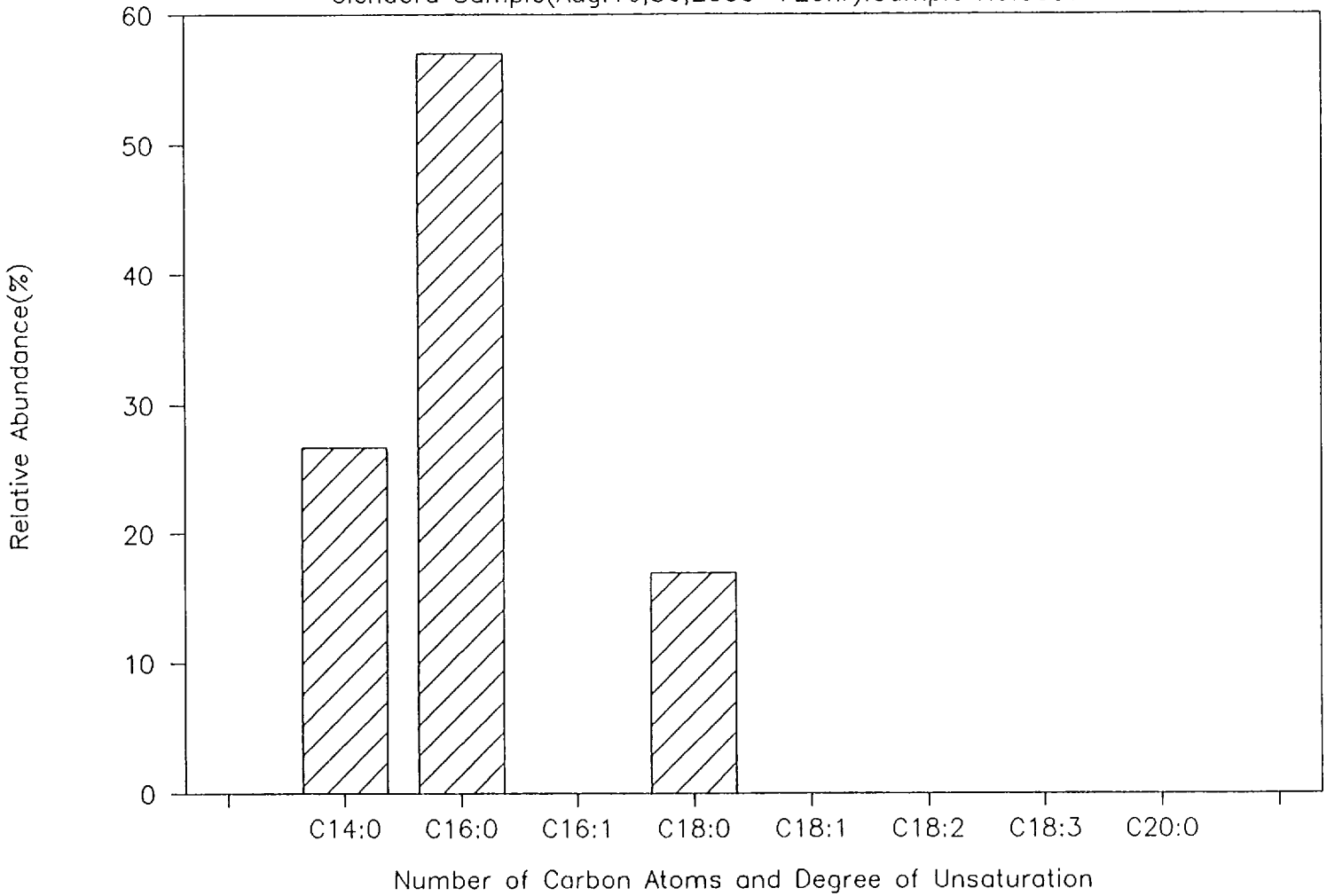


Figure VIII-13

Fatty Acid Distribution,Day

Glendora Sample(Aug.17,86;1200-2000hr):Sample No.8043+8044

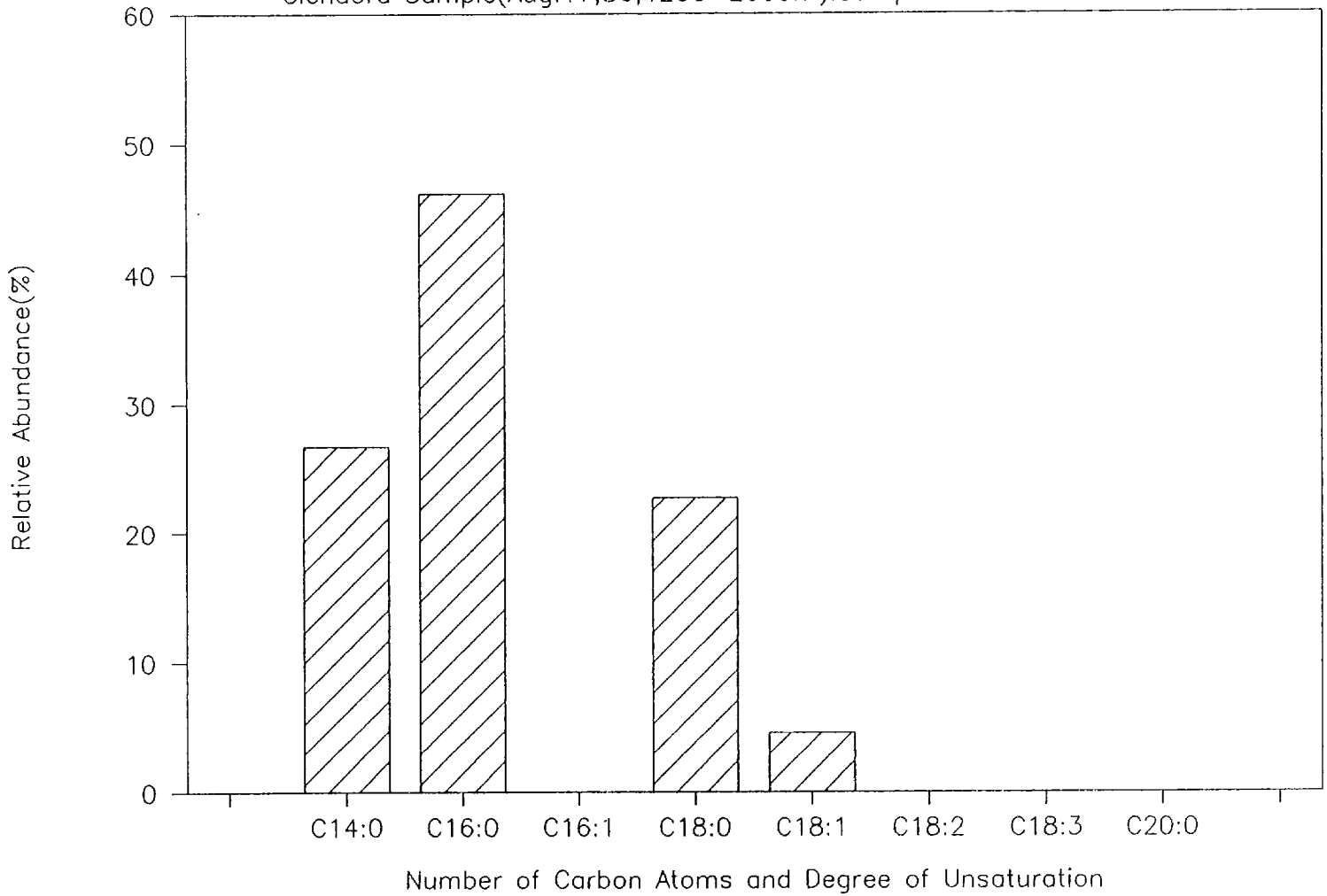


Figure VIII-14

Fatty Acid Distribution,Night

Glendora Sample(Aug.17,86;2005-800hr):Sample No.8045

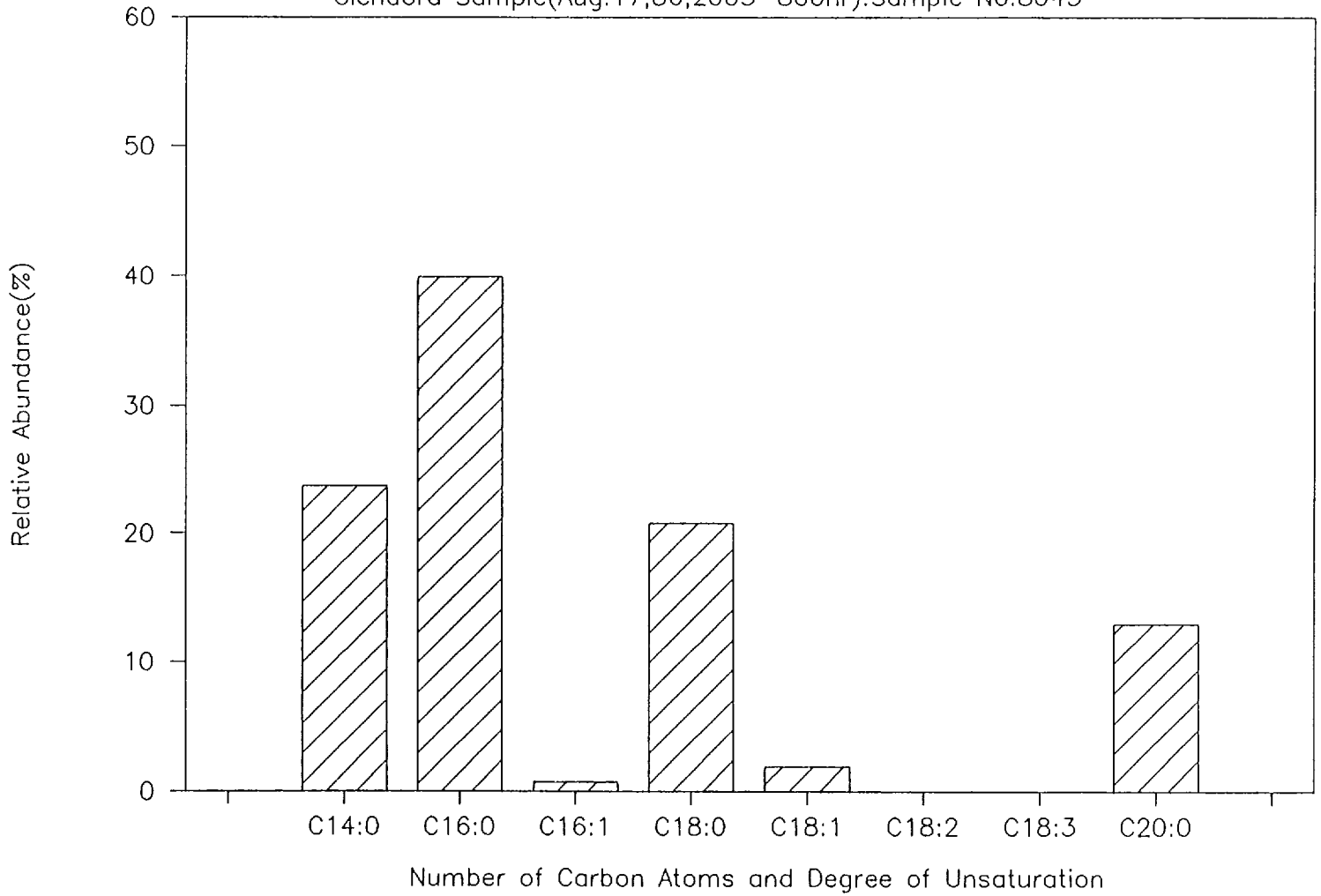


Figure VIII-15

Fatty Acid Distribution,Day

Glendora Sample(Aug.18+19,86;0800−1200h):Sample No.8047+8051

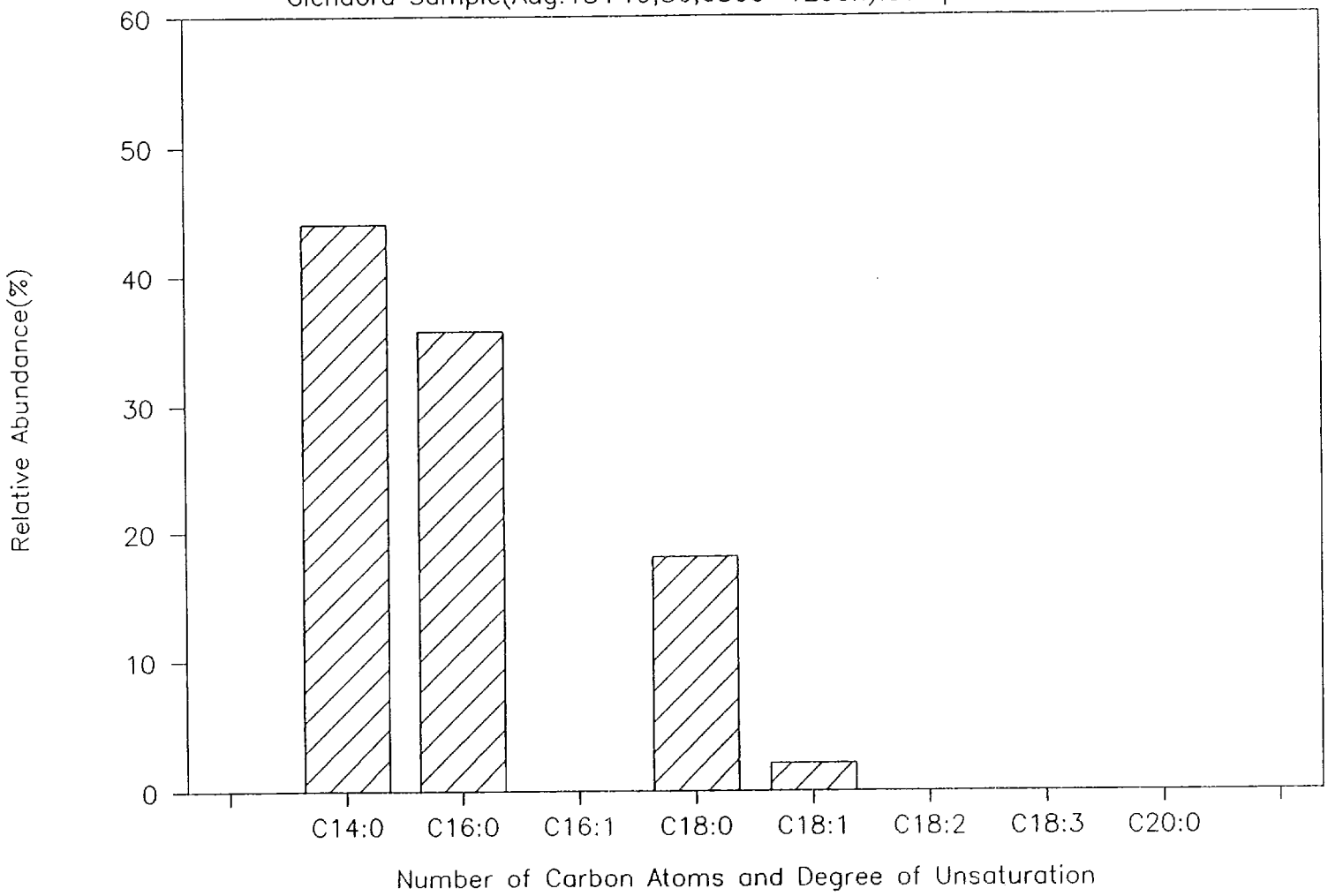


Figure VIII-16

Fatty Acid Distribution,Day

Glendora Sample(Aug.18,86;1200–2000hr):Sample No.8048+8049

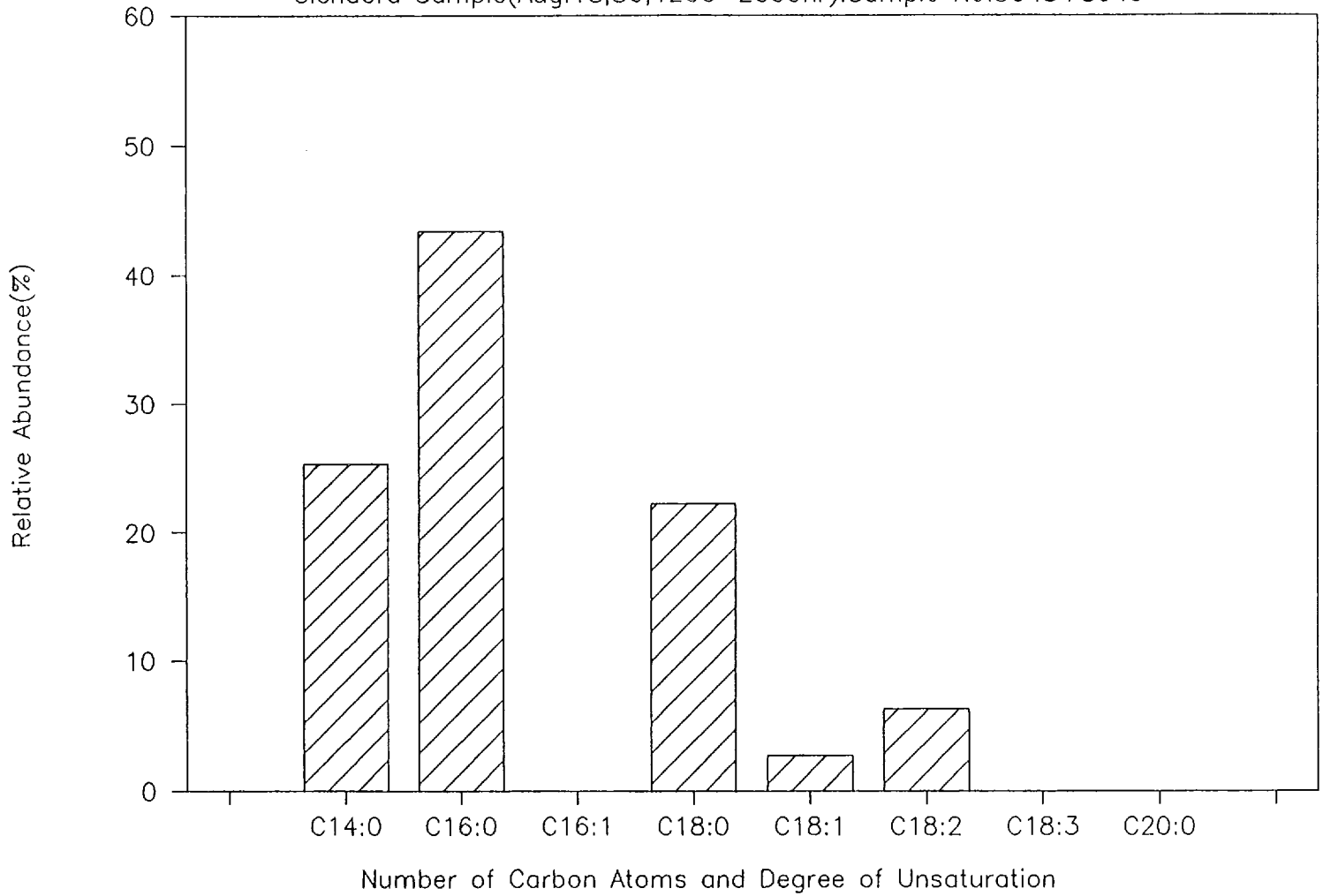


Figure VIII-17

Fatty Acid Distribution,Night

Glendora Sample(Aug.18,86;2000–0800hr):Sample No.8050

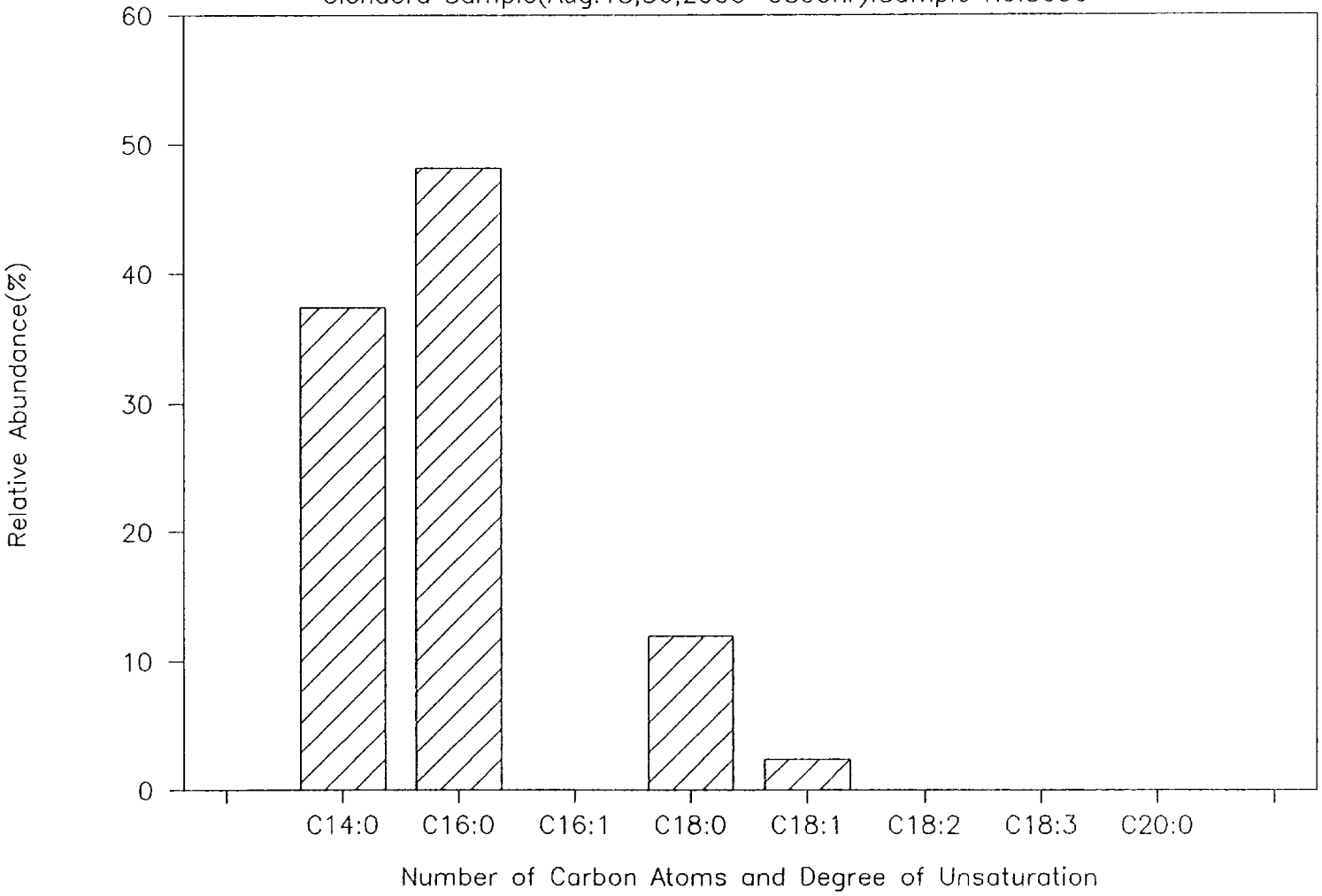


Figure VIII-18

Fatty Acid Distribution,Day

Glendora Sample(Aug.19,86;1200-2015hr):Sample No.8054+8055

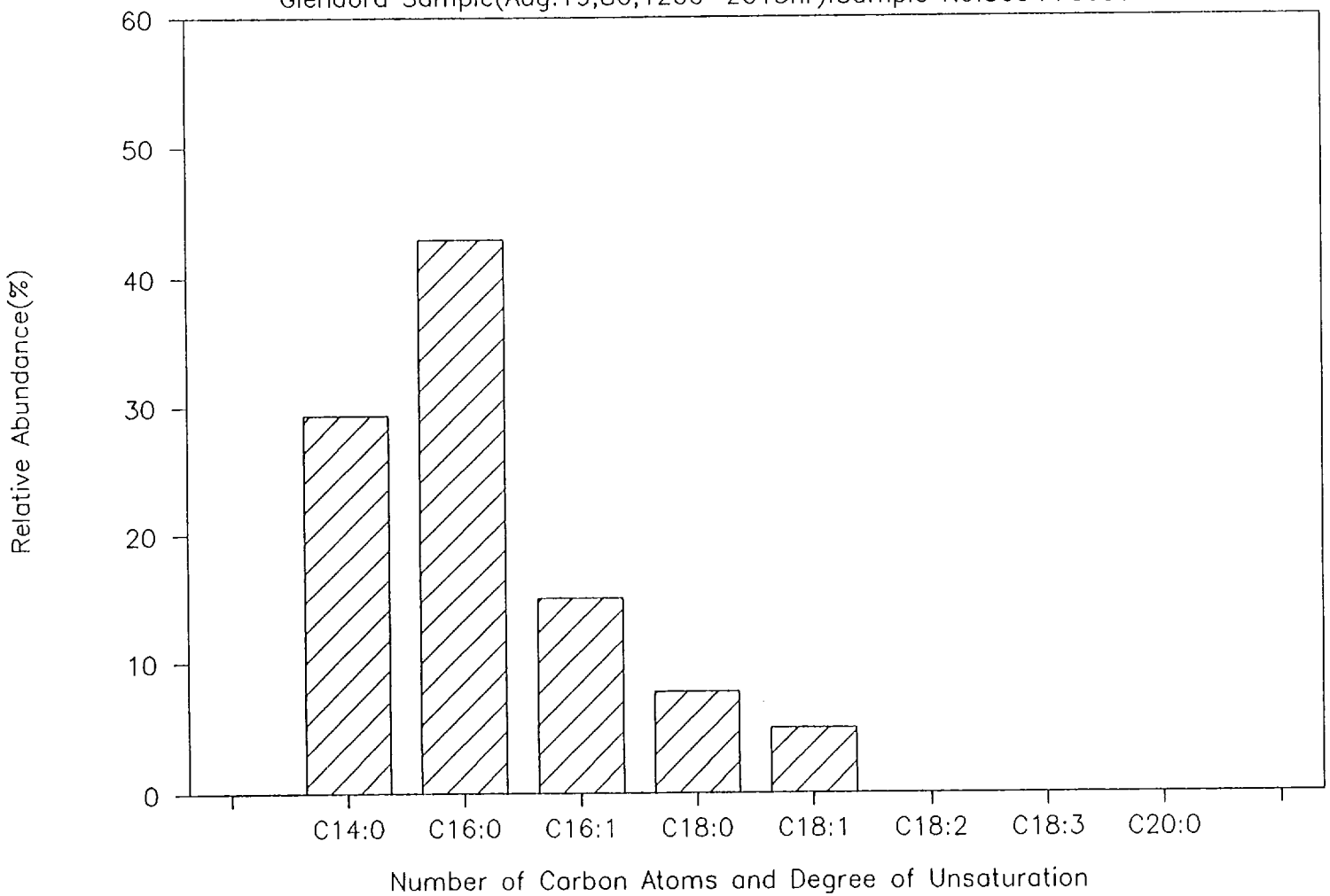


Figure VII1-19

Fatty Acid Distribution,Night

Glendora Sample(Aug.19,86;2020–0800hr):Sample No.8056

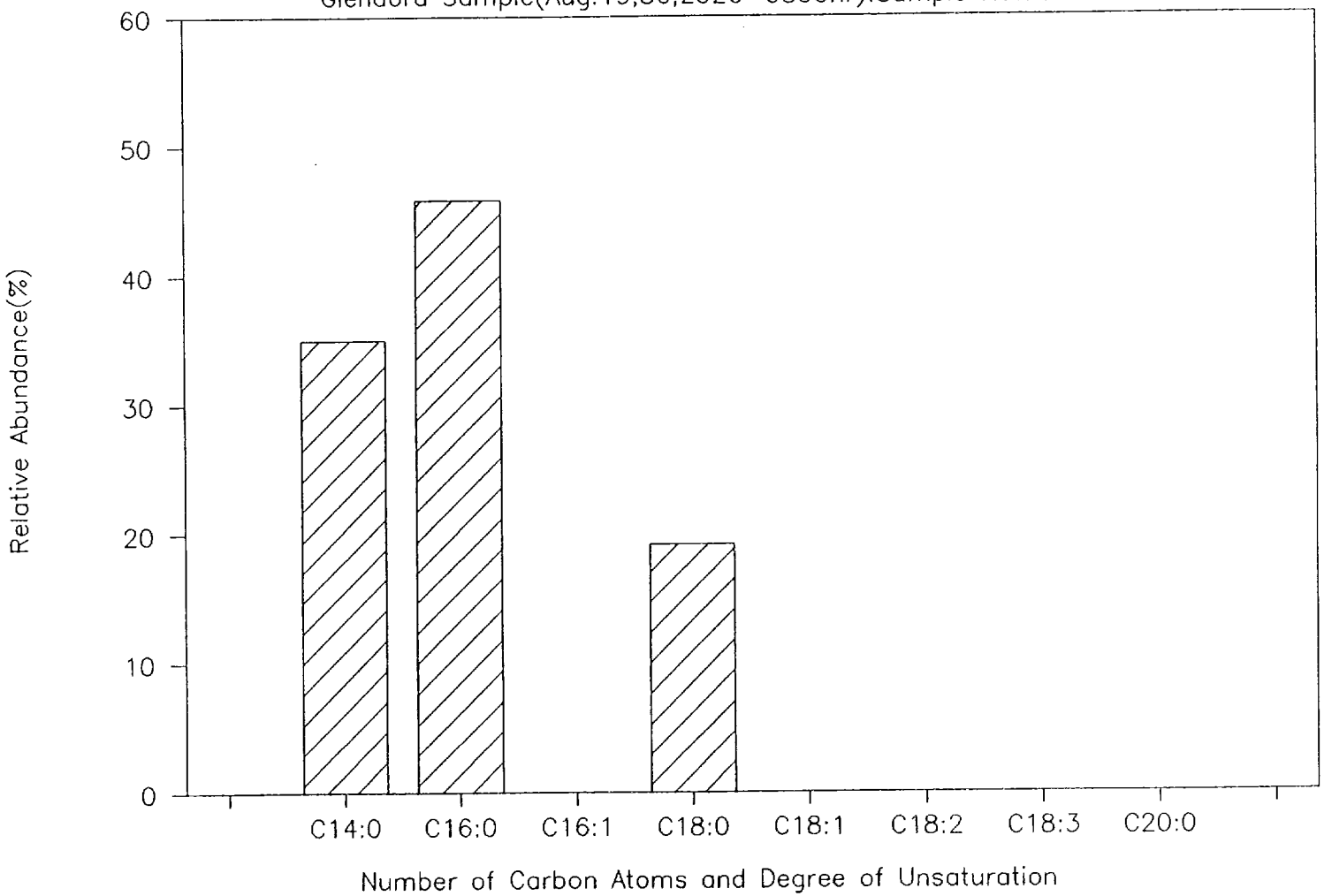


Figure VIII-20

Fatty Acid Distribution,Day

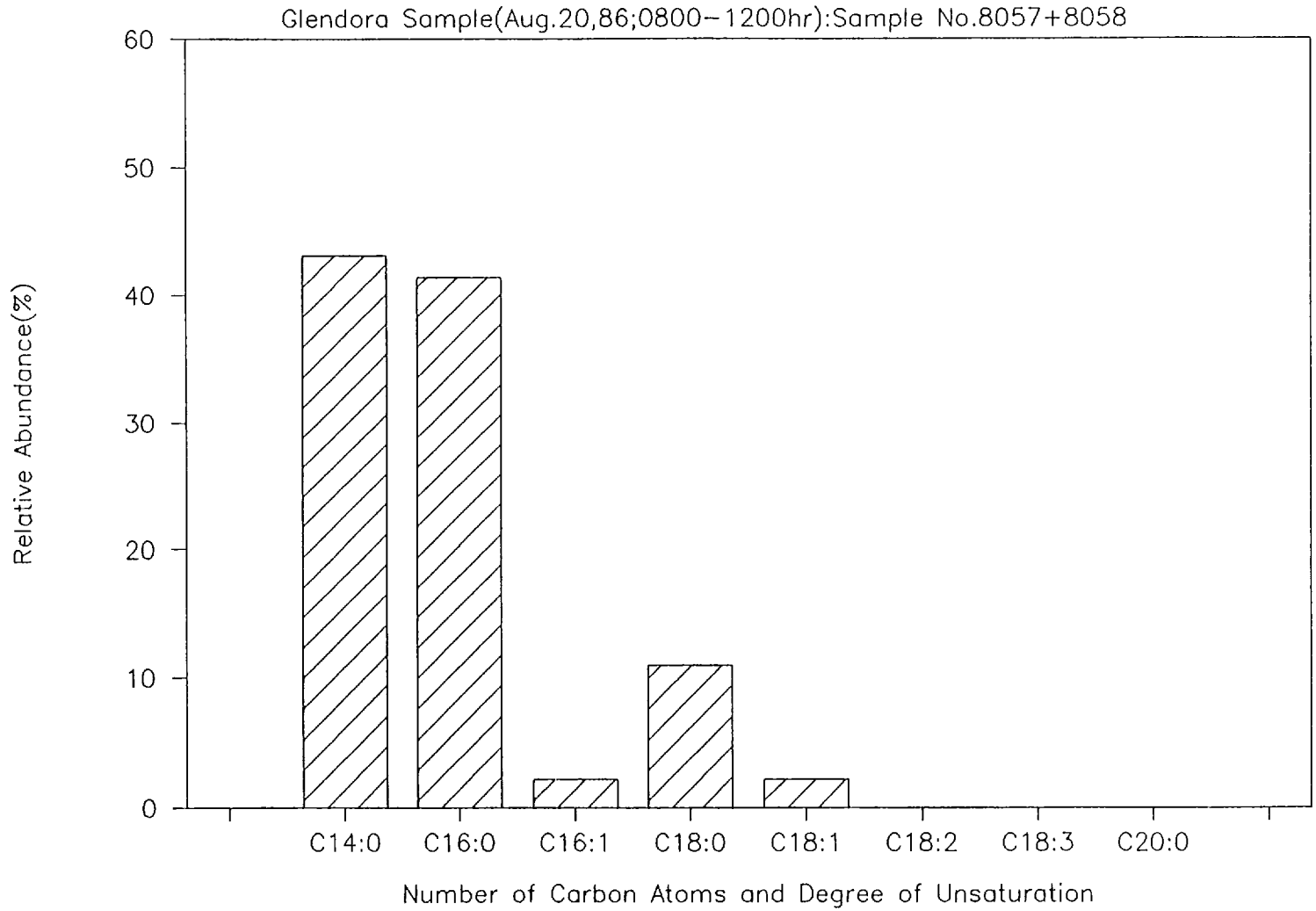


Figure VIII-21

Fatty Acid Distribution,Day

Glendora Sample(Aug.20,86;1200-2000hr):Sample No.8060+8061

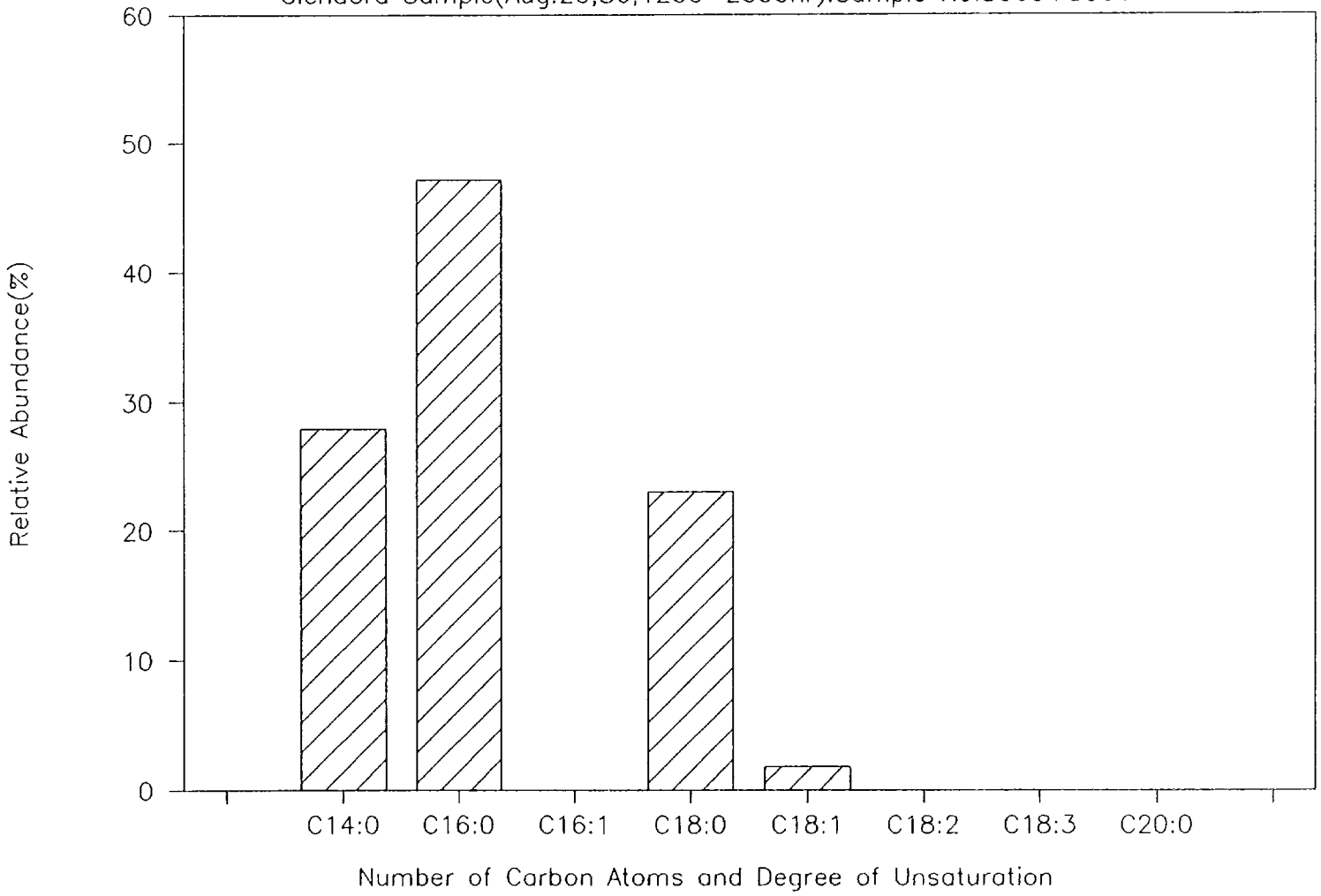
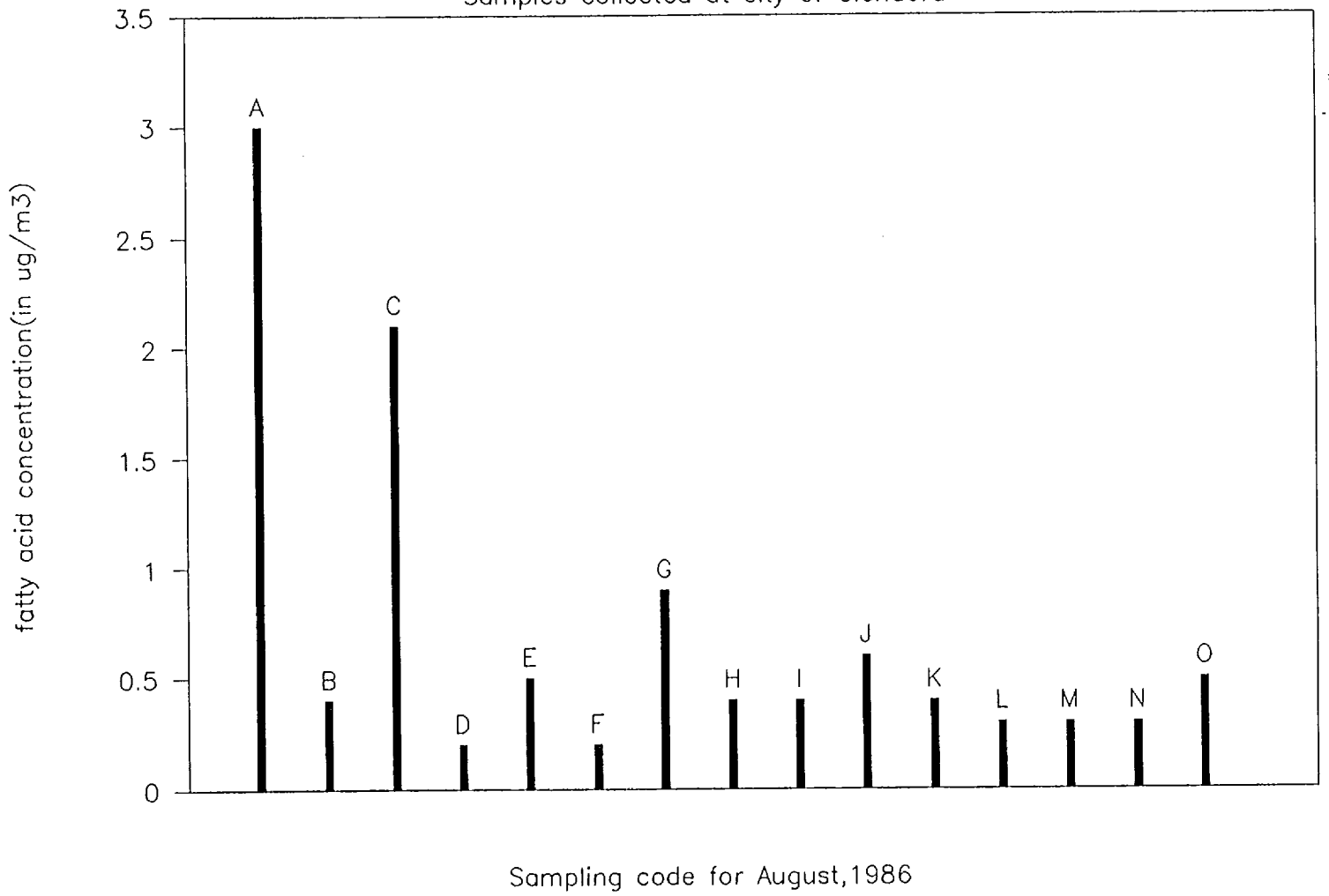


Figure VIII-22

Total Fatty Acid Concentration(ug/m3)

Samples collected at city of Glendora



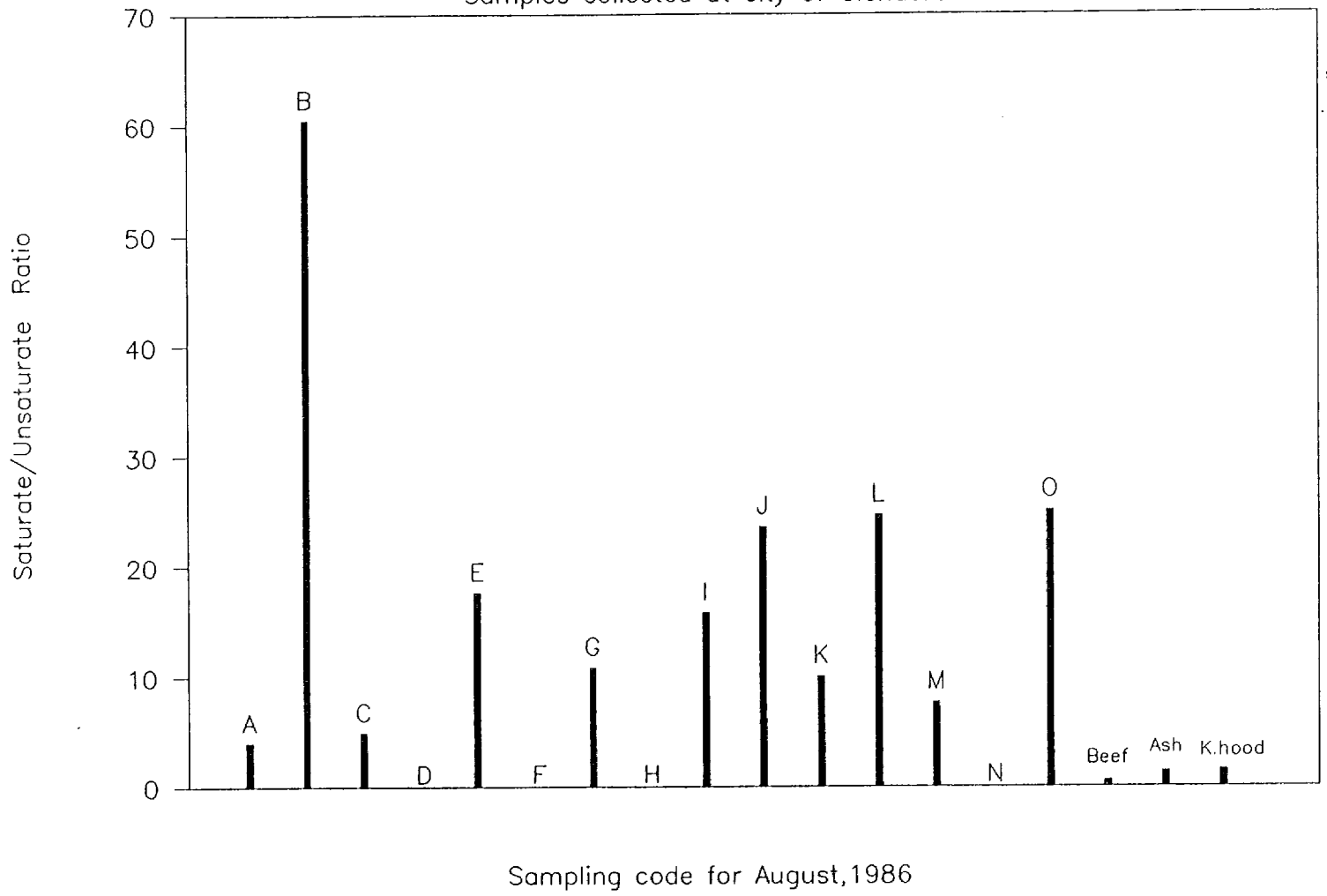
Key

Sample ID	Sampling Date	Sampling Time: Day or Night	Sampling Time: Time
A	8/13/86	D	0800-2000
B	8/13/86	N	2000-0800
C	8/14/86	D	0800-2000
D	8/14/86	N	2000-0800
E	8/15/86	D	0800-2000
F	8/15/86	N	2000-0800
G	8/16/86	D	0800-2000
H	8/16/86	N	2000-0720
I	8/17/86	D	0800-2000
J	8/17/86	N	2005-0800
K	8/18/86	D	0800-2000
L	8/18/86	N	2000-0800
M	8/19/86	D	0800-2015
N	8/19/86	N	2020-0800
O	8/20/86	D	0800-2000

Figure VIII-23

Saturated to Unsaturated Fatty Acid Ratio

Samples collected at city of Glendora



Key

Sample ID	Sampling Date	Sampling Time: Day or Night	Sampling Time: Time
A	8/13/86	D	0800-2000
B	8/13/86	N	2000-0800
C	8/14/86	D	0800-2000
D	8/14/86	N	2000-0800
E	8/15/86	D	0800-2000
F	8/15/86	N	2000-0800
G	8/16/86	D	0800-2000
H	8/16/86	N	2000-0720
I	8/17/86	D	0800-2000
J	8/17/86	N	2005-0800
K	8/18/86	D	0800-2000
L	8/18/86	N	2000-0800
M	8/19/86	D	0800-2015
N	8/19/86	N	2020-0800
O	8/20/86	D	0800-2000

Table VIII-4. Individual fatty acid weight per filter (μg) of samples collected at city of Duarte.

Collection Date (AUG 1986)	Filter No.	D/N*	C14:01	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	C20:0
13/14	8006,8018	D	86.7	60.7	nd2	27.3	nd	nd	nd	nd
13/15	8010,8025	D	68.0	77.3	nd	14.0	4.7	nd	nd	nd
17	8041	D	62.0	86.7	16.0	39.3	12.0	nd	nd	nd
19/20	8053,8059	D	43.3	53.3	nd	25.0	2.0	nd	nd	nd
13	8015	N	63.3	52.7	nd	28.7	4.7	nd	nd	nd

* D = day; N = night

1 Terminology for extent of unsaturation. 18:0 means totally saturated. 18:1 to 18:3 means from 1 to 3 unsaturated bonds.

2 nd = not detected

Table VIII-5. Individual fatty acid weight as function of air volume (ng/m3) of samples collected at city of Duarte.

Collection Date (AUG 1986)	Filter No.	D/N*	C14:01	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	C20:0
13/14	8006,8018	D	172.6	120.8	nd2	54.3	nd	nd	nd	nd
13/15	8010,8025	D	73.6	83.7	nd	15.2	5.1	nd	nd	nd
17	8041	D	154.3	187.7	34.6	85.1	26.0	nd	nd	nd
19/20	8053,8059	D	46.9	57.7	nd	27.1	2.2	nd	nd	nd
13	8015	N	91.4	76.1	nd	41.4	6.8	nd	nd	nd

* D = day; N = night

1 Terminology for extent of unsaturation. 18:0 means totally saturated. 18:1 to 18:3 means from 1 to 3 unsaturated bonds.

2 nd = not detected

Table VIII-6. Total saturated to unsaturated fatty acid ratio calculated for samples collected at city of Duarte.

Collection Date (AUG 1986)	Filter No.	D/N*	$C_{16} + C_{18}$** Ratio
13/14	8006,8018	D	***
13/15	8010,8025	D	19.4
17	8041	D	4.5
19/20	8053,8059	D	39.2
13	8015	N	17.3
Beef Fat Vapor			0.5
Fireplace Ash			1.2
Kitchen Hood Ex			1.2

* D = day; N = night

** $C_{16:0} + C_{18:0} / C_{16:1} + C_{18:1} + C_{18:2} + C_{18:3}$

*** No unsaturated fatty acid

Figure VIII- 24

Fatty Acid Distribution,Day

Duarte Sample(Aug.13+14,86;0810-1252hr):Sample No.8006+8018

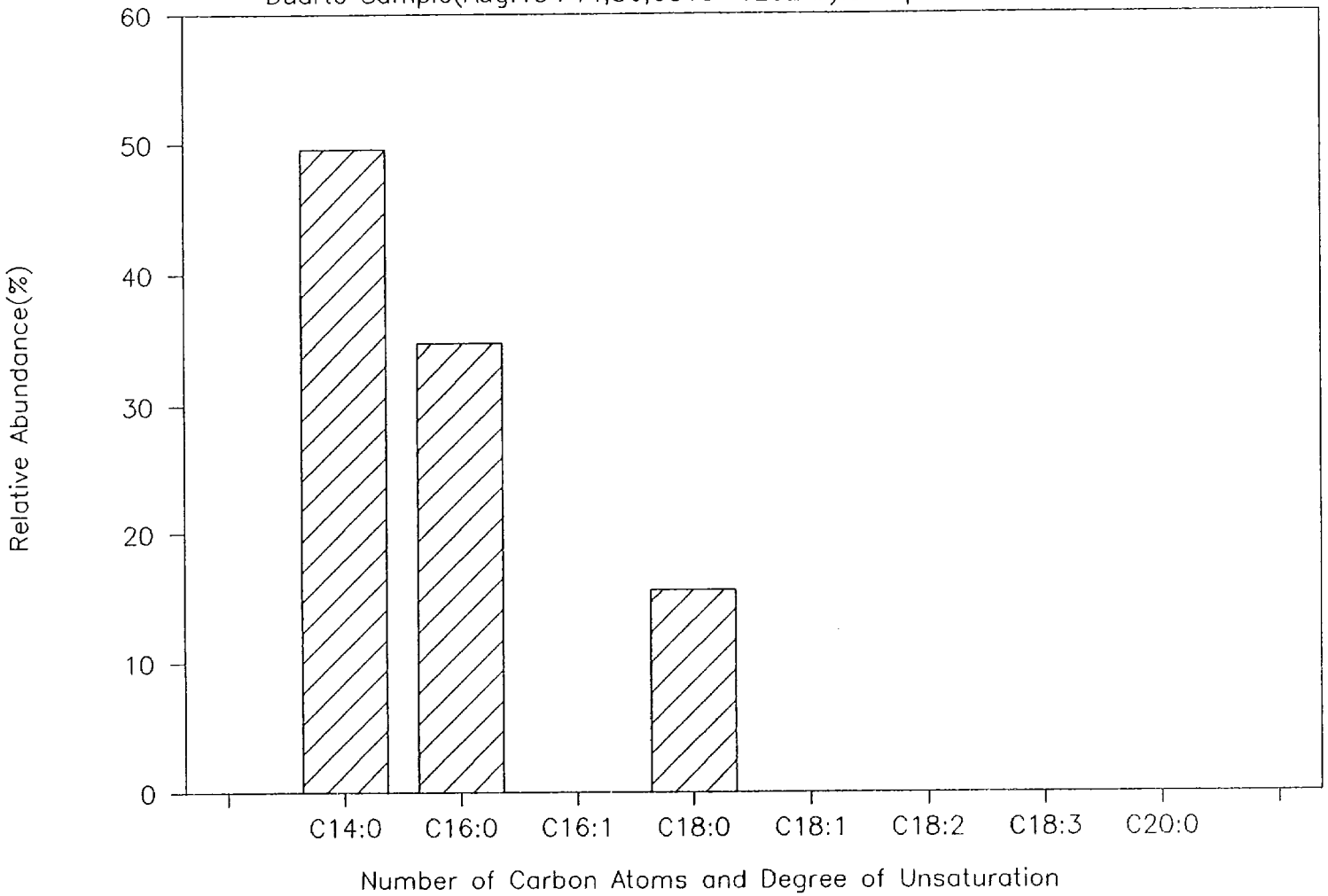


Figure VIII- 25

Fatty Acid Distribution,Day

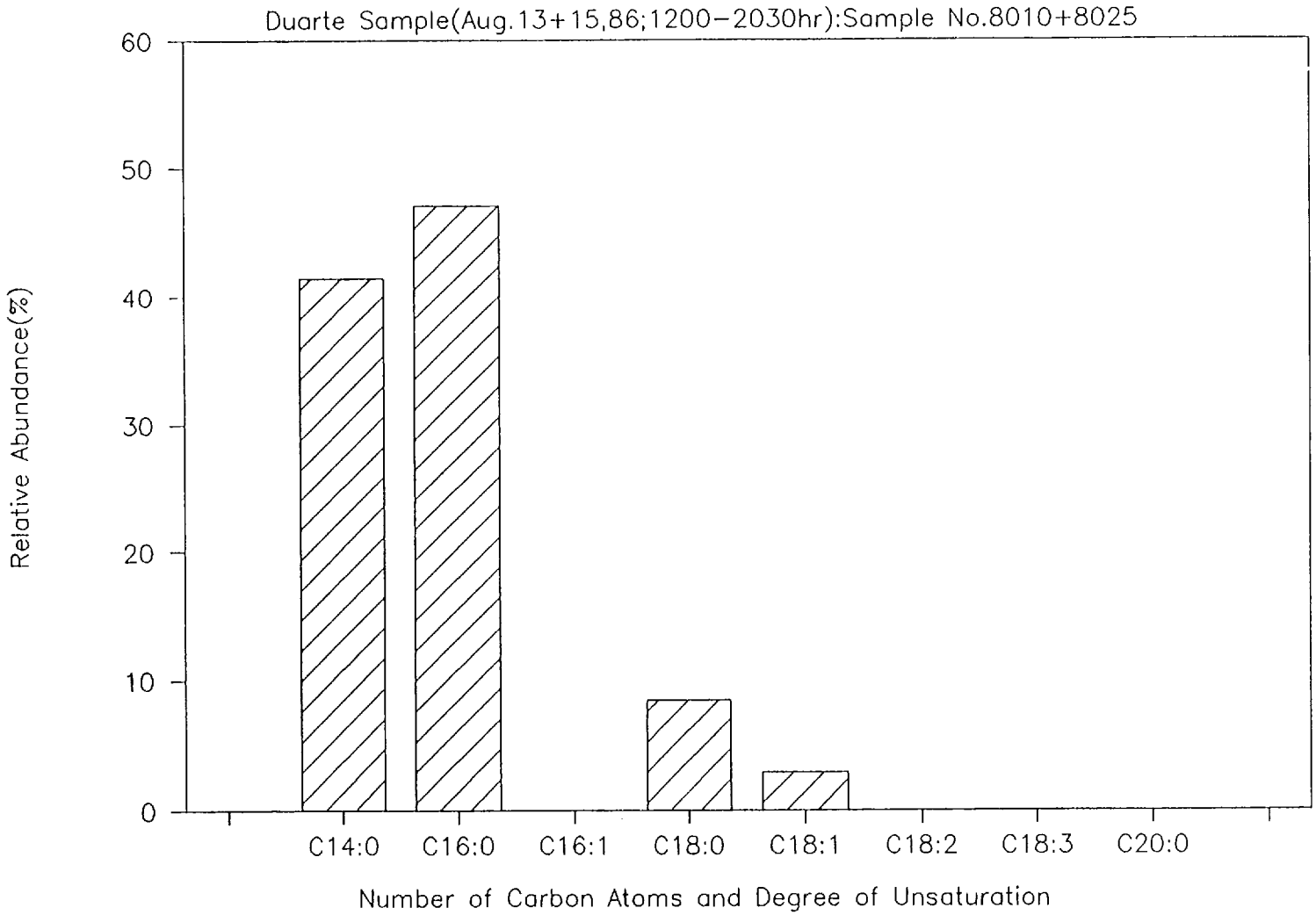


Figure VIII- 26

Fatty Acid Distribution,Night

Duarte Sample(Aug.13,86;2030–0830hr):Sample No.8015

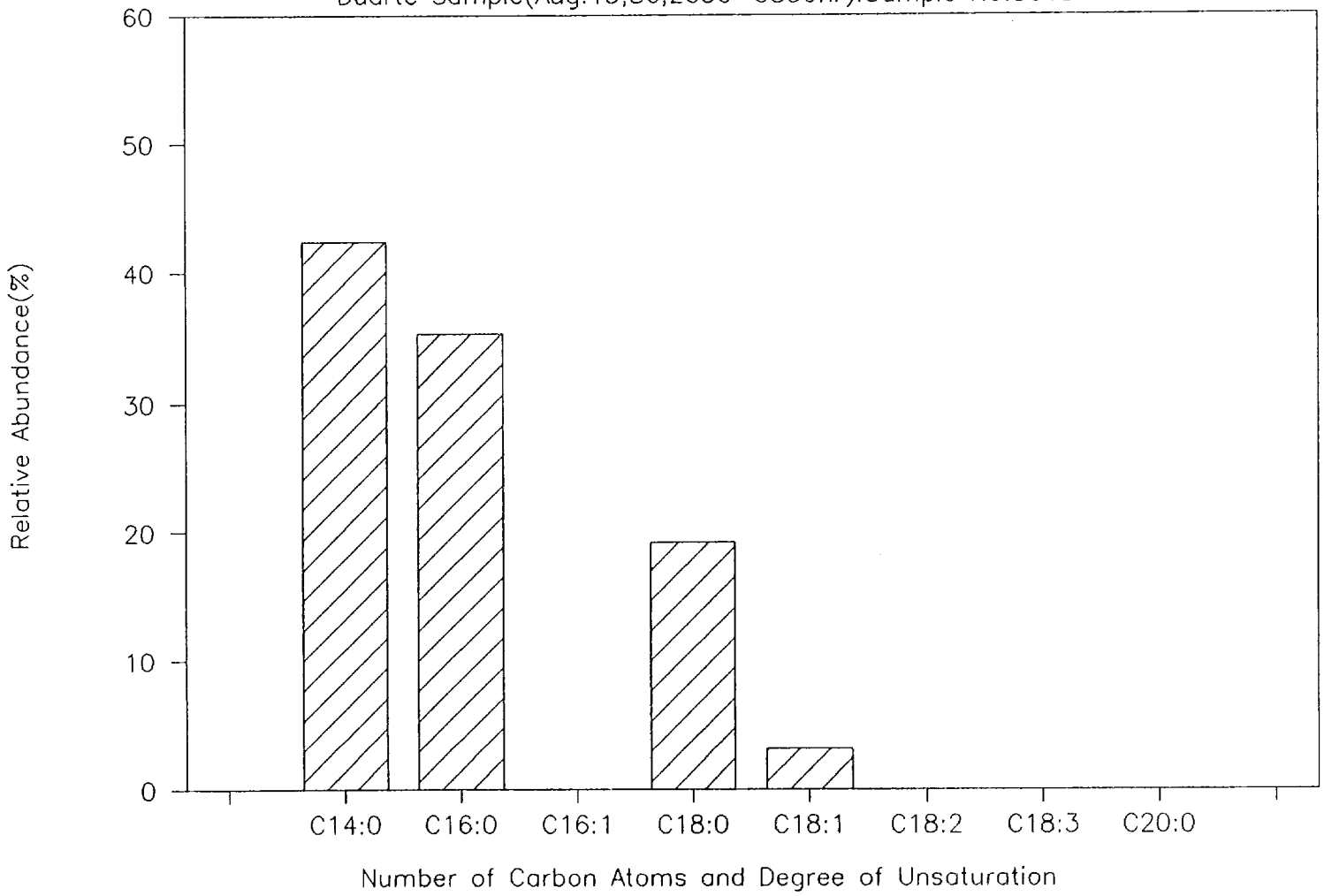


Figure VIII- 27

Fatty Acid Distribution,Day

Duarte Sample(Aug.17,86;1200-2000hr):Sample No.8041

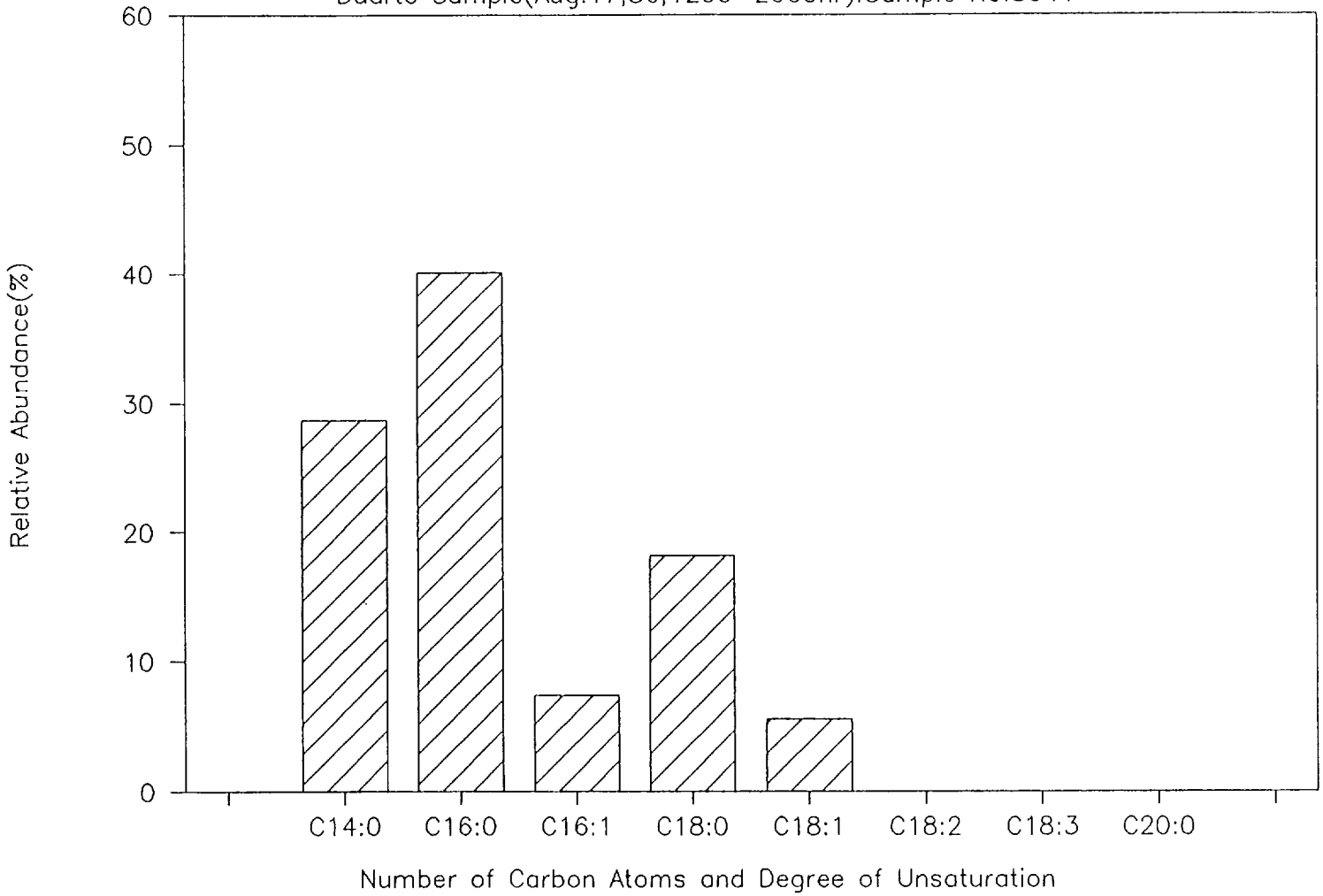


Figure VIII-28

Fatty Acid Distribution,Day

Duarte Sample(Aug.19+20,86;1200−2000hr):Sample No.8053+8059

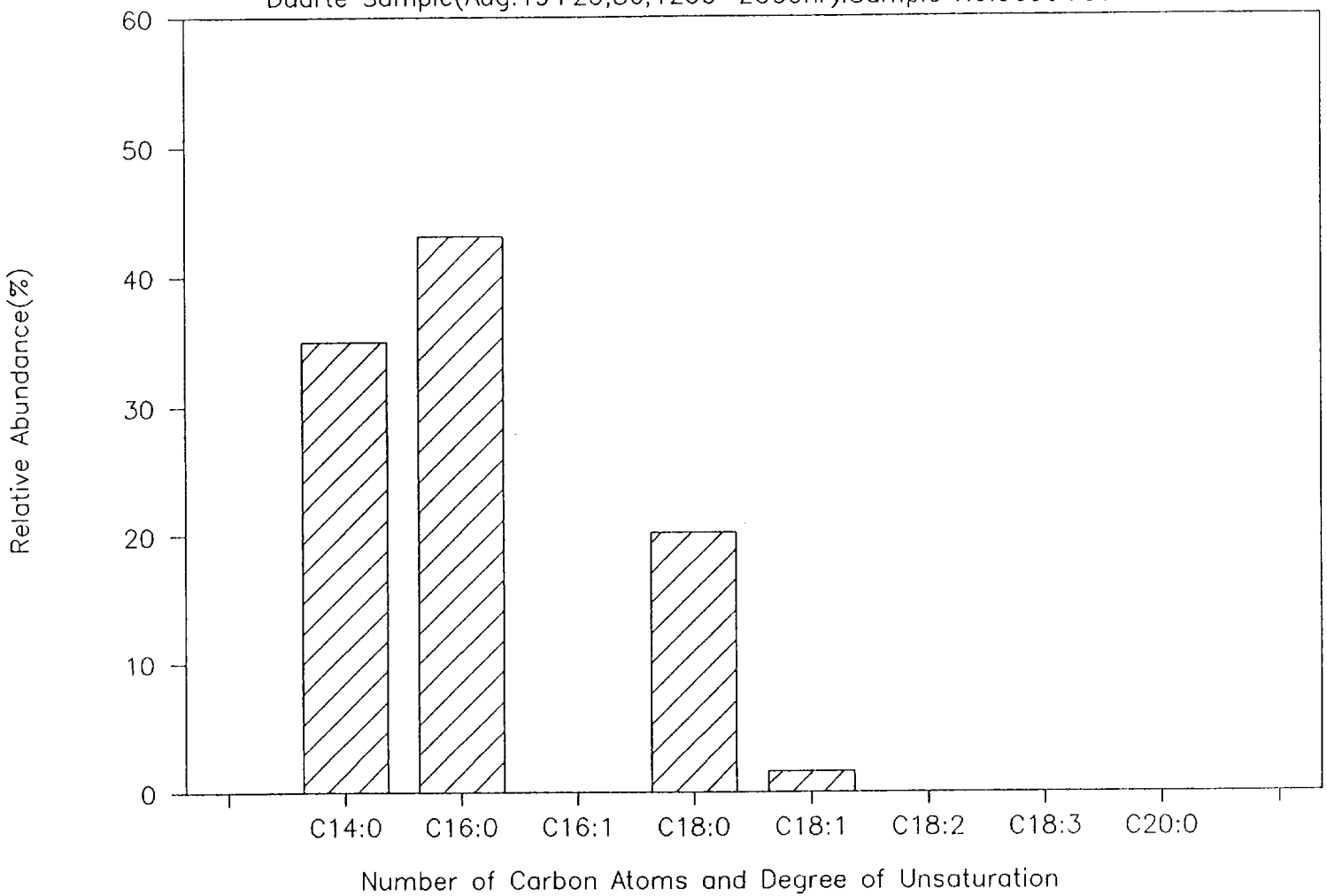
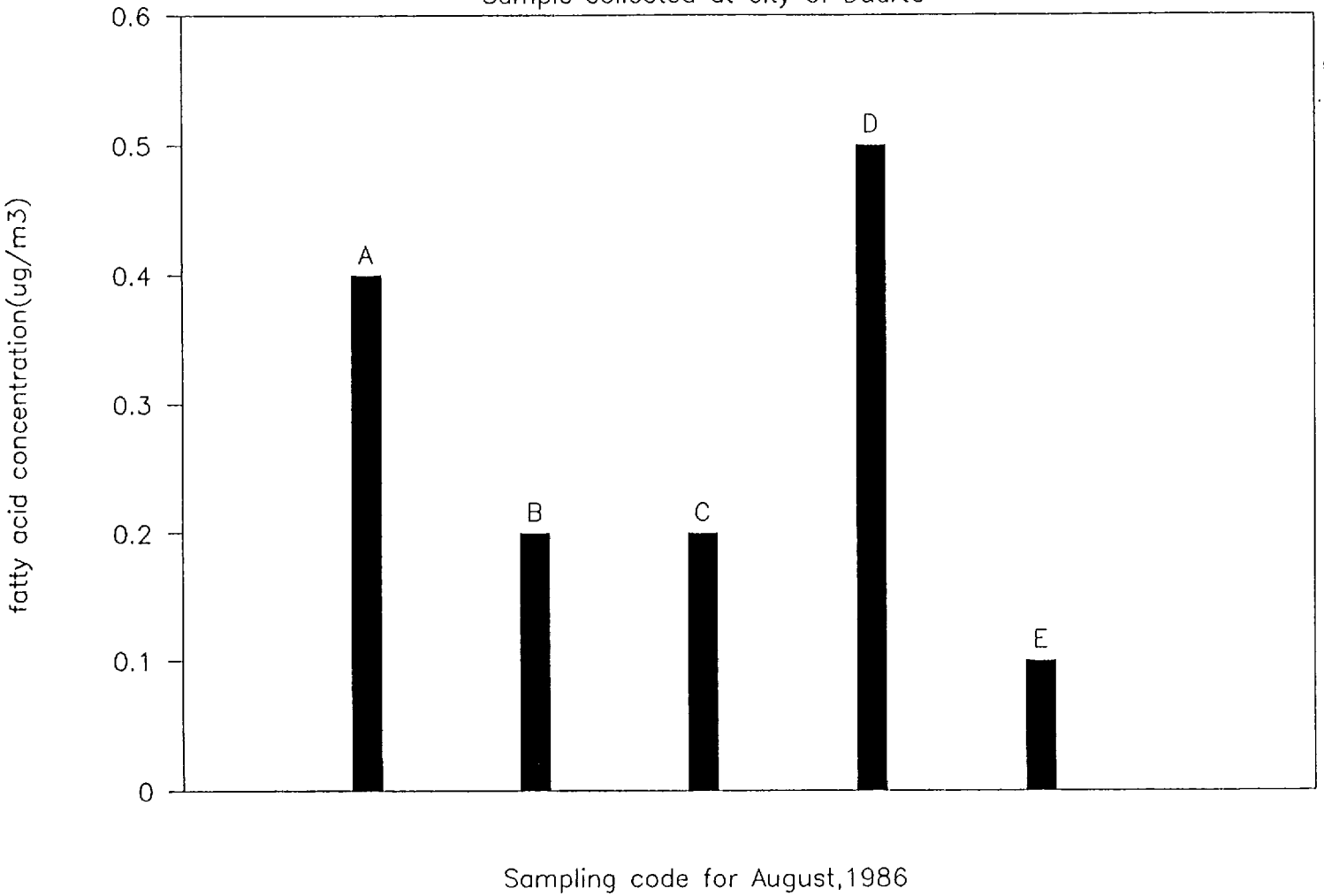


Figure VIII-.29

Total Fatty Acid Concentration(ug/m3)

Sample collected at city of Duarte



Key

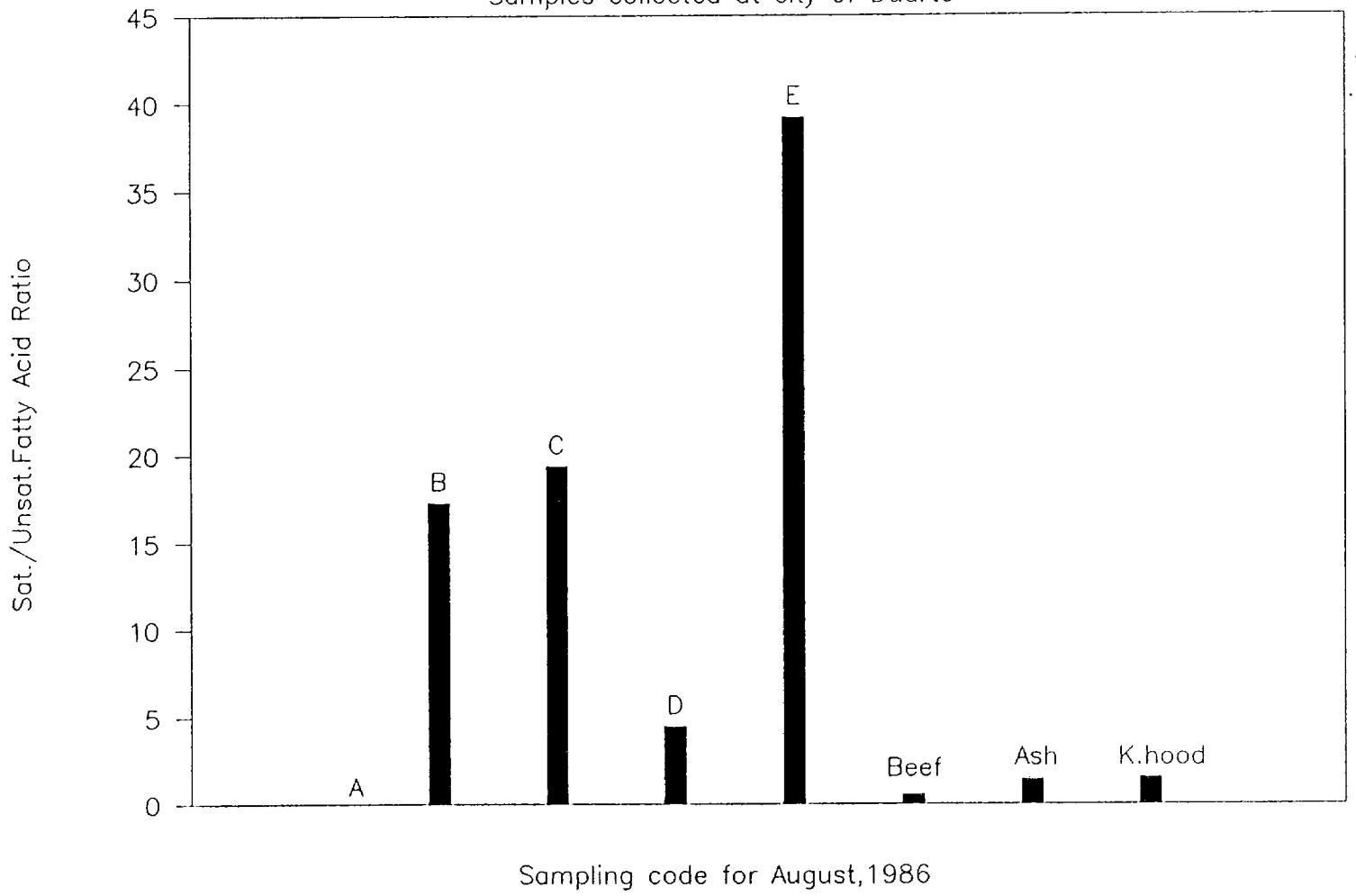
Sample ID	Sampling Date	Sampling Time: Day or Night	Sampling Time: Time
A	8/13/86	D	0810-1230
A	8/14/86	D	0830-1252
B	8/13/86	N	2030-0830
C	8/13/86	D	1230-2030
C	8/15/86	D	1200-2000
D	8/17/86	D	1200-2000
E	8/19/86	D	1200-2000
E	8/20/89	D	1200-2000

} combined samples

Figure VIII-30

Saturated to Unsaturated Fatty Acid Ratio

Samples collected at city of Duarte



Key

Sample ID	Sampling Date	Sampling Time: Day or Night	Sampling Time: Time
A }	8/13/86	D	0810-1230
A }	8/14/86	D	0830-1252
B	8/13/86	N	2030-0830
C }	8/13/86	D	1230-2030
C }	8/15/86	D	1200-2000
D	8/17/86	D	1200-2000
E }	8/19/86	D	1200-2000
E }	8/20/89	D	1200-2000

} combined samples

Table VIII-7. Individual fatty acid weight per filter (μg) for samples collected at Caldecott Tunnel.

Collection Date (AUG 1989)	Filter No.	D/N*	C14:0[1]	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	C20:0
10	3809	D	177.2	110.8 -	19.6	45.6	18.0	44.4	nd[2]	nd
10	3813	N	176.0	208.0	4.4	118.8	62.0	tr[3]	nd	nd

* D = day; N = night

[1] Terminology for extent of unsaturation. 18:0 means totally saturated. 18:1 to 18:3 means from 1 to 3 unsaturated bonds.

[2] nd = not detected

[3] tr = trace

Table VIII-8. Individual fatty acid weight as function of air volume (ng/m3) for samples collected at Caldecott Tunnel.

Collection Date (AUG 1986)	Filter No.	D/N*	C14:0[1]	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	C20:0
10	3809	D	684	428	76	176	69	171	nd[2]	nd
10	3813	N	226	267	6	152	80	tr[3]	nd	nd

* D = day; N = night

[1] Terminology for extent of unsaturation. 18:0 means totally saturated. 18:1 to 18:3 means from 1 to 3 unsaturated bonds.

[2] nd = not detected

[3] tr = trace

Table VIII-9. Total saturated to unsaturated fatty acid ratio calculated for samples collected at Caldecott Tunnel.

Collection Date (AUG 1989)	Filter No.	$C_{16} + C_{18}$* Ratio
10	3809	1.9
10	3813	4.9
	Beef Fat Vapor	0.5
	Fireplace Ash	1.2
	Kitchen Hood Exhaust	1.2

* $C_{16:0} + C_{18:0} / C_{16:1} + C_{18:1} + C_{18:2} + C_{18:3}$

Figure VIII-31

Fatty Acid Distribution,Day

Tunnel Sample(Aug.10,89,0950-1405hr):Sample No.3809

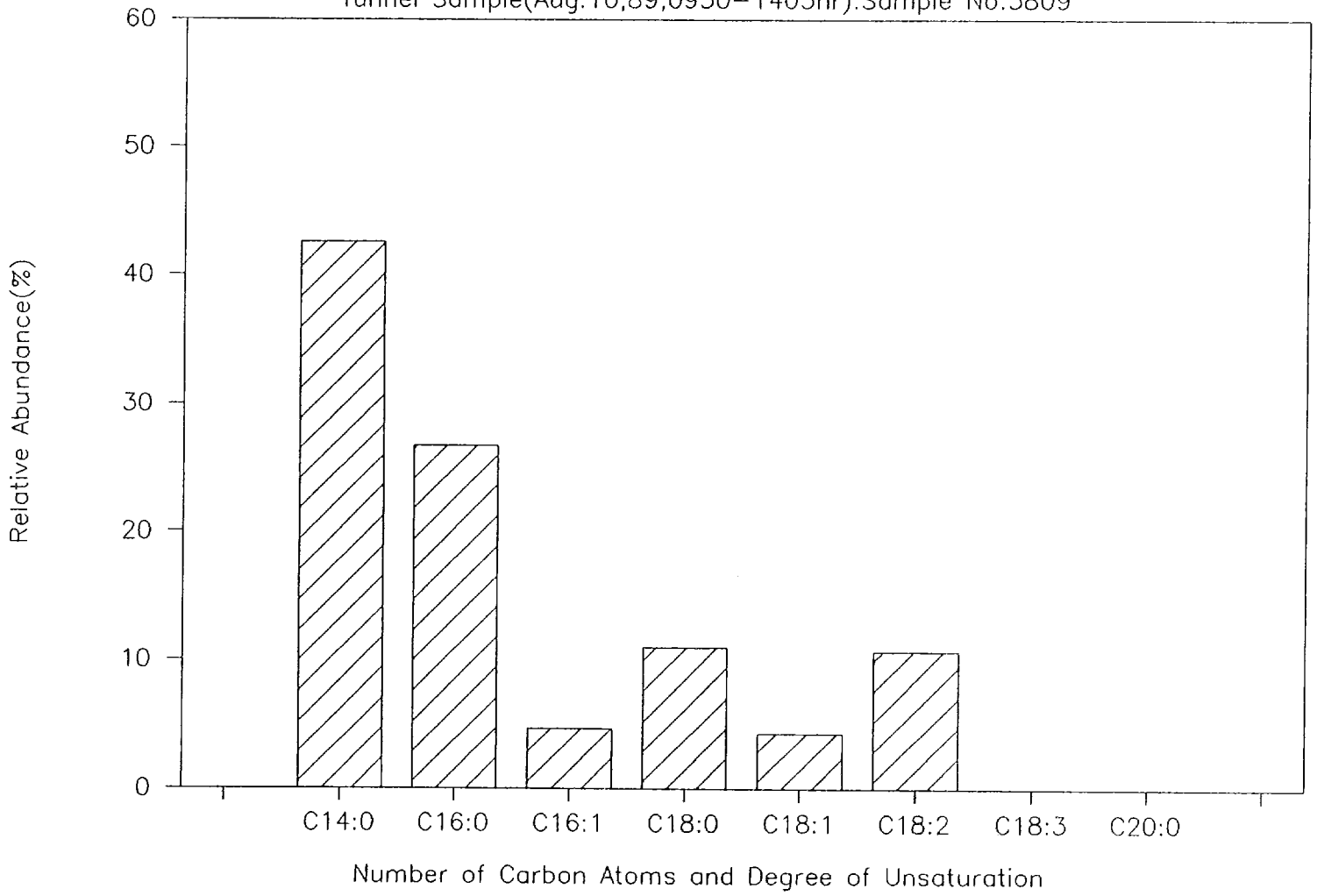


Figure VIII-32

Fatty Acid Distribution,Night

Tunnel Sample(Aug.10,89,1850-0556hr):Sample No.3813

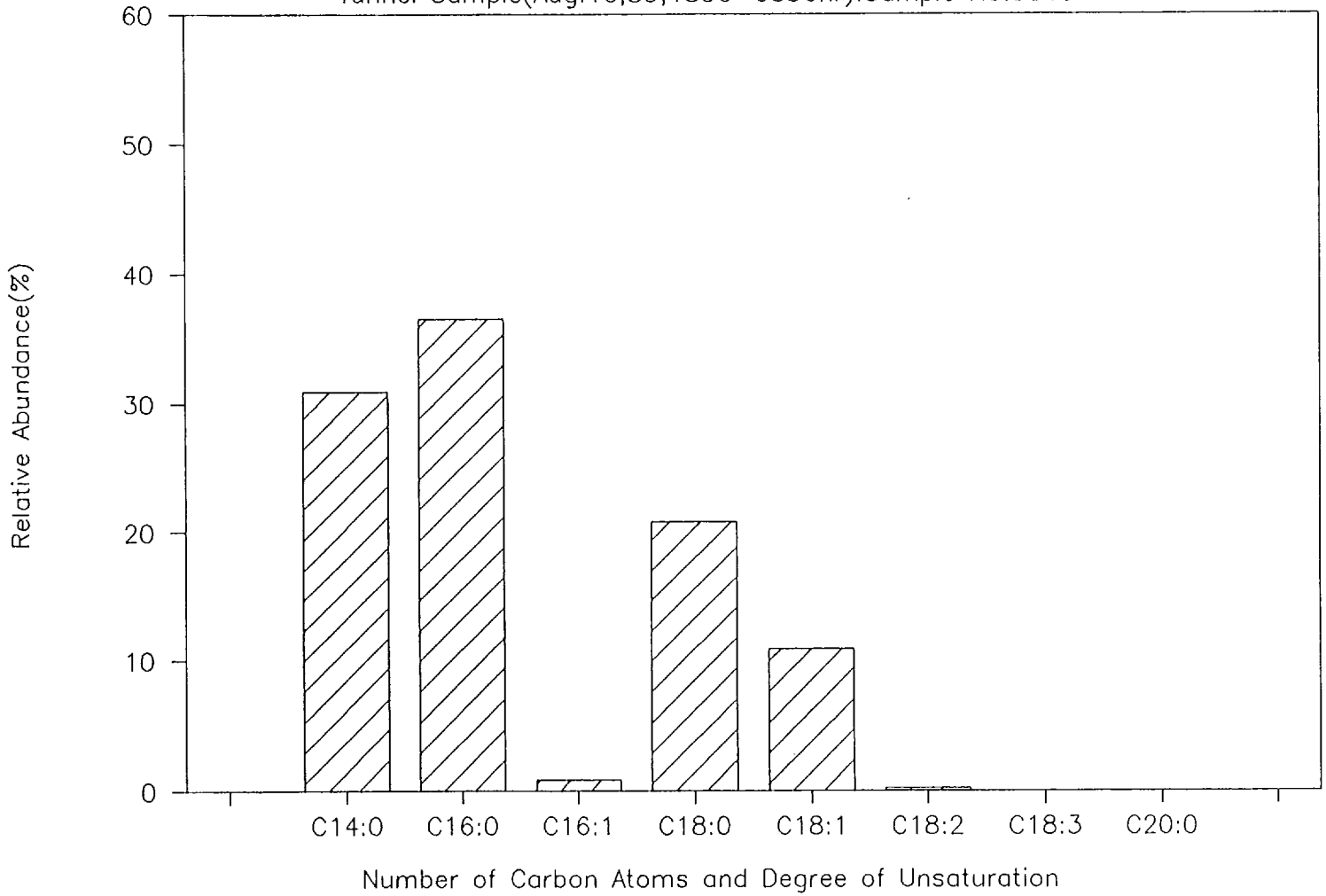
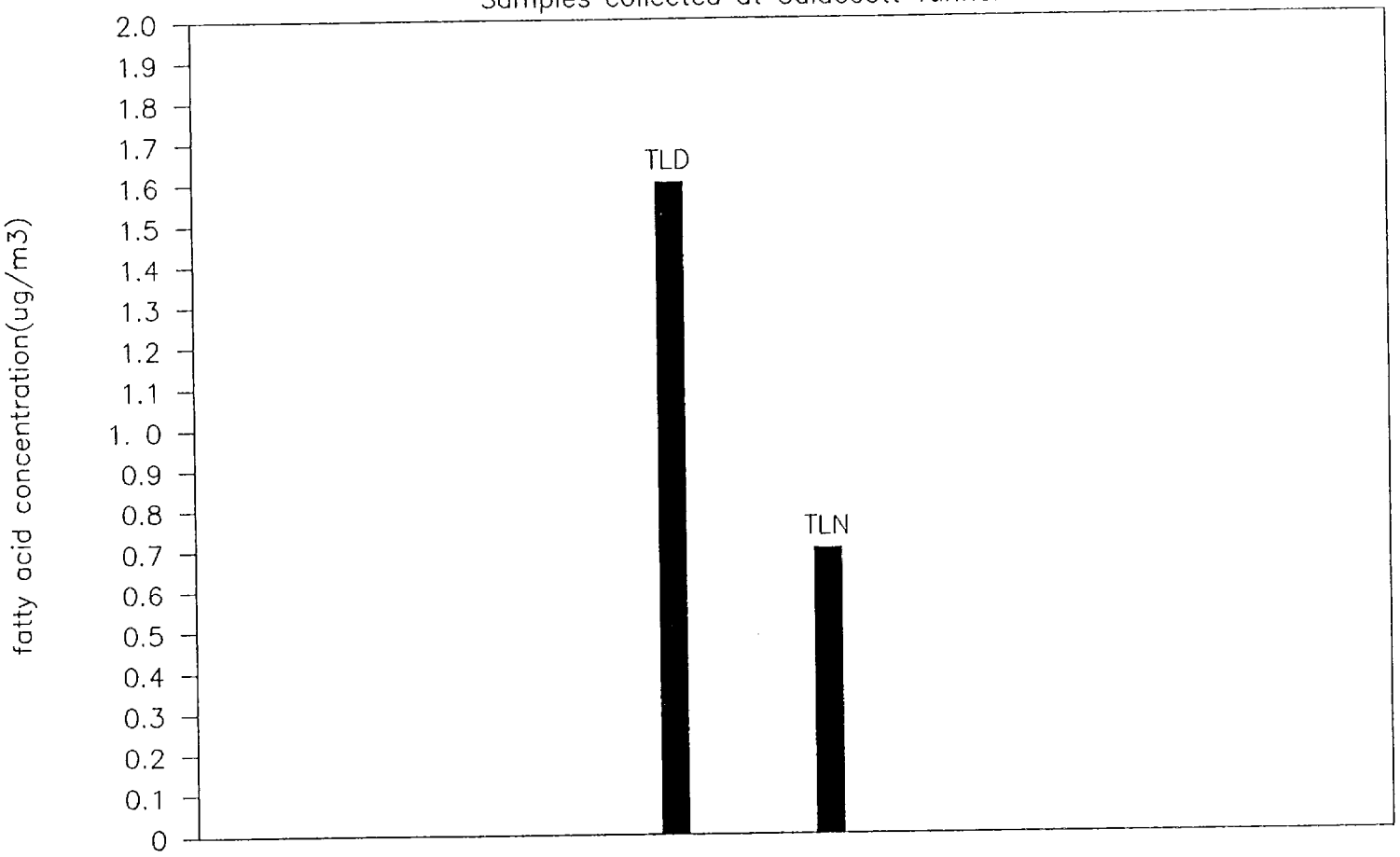


Figure VIII-33

Total Fatty Acid Concentration(ug/m3)

Samples collected at Caldecott Tunnel



Key

	Filter No.	Sampling Date	Sampling Time
TLD	3809	08/10/89	day
TLN	3813	08/10/89	night
TLN2	3814	08/10/89	night

TLD=Tunnel,day

TLN=Tunnel,night

Sampling code for August,1989

Figure VIII-34

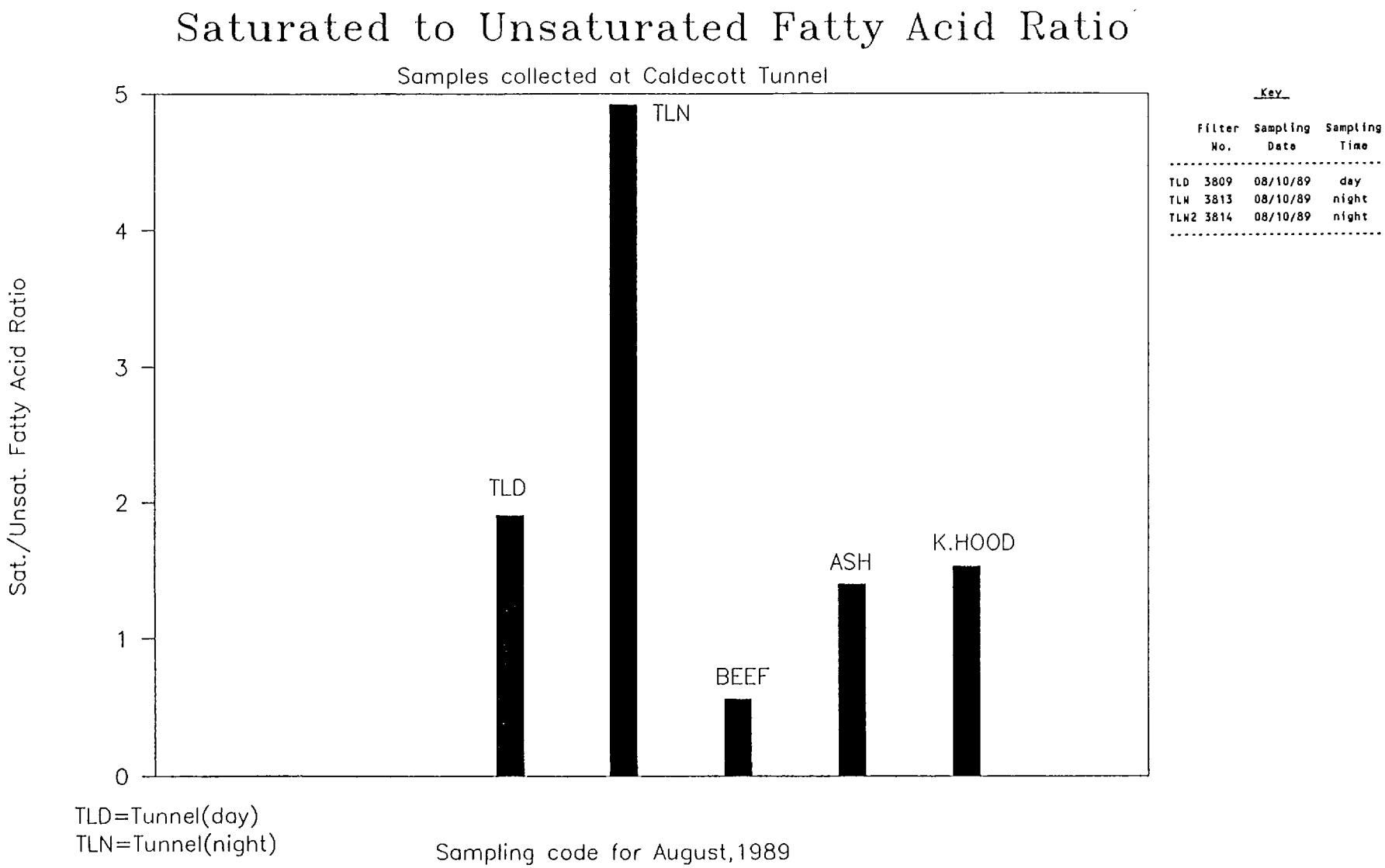


Table VIII-10. Individual fatty acid content (% relative to total extract) of beef fat vapor, fireplace ash and kitchen hood exhaust.

SAMPLE ID	C14:0[1]	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	C20:0
Beef Fat Vapor	2.6	4.5	2.9	1.7	5.3	4.8	nd[2]	nd
Fireplace Ash	1.6	2.4	0.7	0.7	1.1	0.8	nd	nd
Kitchen Hood Exhaust	2.9	9.3	1.8	3.3	4.5	3.9	nd	nd

[1] Terminology for extent of unsaturation. 18:0 means totally saturated. 18:1 to 18:3 means from 1 to 3 unsaturated bonds.
[2] nd = not detected

Figure VIII-35

Fatty Acid Distribution

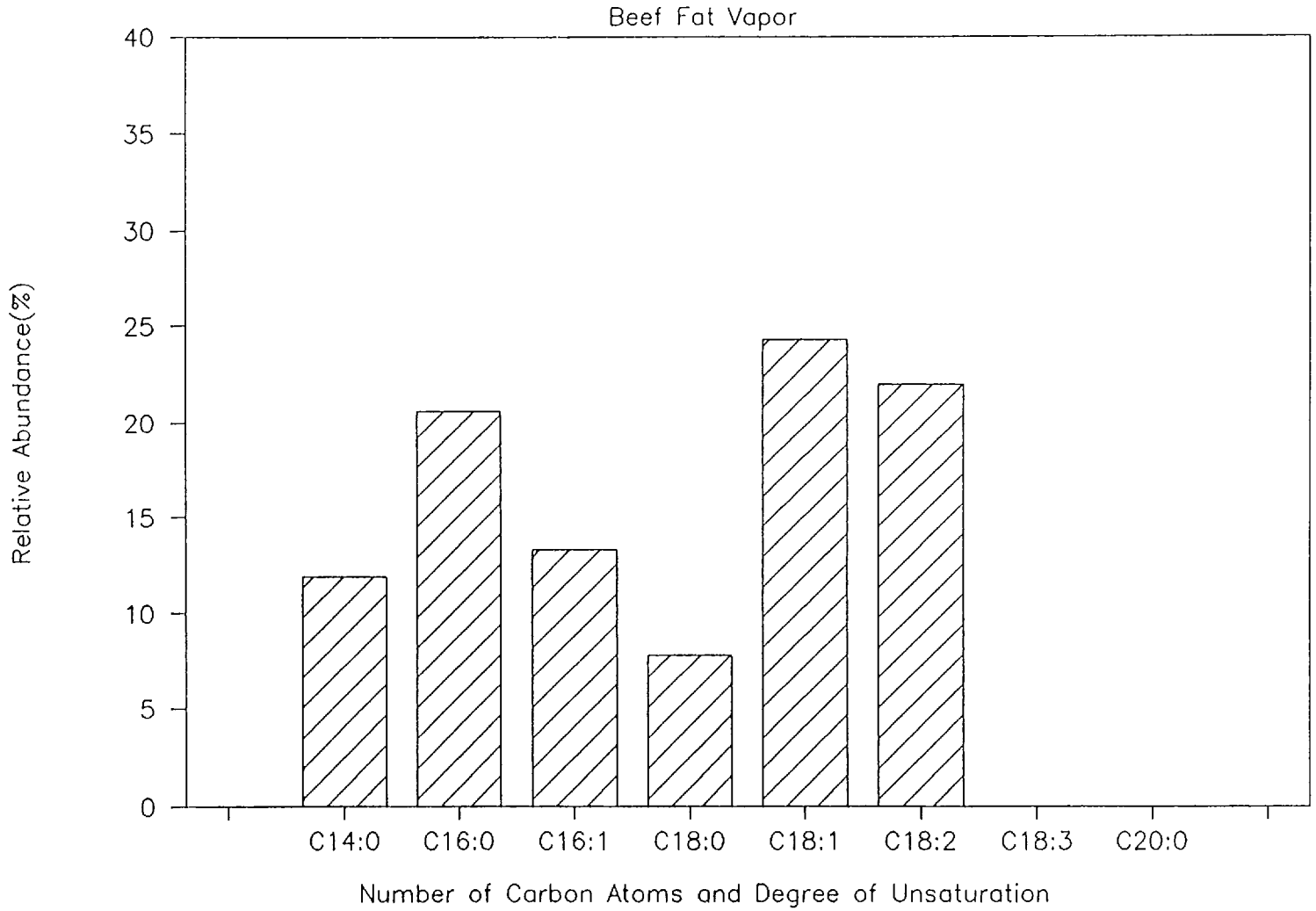


Figure VIII-36

Fatty Acid Distribution

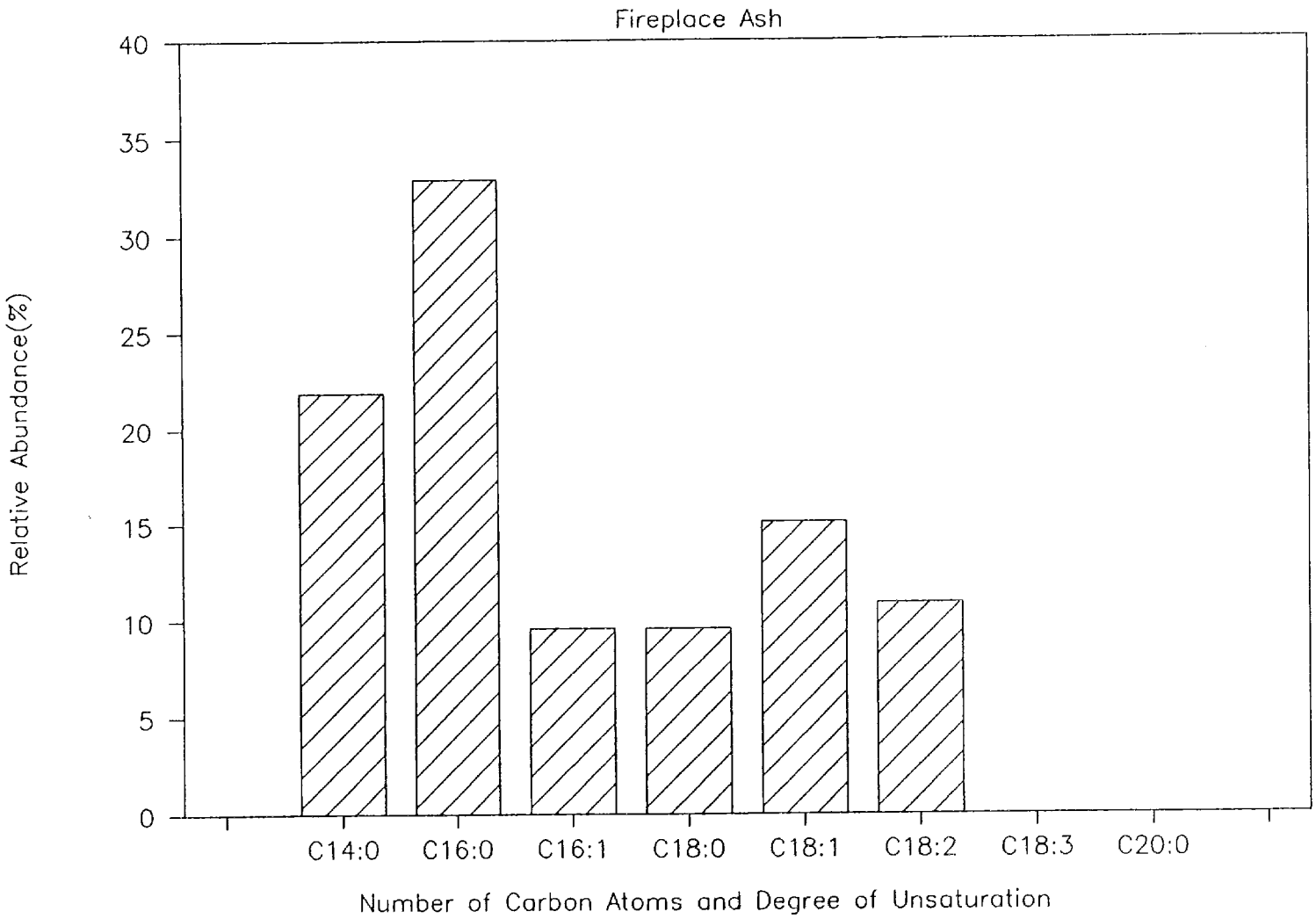
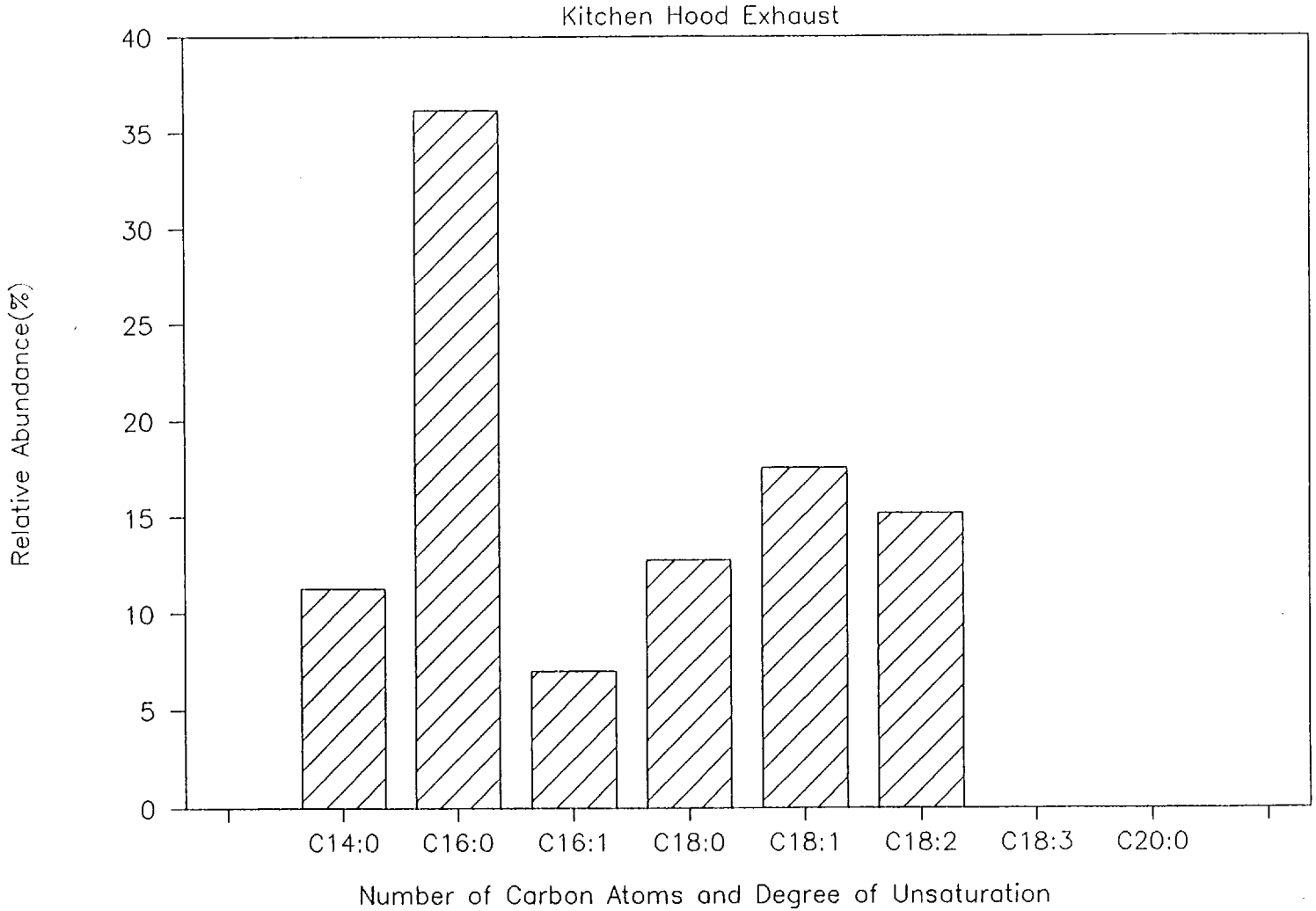


Figure VIII-37

Fatty Acid Distribution



IX. DISTRIBUTION OF CARBON, HYDROGEN AND NITROGEN IN FILTER EXTRACTS AND RESIDUE

IX. DISTRIBUTION OF CARBON, HYDROGEN AND NITROGEN IN FILTER EXTRACTS AND RESIDUE

The elemental composition of the first and second fractions and the residue was examined to determine differences and also to possibly evaluate contamination where the ratios are aberrant. This was accomplished by combusting the filter extracts and measuring CO_2, N_2 and H_2 gases as described in Minagawa et al. (1984). The gas volumes were then converted to an atomic mass and ratios were calculated for H/C and N/C. As a rule, the hydrocarbon fraction displays an atomic H/C ratio of 1.30-1.40, typical of a high molecular weight hydrocarbon mixture with a general H/C ratio of 2 for alkanes and 1 for PAH.

The majority of the polar fraction analyses show H/C values between 1.09-1.40 with some samples >2. The residual samples showed much more variation, with ratios ranging from 0.58 to 2.13 for Glendora, 0.82 to 1.10 for Duarte, and 2.3 for the day and 0.8 for the night tunnel samples. The Duarte samples are the most consistent. We do not understand the reason for the variability in hydrogen content of the residual non-extractable component in extracted filters (Tables IX-1 to IX-9). One reasonable explanation is that where the volume of hydrogen was very low, errors in measurement may have resulted.

The nitrogen to carbon ratio was measured in the polar and residual fractions. The N/C ratio varied from <0.01 to 0.1. Again, Duarte was more consistent than Glendora. The tunnel samples have the lowest N/C ratio.

Table IX-1. Elemental analysis results of the saturate/aromatic hydrocarbon fraction sample collected at city of Glendora.

Collection Date AUG 1986	Filter No.	D/N*	GGCID	CO2 Volume ml	Hydrogen Volume ml	H/C Ratio
13	8007,8008	D	4672-20	3.16	2.29	1.34
13	8009	D	4672-12	3.23	2.36	1.36
14/15	8017,8027	D	4672-19	3.81	2.86	1.39
14	8019	D	4672-2	4.50	3.28	1.33
14	8020	D	4672-7	2.32	1.67	1.32
15	8026,8029	D	4672-18	5.80	4.32	1.35
16	8033,8036	D	4672-15	4.31	3.25	1.38
16/17	8034,8040**	D	4672-13	--	--	--
17	8043,8044	D	4672-14	3.63	2.62	1.32
18/19	8047,8051	D	4672-30	4.50	3.41	1.38
18	8048,8049	D	4672-17	6.56	4.88	1.36
19	8054,8055	D	4672-28	5.51	4.13	1.37
20	8057,8058	D	4672-29	5.29	4.01	1.39
20	8060,8061	D	4672-27	5.58	4.17	1.37
13	8013,8014	N	4672-21	7.76	6.02	1.42
14	8024	N	4672-8	3.41	2.54	1.36
15	8031	N	4672-10	3.88	2.95	1.40
16	8037***	N	4672-11	--	--	--
17	8045	N	4672-9	3.37	2.38	1.29
18	8050	N	4672-4	2.51	1.79	1.33
19	8056	N	4672-3	3.23	2.26	1.28
	FIREPLACE ASH		4672-37	0.20	--	--
	KITCHEN HOOD EX		4672-35	2.47	--	--
	STANDARDS:					
	4672-NBS-1-342			5.18	2.84	1.55
	4672-NBS-2-342			6.44	3.86	1.54

* D = day; N = night
** Contaminated sample
*** Sample lost

Table IX-2. Elemental analysis results of polar fraction samples collected at city of Glendora.

Collection Date AUG 1986	Filter No.	D/N	GGCID	CO_2 Volume ml	Nitrogen Volume ml	Hydrogen Volume ml	N/C Ratio	H/C Ratio
13	8007,8008	D	4672-20	5.95	0.63	4.23	0.09	1.30
13	8009	D	4672-12	2.66	0.05	1.66	0.02	1.16
14/15	8017,8027	D	4672-19	2.29	0.04	1.44	0.02	1.14
14	8019	D	4672-2	2.42	0.05	1.43	0.02	1.10
14	8020	D	4672-7	2.11	0.07	1.58	0.03	1.35
15	8026,8029	D	4672-18	4.64	0.11	2.88	0.02	1.14
16	8033,8036	D	4672-15	6.96	0.10	4.50	0.01	1.17
16/17	8034,8040**	D	4672-13*	40.96	0.04	--	0.002	--
17	8043,8044	D	4672-14	3.52	0.04	2.10	0.01	1.09
18/19	8047,8051	D	4672-30	3.23	0.24	2.62	0.07	1.49
18	8048,8049	D	4672-17	0.26	0.03	0.31	0.13	2.31
19	8054,8055	D	4672-28	2.29	0.04	1.38	0.02	1.11
20	8057,8058	D	4672-29	4.06	0.15	3.02	0.03	1.37
20	8060,8061	D	4672-27	4.17	0.22	3.16	0.05	1.37
13	8013,8014	N	4672-21	3.88	0.12	2.50	0.03	1.19
14	8024	N	4672-8	2.20	0.04	1.40	0.02	1.15
15	8031	N	4672-10	2.72	0.03	1.63	0.01	1.09
16	8037	N	4672-11	4.46	0.23	5.87	0.05	2.42
17	8045	N	4672-9	3.56	0.09	2.62	0.02	1.35
18	8050	N	4672-4	3.63	0.07	2.30	0.02	1.16
19	8056	N	4672-3	2.40	0.09	1.47	0.03	1.14
	FIREPLACE ASH		4672-37	0.21	--	--	--	--
	KITCHEN HOOD EX		4672-35	16.30	--	--	--	--

Table IX-2. Elemental analysis results of polar fraction samples collected at city of Glendora (continued).

Filter No.	D/N	GGCID	CO_2 Volume ml	Nitrogen Volume ml	Hydrogen Volume ml	N/C Ratio	H/C Ratio
SOLVENT 1		4672-33	0.08		0.15		3.00
SOLVENT 2		4672-34	0.11		0.16		3.00
STANDARDS:							
4672-NBS-1-345			14.16		11.76		1.53
4672-NBS-1-352			11.29		9.28		1.51
4672-NBS-2-345			17.51		14.78		1.55
4672-NBS-2-352			18.12		15.07		1.52
4672-NBS-3-345			14.20		11.48		1.48
4672-NBS-4-345			18.83		15.94		1.55
4672-VAL-1-345			10.67				
4672-VAL-2-345			9.64				

* 4672-13 - Hydrogen not collected
** Contamination suspected
D = day
N = night

Table IX-3. Elemental analysis results of residual fraction samples collected at city of Glendora.

Collection Date AUG 1986	Filter No.	D/N#	GGCID	CO_2 Volume ml	Nitrogen Volume ml	Hydrogen Volume ml	N/C Ratio	H/C Ratio
13	8007,8008*	D	4672-20	9.95	0.50	3.16	0.05	0.58
13	8009	D	4672-12	5.67	0.17	4.71	0.03	1.50
14/15	8017,8027*	D	4672-19	7.83	0.54	4.33	0.06	1.02
14	8019	D	4672-2	6.81	0.36	7.94	0.05	2.13
15	8020	D	4672-7	6.71	0.46	7.49	0.06	2.04
16	8026,8029*	D	4672-18	9.66	0.74	6.78	0.07	1.29
16/17	8033,8036*+	D	4672-15	7.80	--	--	--	--
17	8034,8040*+	D	4672-13++	9.30	--	--	--	--
17	8043,8044*+	D	4672-14	11.70	--	--	--	--
18/19	8047,8051*	D	4672-30	10.00	0.25	2.60	0.02	0.47
18	8048,8049*+	D	4672-17	11.60	--	--	--	--
19	8054,8055*	D	4672-28	10.56	0.46	5.18	0.04	0.90
20	8057,8058	D	4672-29	14.78	0.43	6.63	0.03	0.83
20	8060,8061*	D	4672-27	12.53	0.67	5.51	0.05	0.80
13	8013,8016*	N	4672-21	11.27	1.34	6.33	0.11	1.03
14	8024	N	4672-8	6.60	0.19	6.52	0.03	1.13
15	8031**	N	4672-10	--	--	--	--	--
16	8037	N	4672-11	5.57	0.29	5.08	0.05	1.66
17	8045	N	4672-9	6.16	0.13	4.82	0.02	1.43
18	8050	N	4672-4	7.32	0.20	5.11	0.02	1.28
19	8056	N	4672-3	6.52	0.12	5.38	0.02	1.52

Table IX-3. Elemental analysis results of residual fraction samples collected at city of Glendora (continued).

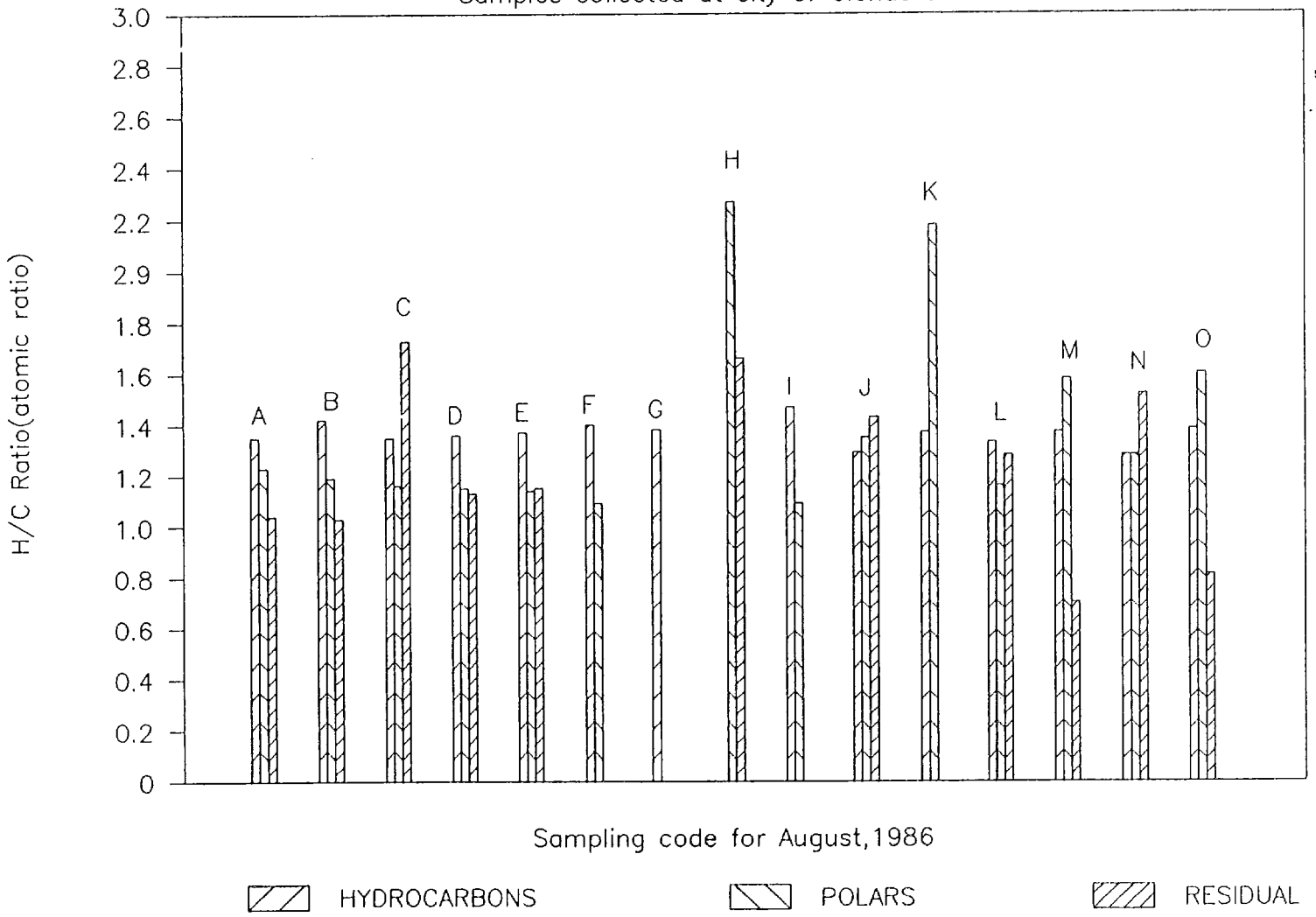
Filter	D/N# GGCID	CO_2 Volume ml	Nitrogen Volume ml	Hydrogen Volume ml	N/C Ratio	H/C Ratio
STANDARDS:						
4672-HST-1-036		10.62	2.59		0.22	
4672-HST-3-036		10.87	2.66		0.22	
4672-LB-1-032		<0.001	<0.001	0.05		
4672-NBS-1-048		14.82		12.03		1.49
4672-NBS-4-015		16.64				
4672-NBS-5-015		17.06				
4672-NBS-6-015		18.30		14.83		1.49
4672-OXA-1-015		9.26				
4672-OXA-2-015		9.38				
4672-OXA-3-015		8.84				
4672-OXA-4-015		7.94				
4672-RB-1-016		0.03	0.001	0.09		6.47
4672-RB-2-016		0.03	0.001	0.10		5.36

* No Cu Added, Combusted at 550°C (all others 850°C)
** Lost
\+ N_2, H_2 Not collected
++ Contamination Suspected
\# D = day; N = night

Figure IX-1

Hydrogen/Carbon Ratios

Samples collected at city of Glendora



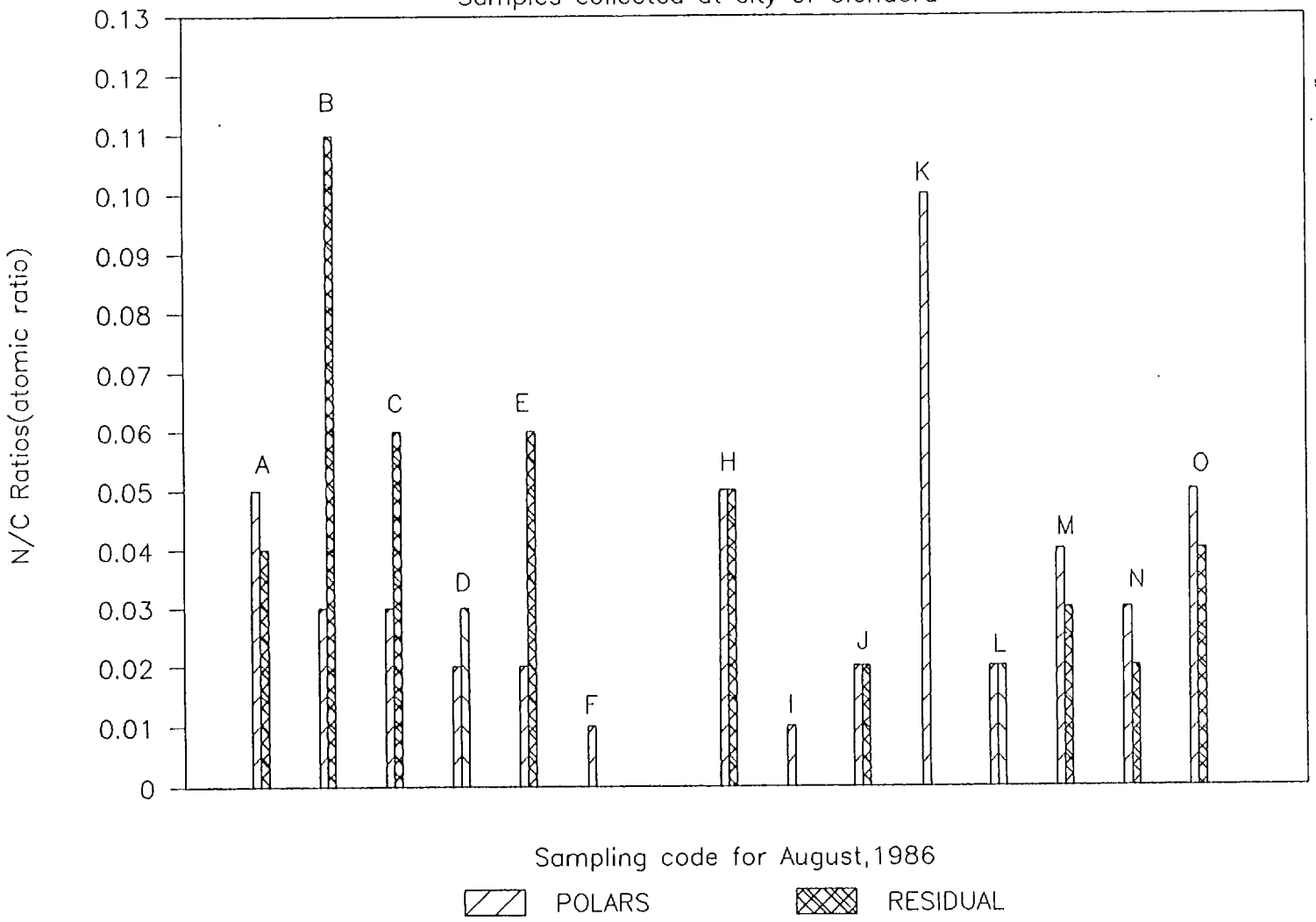
Key

Sample ID	Sampling Date	Sampling Time: Day or Night	Sampling Time: Time
A	8/13/86	D	0800-2000
B	8/13/86	N	2000-0800
C	8/14/86	D	0800-2000
D	8/14/86	N	2000-0800
E	8/15/86	D	0800-2000
F	8/15/86	N	2000-0800
G	8/16/86	D	0800-2000
H	8/16/86	N	2000-0720
I	8/17/86	D	0800-2000
J	8/17/86	N	2005-0800
K	8/18/86	D	0800-2000
L	8/18/86	N	2000-0800
M	8/19/86	D	0800-2015
N	8/19/86	N	2020-0800
O	8/20/86	D	0800-2000

Figure IX-2

Nitrogen/Hydrogen Ratios

Samples collected at city of Glendora



Key

Sample ID	Sampling Date	Sampling Time: Day or Night	Sampling Time: Time
A	8/13/86	D	0800-2000
B	8/13/86	N	2000-0800
C	8/14/86	D	0800-2000
D	8/14/86	N	2000-0800
E	8/15/86	D	0800-2000
F	8/15/86	N	2000-0800
G	8/16/86	D	0800-2000
H	8/16/86	N	2000-0720
I	8/17/86	D	0800-2000
J	8/17/86	N	2005-0800
K	8/18/86	D	0800-2000
L	8/18/86	N	2000-0800
M	8/19/86	D	0800-2015
N	8/19/86	N	2020-0800
O	8/20/86	D	0800-2000

Table IX-4. Elemental analysis results of the saturate/aromatic hydrocarbon fraction of samples collected at city of Duarte.

Collection Date (AUG 1986)	Filter No.	D/N*	GGCID	CO_2 Volume ml	Hydrogen Volume ml	H/C Ratio
13/14	8006,8018	D	4672-22	5.69	4.53	1.46
13/15	8010,8025	D	4672-32	5.33	4.04	1.38
17	8041	D	4672-24	1.71	1.27	1.33
19/20	8053,8059	D	4672-23	2.47	1.86	1.37
13	8015	N	4672-31	3.83	2.88	1.36

STANDARDS:

4672-NBS-1-342	15.18	12.84	1.7
4672-NBS-2-342	16.44	13.86	1.7

* D = day; N = night

Table IX-5. Elemental analysis results of polar fraction of samples collected at city of Duarte.

Collection Date (AUG 1986)	Filter No.	D/N*	GGCID	CO2 Volume ml	Nitrogen Volume ml	Hydrogen Volume ml	N/C Ratio	H/C Ratio
13/14	8006,8018	D	4672-22	2.77	0.11	1.79	0.03	1.17
13/15	8010,8025	D	4672-32	4.90	0.10	3.01	0.02	1.12
17	8041	D	4672-24	3.08	0.07	2.32	0.02	1.40
19/20	8053,8059	D	4672-23	5.44	0.17	4.03	0.03	1.36
13	8015	N	4672-31	0.12	0.01	0.17	0.05	2.63
	SOLVENT 1		4672-33	0.08		0.15		3.00
	SOLVENT 2		4672-34	0.11		0.16		3.00

* D = day; N = night

Table IX-6. Elemental analysis results of residual fraction of samples collected at city of Duarte.

Collection Date (AUG 1986)	Filter	D/N+	GGCID	CO2 Volume ml	Nitrogen Volume ml	Hydrogen Volume ml	N/C Ratio	H/C Ratio
13/14	8006,8018*	D	4672-22	9.00	0.67	4.06	0.07	0.82
13/15	8010,8025*	D	4672-32	13.5	1.06	6.00	0.07	0.81
17	8041*	D	4672-24	5.08	0.29	3.08	0.05	1.10
19/20	8053,8059*	D	4672-23	9.93	0.50	3.85	0.05	0.71
13	8015	N	4672-31	8.61	1.17	6.65	0.12	1.42

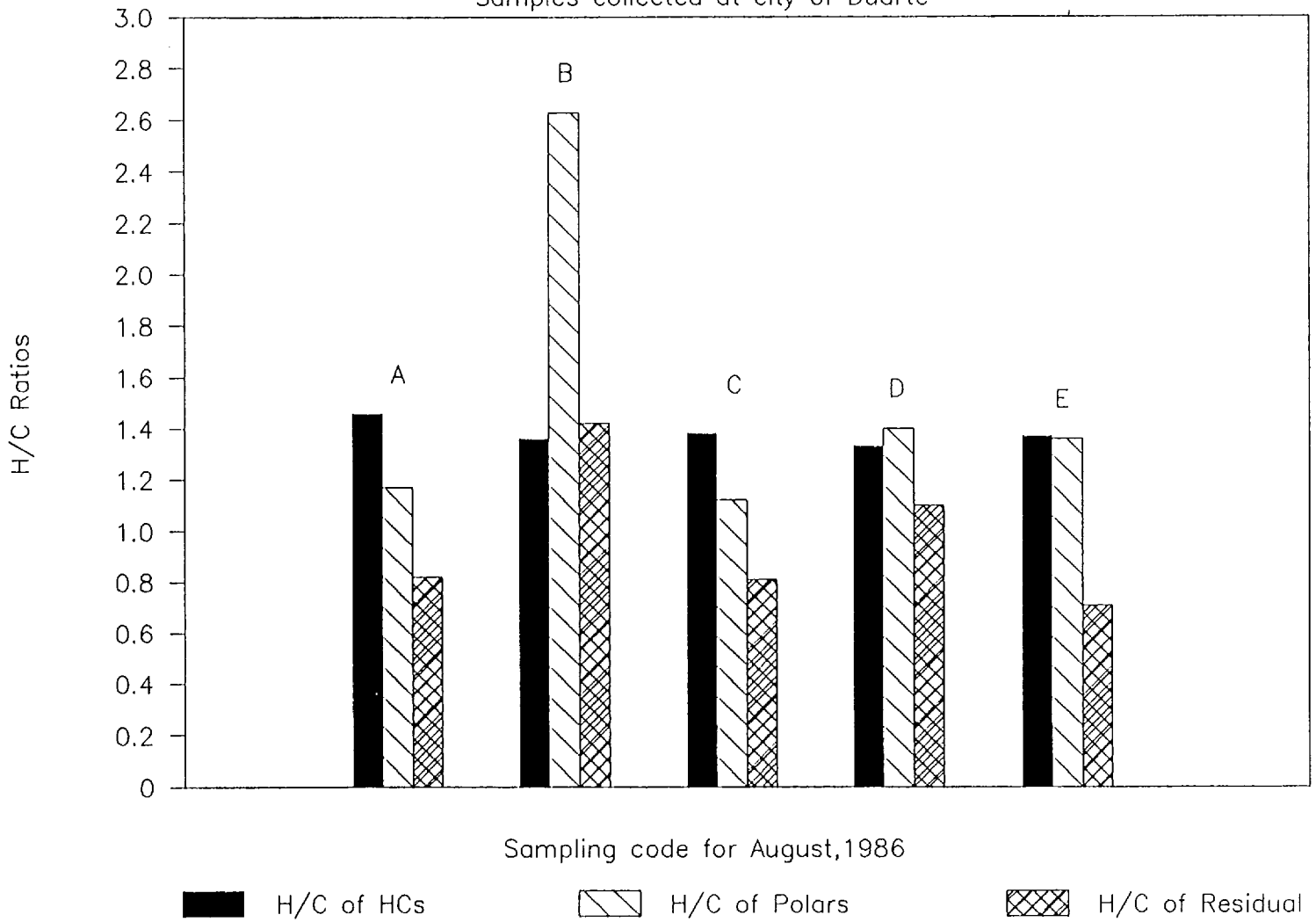
* No Cu added; combusted at 500C

\+ D = day; N = night

Figure IX-3

Hydrogen/Carbon Ratio

Samples collected at city of Duarte



Key

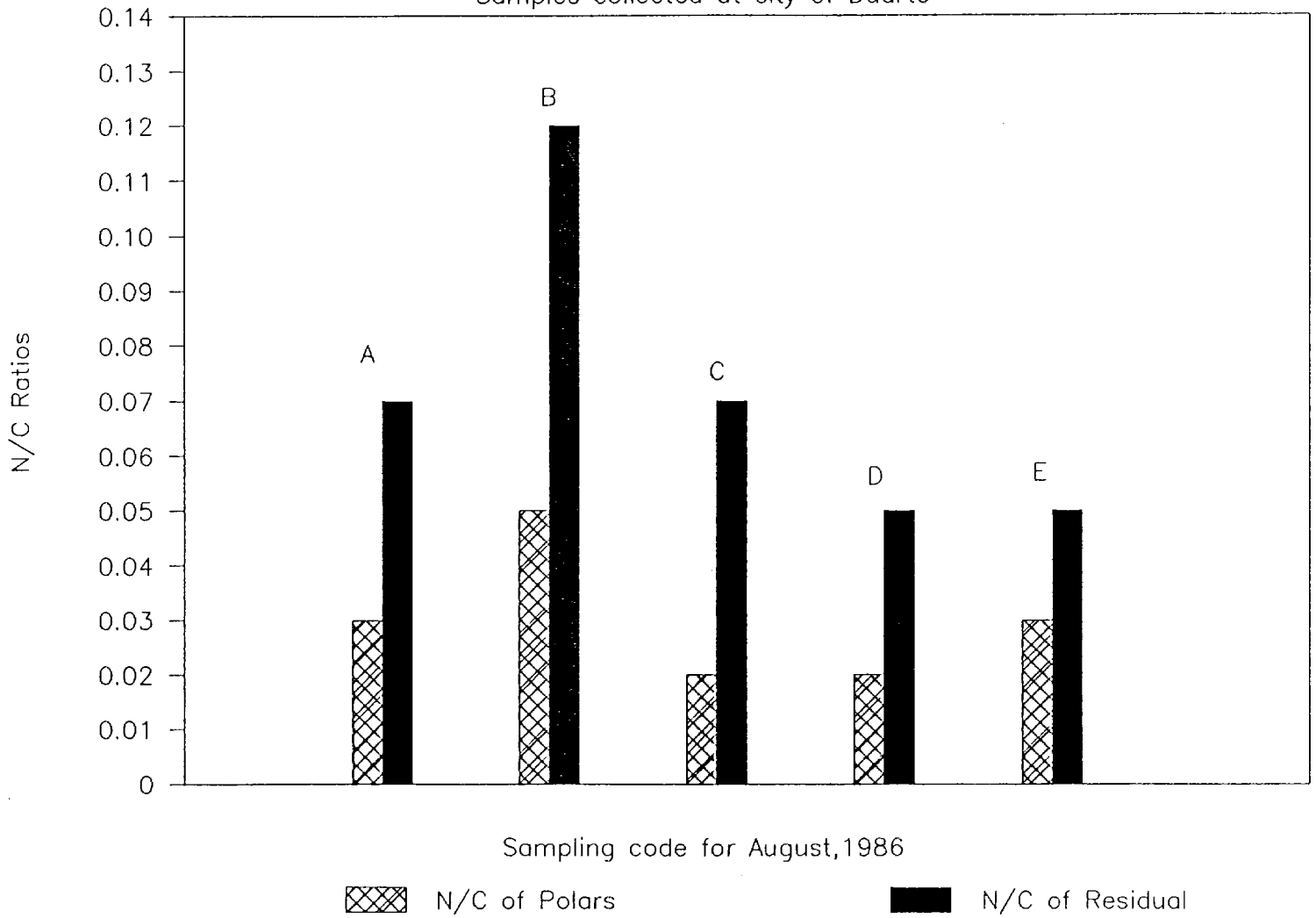
Sample ID	Sampling Date	Sampling Time: Day or Night	Sampling Time: Time
A	8/13/86	D	0810-1230
A	8/14/86	D	0830-1252
B	8/13/86	N	2030-0830
C	8/13/86	D	1230-2030
C	8/15/86	D	1200-2000
D	8/17/86	D	1200-2000
E	8/19/86	D	1200-2000
E	8/20/89	D	1200-2000

} combined samples

Figure IX-4

Nitrogen/Carbon Ratio

Samples collected at city of Duarte



Key

Sample ID	Sampling Date	Sampling Time: Day or Night	Sampling Time: Time
A	8/13/86	D	0810-1230
A	8/14/86	D	0830-1252
B	8/13/86	N	2030-0830
C	8/13/86	D	1230-2030
C	8/15/86	D	1200-2000
D	8/17/86	D	1200-2000
E	8/19/86	D	1200-2000
E	8/20/89	D	1200-2000

} combined samples

Table IX-7. Elemental analysis results of the saturate/aromatic hydrocarbon fraction of samples collected at Caldecott Tunnel.

Collection Date (AUG 1989)	Filter	D/N*	GGCID	CO_2 Volume ml	Hydrogen Volume ml	H/C Ratio
10	3809	D	4672-1	4.39	3.34	1.42
10	3813	N	4672-6	4.21	3.11	1.35

* D = day; N = night

Table IX-8. Elemental analysis of polar fraction of samples collected at Caldecott Tunnel.

Collection Date (AUG 1989)	Filter No.	D/N*	GGCID	CO_2 Volume ml	Nitrogen Volume ml	Hydrogen Volume ml	N/C Ratio	H/C Ratio
10	3809	D	4672-1	3.37	0.04	2.06	0.01	1.1
10	3813	D	4672-6	2.59	0.03	1.53	0.01	1.06
	SOLVENT 1		4672-33	0.08		0.15		3.0
	SOLVENT 2		4672-34	0.11		0.16		3.0

* D = day; N = night

Table IX-9. Elemental analysis of residual fraction of samples collected at Caldecott Tunnel.

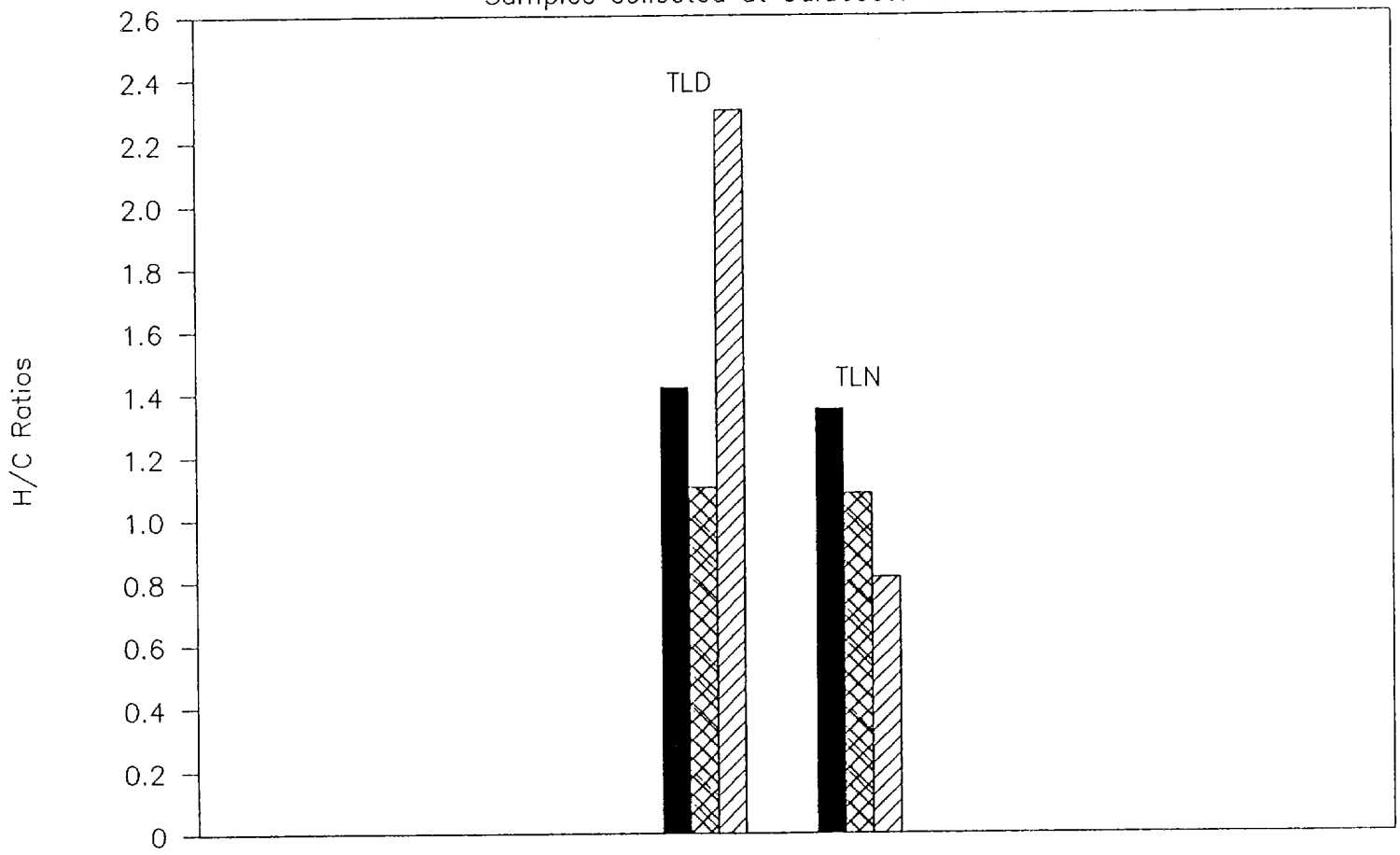
Collection Date (AUG 1989)	Filter No.	D/N* GGCID	CO_2 Volume ml	Nitrogen Volume ml	Hydrogen Volume ml	N/C Ratio	H/C Ratio
10	3809	D 4672-1	4.57	0.07	5.66	0.01	2.3
10	3813	N 4672-6	49.25	1.06	21.65	0.02	0.8

* D = day; N = night

Figure IX-5

Hydrogen/Carbon Ratio

Samples collected at Caldecott Tunnel



TLD=Tunnel(day)
TLN=Tunnel(night)

H/C of HCs H/C of Polars H/C of Residual

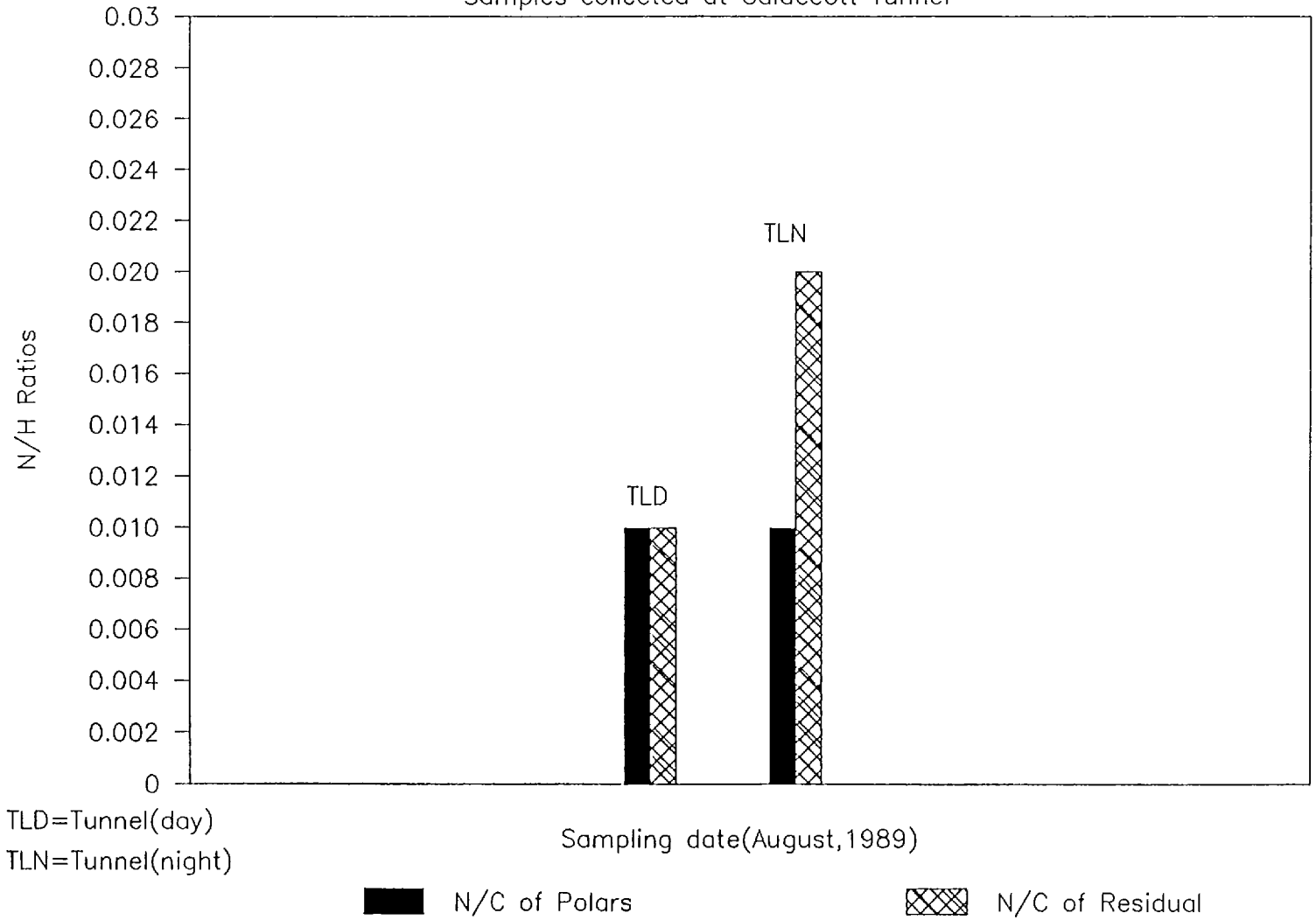
Key

	Filter No.	Sampling Date	Sampling Time
TLD	3809	08/10/89	day
TLN	3813	08/10/89	night
TLN2	3814	08/10/89	night

Figure IX-6

Nitrogen/Hydrogen Ratio

Samples collected at Caldecott Tunnel



TLD=Tunnel(day)
TLN=Tunnel(night)

Key

	Filter No.	Sampling Date	Sampling Time
TLD	3809	08/10/89	day
TLN	3813	08/10/89	night
TLN2	3814	08/10/89	night

X. STABLE ISOTOPE RATIOS FOR $^{13}C/^{12}C$, D/H, $^{15}N/^{14}N$ ($\delta^{13}C$, δD AND $\delta^{15}N$)

X. STABLE ISOTOPE RATIOS FOR $^{13}C/^{12}C$, D/H, $^{15}N/^{14}N$

Stable isotope ratios of the light elements have been widely used in geochemistry for the past 40 years to identify sources and processes in nature. By convention, the least abundant isotope is given as a ratio against the most abundant isotope. Hence, for example $^{13}C/^{12}C$ = 1/100, $^{15}N/^{14}N$ = 1/250 and D/H = 1/2500. Also by convention, the ratio is given in the delta notation against a standard as follows:

$$\delta_E \ ^o/oo = \frac{H_I/L_{I_{sample}} - H_I/L_{I_{standard}}}{H_I/L_{I_{standard}}} \times 1000$$

Where E is the element, I is the isotope of a particular element, H is the heavy isotope and L is the light isotope. For each element an international set of standards is recognized.

Conventionally, the isotope ratio of the standard is given a value of $^o/oo$. If the element is enriched in the heavy isotope it is positive and if it is enriched in the light isotope it is negative.

The average carbon isotope value for gasoline in the Los Angeles area has a $\delta^{13}C$ = -26$^o/oo$. It is apparent that for both Glendora and Duarte, $\delta^{13}C$ is ~-27$^o/oo$ for the hydrocarbon fraction. For the Caldecott Tunnel sample it is ~-28$^o/oo$, which may reflect a different mix of gasoline/diesel usage or less hydrocarbons from biogenic sources. In all cases [except for the combined filter samples 8034, 8040 (Table VIII-1), which was assumed to be contaminated], the polar and the residual fractions are enriched in ^{13}C relative to the hydrocarbon fraction and are generally very similar to each other. This could signify different source mixtures in the hydrocarbon fraction and the polar/residual fractions. Values for $\delta^{13}C$ of the kitchen hood extract show both the

hydrocarbon fraction ($\delta^{13}C$ = -25.13^{o}/oo) as well as the polar fraction ($\delta^{13}C$ = -24.94^{o}/oo), to be somewhat enriched in ^{13}C.

The δD hydrogen isotope values are in the range of -100 to -110°/oo for the hydrocarbon fraction, and -60 to -100°/oo for the polar and residual fractions. These values are considerably more enriched in deuterium than gasoline sold in the Los Angeles area which has a δD ~-140°/oo. This suggests that the atmospheric residues have lost the light isotope by evaporation and exchange with water.

The nitrogen isotope data show very great variation. Whereas the values for the residual fraction are all enriched in ^{15}N relative to the atmospheric nitrogen gas standard, the polar fraction displays a wide variation in $\delta^{15}N$. Most of the values are either close to zero (atmospheric nitrogen) or enriched in the light isotope. These variations are probably due to the different amount of NO_3^- and NH_4^+ in the extract. The former ion is probably isotopically enriched in ^{15}N and the latter depleted in ^{15}N. Because the polar sample was only partially eluted from the chromatographic column, the samples analyzed may not be representative of the entire polar fraction.

Data for the measured stable isotope values are given in Tables X-1 to X-3 and plotted in Figures X-1 to X-3.

Table X-1. Stable isotope ratios ($\delta^{13}C$, δD and $\delta^{15}N$) of samples collected at city of Glendora.

Collection Date (AUG 1986)	Filter No.	D/N+	GGCID	Residual del13C	Residual delD	Residual delD Dup	Residual del15N	Residual del15N Dup	Aliphatic and Aromatic del13C	Aliphatic and Aromatic del13C Dup	Aliphatic and Aromatic delD	Aliphatic and Aromatic delD Dup	Polar del13C	Polar del13C Dup	Polar delD	Polar delD Dup	Polar del15N	Polar del15N Dup
13	8007,8008	D	4672-20	-25.91	-76		20.39		-27.16	-27.27	-108	-115	-24.70		-90		8.74	10.19
13	8009	D	4672-12	-29.44	-113		18.40		-27.07		-103		-25.04		-61		-13.04	
14/15	8017,8027	D	4672-19	-26.13	-83		14.06		-27.68		-104		-25.71		-84		-4.09	
14	8019	D	4672-2	-24.50	-96		29.79		-26.35		-90		-24.84		-59		-13.27	
14	8020	D	4672-7	-24.65	-87		27.26		-26.78		-108		-24.81	-25.05	-52		-6.96	
15	8026,8029	D	4672-18	-24.68	-79		-8.73	-10.23	-26.54		-103		-24.91		-76		-6.46	
16	8033,8036	D	4672-15	-24.59	--		--		-27.18		-111		-25.21		-51		-11.09	
16/17	8034,8040	D	4672-13++	-25.86	Contaminated sample				-27.73		-111		-29.46	-29.43	--		-0.65	-0.67
17	8043,8044	D	4672-14	-25.21	--		--		-26.53	-26.53	-105	-107	-25.02		-72		-8.14	
18/19	8047,8051	D	4672-30	-26.08	-79		7.14		-27.53		-109		-26.31		-93		1.35	
18	8048,8049	D	4672-17	-25.19	--		--		-26.71		-105		-24.91		-79		3.51	
19	8054,8055	D	4672-28	-25.26	-80		10.98		-26.40		-104		-25.14		-56		-4.64	
20	8057,8058	D	4672-29	-25.41	-98		11.57		-27.26		-110		-25.58	-25.19	-89		-0.31	
20	8060,8061	D	4672-27	-25.40	-70		9.49		-26.38		-104		-25.59	-25.06	-84		-1.54	
13	8013,8014	N	4672-21	-24.90	-60		8.58		-27.09		-114		-25.07		-94		-0.01	
14	8024	N	4672-8	-25.12	-106		19.40		-27.55		-115		-25.17		-94		0.03	
15	8031	N	4672-10	*	--		--		-27.72		-117		-25.22		-106		0.02	
16	8037	N	4672-11	-24.32	-92		47.24		*		--		-24.61	-24.41	-77		1.57	
17	8045	N	4672-9	-24.62	-105		18.58		-27.78		-114		-25.42		-59		-0.40	
18	8050	N	4672-4	-24.96	-101		14.94		-26.86		-125		-25.28		-79		-4.08	
19	8056	N	4672-3	-24.17	-103		5.79		-26.66		-119		-25.29		-83		-3.23	
FIREPLACE ASH			4672-37	--	--		--		-28.61		--		-27.27		--		--	
KITCHEN HOOD			4672-35	--	--		--		-25.13		--		-24.94		--		--	

Table X-1. Stable isotope ratios ($\delta^{13}C$, δD and $\delta^{15}N$) of samples collected at city of Glendora (continued).

Filter No.	D/N+ GGCID	Residual del13C	Residual delD	Residual del15N	Residual del15N Dup	Aliphatic and Aromatic del13C	Aliphatic and Aromatic del13C Dup	Aliphatic and Aromatic delD	Aliphatic and Aromatic delD Dup	Polar del13C	Polar del13C Dup	Polar delD	Polar delD Dup	Polar del15N	Polar del15N Dup
SOLVENT 1	4672-33	--	--	--		-26.02		-87		--		--		--	
SOLVENT 2	4672-34	--	--	--		-25.64		-94		--		--		--	
STANDARDS:															
4672-HST-1-036		-8.97		-5.70											
4672-HST-3-036		-8.75		-5.45											
4672-NBS-1-036		-29.84													
4672-NBS-1-048		-29.82	-120												
4672-NBS-1-342		-29.79	-119												
4672-NBS-1-352		-29.82	-117												
4672-NBS-2-036		-29.73													
4672-NBS-2-342		-29.81	-121												
4672-NBS-2-345		-29.84	-122												
4672-NBS-2-352		-29.78	-120												
4672-NBS-3-345		-29.78	-118												
4672-NBS-4-015		-29.84													
4672-NBS-4-345		-29.76													
4672-NBS-5-015		-29.80													
4672-NBS-6-015		-29.75													
4672-OXA-1-015		-17.52													
4672-OXA-2-015		-17.46													
4672-OXA-3-015		-17.41													
4672-OXA-4-015		-17.44													
4672-RB-1-016		-24.11	-90												
4672-RB-2-016		-24.40	-81												
4672-VAL-1-345		-28.27	-20	11.60											
4672-VAL-2-345		-28.29	-19	11.62											

* Lost

\+ D = day; N = night

++ Contamination Suspected

Table X-2. Stable isotope ratios ($\delta^{13}C$, δD and $\delta^{15}N$) of samples collected at city of Duarte.

Collection Date (AUG 1986)	Filter No.	D/N*	GGCID	Residual del13C	Residual delD	Residual del15N	Aliphatic and Aromatic del13C	Aliphatic and Aromatic delD	Polar del13C	Polar del13C Dup	Polar delD	Polar del15N
13/14	8006,8018	D	4672-22	-25.61	-70	0.83	-27.31	-105	-25.39		-51	-0.24
13/15	8010,8025	D	4672-32	-25.26	-65	10.11	-26.91	-104	-25.34		-70	-11.09
17	8041	D	4672-24	-25.52	-75	11.69	-27.90	-112	-25.69		-34	-3.46
19/20	8053,8059	D	4672-23	-25.28	-70	9.21	-27.24	-108	-25.60	-25.06	-85	-8.00
13	8015	N	4672-31	-24.58	-74	8.99	-26.89	-119	-24.82		-90	6.42

Table X-3. Stable isotope ratios ($\delta^{13}C$, δD and $\delta^{15}N$) of samples collected at Caldecott Tunnel.

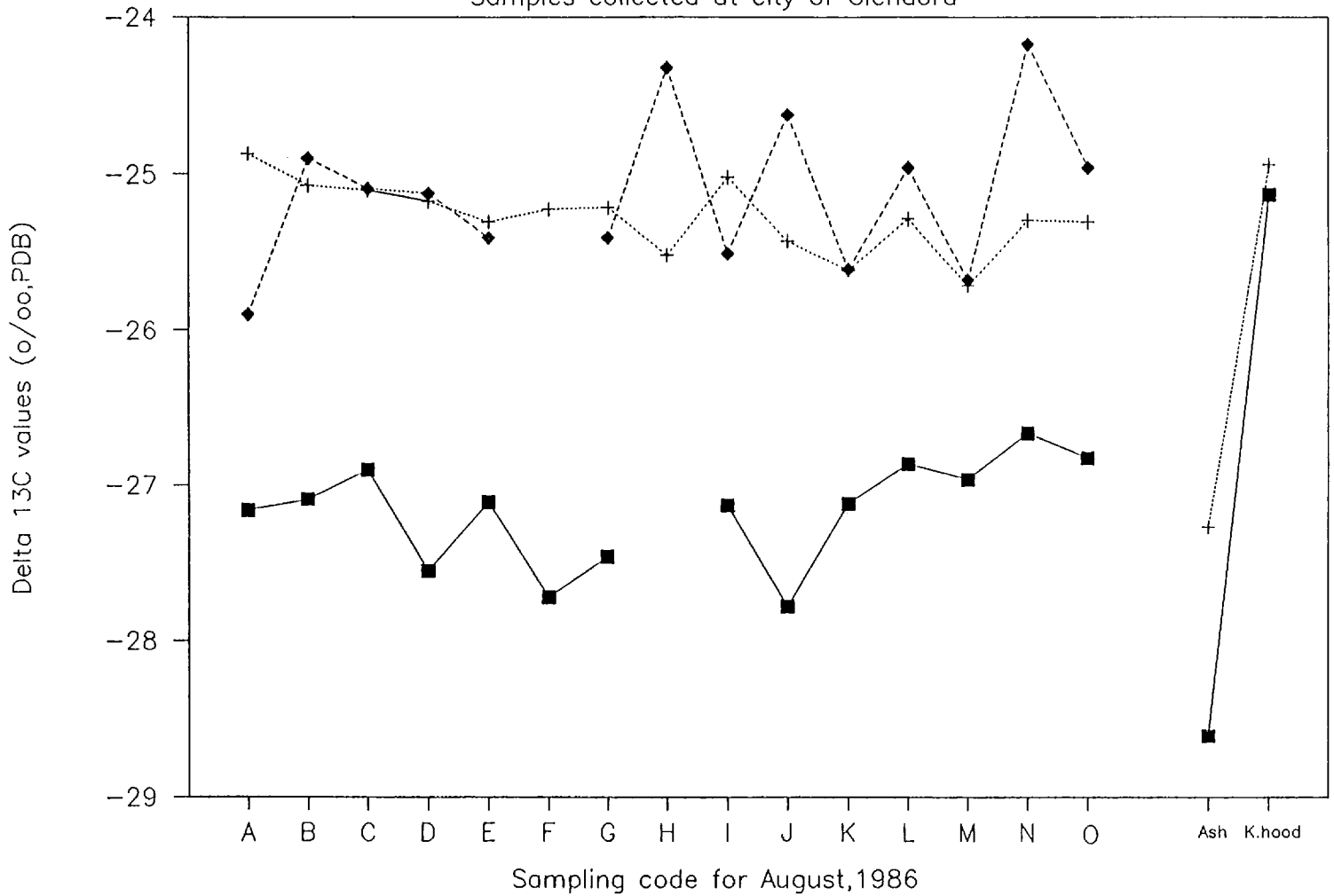
Collection Date (AUG 1986)	Filter No.	D/N*	GGCID	Residual del13C	Residual delD	Residual del15N	Aliphatic and Aromatic del13C	Aliphatic and Aromatic delD	Polar del13C	Polar delD	Polar del15N
10	3809	D	4672-1	-26.86	-137	22.57	-28.04	-121	-26.88	-97	7.38
10	3813	N	4672-6	-26.05	-98	30.33	-27.70	-120	-26.50	-87	7.23

* D = day; N = night

Figure X-1

Carbon Isotope Ratios

Samples collected at city of Glendora



Key

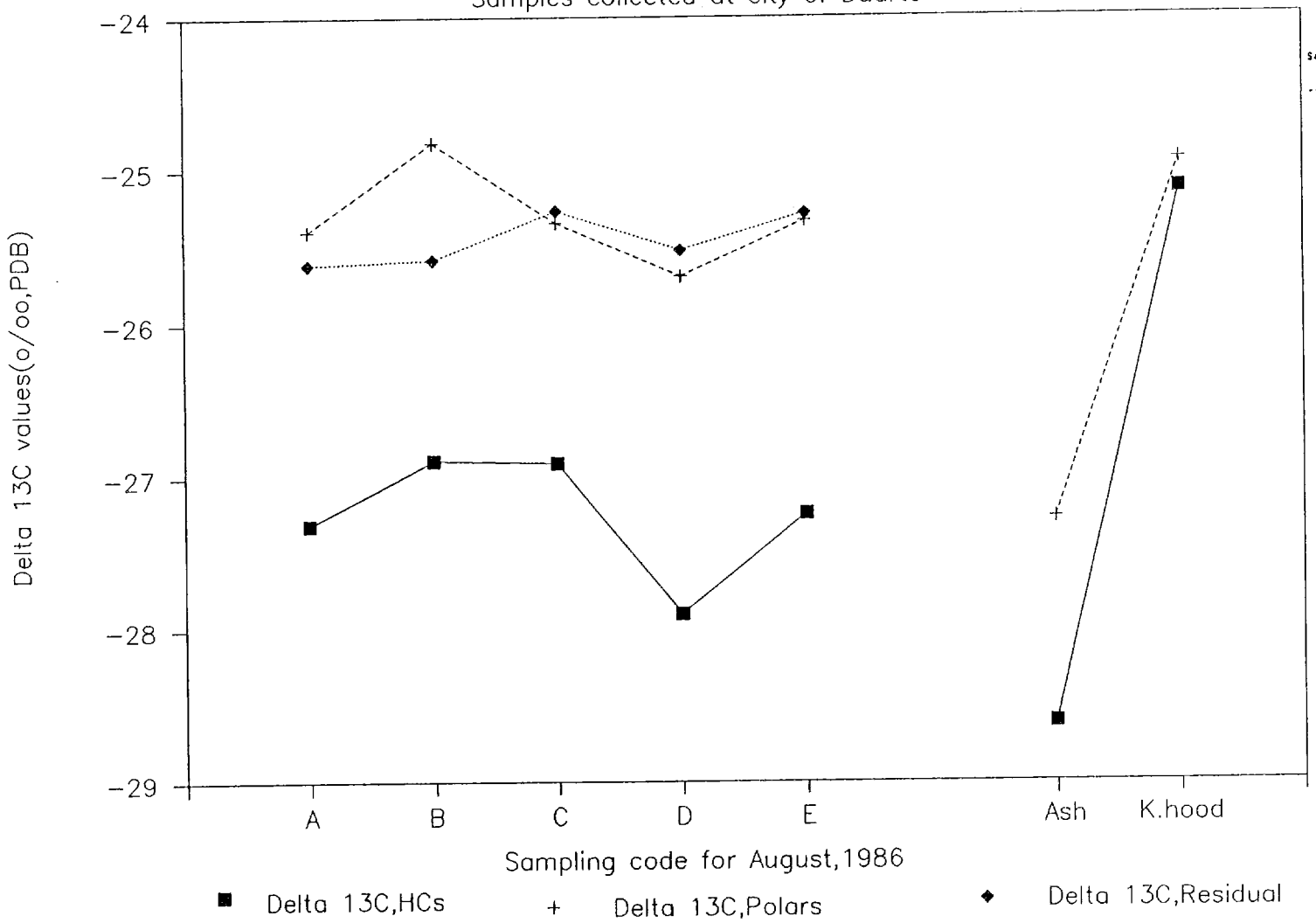
Sample ID	Sampling Date	Sampling Time: Day or Night	Sampling Time: Time
A	8/13/86	D	0800-2000
B	8/13/86	N	2000-0800
C	8/14/86	D	0800-2000
D	8/14/86	N	2000-0800
E	8/15/86	D	0800-2000
F	8/15/86	N	2000-0800
G	8/16/86	D	0800-2000
H	8/16/86	N	2000-0720
I	8/17/86	D	0800-2000
J	8/17/86	N	2005-0800
K	8/18/86	D	0800-2000
L	8/18/86	N	2000-0800
M	8/19/86	D	0800-2015
N	8/19/86	N	2020-0800
O	8/20/86	D	0800-2000

■ Delta 13C Hydrocarbons + Delta 13C Polars ◆ Delta 13C Residual

Figure X-2

Carbon Isotope Ratios

Samples collected at city of Duarte



Key

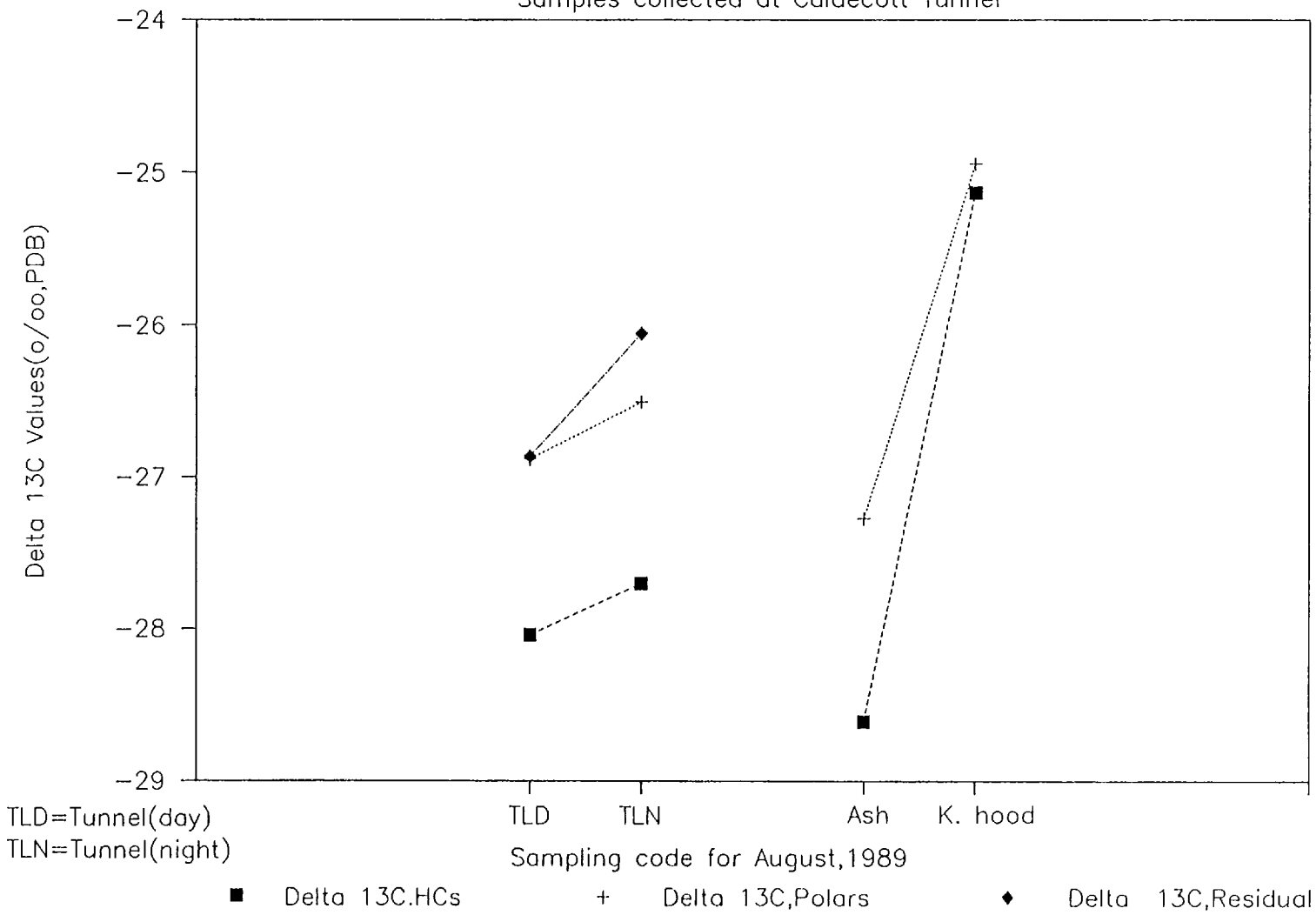
Sample ID	Sampling Date	Sampling Time: Day or Night	Sampling Time: Time
A	8/13/86	D	0810-1230
A	8/14/86	D	0830-1252
B	8/13/86	N	2030-0830
C	8/13/86	D	1230-2030
C	8/15/86	D	1200-2000
D	8/17/86	D	1200-2000
E	8/19/86	D	1200-2000
E	8/20/89	D	1200-2000

} combined samples

Figure X-3

Carbon Isotope Ratios

Samples collected at Caldecott Tunnel



TLD=Tunnel(day)
TLN=Tunnel(night)

Key

	Filter No.	Sampling Date	Sampling Time
TLD	3809	08/10/89	day
TLN	3813	08/10/89	night
TLN2	3814	08/10/89	night

XI. ^{14}C ESTIMATION OF MODERN CARBON IN AEROSOLS

XI. ^{14}C ESTIMATION OF MODERN CARBON IN AEROSOLS

The measurement of ^{14}C in the aerosols is based on the fact that ^{14}C forms continuously in the atmosphere by cosmic ray impact on nitrogen and decays by β particle loss to nitrogen with a half life of 5730 years. When plants grow, they incorporate carbon dioxide with a modern (atmospheric) ^{14}C content. Respiration and biological production of gases and aerosols liberate chemical species with a modern ^{14}C signature. The lowest content of ^{14}C which can be measured with very sensitive instruments represents about ten half lives. When ^{14}C can no longer be measured in the sample it is considered "dead". Hence to evaluate the amount of modern carbon in a sample one measures the amount of ^{14}C in the total sample and ratios it to the ^{12}C which is considered to remain relatively constant. The change in the $^{14}C/^{12}C$ ratio (or $D^{14}C$) relative to international standards will allow a calculation of the amount of modern carbon.

To evaluate the amount of modern carbon, the assumption was made that the hydrocarbon fraction was entirely or largely produced from fossil fuels and therefore should have the lowest content of ^{14}C (modern carbon), whereas the polar fraction, which represents photochemical reactions including possible contributions of biological material, could have the largest content of modern carbon. The solvent extracted samples were separated into hydrocarbon and polar fractions, which, together with the non-extractable residue were prepared for ^{14}C measurement by an accelerator mass spectrometer.

The data presented in Tables XI-1 to XI-3 and in Figures XI-1 to XI-12 clearly show that in fact the lowest content of ^{14}C (or least amount of modern carbon) is present in the hydrocarbon fraction. The lowest content of all was measured in the Caldecott Tunnel samples, which should have had the least mixing with biological material. Here, the measured modern carbon content is

only an average of 3%. For Glendora and Duarte, the amount is 16-17%, with the exception of sample 8015 (a night sample) at Duarte.

The polar fraction of Glendora and Duarte was measured to contain 37% and 28% modern carbon respectively, whereas the residue contains a range varying from 33% modern carbon for Glendora and 29% for Duarte.

For the tunnel samples, the percent modern carbon is significantly lower than for the ambient air samples. The polar fraction was measured to contains 13.4% modern carbon and the residual fraction was found to contain 8.9%.

These data are consistent with the fact that modern carbon is present in all fractions, but particularly in the polar and to a lesser extent the residual (elemental carbon) fraction.

The measured data suggest that biogenic carbon components enter particulate aerosols in the ambient atmosphere. The amount present in the hydrocarbon fraction is approximately one half that in the polar or residual fraction. The amount of modern carbon in the latter two fractions is remarkably close, suggesting a generic relationship between them.

Table XI-1. Determination of modern carbon content from D14C measurements on samples collected at city of Glendora.

Collection Date AUG 1986	Filter No.	D/N*	GGCID	Aliphatic + Aromatic D14C (o/oo)	Aliphatic + Aromatic D14C (Dup)	Aliphatic + Aromatic % Modern First/Dup.	Polar D14C (o/oo)	Polar D14C (Dup)	Polar % Modern First/Dup.	Residual D14C (o/oo)	Residual D14C (Dup)	Residual % Modern First/Dup.
13	8007, 8008	D	4672-20	-839.5		16.1	-751.4	-779.5	24.9/22.1	-702.5		29.8
13	8009	D	4672-12	-901.5		9.9	-766.6		23.3	-650.5		35.0
14/15	8017, 8027	D	4672-19	-854.7		14.5	-583.6		41.6	-620.7		37.9
14	8019	D	4672-2	-857.8		14.2	-764.6		23.5	-705.9		29.4
14	8020	D	4672-7	-890.8		10.9	-772.1	-750.9	22.8/24.8	-683.8	-671.1	31.6/32.
15	8026,8029	D	4672-18	-833.7		16.4	-731.2		26.9	-745.6		25.4
16/17	8034,8040	D	4672-13	Contaminated sample			-940.2	-941.9		-295.8		
16	8033,8036	D	4672-15	-826.2		17.4	-705.8		29.4	-693.8		30.6
17	8043,8044	D	4672-14	-768.9		23.1	-745.3		25.5	-661.5		33.9
18/19	8047,8051	D	4672-30	-866.8		13.3	-646.5		35.4	-645.0		35.1
18	8048,8049	D	4672-17	-779.4	-764.1	22.1/23.6	Lost			-633.0		36.7
19	8054,8055	D	4672-28	-813.4		18.7	-725.5		27.5			
20	8057,8058	D	4672-29	-855.0		14.5	-640.1		36.0	-695.5		30.5
20	8060,8061	D	4672-27	-805.3		19.5	-299.9		70.0	-680.8		31.9
13	8013,8014	N	4672-21	-786.3	-789.3	21.4/21.1	-482.6		51.7	-744.0	-752.9	25.6/24.
14	8024	N	4672-8	-869.0		13.1	-517.2		48.3	-699.4		30.1
15	8031	N	4672-10	-869.3		13.1	-533.4		46.7	Lost		
16	8037	N	4672-11	Lost			-599.5		40.1	-666.7		33.3
17	8045	N	4672-9	-862.5		13.8	-533.5		46.7	-645.5		35.5
18	8050	N	4672-4	-794.2		20.6	-592.8		40.7	-573.1		42.7
19	8056	N	4672-3	-727.4		27.3	-528.4		47.2	-626.4		37.4
Mean values (X)						16.9			37.3			32.9
Standard Deviation (SD)						(±4.6)			(±12.7)			(±4.4)

Mean value (% modern) for all three fractions: 28.9 (±12.0)

Table XI-1. Determination of modern carbon content from D14C measurements on samples collected at city of Glendora. (continued)

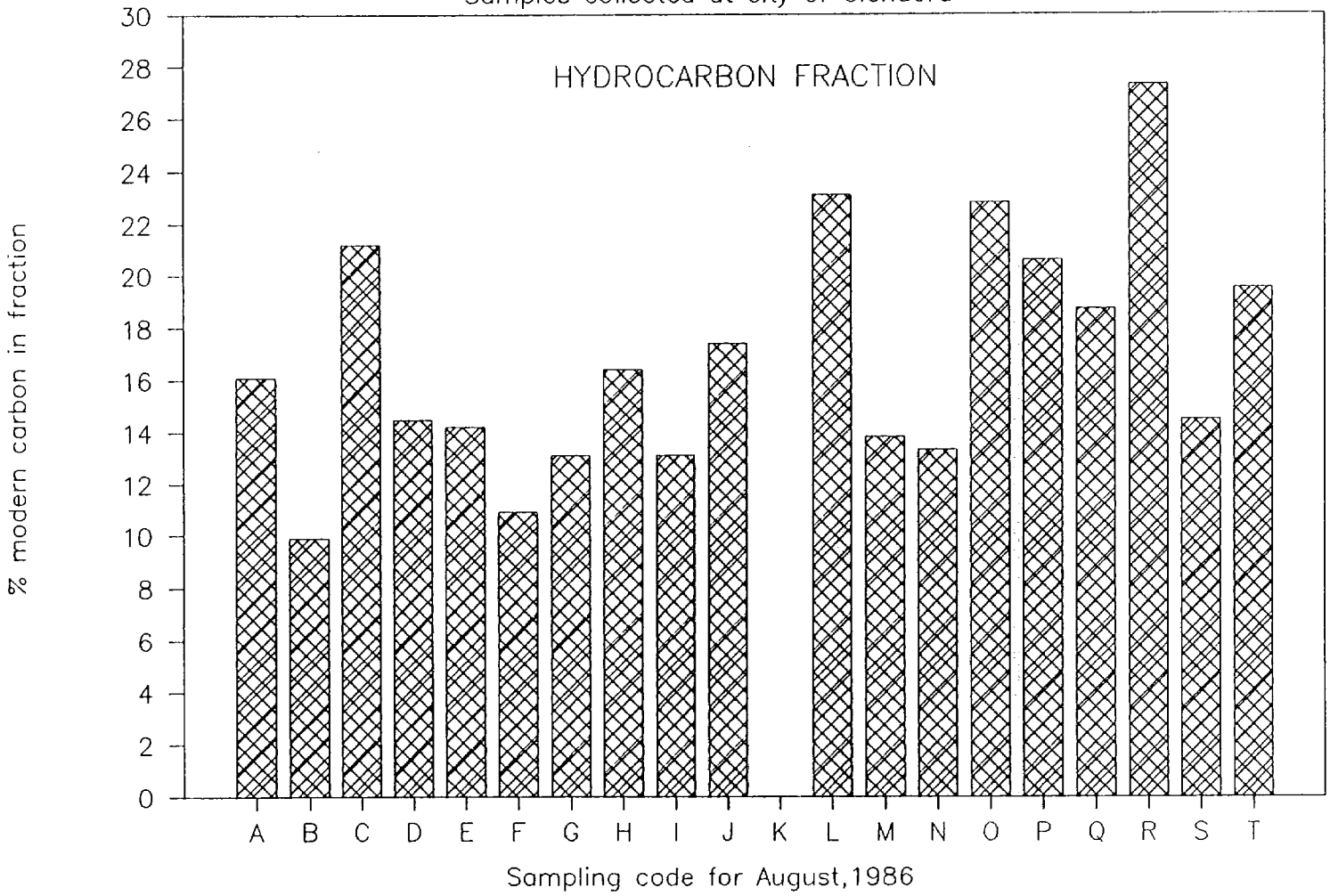
Collection Date AUG 1986	Filter No.	D/N*	GGCID	Aliphatic + Aromatic D14C (o/oo)	Aliphatic + Aromatic D14C (Dup)	Aliphatic + Aromatic % Modern First/Dup.	Polar D14C (o/oo)	Polar D14C (Dup)	Polar % Modern First/Dup.	Residual D14C (o/oo)	Residual D14C (Dup)	Residual % Modern First/Dup.
			OXA4672-15			0.0				338.5		0.0
			OXA-088							366.1		
			OXA-4-088							353.1		
	KITCHEN HOOD EXTRACT		4672-35	-175.0		82.5	179.5		117.9			

* D = day; N = night

Figure XI-1

D 14C Determination of Modern Carbon Content

Samples collected at city of Glendora



Key

	Filter No.	Sampling Date	Sampling Time
A	8007	13/08/86	0800-1200
A	8008	13/08/86	0800-1200
B	8009	13/08/86	1200-2000
C	8013	13/08/86	2000-0800
C	8014	13/08/86	2000-0800
D	8017	14/08/86	0800-1200
D	8027	15/08/86	0800-1200
E	8019	14/08/86	1200-2000
F	8020	14/08/86	1200-2000
G	8024	14/08/86	2000-0800
H	8026	15/08/86	1200-2000
H	8029	15/08/86	1200-2000
I	8031	15/08/86	2005-0800
J	8033	16/08/86	1205-2000
J	8036	16/08/86	1205-2000
K	8037	16/08/86	2000-0720
L	8043	17/08/86	1200-2000
L	8044	17/08/86	1200-2000
M	8045	17/08/86	2000-0800
N	8047	18/08/86	0800-1200
N	8051	19/08/86	0800-1200
O	8048	18/08/86	1200-2000
O	8049	18/08/86	1200-2000
P	8050	18/08/86	2000-0800
Q	8054	19/08/86	1200-2000
Q	8055	19/08/86	1200-2000
R	8056	19/08/86	2020-0800
S	8057	20/08/86	0800-1200
S	8058	20/08/86	0800-1200
T	8060	20/08/86	1200-2000
T	8061	20/08/86	1200-2000

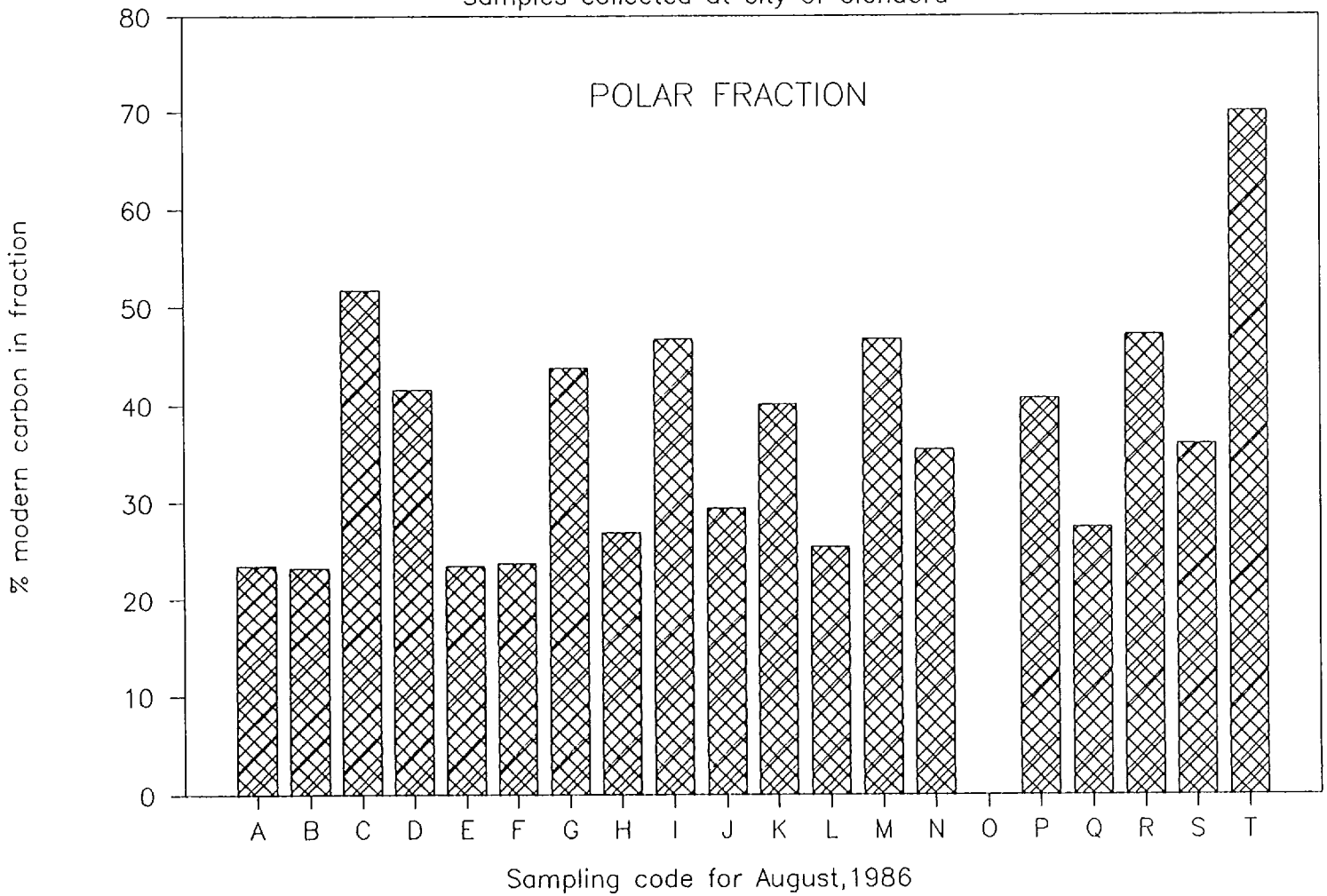
} combined samples

Samples missing were lost either during combustion or preparation for 14C analysis

Figure XI-2

D 14C Determination of Modern Carbon Content

Samples collected at city of Glendora



Key

	Filter No.	Sampling Date	Sampling Time
A	8007	13/08/86	0800-1200
A	8008	13/08/86	0800-1200
B	8009	13/08/86	1200-2000
C	8013	13/08/86	2000-0800
C	8014	13/08/86	2000-0800
D	8017	14/08/86	0800-1200
D	8027	15/08/86	0800-1200
E	8019	14/08/86	1200-2000
F	8020	14/08/86	1200-2000
G	8024	14/08/86	2000-0800
H	8026	15/08/86	1200-2000
H	8029	15/08/86	1200-2000
I	8031	15/08/86	2005-0800
J	8033	16/08/86	1205-2000
J	8036	16/08/86	1205-2000
K	8037	16/08/86	2000-0720
L	8043	17/08/86	1200-2000
L	8044	17/08/86	1200-2000
M	8045	17/08/86	2000-0800
N	8047	18/08/86	0800-1200
N	8051	19/08/86	0800-1200
O	8048	18/08/86	1200-2000
O	8049	18/08/86	1200-2000
P	8050	18/08/86	2000-0800
Q	8054	19/08/86	1200-2000
Q	8055	19/08/86	1200-2000
R	8056	19/08/86	2020-0800
S	8057	20/08/86	0800-1200
S	8058	20/08/86	0800-1200
T	8060	20/08/86	1200-2000
T	8061	20/08/86	1200-2000

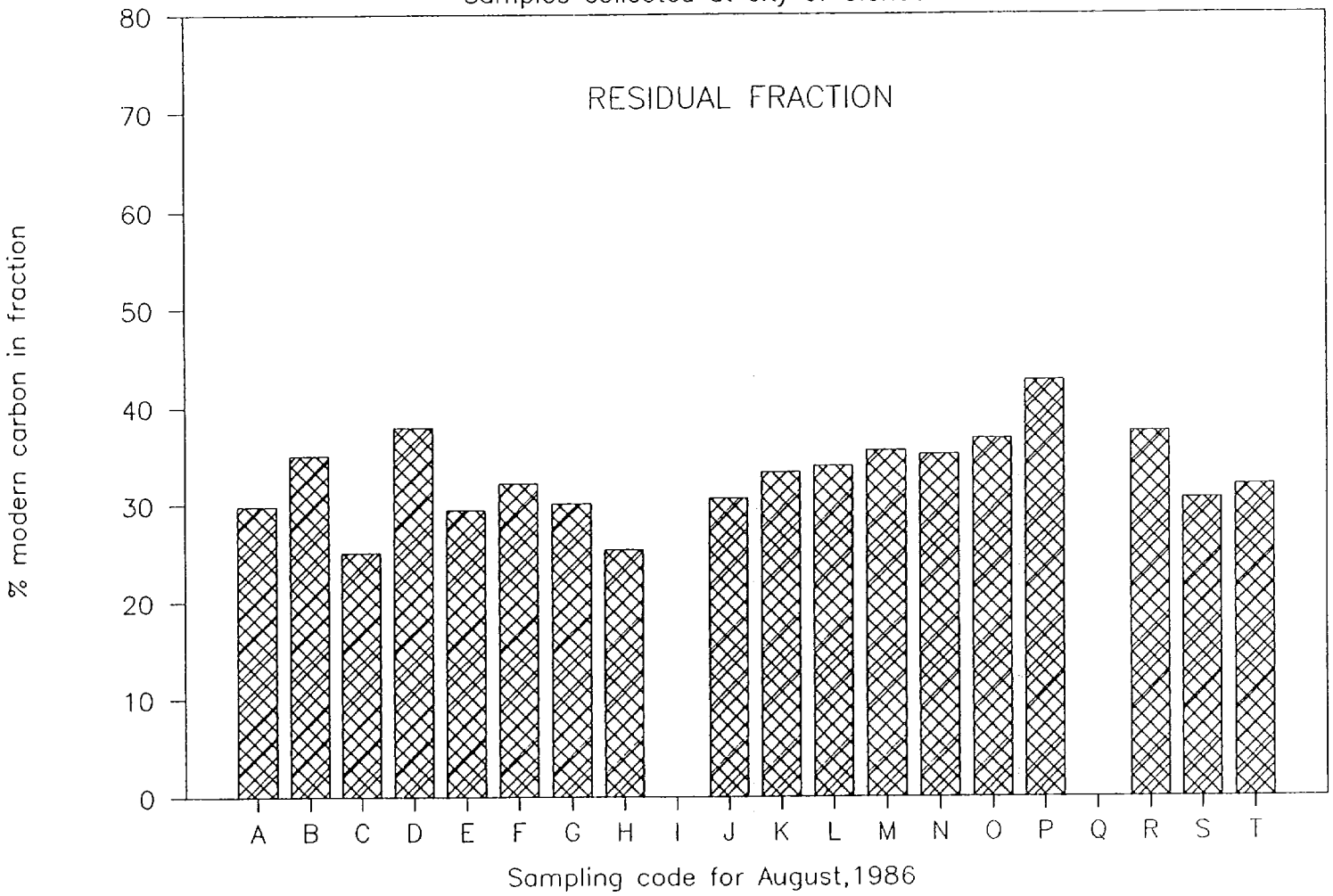
} combined samples

Samples missing were lost either during combustion or preparation for 14C analysis

Figure XI-3

D 14C Determination of Modern Carbon Content

Samples collected at city of Glendora



Key

	Filter No.	Sampling Date	Sampling Time
A	8007	13/08/86	0800-1200
A	8008	13/08/86	0800-1200
B	8009	13/08/86	1200-2000
C	8013	13/08/86	2000-0800
C	8014	13/08/86	2000-0800
D	8017	14/08/86	0800-1200
D	8027	15/08/86	0800-1200
E	8019	14/08/86	1200-2000
F	8020	14/08/86	1200-2000
G	8024	14/08/86	2000-0800
H	8026	15/08/86	1200-2000
H	8029	15/08/86	1200-2000
I	8031	15/08/86	2005-0800
J	8033	16/08/86	1205-2000
J	8036	16/08/86	1205-2000
K	8037	16/08/86	2000-0720
L	8043	17/08/86	1200-2000
L	8044	17/08/86	1200-2000
M	8045	17/08/86	2000-0800
N	8047	18/08/86	0800-1200
N	8051	19/08/86	0800-1200
O	8048	18/08/86	1200-2000
O	8049	18/08/86	1200-2000
P	8050	18/08/86	2000-0800
Q	8054	19/08/86	1200-2000
Q	8055	19/08/86	1200-2000
R	8056	19/08/86	2020-0800
S	8057	20/08/86	0800-1200
S	8058	20/08/86	0800-1200
T	8060	20/08/86	1200-2000
T	8061	20/08/86	1200-2000

} combined samples

Samples missing were lost either during combustion or preparation for 14C analysis

Table XI-2. Determination of modern carbon content from D14C measurements on samples collected at city of Duarte.

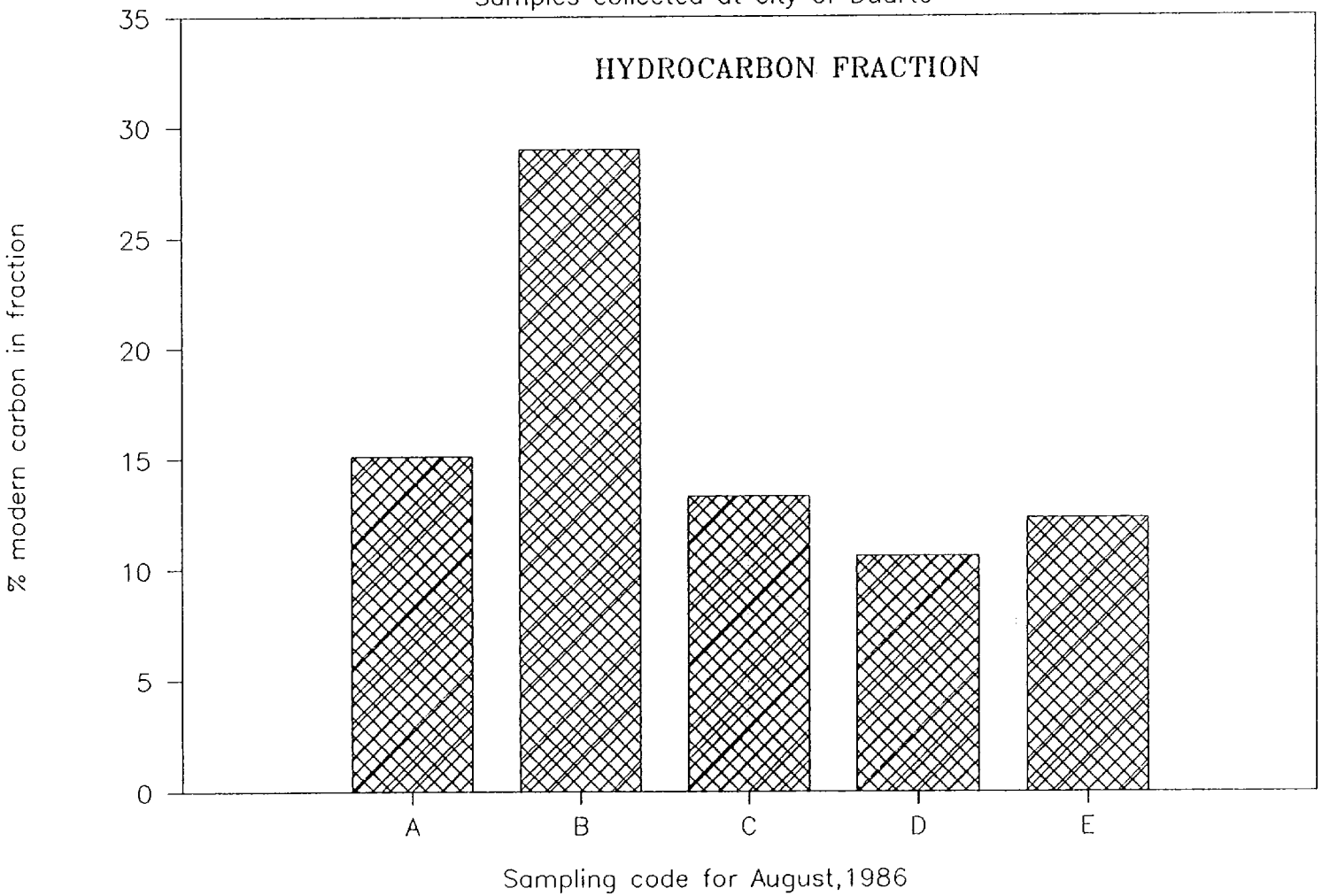
Collection Date (AUG 1986)	Filter No.	D/N*	GGC ID	Aliphatic + Aromatic D14C (o/oo)	Aliphatic + Aromatic D14C (Dup)	Aliphatic + Aromatic % Modern First/Dup.	Polar D14C (o/oo)	Polar D14C (Dup)	Polar % Modern First/Dup.	Residual D14C (o/oo)	Residual D14C (Dup)	Residual % Mode First/
13/14	8006,8018	D	4672-22	-849.4		15.1	-617.3		38.3	-663.2		33.7
13/15	8010,8025	D	4672-32	-867.2		13.3	-782.8		21.7	-745.5		25.3
17	8041	D	4672-24	-894.5		10.6	-722.4		27.8	-693.6		30.6
19/20	8053,8059	D	4672-23	-876.8		12.3	768.5		23.2	-686.8		31.3
13	8015	N	4672-31	-709.6		29.0			Lost	-762.7		23.7
Mean values ($\bar{x}$)						16.1			27.8			28.9
Standard Deviation (SD)						(±7.4)			(±7.5)			(±4.2)
Mean value (% modern) for all three fractions: 24.0 (+8.6)												
			OXA4672-15 (standard)							338.5		
			OXA-088 (standard)							366.1		
			OXA-4-088 (standard)							353.1		
	KITCHEN		4672-35	-175.0		82.5	179.5		117.9			

* D = day; N = night

Figure XI-4

D 14C Determination of Modern Carbon Content

Samples collected at city of Duarte



Key

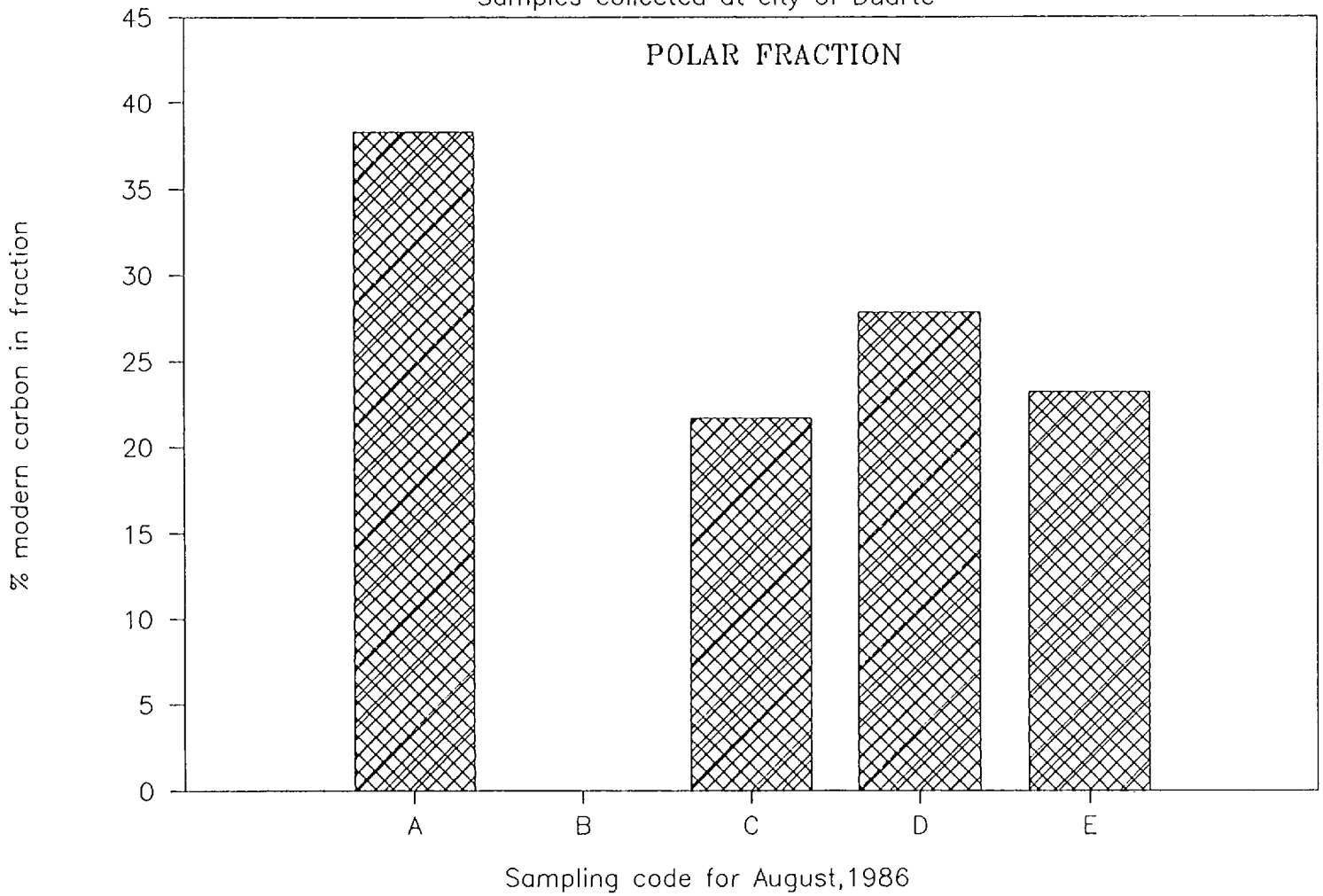
	Filter No.	Sampling Date	Sampling Time
A	8006	13/08/86	0830-1230
A	8018	14/08/86	0830-1230
B	8015	13/08/86	2030-0830
C	8010	13/08/86	1230-2030
C	8025	15/08/86	1230-2030
D	8041	17/08/86	1200-2000
E	8053	19/08/86	1200-2000
E	8059	20/08/86	1200-2000

} combined samples

Figure XI-5

D 14C Determination of Modern Carbon Content

Samples collected at city of Duarte



Key

	Filter No.	Sampling Date	Sampling Time
A	8006	13/08/86	0830-1230
A	8018	14/08/86	0830-1230
B	8015	13/08/86	2030-0830
C	8010	13/08/86	1230-2030
C	8025	15/08/86	1230-2030
D	8041	17/08/86	1200-2000
E	8053	19/08/86	1200-2000
E	8059	20/08/86	1200-2000

} combined samples

Sample missing was lost either during combustion or preparation for 14C analysis

Figure XI-6

D 14C Determination of Modern Carbon Content

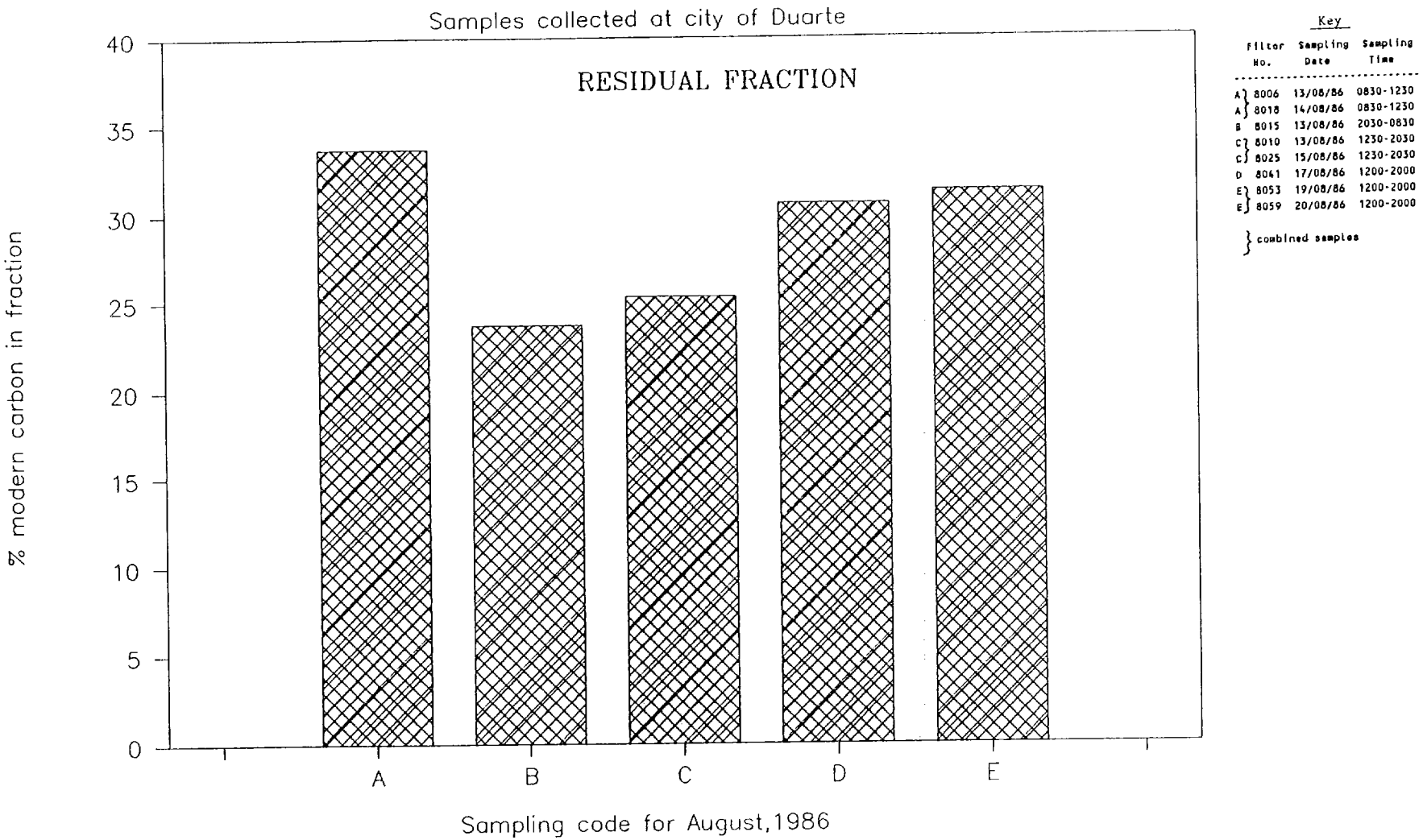


Table XI-3. Determination of modern carbon content from D14C measurements on samples collected at Caldecott Tunnel.

Collection Date (AUG 1989)	Filter No.	D/N*	GGC ID	Aliphatic + Aromatic D14C (o/oo)	Aliphatic + Aromatic D14C (Dup)	Aliphatic + Aromatic % Modern First/Dup.	Polar D14C (o/oo)	Polar D14C (Dup)	Polar % Modern First/Dup.	Residual D14C (o/oo)	Residual D14C (Dup)	Residual % Modern First/Dup.
10	3809	D	4672-1	-966.3		3.4	-856.2		14.4	-911.1		8.9
10	3813	N	4672-6	-959.3		4.1	Lost			-949.3		5.1
10	3814	N	4672-41	-987.7		1.2	-877.1		12.3	-873.8		12.6
Mean values ($\bar{X}$)						2.9			13.4			8.9
Standard deviation (SD)						(±1.5)			(±1.5)			(±3.8)

Mean value (% modern) for all three fractions: 7.2 (+4.6)

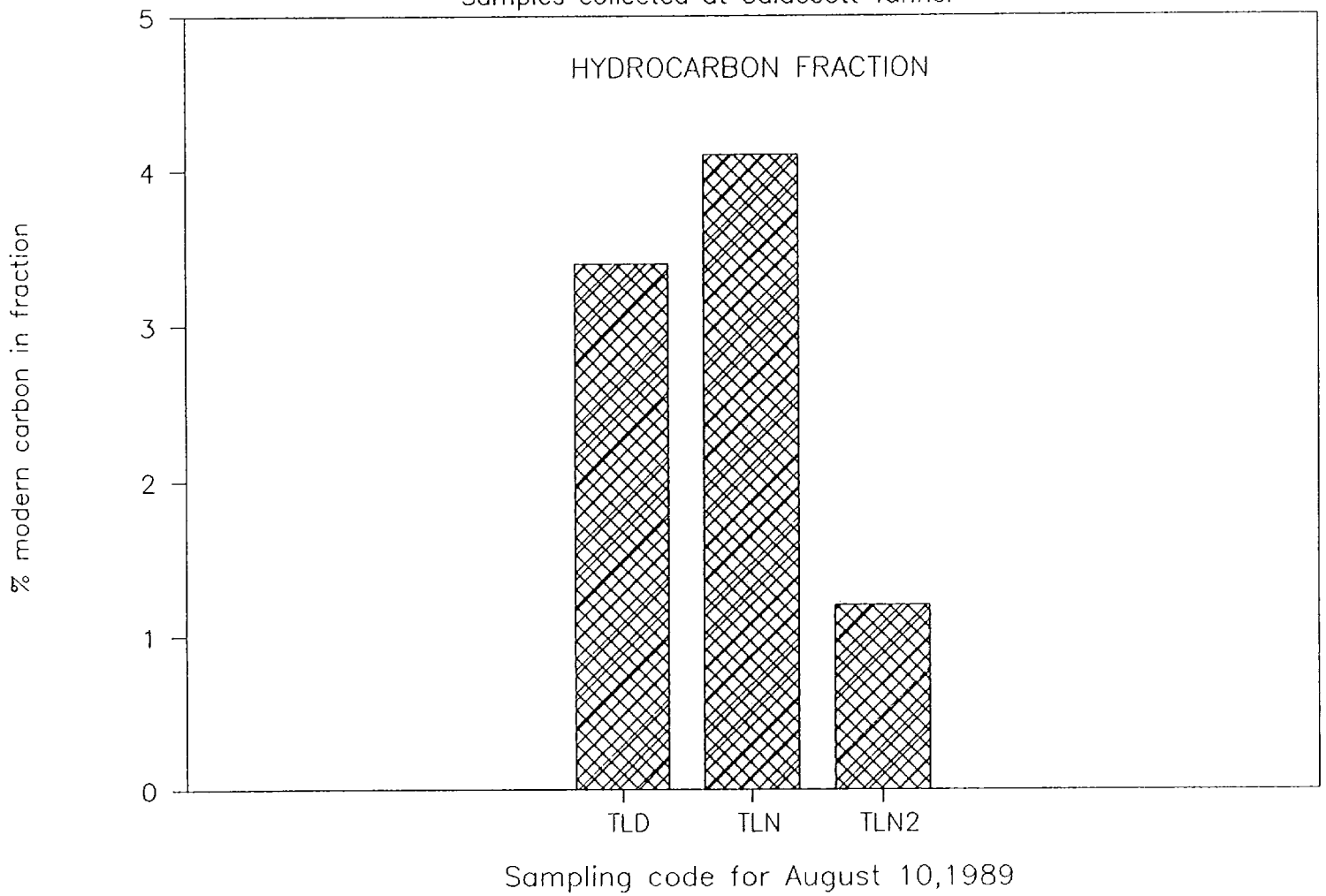
OXA4672-15 (standard)	338.5
OXA-088 (standard)	366.1
OXA-4-088 (standard)	353.1

* D = day; N = night

Figure XI-7

D 14C Determination of Modern Carbon Content

Samples collected at Caldecott Tunnel



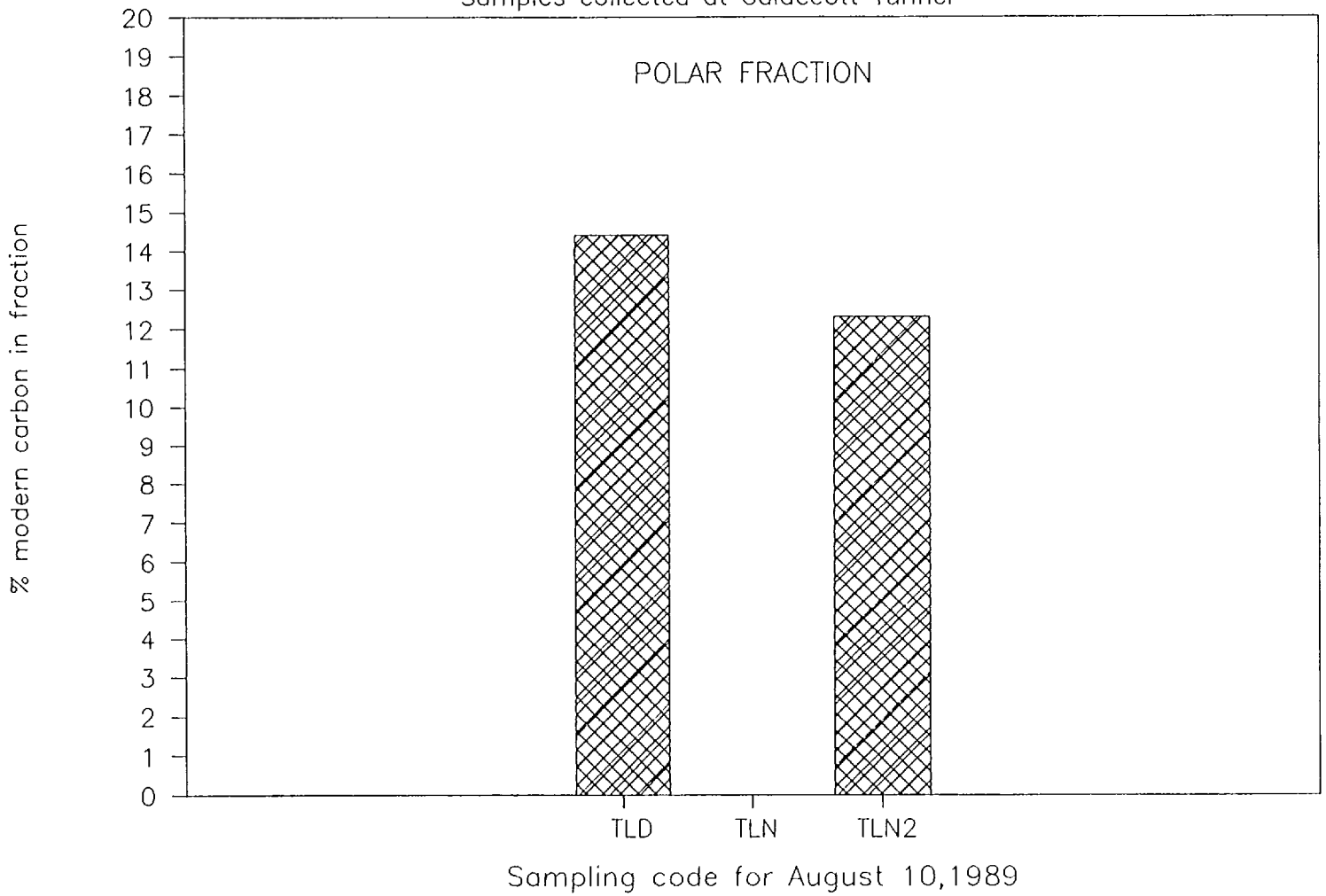
Key

Filter No.		Sampling Date	Sampling Time
TLD	3809	08/10/89	day
TLN	3813	08/10/89	night
TLN2	3814	08/10/89	night

Figure XI-8

D 14C Determination of Modern Carbon Content

Samples collected at Caldecott Tunnel



Key

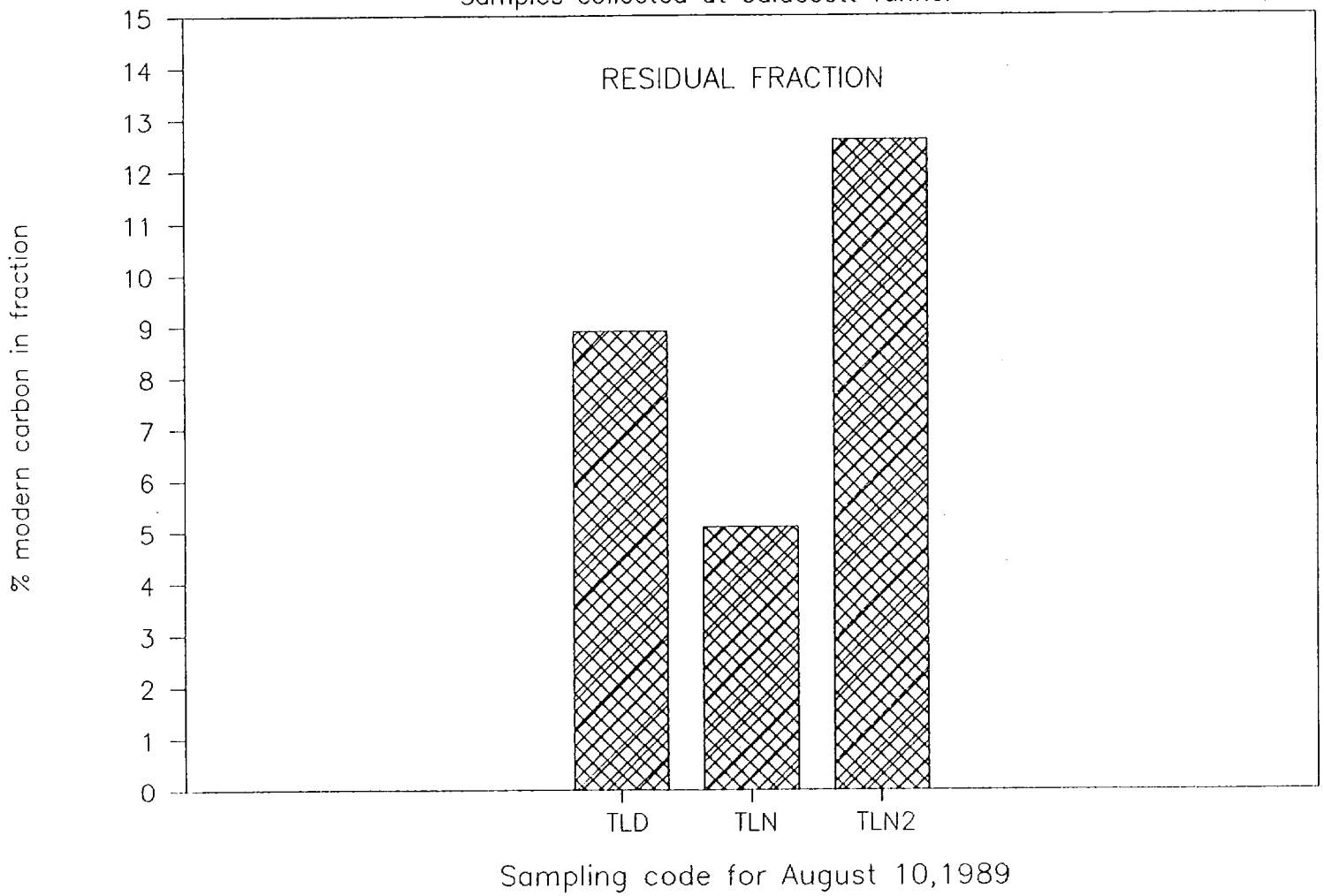
	Filter No.	Sampling Date	Sampling Time
TLD	3809	08/10/89	day
TLN	3813	08/10/89	night
TLN2	3814	08/10/89	night

Sample missing was lost either during combustion or preparation for 14C analysis

Figure XI-9

D 14C Determination of Modern Carbon Content

Samples collected at Caldecott Tunnel



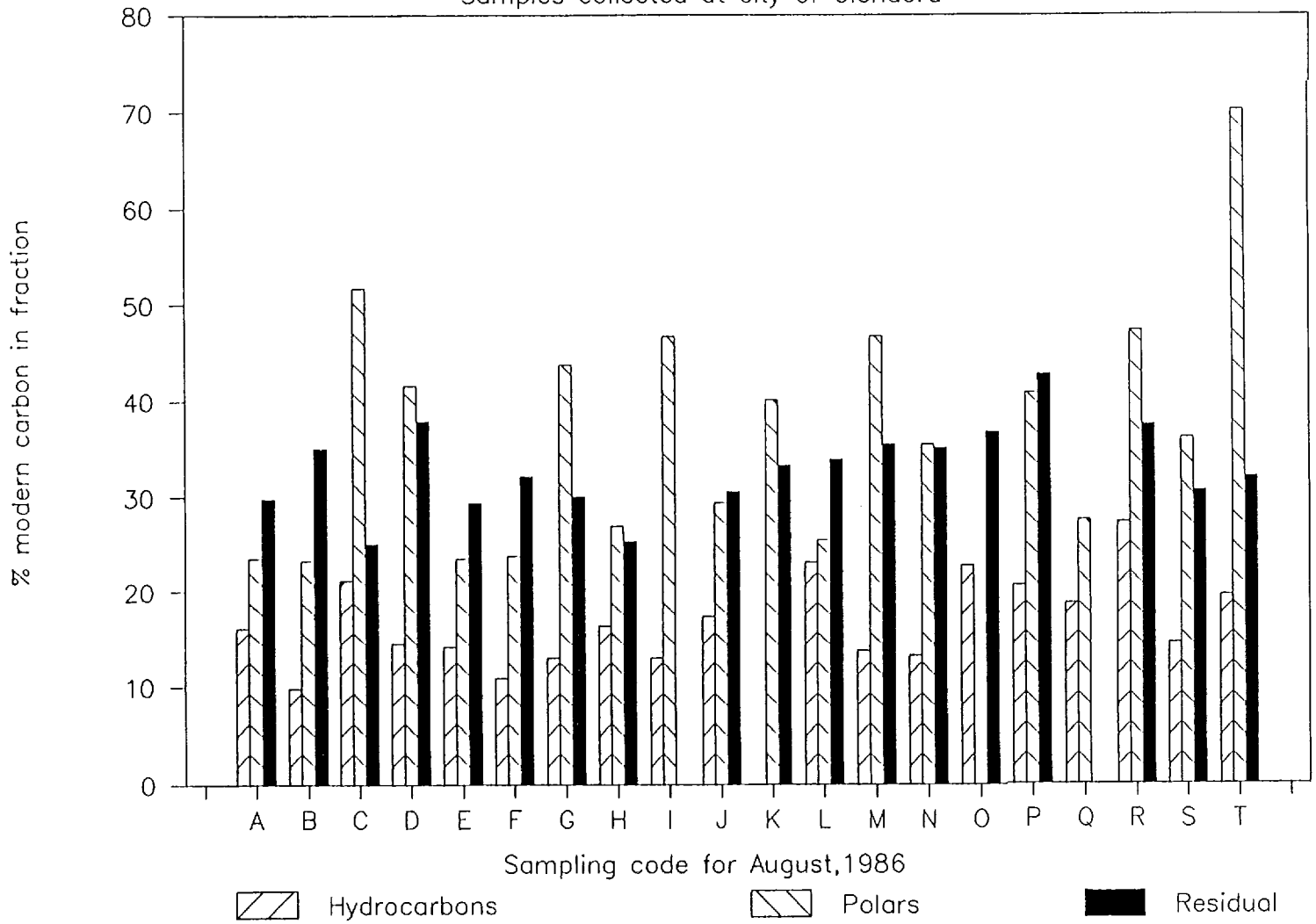
Key

	Filter No.	Sampling Date	Sampling Time
TLD	3809	08/10/89	day
TLN	3813	08/10/89	night
TLN2	3814	08/10/89	night

Figure XI-10

D 14C Determination of Modern Carbon Content

Samples collected at city of Glendora



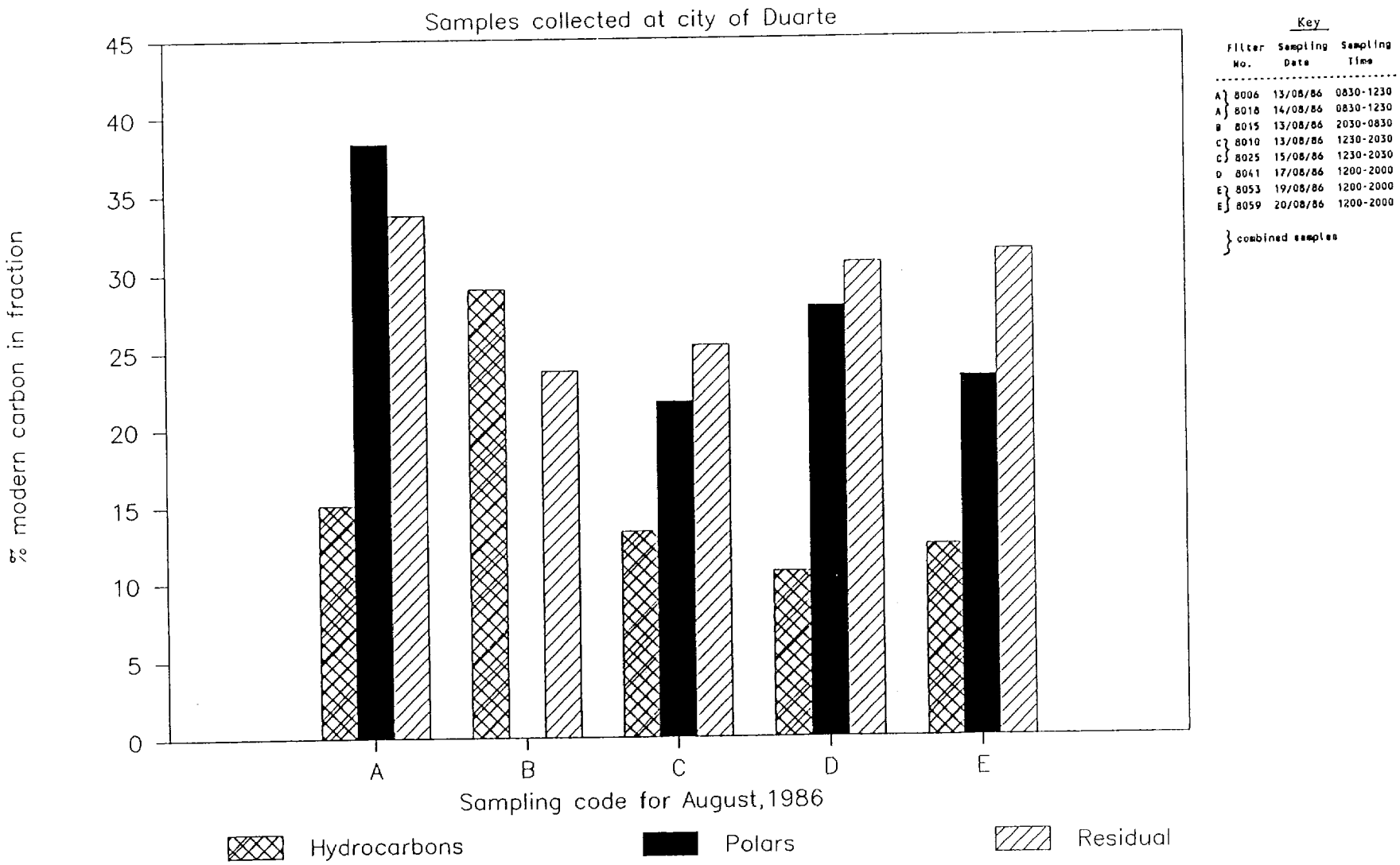
Key

	Filter No.	Sampling Date	Sampling Time
A	8007	13/08/86	0800-1200
A	8008	13/08/86	0800-1200
B	8009	13/08/86	1200-2000
C	8013	13/08/86	2000-0800
C	8014	13/08/86	2000-0800
D	8017	14/08/86	0800-1200
D	8027	15/08/86	0800-1200
E	8019	14/08/86	1200-2000
F	8020	14/08/86	1200-2000
G	8024	14/08/86	2000-0800
H	8026	15/08/86	1200-2000
H	8029	15/08/86	1200-2000
I	8031	15/08/86	2005-0800
J	8033	16/08/86	1205-2000
J	8036	16/08/86	1205-2000
K	8037	16/08/86	2000-0720
L	8043	17/08/86	1200-2000
L	8044	17/08/86	1200-2000
M	8045	17/08/86	2000-0800
N	8047	18/08/86	0800-1200
N	8051	19/08/86	0800-1200
O	8048	18/08/86	1200-2000
O	8049	18/08/86	1200-2000
P	8050	18/08/86	2000-0800
Q	8054	19/08/86	1200-2000
Q	8055	19/08/86	1200-2000
R	8056	19/08/86	2020-0800
S	8057	20/08/86	0800-1200
S	8058	20/08/86	0800-1200
T	8060	20/08/86	1200-2000
T	8061	20/08/86	1200-2000

} combined samples

Figure XI-11

D 14C Determination of Modern Carbon Content

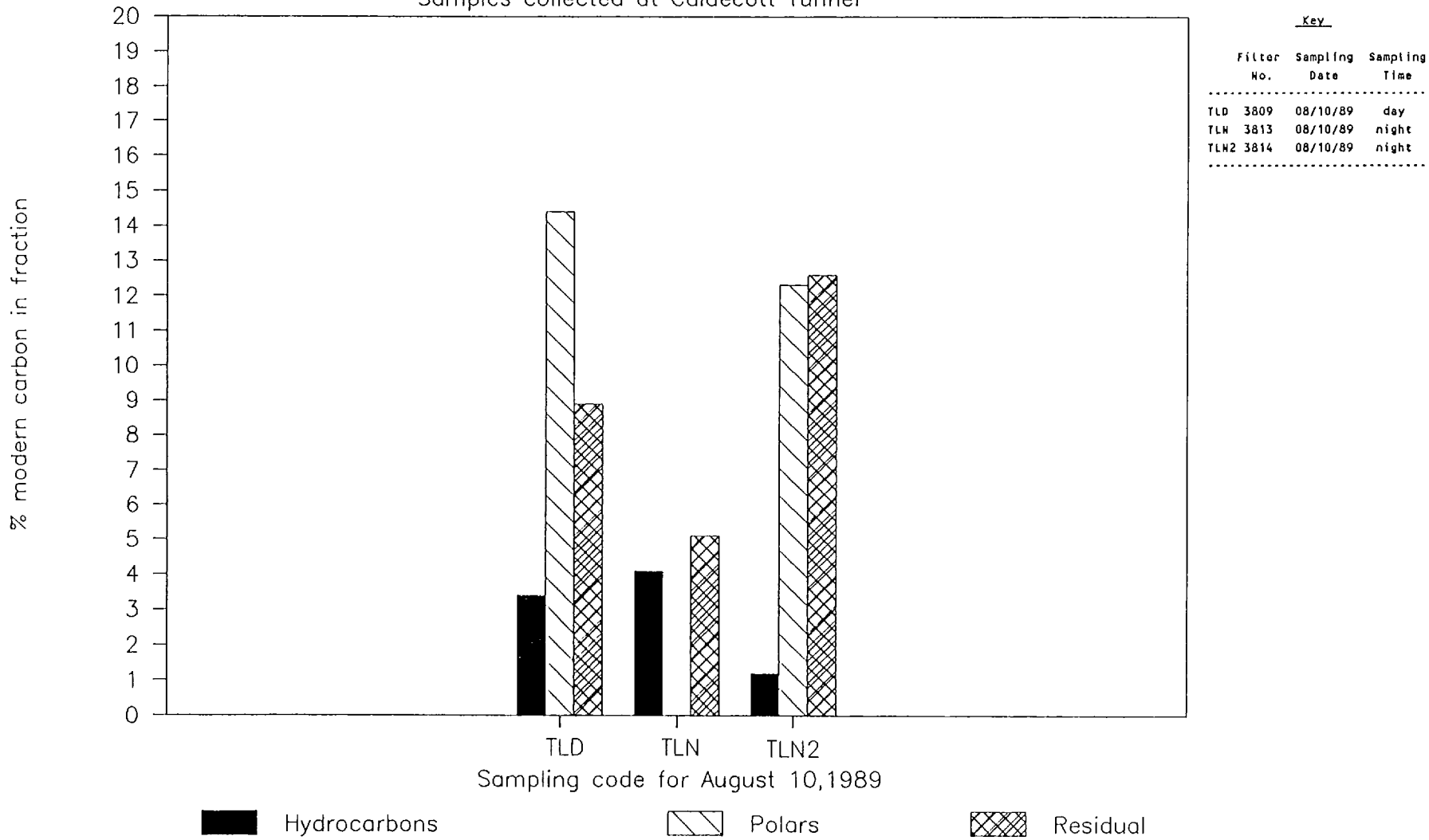


Sample missing was lost either during combustion
or preparation for 14C analysis

Figure XI-12

D 14C Determination of Modern Carbon Content

Samples collected at Caldecott Tunnel



Sample missing was lost either during combustion or preparation for 14C analysis

XII. ANALYSES OF BLANK FILTERS

XII. ANALYSES OF BLANK FILTERS

Although all the filters used in this project were documented to have been "fired" at 700°C, when analyses were performed on replicate blanks to determine the total carbon content, it was determined that measurable quantities of total carbon were identified. Therefore, a series of available blank filters, representing the series run for the tunnel samples (3000 filter series) and the Glendora/Duarte samples (8000 filter series) were analyzed in some detail in order to evaluate the data obtained on the samples.

XII-1 Total Carbon in Blank Filters

Table XII-1 presents data for ten blank filters for total carbon, organic carbon and elemental carbon. By contrast with the means for the samples shown in Table XII-2, it is apparent that the filters have a significant and unexplainable content of organic carbon. The total carbon on the blank filters represents about 30% of the total carbon from the Glendora and Duarte samples but only about 3-4% of the Caldecott Tunnel samples. It is further evident that the major carbon form in the blank filters is organic carbon (Table XII-1) and that only a small fraction (12%) can be described as "elemental carbon" or residual carbon.

Hence, for Glendora and Duarte, the total "organic carbon" of the blank filters represents up to 40% of the collected samples, whereas the elemental fraction is <10% of the elemental fraction of the samples (Table XII-3). For Caldecott Tunnel samples, the total "organic carbon" of the blank filter represents about 13% of the organic carbon in the sample, whereas the "elemental carbon" in the blank filter is only 0.5% of the elemental carbon in the tunnel aerosol sample.

Table XII-1. Measured, Total C and Organic C for blank filters and calculated Elemental Carbon and Organic/Elemental carbon ratios.

Filter No.	Total C (mg)	Organic C (mg)	Elemental C (mg)	Organic C / Elemental C
3413	2.75	2.37	0.42	5.6
3459	2.46	2.38	0.08	29.7
8012	2.06	1.99	0.07	28.0
8016	1.22	1.07	0.15	7.1
8022	1.62	1.60	0.02	80.0
8023	1.74	1.53	0.21	7.3
8028	2.38	1.78	0.60	3.0
8030	1.41	1.38	0.03	46.0
8039	2.67	2.36	0.31	7.6
8052	1.43	1.16	0.27	4.3
Mean	1.97	1.76	0.21	8.4

Table XII-2. Calculated mean values for TC, OC, EC (in mg) and OC/EC ratios of sampled filters.

	TC	OC	EC	OC / EC
Glendora(day)	6.7	4.4	2.3	1.9
Glendora(night)	6.7	4.1	2.6	1.8
Duarte(day)	6.4	4.2	2.2	1.9
Duarte(night)	6.8	3.9	2.9	1.3
Tunnel(day)	51.1	12.8	38.3	0.3
Tunnel(night)	54.2	13.6	40.6	0.3

XII-2 Extractable Organic Carbon in Blank Filters

To further evaluate the content of extractable organic material and the content of Fraction 1 and Fraction 2, which were used for ^{14}C analyses and detailed chemical identification purposes, each of the ten blank filters was extracted and the extracts of eight filters were weighed, fractionated by column chromatography and weighed again. The data are shown in Table XII-3. Here again it can be seen that the extractable carbon in the blanks represents about 78% of the total carbon in the filters measured by a combustion technique.

XII-3 Fraction 1 and Fraction 2 in Blank Filter Extracts

In order to correct for ^{14}C measurements it is of value to compare the same fraction mass in the sample filter and the blank filter. This can be seen for elemental carbon in Table XII-4 and for Fraction 1 and Fraction 2 in Table XII-5. For Glendora and Duarte, the average content of Fraction 1 in blank filters relative to day and night samples is about 8%, whereas for the Caldecott Tunnel samples it is ~15%, for the day sample and 12% for the night sample.

For Fraction 2 the average of the blank to the Glendora and Duarte day and night samples is 11%, and for the tunnel samples it is ~17.5 for the day sample and ~10% for the night samples. For the elemental fraction it is 8.5% for the Glendora and Duarte samples and 0.5% for the tunnel samples.

XII-4 Fraction 1 Composition in Blank Filters

To determine what the dominant components were in Fraction 1 from the blank filters, aliquots of the fraction were measured by GC-mass spectrometer. The mass fragmentograms for nine filter blank extracts are shown in Figures

Table XII-3. Total extract and fraction weights for blank filters.

Filter No.	Total Extract Wt (mg)	Fraction 1 (Aliphatic & Aromatic) Wt (mg)	Fraction 1 % Total Extract	Fraction 2 (Polar) Wt (mg)	Fraction 2 % Total Extract	% Extract Remaining in Column	Fatty Acids % Total Extract	Organic C / Total C	Extract / Total C
3413	1.52	0.2	14.4	0.3	17.3	68.3	nd	0.86	0.55
3459	1.89	0.3	13.5	0.4	19.9	66.6	nd	0.97	0.77
8012	1.90	0.2	10.3	0.4	18.0	71.7	0.5	0.97	0.92
8016	1.35	nd	nd	nd	nd	nd	nd	0.88	1.11
8022	1.38	nd	nd	nd	nd	nd	nd	0.99	0.85
8023	0.90	0.1	11.1	0.2	22.2	66.7	nd	0.88	0.52
8028	1.40	0.2	14.3	0.4	28.6	57.1	nd	0.75	0.59
8030	1.90	0.2	7.9	0.3	13.2	78.9	ND	0.98	1.35
8039	1.82	0.2	11.0	0.3	17.3	71.7	nd	0.88	0.68
8052	0.70	0.1	14.2	0.2	28.4	57.2	nd	0.81	0.49
Mean	1.48	0.2		0.3				0.90	0.78

nd = not determined
ND = not detected

Table XII-4. Calculated mean ratios (total sample filter/blank filter) of Total C, Organic C, Elemental C.

	Total C	Organic C	Elemental C
Glendora(day)	3.4	2.5	10.9
Glendora(night)	3.4	2.3	12.4
Duarte(day)	3.2	2.5	10.5
Duarte(night)	3.5	2.2	13.8
Tunnel(day)	25.9	7.3	182.4
Tunnel(night)	27.5	7.7	193.3

Table XII-5. Mean values of total extract and fraction weights (in mg) of sampled filters and their ratios to blank filters.

	Total Extract		Fraction 1		Fraction 2	
	Sample	Sample/Blank	Sample	Sample/Blank	Sample	Sample/Blank
Glendale(day)	15.7	10.6	3.0	15.0	3.4	11.3
Glendale(night)	13.4	9.0	2.6	13.0	2.8	9.5
Duarte(day)	13.3	9.0	2.1	10.5	2.7	9.0
Duarte(night)	12.7	8.6	2.3	11.5	1.8	6.0
Tunnel(day)	12.6	8.5	1.3	6.5	1.7	5.7
Tunnel(night)	16.0	10.8	1.9	8.5	2.9	9.7

XII-1 to XII-9. It is immediately evident that the major identifiable peaks in filter Nos. 8016, 8022 and 8030 is the TXIB plasticizer. Smaller amounts were found in filter Nos. 8028 and 8052. In filter 8030 di-n-butylphthalate and bis(1-ethylhexyl) phthalate were also present in significant measurable quantities (see Table XII-6). No plasticizers were found in the 3000 series filters or in the Caldecott Tunnel samples. The ratio of the plasticizers amount in the samples relative to the mean in the filter blanks is shown in Table XII-7. The values are all >1.0. For TXIB the mean for the Glendora day and night samples and for the Duarte day samples is 4.0. For the Duarte night sample the ratio is 1.7. The ratios are much higher for the two phthalate plasticizers. In every case, the day samples contain significantly more plasticizer than the night samples at the same station.

Although the source of the plasticizers is not known, the high content of TXIB in some of the blank filters may argue for a manufacturing additive in the filters. However, because it is not uniformly present in all the blank filters and was not detected in Caldecott Tunnel samples, we would argue that the plasticizers were sampled from the atmosphere. This argument is further strengthened by the presence of larger quantities of the plasticizers (by a factor of 2) in samples collected during the day (when construction activity occurs) over samples collected at night (Table XII-7).

A very small proportion of the Fraction 1 blank extract is normal alkanes. The distribution of hydrocarbons in eight filter extracts is shown in Figures XII-10 to XII-17. The pattern is not uniform. In filter Nos. 3413, 8023, 8028 and 8052 and probably 8030, the low molecular weight hydrocarbons ($<C_{20}$) are the most abundant. This pattern is unlike the aerosol sample pattern of hydrocarbons. In filters 3459 and 8012, the maximum is reached at C_{22} similar to that in the tunnel samples, whereas in filter 8039 it optimizes at C_{25}, similar

Table XII-6. Estimated concentration (μg/filter) plasticizer (compound 1) and two phthalates (compounds 2 and 3) in blank filters.

Filter No.	Compound 1*	Compound 2*	Compound 3*
	μg/filter	μg/filter	μg/filter
3413	ND	Tr	Tr
3459	ND	Tr	Tr
8012	ND	ND	ND
8016	132	2	ND
8022	138	2	ND
8023	ND	Tr	Tr
8028	<50	Tr	<5
8030	205	19	16
8039	ND	Tr	Tr
8052	<20	Tr	Tr

ND = not detected
Tr = Trace

*1 = TXIB
*2 = Di-n-butylphthalate
*3 = Bis(1-ethylhexyl) phthalate

Table XII-7. Average concentration (μg/filter) of Plasticizer TXIB (Compound 1) and two phthalates (Compounds 2 and 3) in samples collected at city of Glendora and city of Duarte.

Location	Compound 1 Concentration (μg/filter)				Compound 2 Concentration (μg/filter)				Compound 3 Concentration (μg/filter)			
	Average in Samples	Average in Blanks	Samples-Blanks	Samples/Blanks Ratio	Average in Samples	Average in Blanks	Samples-Blanks	Samples/Blanks Ratio	Average in Samples	Average in Blanks	Samples-Blanks	Samples/Blanks Ratio
Glendora (day)	276	54	222	5.1	57	2	55	28.5	98	2	96	49.0
Glendora (night)	155	54	101	2.9	35	2	33	17.5	63	2	61	31.5
Duarte (day)	218	54	164	4.0	31	2	29	15.5	88	2	86	44.0
Duarte (night)	91	54	37	1.7	14	2	12	7.0	12	2	10	6.0

Table XII-8. Relative amounts of saturated hydrocarbons in blank filters.

Carbon Number	Relative Percent							
	3413	3459	8012	8023	8028	8030	8039	8052
19	24.1	7.9	6.7	18.3	17.6	11.3	1.6	19.2
20	18.8	7.3	13.7	16.0	15.2	18.9	1.3	15.0
21	14.6	13.0	13.3	14.2	13.5	17.6	1.9	14.1
22	13.5	21.4	19.1	15.0	14.0	16.1	4.5	14.5
23	9.6	21.9	16.3	13.6	12.2	14.7	10.3	12.7
24	6.6	13.2	12.1	10.3	9.2	10.3	18.8	9.3
25	4.5	7.2	8.6	6.8	6.8	6.6	25.7	6.8
26	2.9	3.8	3.9	2.9	3.2	2.5	18.7	3.1
27	1.8	2.4	1.2	1.3	1.9	1.5	10.9	2.2
28	1.4	1.1		0.4	1.1	0.7	3.9	1.0
29	2.2	0.7		0.5	1.7		1.6	2.3
30	1.5	0.5		0.1	1.1		0.5	
31				0.5	1.9		0.4	
32					0.6			
CPI*	1.1	1.2	1.6	1.7	1.5	1.5	1.3	1.7

* CPI is calculated from the following ratio.

$$CPI = 1/2 \left(\frac{C25 + C27 + \ldots + C33}{C24 + C26 + \ldots + C32} + \frac{C25 + C27 + \ldots + C33}{C26 + C28 + \ldots + C34} \right)$$

Figure XII-1

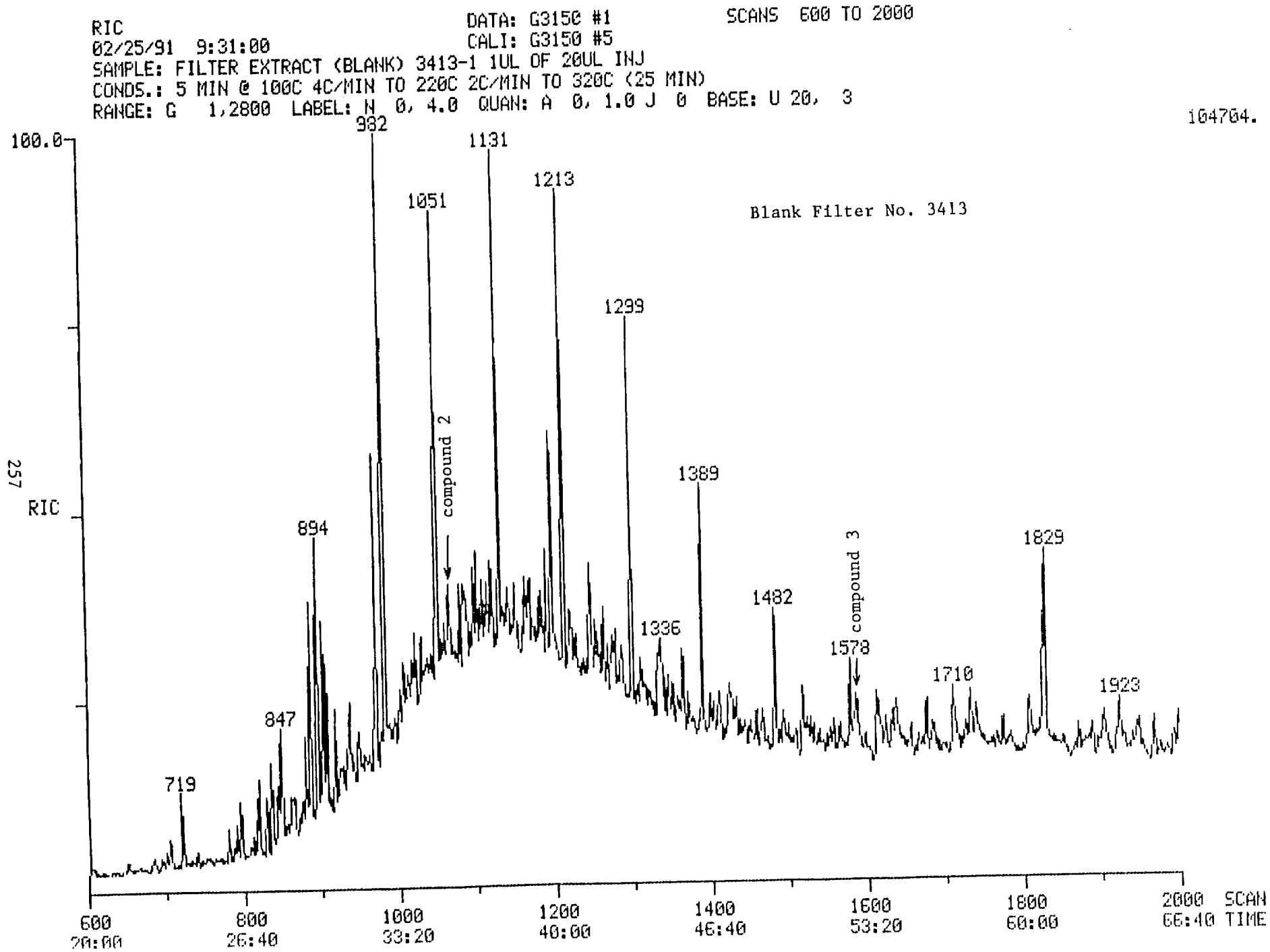

RIC
02/25/91 9:31:00
SAMPLE: FILTER EXTRACT (BLANK) 3413-1 1UL OF 20UL INJ
CONDS.: 5 MIN @ 100C 4C/MIN TO 220C 2C/MIN TO 320C (25 MIN)
RANGE: G 1,2800 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3
DATA: G3150 #1
CALI: G3150 #5
SCANS 600 TO 2000
104704.
Blank Filter No. 3413
100.0
RIC
257
719
847
894
932
1051
compound 2
1131
1213
1299
1336
1389
1482
1578
compound 3
1710
1829
1923
600
20:00
800
26:40
1000
33:20
1200
40:00
1400
46:40
1600
53:20
1800
60:00
2000
66:40
SCAN
TIME

Figure XII-2

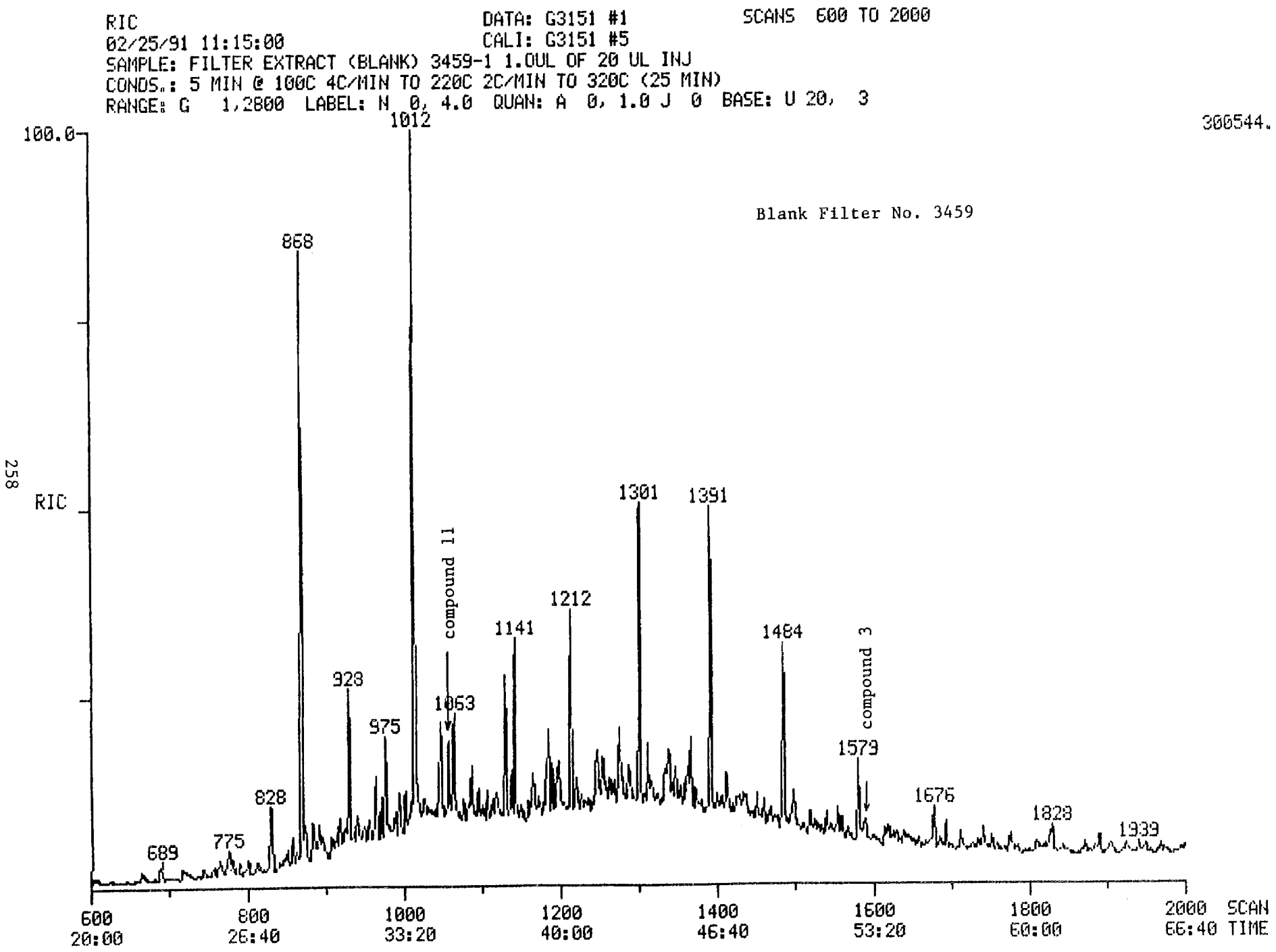

RIC
02/25/91 11:15:00
SAMPLE: FILTER EXTRACT (BLANK) 3459-1 1.0UL OF 20 UL INJ
CONDS.: 5 MIN @ 100C 4C/MIN TO 220C 2C/MIN TO 320C (25 MIN)
RANGE: G 1,2800 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3
DATA: G3151 #1
CALI: G3151 #5
SCANS 600 TO 2000
300544.
Blank Filter No. 3459
100.0
RIC
1012
868
compound 11
1301
1391
1212
1141
1484
compound 3
928
1053
975
1579
828
1676
1828
1939
689
775
600
20:00
800
26:40
1000
33:20
1200
40:00
1400
46:40
1600
53:20
1800
60:00
2000
66:40
SCAN
TIME

Figure XII- 3

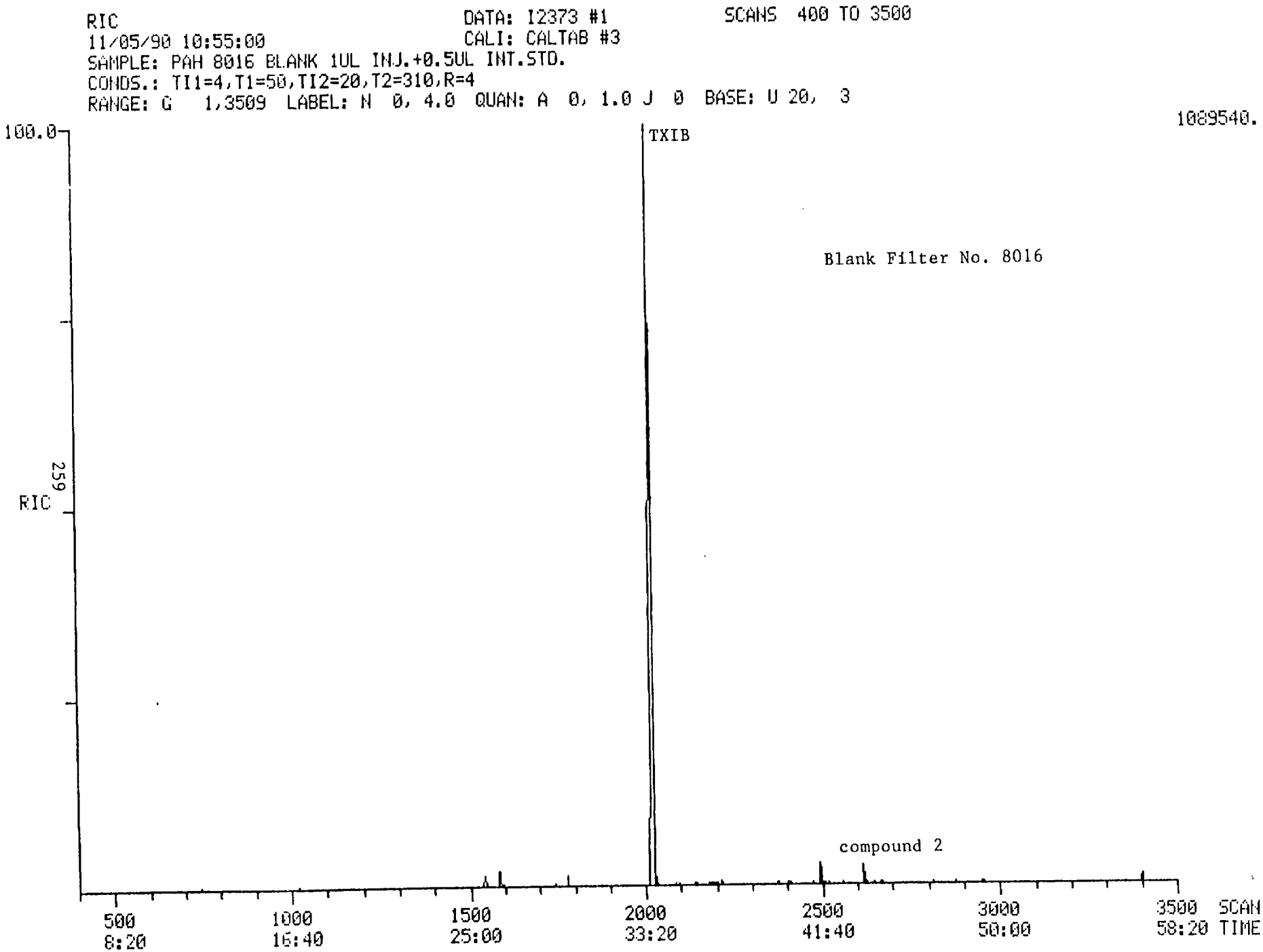

RIC
11/05/90 10:55:00
DATA: I2373 #1
CALI: CALTAB #3
SCANS 400 TO 3500
SAMPLE: PAH 8016 BLANK 1UL INJ.+0.5UL INT.STD.
CONDS.: TI1=4,T1=50,TI2=20,T2=310,R=4
RANGE: G 1,3509 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3
1089540.
100.0
TXIB
Blank Filter No. 8016
259
RIC
compound 2
500
8:20
1000
16:40
1500
25:00
2000
33:20
2500
41:40
3000
50:00
3500
58:20
SCAN
TIME

Figure XII-4

RIC DATA: I2374 #1 SCANS 400 TO 3500
11/05/90 12:03:00 CALI: CALTAB #3
SAMPLE: 8022 FILTER
CONDS.: TI1=4,T1=50,TI2=20,T2=310,R=4
RANGE: G 1,4700 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

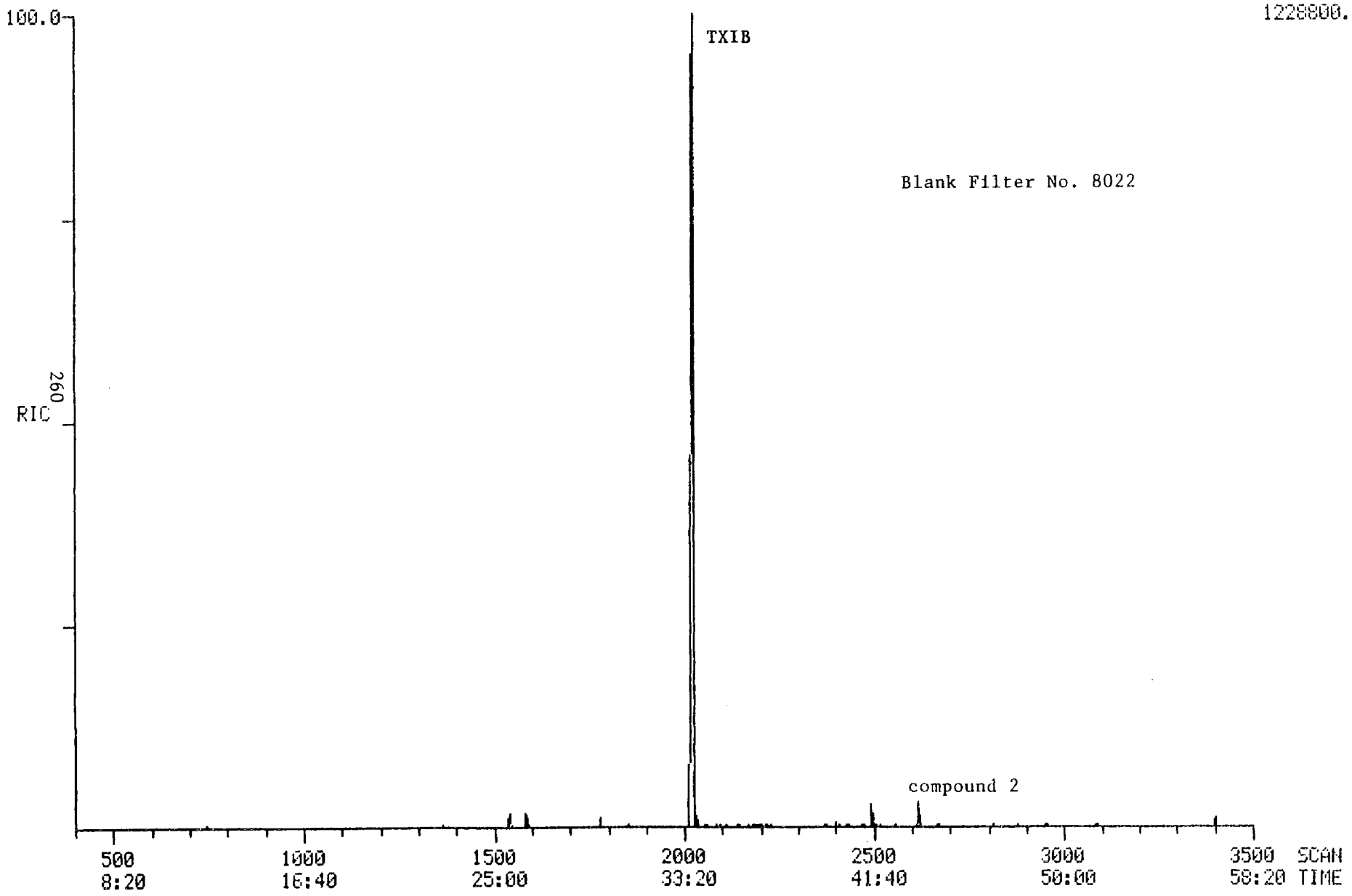


Figure XII-5

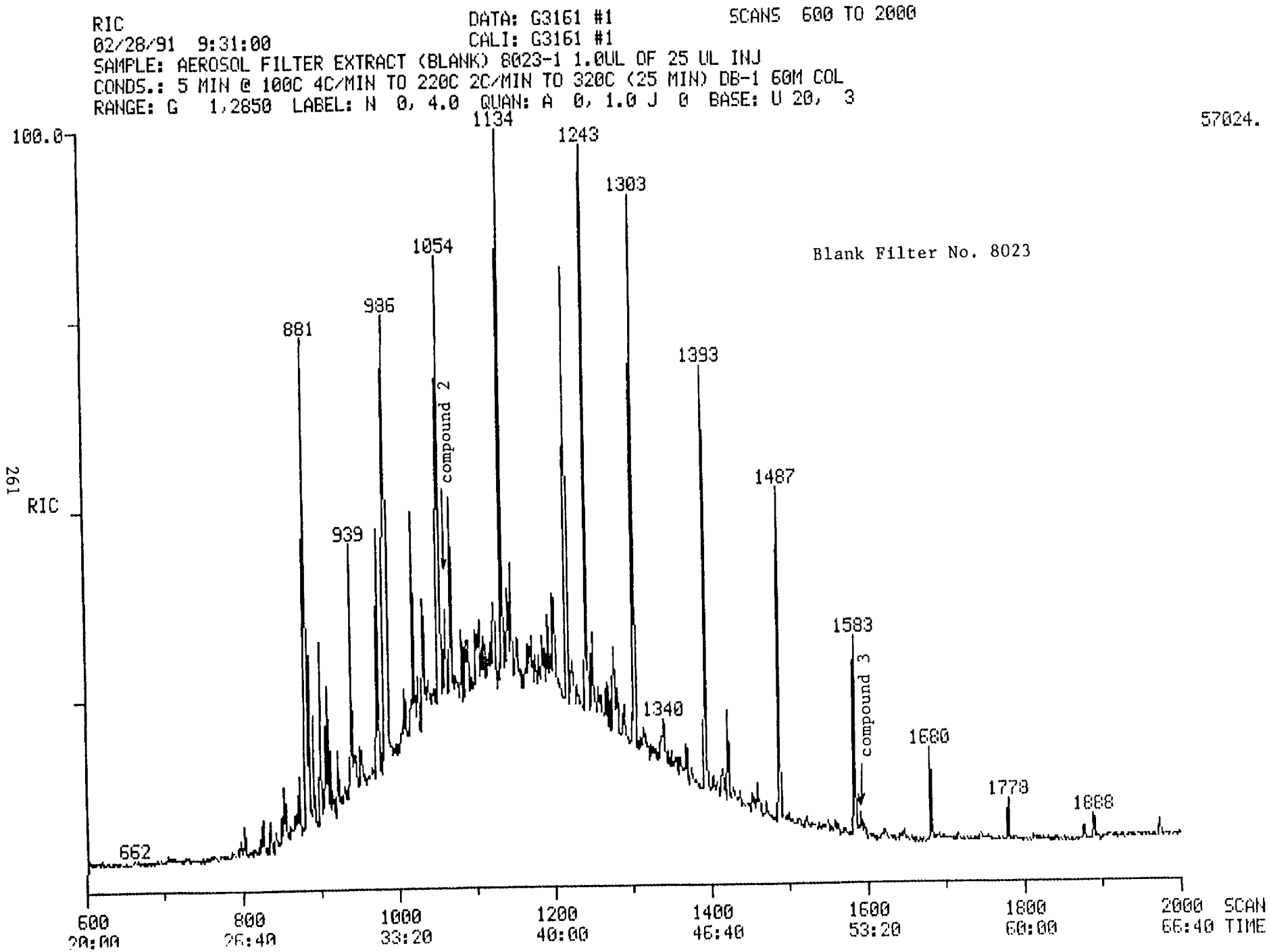

RIC
02/28/91 9:31:00
DATA: G3161 #1
CALI: G3161 #1
SCANS 600 TO 2000
SAMPLE: AEROSOL FILTER EXTRACT (BLANK) 8023-1 1.0UL OF 25 UL INJ
CONDS.: 5 MIN @ 100C 4C/MIN TO 220C 2C/MIN TO 320C (25 MIN) DB-1 60M COL
RANGE: G 1,2850 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3
57024.
100.0
RIC
Blank Filter No. 8023
662
881
939
986
1054
compound 2
1134
1243
1303
1340
1393
1487
1583
compound 3
1680
1778
1888
600
20:00
800
26:40
1000
33:20
1200
40:00
1400
46:40
1600
53:20
1800
60:00
2000 SCAN
66:40 TIME

Figure XII- 6

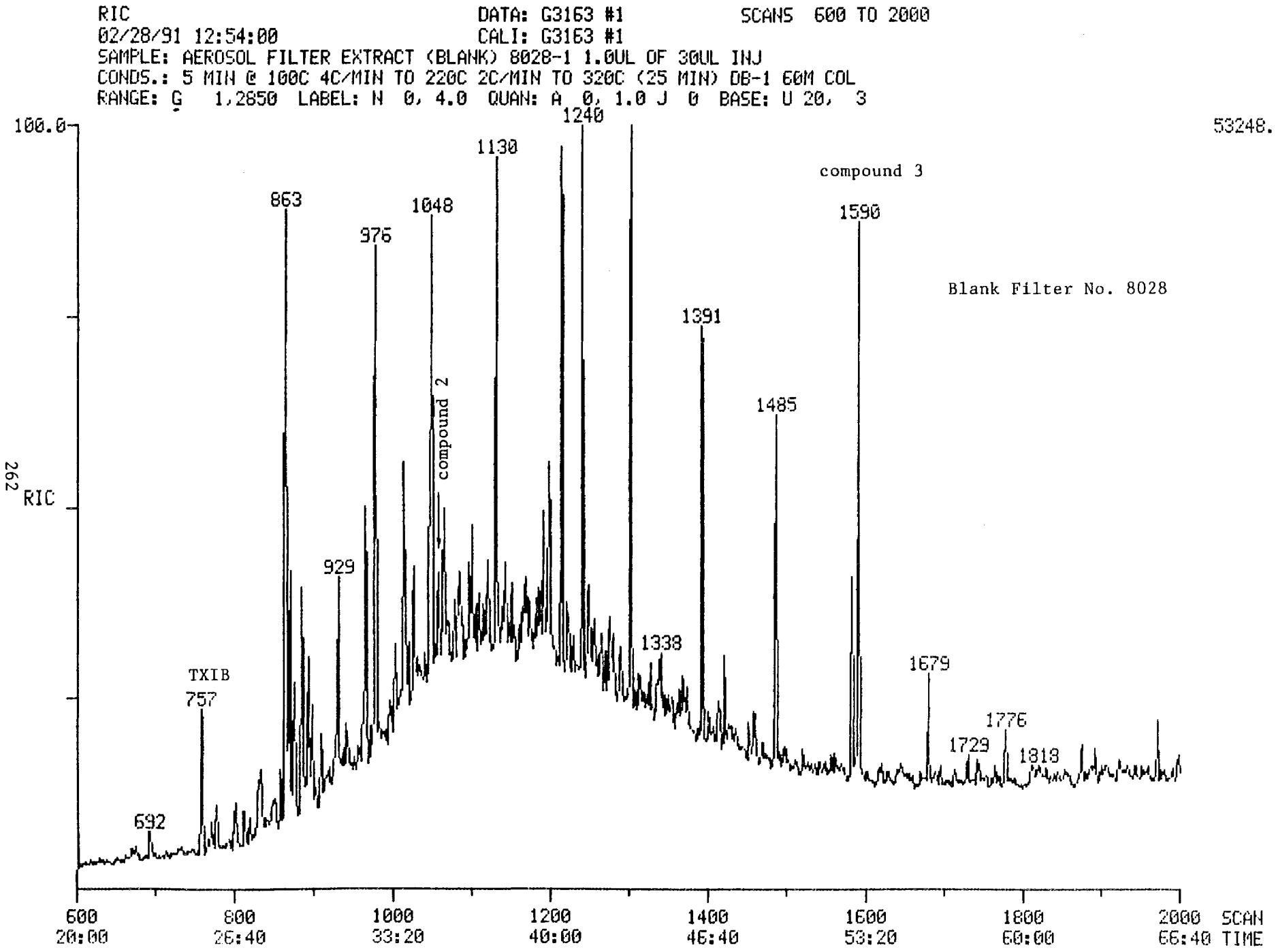

RIC
02/28/91 12:54:00
DATA: G3163 #1
CALI: G3163 #1
SCANS 600 TO 2000
SAMPLE: AEROSOL FILTER EXTRACT (BLANK) 8028-1 1.0UL OF 30UL INJ
CONDS.: 5 MIN @ 100C 4C/MIN TO 220C 2C/MIN TO 320C (25 MIN) DB-1 60M COL
RANGE: G 1,2850 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3
100.0
53248.
RIC
262
692
TXIB
757
863
929
975
1048
compound 2
1130
1240
1338
1391
1485
compound 3
1590
1679
1729
1776
1813
Blank Filter No. 8028
600
20:00
800
26:40
1000
33:20
1200
40:00
1400
46:40
1600
53:20
1800
60:00
2000
66:40
SCAN
TIME

Figure XII- 7

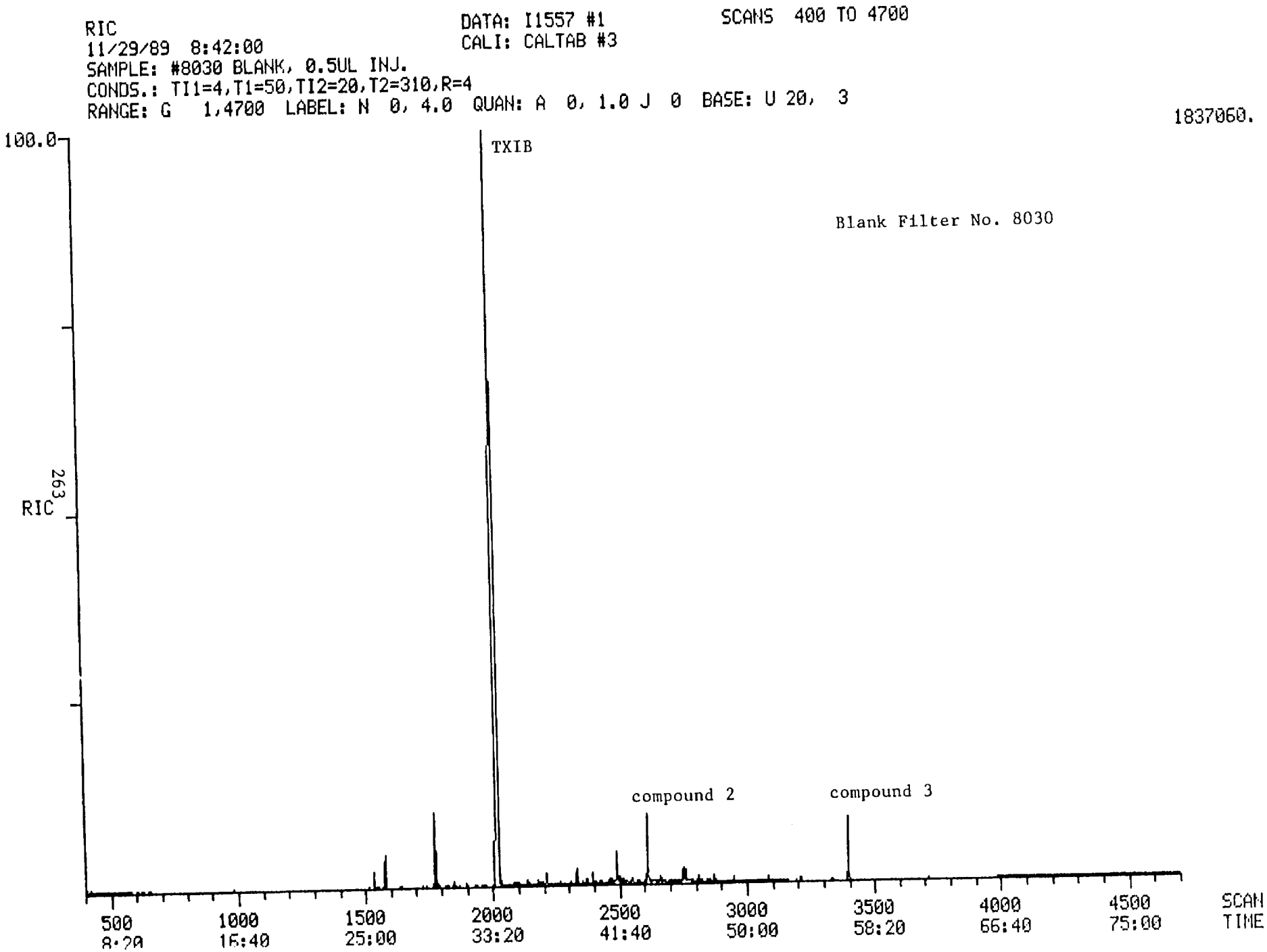

RIC
11/29/89 8:42:00
SAMPLE: #8030 BLANK, 0.5UL INJ.
CONDS.: TI1=4,T1=50,TI2=20,T2=310,R=4
RANGE: G 1,4700 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3
DATA: I1557 #1
CALI: CALTAB #3
SCANS 400 TO 4700
1837060.
100.0
263
RIC
TXIB
Blank Filter No. 8030
compound 2
compound 3
500
8:20
1000
16:40
1500
25:00
2000
33:20
2500
41:40
3000
50:00
3500
58:20
4000
66:40
4500
75:00
SCAN
TIME

Figure XII- 8

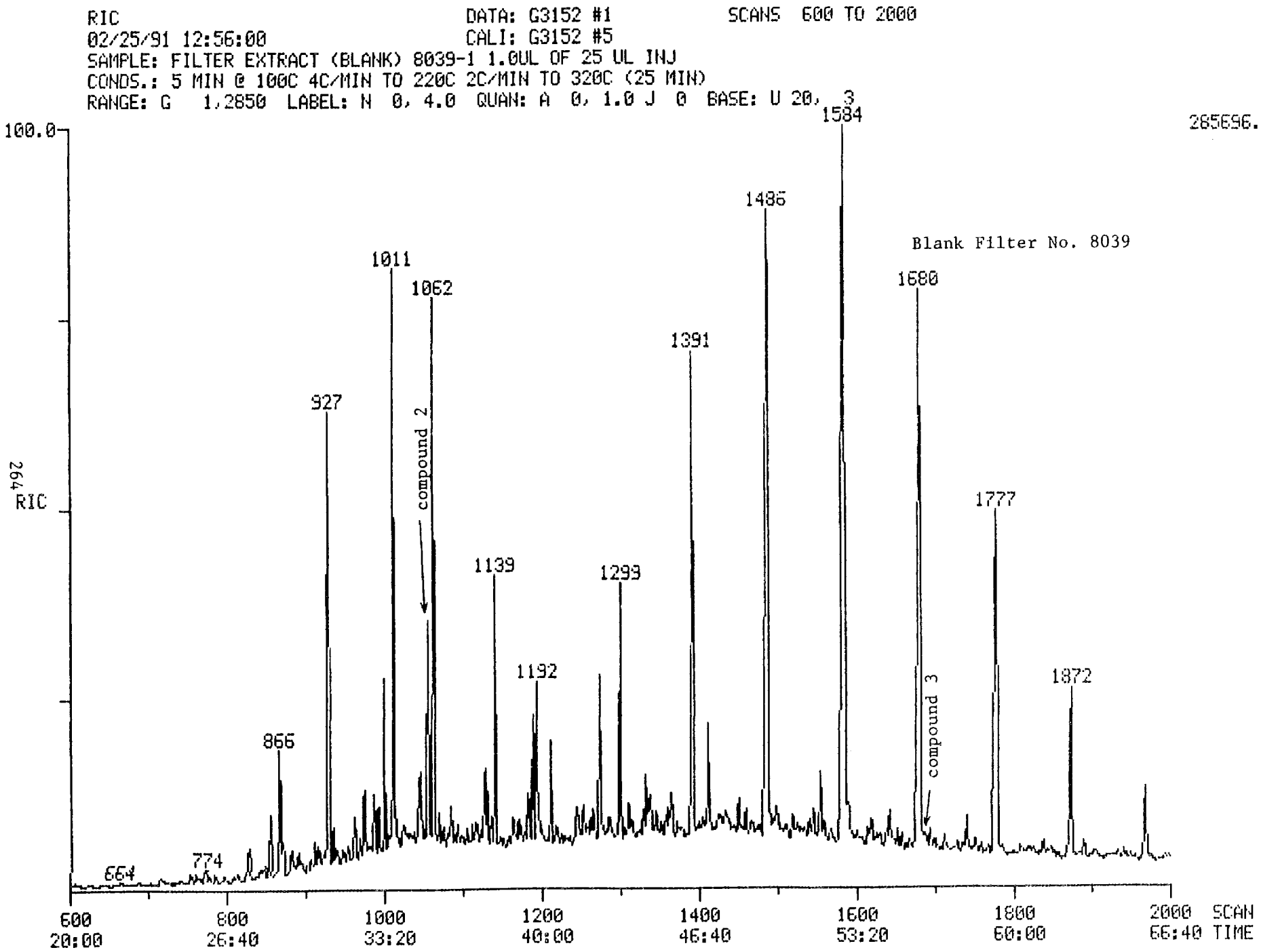

RIC
02/25/91 12:56:00
DATA: G3152 #1
CALI: G3152 #5
SCANS 600 TO 2000
SAMPLE: FILTER EXTRACT (BLANK) 8039-1 1.0UL OF 25 UL INJ
CONDS.: 5 MIN @ 100C 4C/MIN TO 220C 2C/MIN TO 320C (25 MIN)
RANGE: G 1,2850 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3
100.0
264 RIC
265696.
Blank Filter No. 8039
compound 2
compound 3
664
774
866
927
1011
1062
1139
1192
1298
1391
1486
1584
1680
1777
1872
600 20:00
800 26:40
1000 33:20
1200 40:00
1400 46:40
1600 53:20
1800 60:00
2000 SCAN 66:40 TIME

Figure XII-. 9

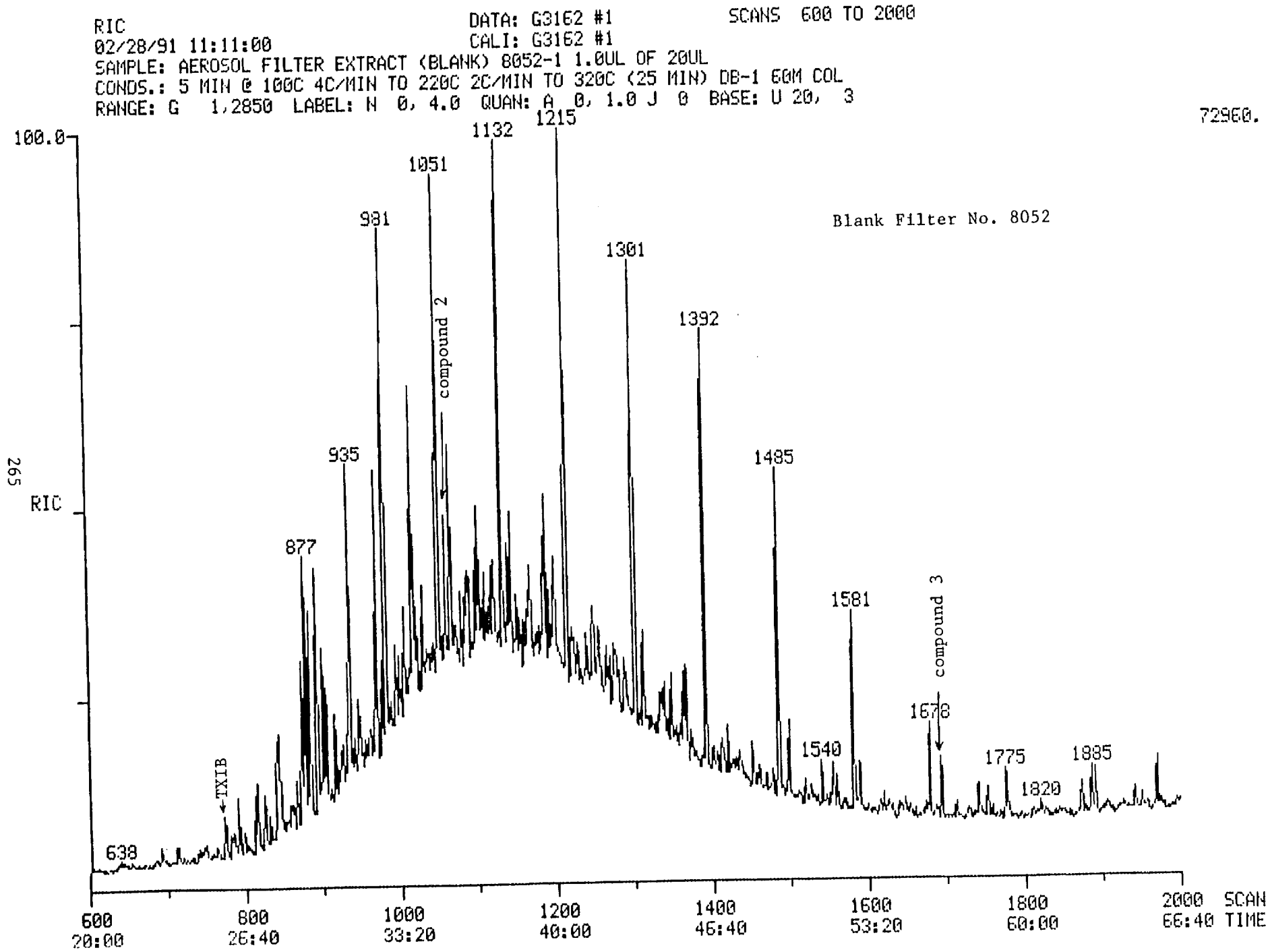

RIC
02/28/91 11:11:00
DATA: G3162 #1
CALI: G3162 #1
SCANS 600 TO 2000
SAMPLE: AEROSOL FILTER EXTRACT (BLANK) 8052-1 1.0UL OF 20UL
CONDS.: 5 MIN @ 100C 4C/MIN TO 220C 2C/MIN TO 320C (25 MIN) DB-1 60M COL
RANGE: G 1,2850 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3
72960.
100.0
RIC
Blank Filter No. 8052
638
TXIB
877
935
981
1051
compound 2
1132
1215
1301
1392
1485
1540
1581
1678
compound 3
1775
1820
1885
600
20:00
800
26:40
1000
33:20
1200
40:00
1400
46:40
1600
53:20
1800
60:00
2000
66:40
SCAN
TIME

Table XII-9. Corrected average total saturated hydrocarbon concentration (μg/filter) in samples collected at city of Glendora, city of Duarte and Caldecott Tunnel.

Sampling Location and Time	Average of Total Saturated Hydrocarbon Concentration (μg/filter)			
	Samples	Blanks	Samples-Blanks	Sample/Blank Ratio
Glendora (day)	81	11	70	7.4
Glendora (night)	103	11	92	9.4
Duarte (day)	40	11	29	3.6
Duarte (night)	20	11	9	1.8
Tunnel (day)	17	11	6	1.5
Tunnel (night)	45	11	34	4.1

Table XII-10. Individual fatty acid weight per filter (μg) for blank filters.

Filter No.	C14:0	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	C20:0
8012	5.3	4.7	ND	ND	ND	ND	ND	ND
8030	ND	ND	ND	ND	ND	ND	ND	ND

ND = not detected

Table XII-11. Elemental analysis results of saturate/aromatic hydrocarbon fraction of blank filters and means for city of Glendora, city of Duarte and Caldecott Tunnel samples.

Filter No.	CO_2 Volume ml	Hydrogen Volume ml	H/C Ratio
8012	0.33	0.34	1.75
8030	0.93	0.91	1.69
	Means		
Glendora(day)	4.48	3.32	1.36
Glendora(night)	4.03	2.99	1.35
Duarte(day)	3.80	2.93	1.36
Duarte(night)	3.83	2.88	1.36
Tunnel(day)	4.39	3.34	1.42
Tunnel(night)	4.21	3.11	1.35

Table XII-12. Elemental analysis results for polar fraction of blank filters and means for city of Glendora, city of Duarte and Caldecott Tunnel samples.

Filter No.	CO_2 Volume ml	Nitrogen Volume ml	Hydrogen Volume ml	N/C Ratio	H/C Ratio
8012	0.23		0.23		1.70
8030	0.71	0.01	0.56	0.02	1.50
			Means		
Glendora(day)	3.42	0.14	2.33	0.04	1.32
Glendora(night)	3.26	0.10	2.54	0.03	1.36
Duarte(day)	4.04	0.11	2.79	0.03	1.26
Duarte(night)	0.12	0.01	0.17	0.05	2.63
Tunnel(day)	3.37	0.04	2.06	0.01	1.10
Tunnel(night)	2.59	0.03	1.53	0.01	1.06

to that in most ambient aerosol samples. The mean CPI for the extracts in the blank filters (Table XII-8) is 1.45, not significantly different from that in the Glendora samples or the Duarte samples. The content of saturated hydrocarbons (alkanes) is considerably higher in the Glendora samples than in the Duarte or Tunnel samples. Hence, the ratio of identifiable sample/blank alkanes varies from 1.5 in the day tunnel sample to 9.4 in the night Glendora sample (Table XII-9). These ratios may reflect the fact that the majority of the day traffic is automobiles which burn gasoline, whereas the night traffic may have a higher proportion of diesel-burning trucks.

XII-5 Fraction 2 Composition of Blank Filters

Fraction 2 was separated from two samples to measure the fatty acid composition. Measurable quantities were only detected in filter No. 8012 (Table XII-10). Here, very small quantities of the saturated acids C_{14}:0 and C_{16}:0 were identified. Their concentration is on the average one to two orders of magnitude less than that found in the aerosol samples (Table VIII-1). Further, no unsaturated acids or C_{18} acids were detected, arguing against a biogenic source.

XII-6 Elemental Analysis in Different Fractions in Blank Filters

To compare the elemental composition in Fractions 1 and 2 from the blank with that from the samples, the H/C ratio in each was compared. For all the three stations sampled, the means of H/C ratios in Fraction 1 fell in the narrow range of 1.35 - 1.42 (Table XII-11). By contrast, the yields from the filters had a range of 1.69 - 1.75. The blanks therefore contain components richer in hydrogen than do the samples. This enrichment of hydrogen over carbon can also be seen in the polar fraction (Table XII-12). Here we also perceive a

Figure XII-10

Alkane Distribution Pattern for Blank Sample

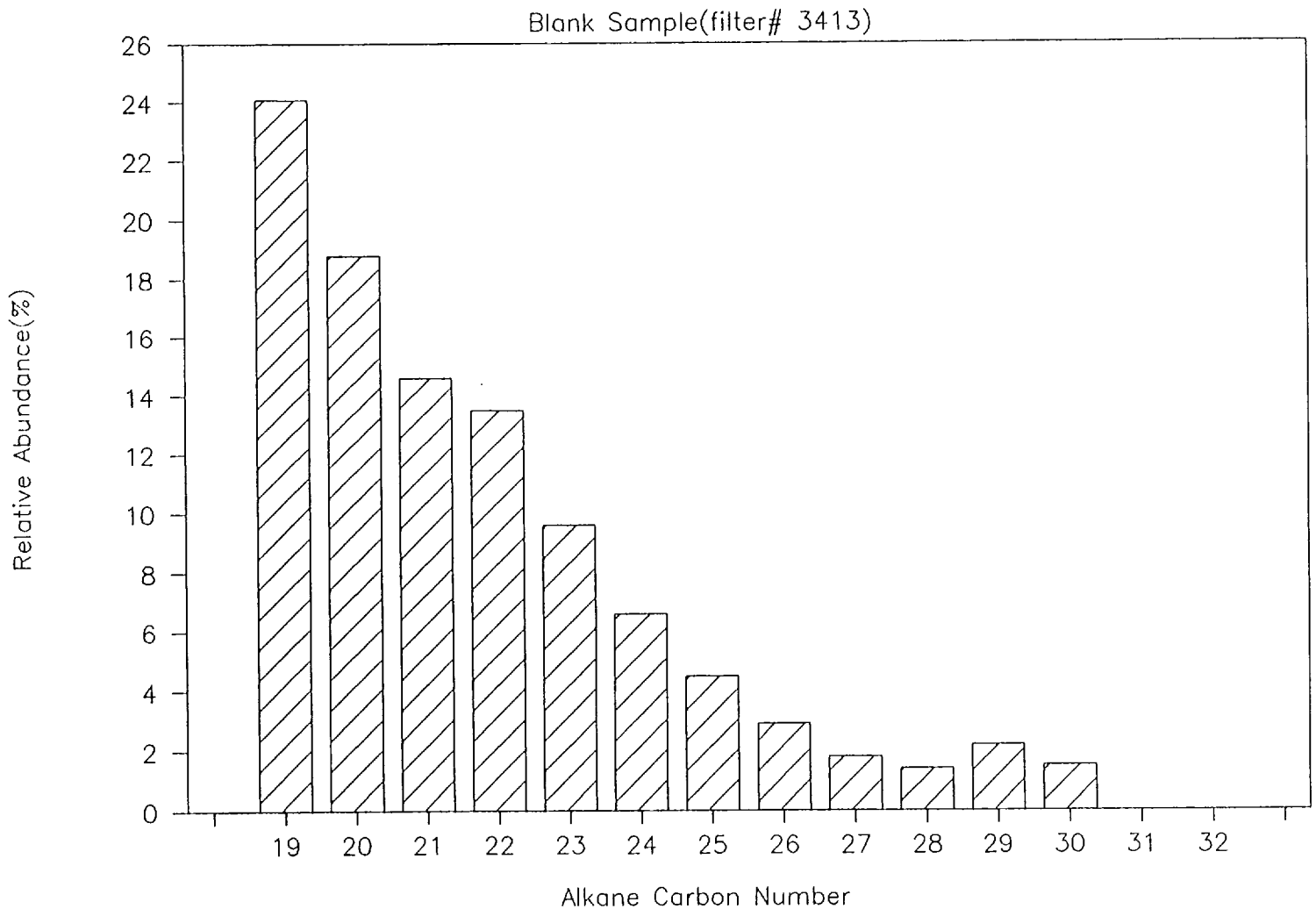


Figure XII-11

Alkane Distribution Pattern for Blank Sample

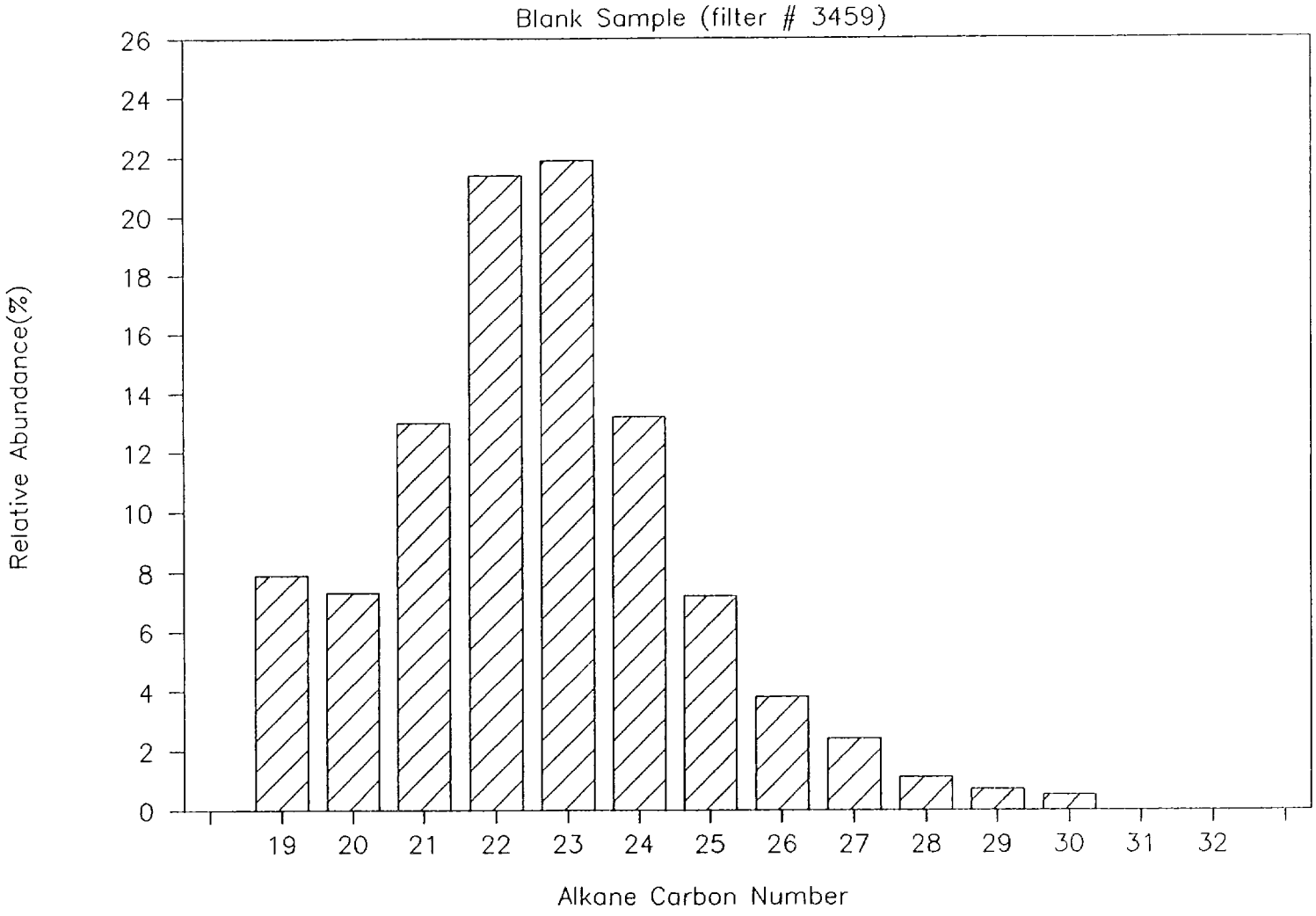


Figure XII- 12

Alkane Distribution Pattern for Blank Sample

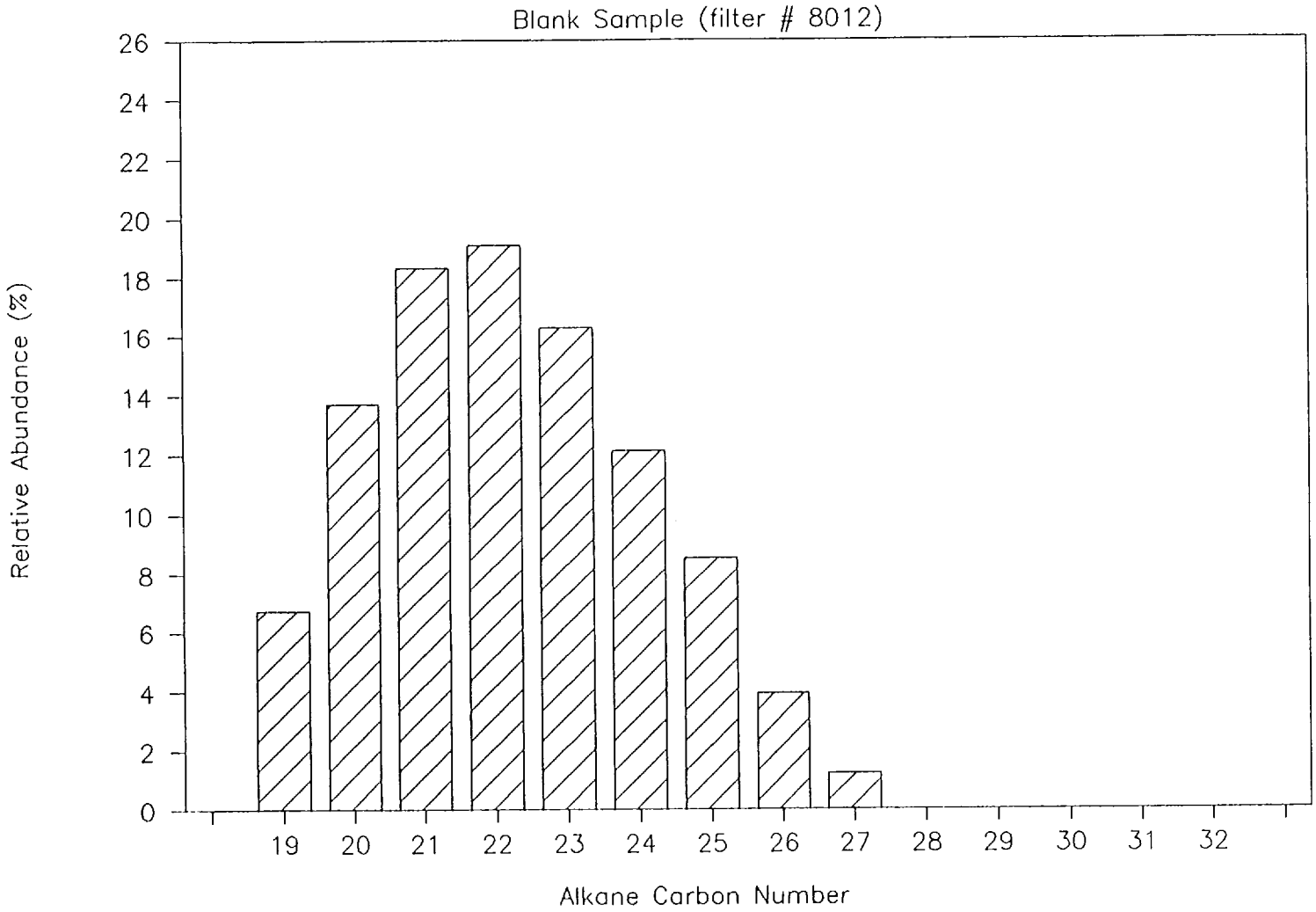


Figure XII-13

Alkane Distribution Pattern for Blank Sample

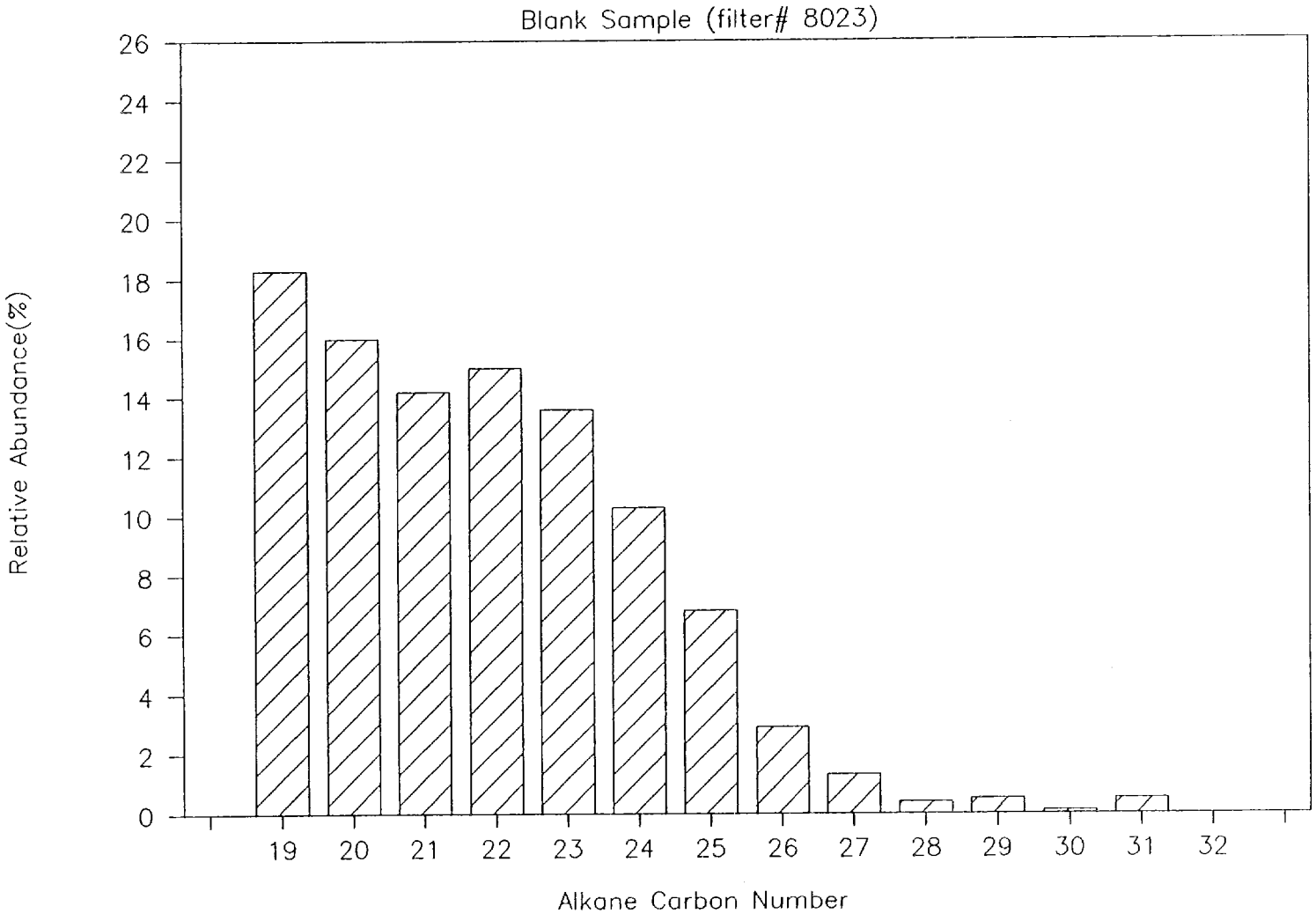


Figure XII-14

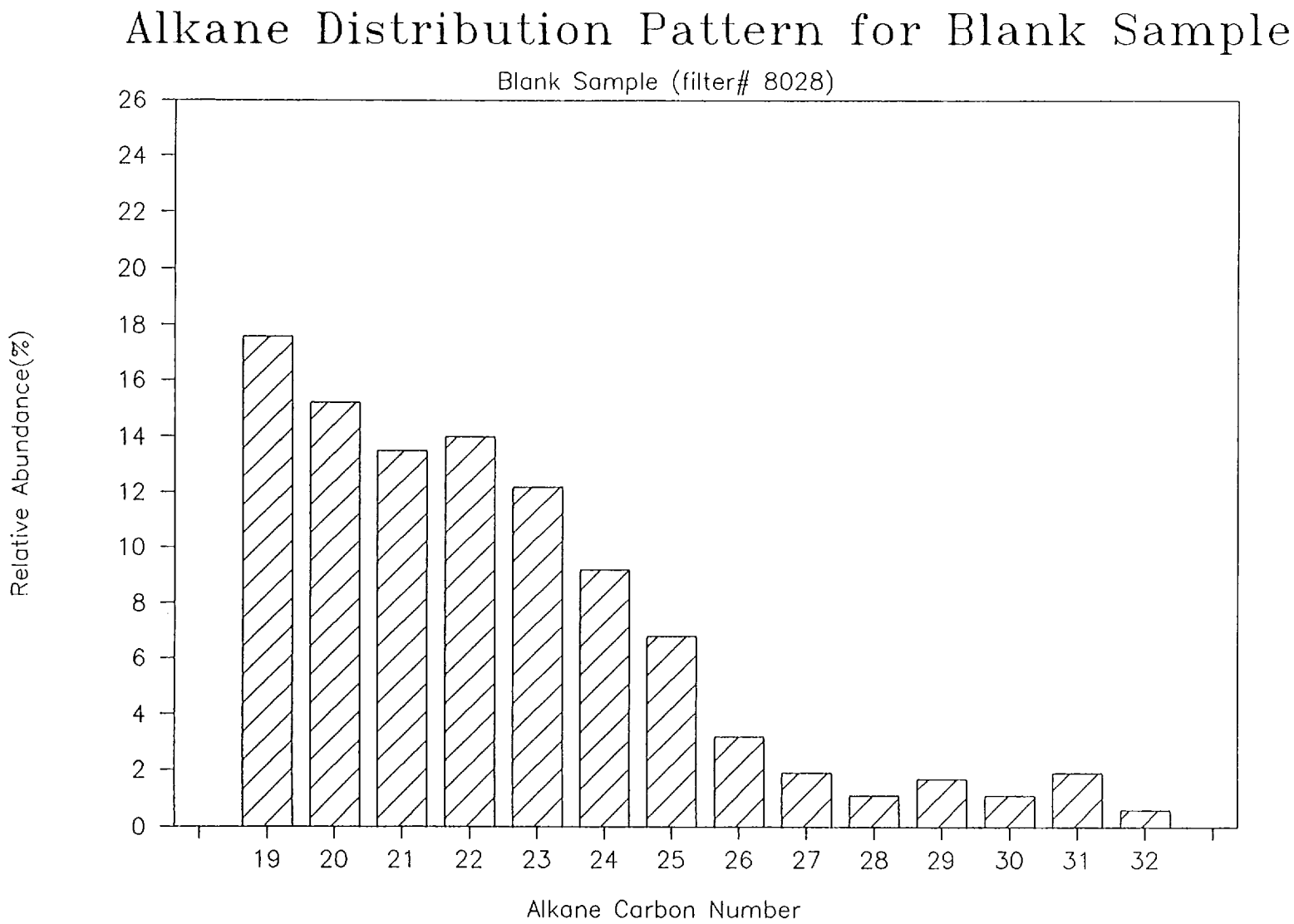


Figure XII-15

Alkane Distribution Pattern for Blank Sample

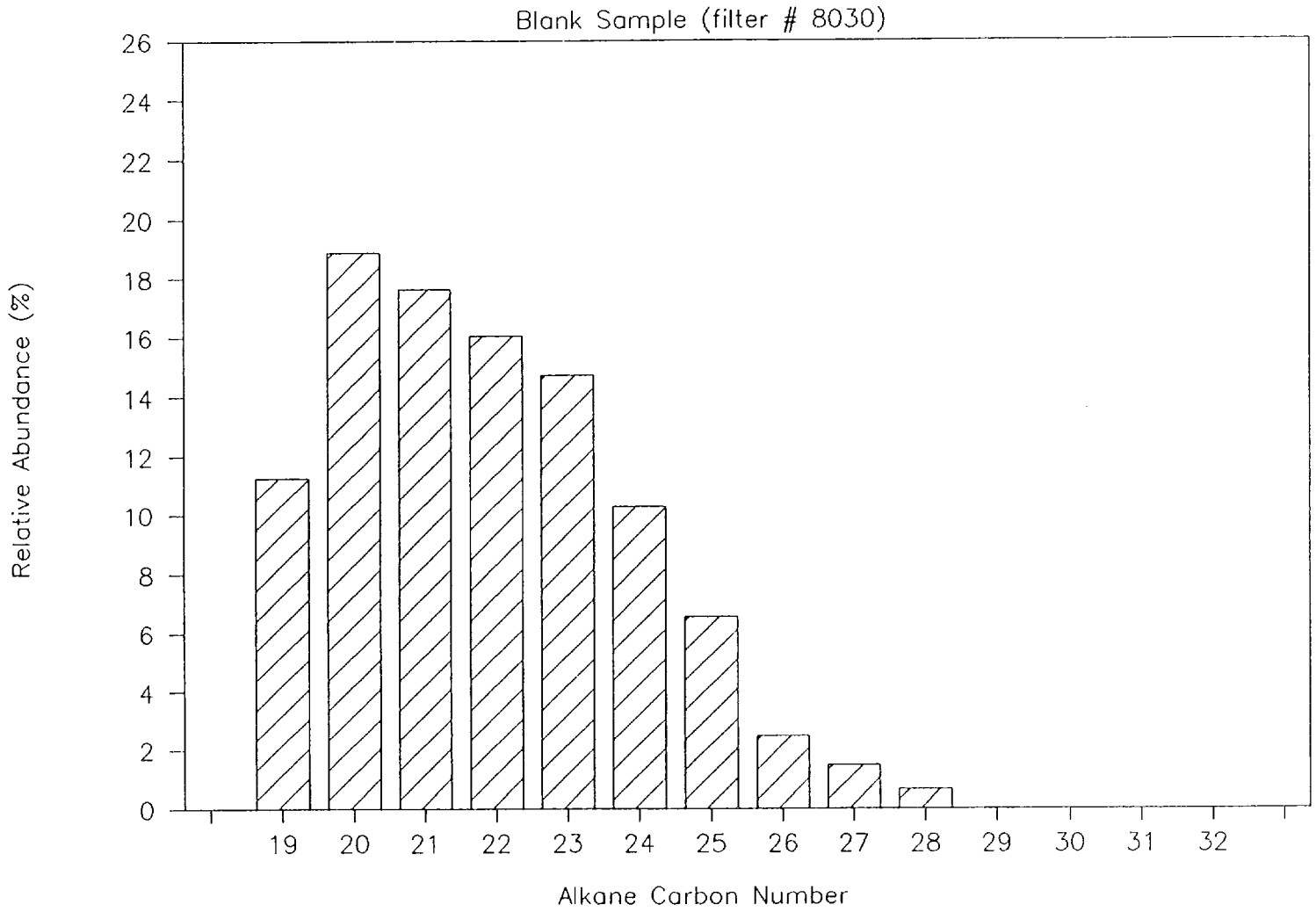


Figure XII-16

Alkane Distribution Pattern for Blank Sample

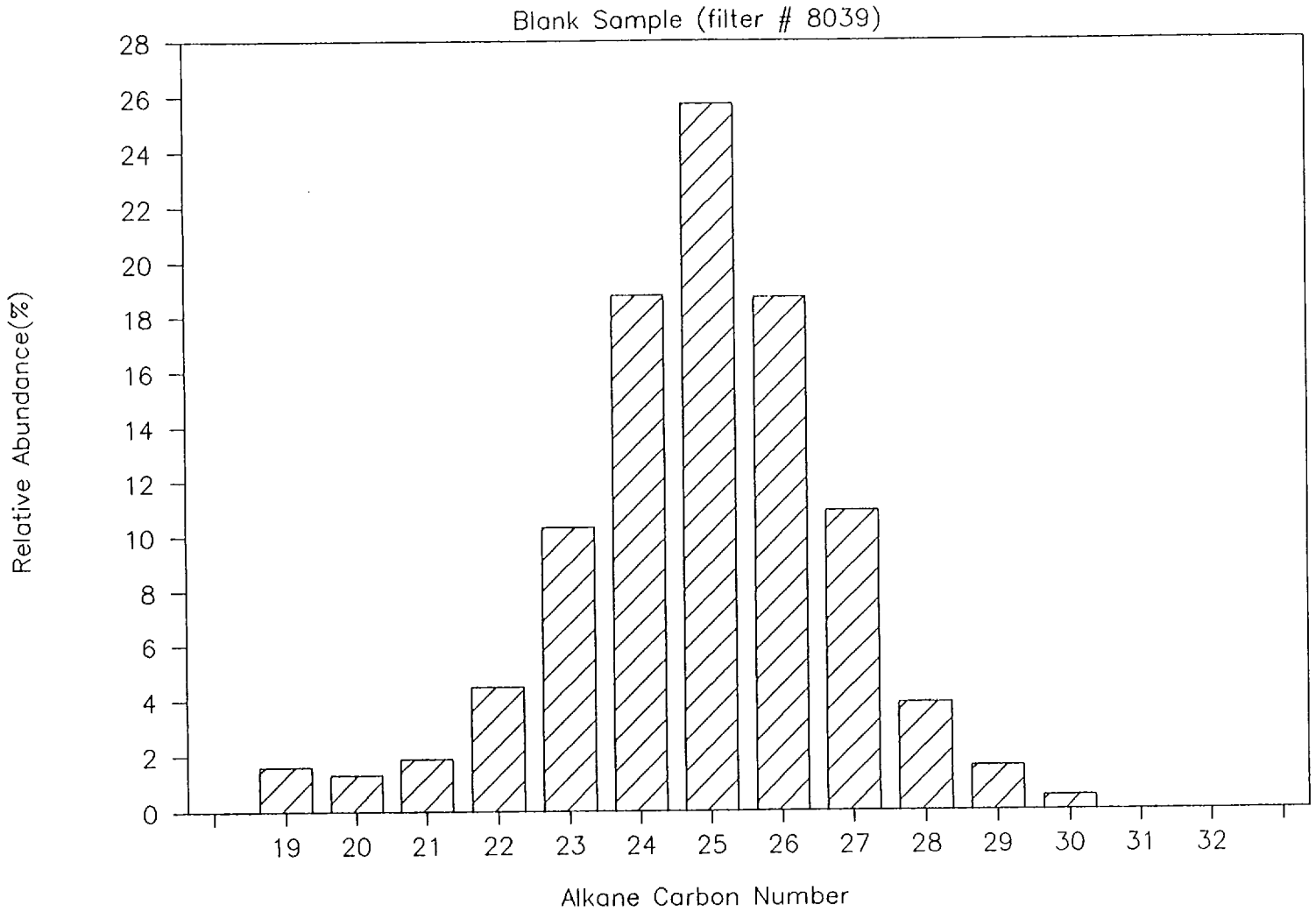


Figure XII-17

Alkane Distribution Pattern for Blank Sample

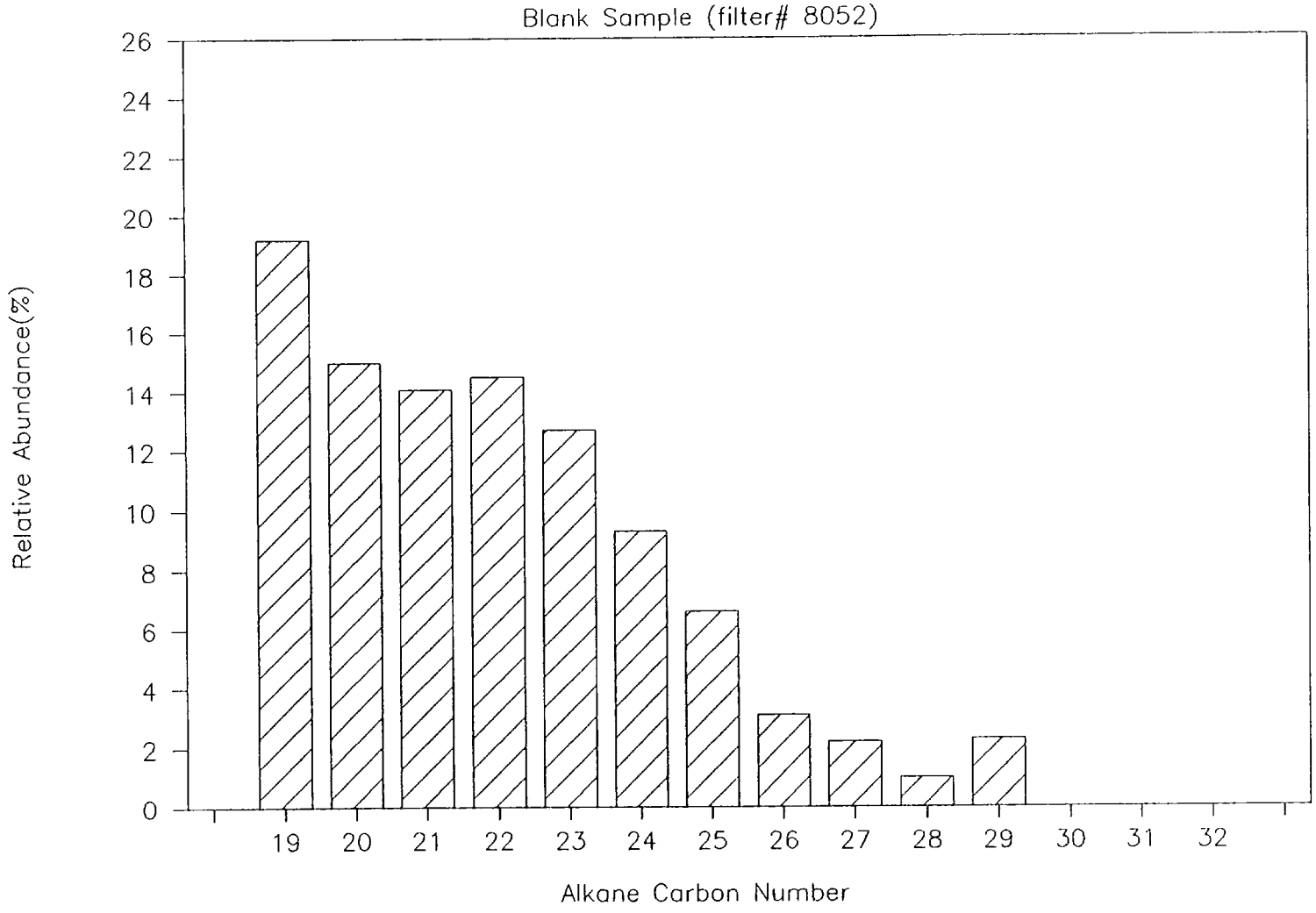


Table XII-13. Stable isotope ratios ($\delta^{13}C$, δD and $\delta^{15}N$) for blank filters.

Filter No.	Aliphatic and Aromatic del13C	Aliphatic and Aromatic delD	Polar del13C	Polar delD
3413,3459	-27.43	nd	-28.26	nd
8012	-27.32	-111	-27.63	-88
8030	-28.66	-109	-27.63	-85
8023,8028 8039,8052	-27.76	nd	-28.59	nd
Plasticizer	-29.73			
	Means			
Glendora (day)	-26.89	-106	-25.19	-72
Glendora (night)	-27.28	-117	-25.06	-85
Duarte (day)	-27.34	-107	-25.41	-60
Duarte (night)	-26.89	-119	-24.82	-90
Tunnel (day)	-28.04	-121	-26.88	-97
Tunnel (night)	-27.70	-120	-26.50	-87

nd = not determined

difference in this ratio between the tunnel sample and the ambient samples. The Caldecott Tunnel samples have a mean H/C ratio of ~1.10, Duarte day samples have a mean H/C ratio of 1.26, whereas the Glendora samples have a mean H/C = 1.34±0.2. The single H/C value of 2.63 for the Duarte night samples is probably an error reflecting imprecision in measurement.

These data illustrate that the blank contaminants contain hydrogen-rich components in both the hydrocarbon and polar fractions. The low value for the tunnel samples would indicate an aromatic type polar material, such as aromatic acids, quinones or phenols. The level of contamination by the high H/C filter extract may be small, due to the similarity of the H/C ratio in both the day/night Glendora and Caldecott Tunnel samples.

XII-7 Stable Isotope Ratios of Extracted Fractions in Blank Filters

To determine if the carbon and hydrogen isotope ratios might be a signature for contaminants in the blank filter extracts, $\delta^{13}C$ and δD were run on Fraction 1 and Fraction 2 (Table XII-13). The $\delta^{13}C$ and δD of Fraction 1 from the blanks and the samples are not significantly different. Within the sample set there are differences which are not readily explainable, and most probably depend on the mix of gasoline fuels. The fact that the ambient samples are enriched in ^{13}C over the tunnel samples might reflect (1) preferential photochemical removal of ^{12}C or (2) introduction of biogenic carbon into the ambient atmospheric samples. This is also noticeable in the enrichment of $^{2}H(D)$ in the ambient aerosol over that in the tunnel samples. The polar samples (Fraction 2) for the blank filter extracts gave $\delta^{13}C$ values which were random in comparison with those in Fraction 1, all falling in the range of -27.32 to -28.59^{o}/oo. By comparison, $\delta^{13}C$ of the Fraction 2 in the sample extracts are isotopically enriched in ^{13}C relative to Fraction 1 by about 2°/oo (Table XII-13).

The $\delta^{13}C$ of the commercially available plasticizer is significantly enriched in ^{12}C over Fraction 1 (by 2-4°/oo) and by 3-5°/oo in the $\delta^{13}C$ of Fraction 2. Hence, its overall influence may not be large.

XII-8 ^{14}C Data for solvent Extracts of Blank Filters and TXIB Plasticizer

To determine the effect of the contaminants in the filter blanks, two filter extracts were combusted to CO_2 and prepared for ^{14}C measurement. Table XII-14 and Figure XII-18 show that the amount of modern carbon calculated from the $D^{14}C$ is 36.2 and 39.2 percent respectively. Four blank prefired filters were composited together, cut up, extracted and separated by column chromatography into hydrocarbon and polar fractions. The $D^{14}C$ measurements on these fractions showed the hydrocarbon fraction had 11.3% modern carbon and the polar fraction had 26.6% modern carbon.

A sample of the plasticizer TXIB was also measured for comparison and was found to contain only 0.5% modern carbon. Therefore, this component can be assumed to have little influence on the ^{14}C of the sample, and will dilute Fraction 1 to give an apparent lower ^{14}C content (less modern carbon) in the fraction.

XII-9 Laboratory Procedures Evaluation

Solvents used for the extraction were passed though the precise procedures that were used for filter extracts, in the same cleaned glassware used for the filter treatment. No residues were detected by this procedure when the solvents were evaporated down to near dryness. Further, no blank contamination was detected during the procedure of derivatization of the polar fraction with BF_3-CH_3OH for fatty acid analysis. Hence, there is no evidence that the blank filter contamination could have arisen from any of the laboratory procedures.

Table XII-14. Modern carbon content in organic carbon of total extract and hydrocarbon and polar fractions of blank filters and plasticizer, TXIB purchased from Eastman Kodak.

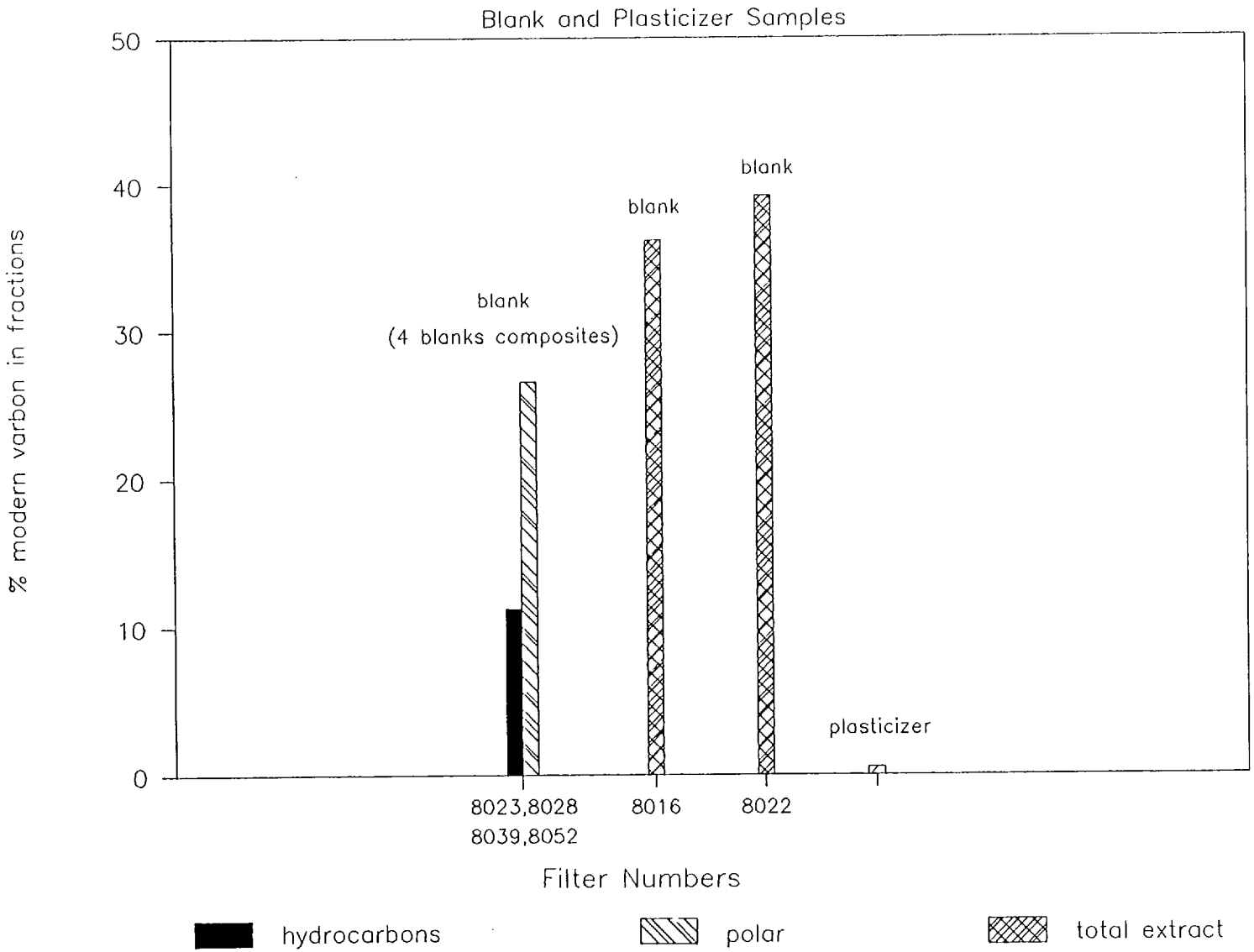
Filter No.	Total Extract		Aliphatic + Aromatic		Polar	
	D14C (o/oo)	% Modern C	D14C (o/oo)	% Modern C	D14C (o/oo)	% Modern C
8016	-637.7	36.2				
8022	-607.9	39.2				
8023, 8028 8039, 8052			-887.9	11.3	-733.6	26.6
Plasticizer (TXIB)	-995.0	0.5				

XII-10 Source of Blank Filter Contamination

At this stage, it is not known what the source of organic contamination in the blank filters could be. One possibility is that during the firing process the filters become very active and adsorbed organic vapors and particles from the atmosphere when they are removed from the furnace or when they were taken into the field. To test this further, a section of blank filter which had been wrapped in aluminum foil and placed in a clean room cabinet at ambient temperature from 1986 to 1991, was combusted at 750°C in a closed quartz vessel according to the method described on p. 8-9. A volume of 1.5 ml CO_2 equivalent to the whole filter was obtained from the combusted products. The filter was then fired at 700°C for 1.5 hrs., cooled, cut up and recombusted in a closed quartz tube again at 750°C with a upper oxide catalyst. This time the volume of CO_2 obtained was 0.6 ml CO_2 for the entire filter. Hence, even combustion at 700°C does not appear to remove all the carbon. Alternatively, the surface of the filter is sufficiently active following combustion that organic particles are adsorbed on it extremely quickly.

Figure XII-18

D 14C Determination of Modern Carbon Content



XIII. DATA EVALUATION AND BLANK CORRECTIONS OF ^{14}C MEASUREMENTS

XIII. DATA EVALUATION AND BLANK CORRECTION OF ^{14}C MEASUREMENT

XIII-1 Inspection of Data

To verify the validity of the measured carbon-14 data for estimation of percent modern carbon in the fractions analyzed, the following procedures were instituted. First, data for each location given in Tables XI-1, XI-2 and XI-3 were separated into day and night sampling. An average and standard deviation was calculated for each set of data. Because the data sets are not large, a qualitative decision was made to accept 90% of the data set that fell into a Gaussian distribution around the mean (CRC Handbook of Chemistry and Physics, 1981-82). This was done by multiplying the standard deviation by 1.7 and then discarding all data falling out of the range of 1.7σ from the mean. In doing this, two datum points were eliminated from the Glendora day samples shown in Table XI-1. These are the polar fraction for filter Nos. 8060/8061 collected on August 20, 1986, where the measured modern carbon content is 70%. The other sample is the residual fraction in filter Nos. 8026/8029 collected on August 15, 1986, where the modern carbon content is 25.4%.

XIII-2 Correlation of Fraction Contents and ^{14}C Measured Values

In order to better review the data, two component plots were constructed to reveal data inconsistencies. The data are presented in a series of figures from Figures XIII-1 to XIII-42. They are plots of ^{14}C for each fraction measured, plotted against ^{14}C of another fraction. The data are also broken up into morning, afternoon and night collections for Glendora and Duarte and day and night collections for the Caldecott Tunnel samples. In these plots, the two samples described above as falling out of the range of acceptable data are not plotted. A statistical evaluation based on a least square fit of the data to a single correlation line eliminated the following samples as falling outside the range of 1.7σ:

In Figure XIII-1: Filter No. 8056

Figure XIII-5: Filter Nos. 8013/8014, 8050, 8056

but these were not eliminated in Figure XIII-8

Figure XIII-13: Filter Nos. 8007/8008, 8019

Figure XIII-15: Filter No 8019

but 8007/8008 was not eliminated in Figure XIII-14

Figure XIII-17: Filter Nos. 8009, 8020

Figure XIII-21: Filter Nos. 8007/8008, 8013/8014, 8050, 8057/8058

Figure XIII-24: Filter Nos. 8013/8014

These plots generally indicate that when all the data for particular sets of data are considered, a significant number of measurements fall out of range of the entire set based on the criterion established of valid data falling within 1.7σ of mean. However, when the entire data set is divided into subsets of data representing specific fractions within constrained sampling time elements, the variance is reduced. This suggests that more than one relationship exists among the data and that these cannot be described by drawing a linear least square fit line through all the data. For that reason, it was decided not to eliminate any other datum points beside the two described for Glendora.

Further, no points have been removed from the day collections in Duarte or any of the samples from Caldecott Tunnel. These data fell into a relatively tight distribution pattern, and the number of individual measurements were too small for a statistical treatment. However, the single night sample at Duarte displayed characteristics which may have resulted either from contamination or

error in sample treatment and ^{14}C measurement. Because no duplicate night sample was measured from this location, we decided not to use the measured ^{14}C results for this sample in the summary table or figures.

XIII-3 Blank Corrections for ^{14}C Measurements

Because it was shown (Chapter XII) that some of the filters contained a background of organic carbon which may not have originated from atmospheric particles, a correction factor was applied to the ^{14}C modern carbon content measured on the aerosol in the filters.

This was first done by determining the percentage of extracted contaminant in Fraction 1 and Fraction 2 of the filters from the data shown in Table XII-5 and then assuming an average as shown in Chapter XII-3 (page 249). The following table (Table XIII-1) was then constructed.

The average residual fraction (elemental carbon) for Glendora and Duarte was 8.5% and for the Caldecott Tunnel samples 0.5%. Therefore in the latter case it was insignificant. For the samples collected at Glendora and Duarte, it was decided not to make a correction for two reasons; one is that some blank filters contained negligible quantities of elemental carbon (see Table XII-4), the second is that no ^{14}C measurement was obtained for this fraction and any assumed correction could generate an error.

Because the total solvent extract content of the blank filters was low, it was not practical to separate the extracts by column chromatography into the two fractions as was done on the sampled filters. For that reason, the total extracted sample from filter No. 8016 and 8022 was combusted to CO_2 and used for ^{14}C measurement. The two values for percent modern carbon (shown in Table XII-14) were averaged and a modern age of 38% was assigned to the extracts. This approach may overestimate the correction factor (f) for the age

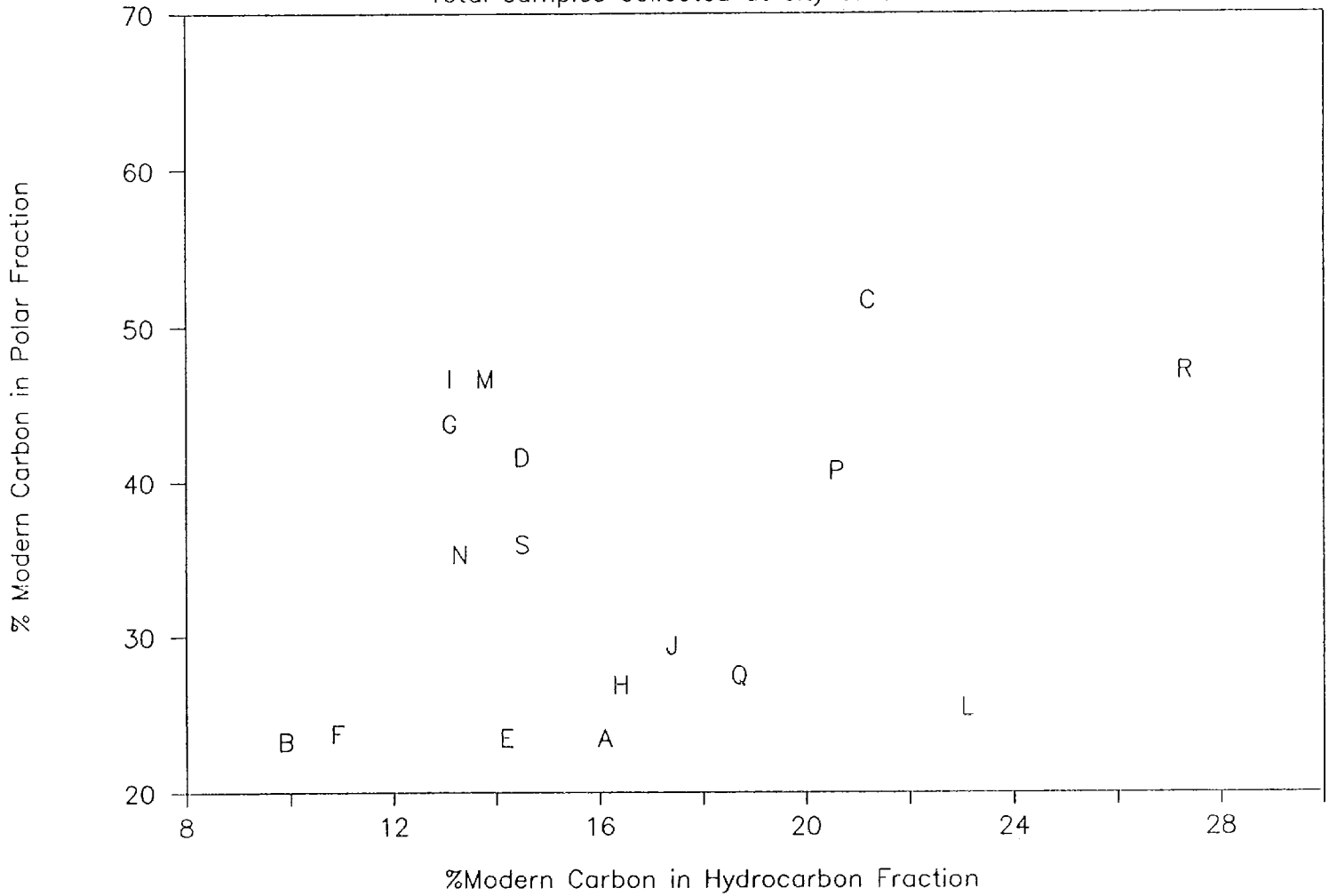
Table XIII-1. Assumed percent contaminant contribution of blank filters to various filter extracts.

Sample Location	Sampling Period	Fraction 1 (y_1)	Correction Factor (f_1)	Fraction 2 (y_2)	Correction Factor (f_2)
Glendora	day	8	3.0	11	4.2
Glendora	night	8	3.0	11	4.2
Duarte	day	8	3.0	11	4.2
Duarte	night	8	3.0	11	4.2
Caldecott Tunnel	day	15	5.7	17.5	6.7
Caldecott Tunnel	night	12	4.6	10	3.8

Figure XIII-1

%Modern Carbon: Hydrocarbon vs. Polar Fractions

Total samples collected at city of Glendora



Key

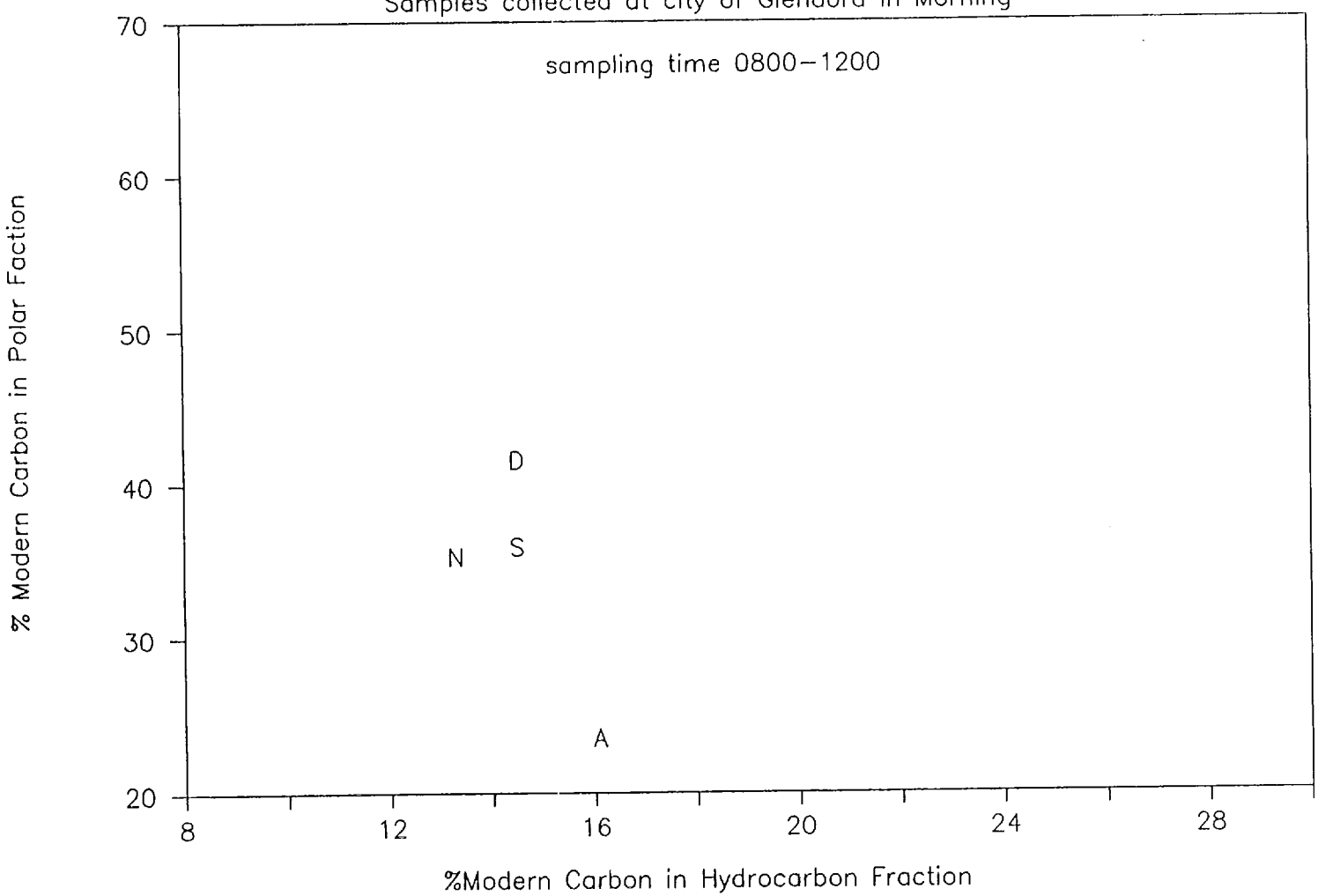
	Filter No.	Sampling Date	Sampling Time
A	8007	13/08/86	0800-1200
A	8008	13/08/86	0800-1200
B	8009	13/08/86	1200-2000
C	8013	13/08/86	2000-0800
C	8014	13/08/86	2000-0800
D	8017	14/08/86	0800-1200
D	8027	15/08/86	0800-1200
E	8019	14/08/86	1200-2000
F	8020	14/08/86	1200-2000
G	8024	14/08/86	2000-0800
H	8026	15/08/86	1200-2000
H	8029	15/08/86	1200-2000
I	8031	15/08/86	2005-0800
J	8033	16/08/86	1205-2000
J	8036	16/08/86	1205-2000
K	8037	16/08/86	2000-0720
L	8043	17/08/86	1200-2000
L	8044	17/08/86	1200-2000
M	8045	17/08/86	2000-0800
N	8047	18/08/86	0800-1200
N	8051	19/08/86	0800-1200
O	8048	18/08/86	1200-2000
O	8049	18/08/86	1200-2000
P	8050	18/08/86	2000-0800
Q	8054	19/08/86	1200-2000
Q	8055	19/08/86	1200-2000
R	8056	19/08/86	2020-0800
S	8057	20/08/86	0800-1200
S	8058	20/08/86	0800-1200
T	8060	20/08/86	1200-2000
T	8061	20/08/86	1200-2000

} combined samples

Figure XIII-2

%Modern Carbon : Hydrocarbon vs. Polar Fractions

Samples collected at city of Glendora in Morning



Key

Filter No.	Sampling Date	Sampling Time
A} 8007	13/08/86	0800-1200
A} 8008	13/08/86	0800-1200
B 8009	13/08/86	1200-2000
C} 8013	13/08/86	2000-0800
C} 8014	13/08/86	2000-0800
D} 8017	14/08/86	0800-1200
D} 8027	15/08/86	0800-1200
E 8019	14/08/86	1200-2000
F 8020	14/08/86	1200-2000
G 8024	14/08/86	2000-0800
H} 8026	15/08/86	1200-2000
H} 8029	15/08/86	1200-2000
I 8031	15/08/86	2005-0800
J} 8033	16/08/86	1205-2000
J} 8036	16/08/86	1205-2000
K 8037	16/08/86	2000-0720
L} 8043	17/08/86	1200-2000
L} 8044	17/08/86	1200-2000
M 8045	17/08/86	2000-0800
N} 8047	18/08/86	0800-1200
N} 8051	19/08/86	0800-1200
O} 8048	18/08/86	1200-2000
O} 8049	18/08/86	1200-2000
P 8050	18/08/86	2000-0800
Q} 8054	19/08/86	1200-2000
Q} 8055	19/08/86	1200-2000
R 8056	19/08/86	2020-0800
S} 8057	20/08/86	0800-1200
S} 8058	20/08/86	0800-1200
T} 8060	20/08/86	1200-2000
T} 8061	20/08/86	1200-2000

} combined samples

Figure XIII-3

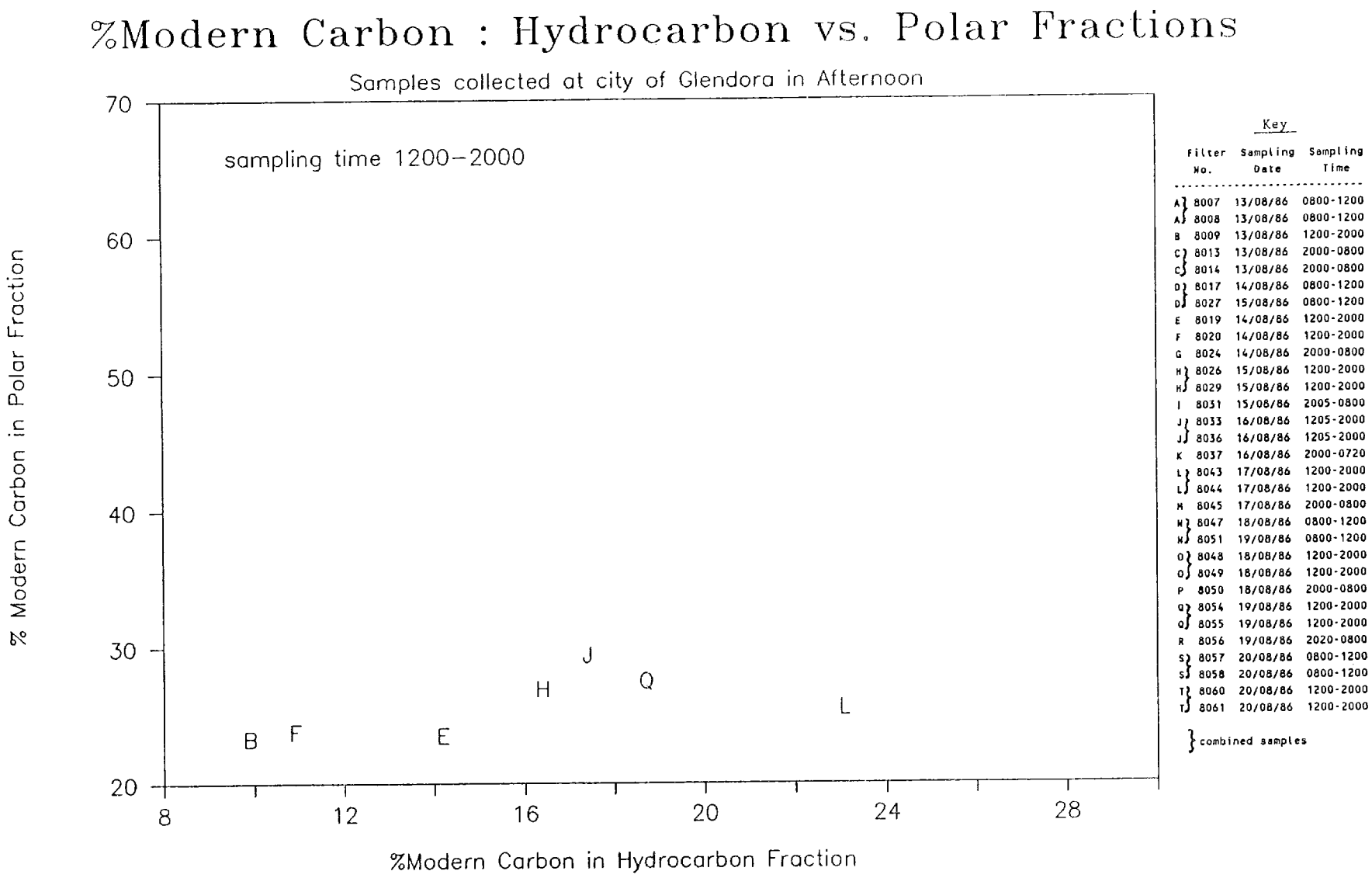
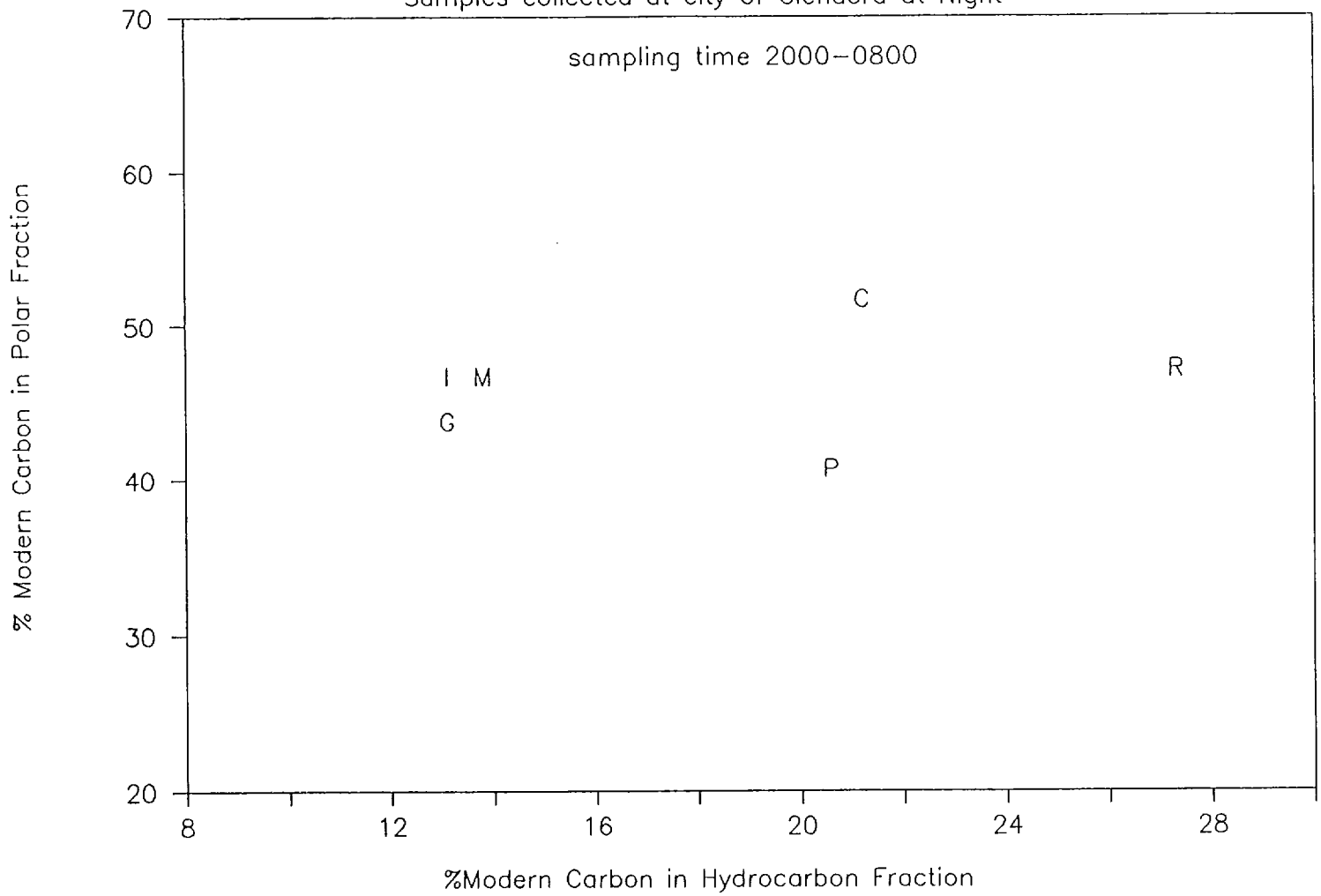


Figure XIII-4

%Modern Carbon : Hydrocarbon vs. Polar Fractions

Samples collected at city of Glendora at Night



Key

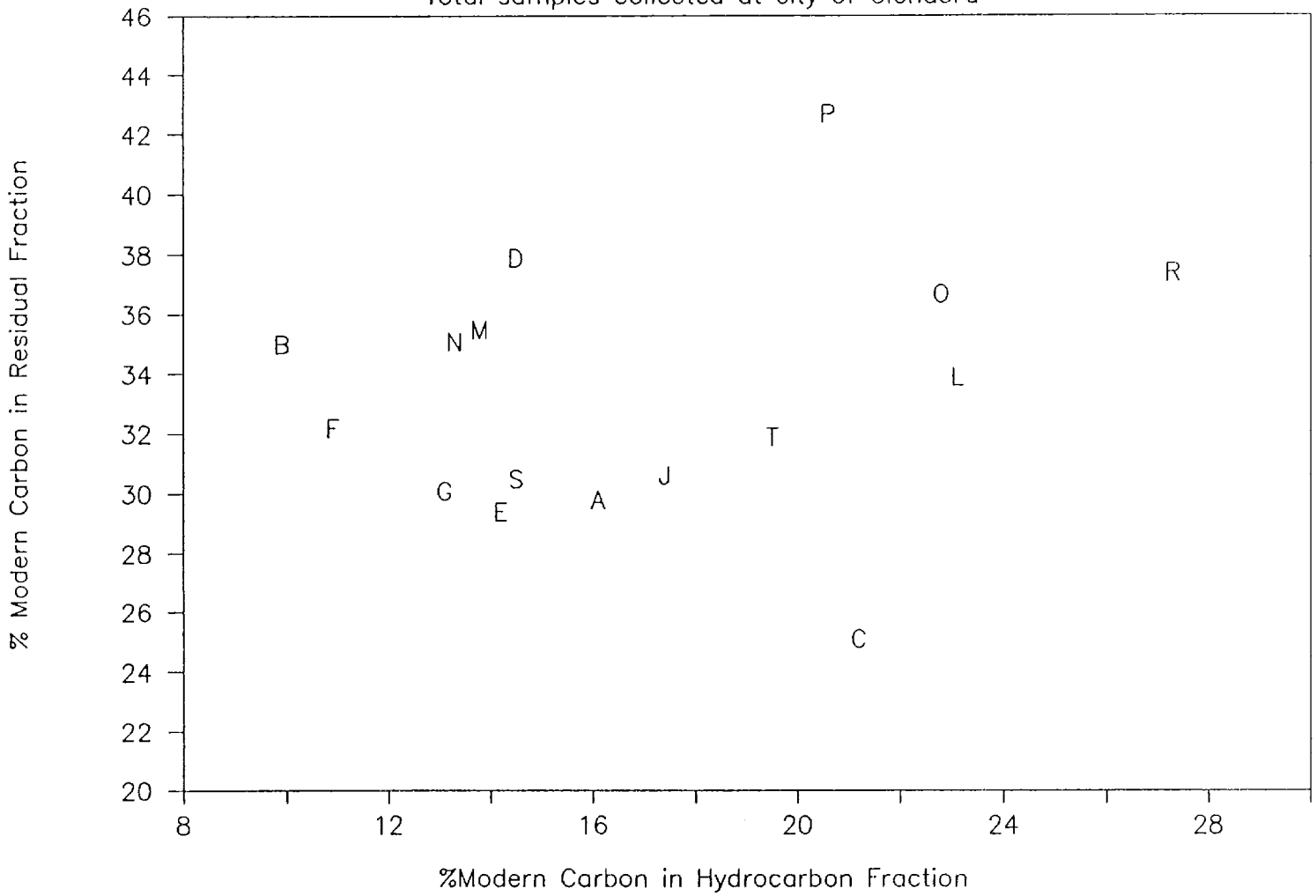
Filter No.	Sampling Date	Sampling Time
A 8007	13/08/86	0800-1200
A 8008	13/08/86	0800-1200
B 8009	13/08/86	1200-2000
C 8013	13/08/86	2000-0800
C 8014	13/08/86	2000-0800
D 8017	14/08/86	0800-1200
D 8027	15/08/86	0800-1200
E 8019	14/08/86	1200-2000
F 8020	14/08/86	1200-2000
G 8024	14/08/86	2000-0800
H 8026	15/08/86	1200-2000
H 8029	15/08/86	1200-2000
I 8031	15/08/86	2005-0800
J 8033	16/08/86	1205-2000
J 8036	16/08/86	1205-2000
K 8037	16/08/86	2000-0720
L 8043	17/08/86	1200-2000
L 8044	17/08/86	1200-2000
M 8045	17/08/86	2000-0800
N 8047	18/08/86	0800-1200
N 8051	19/08/86	0800-1200
O 8048	18/08/86	1200-2000
O 8049	18/08/86	1200-2000
P 8050	18/08/86	2000-0800
Q 8054	19/08/86	1200-2000
Q 8055	19/08/86	1200-2000
R 8056	19/08/86	2020-0800
S 8057	20/08/86	0800-1200
S 8058	20/08/86	0800-1200
T 8060	20/08/86	1200-2000
T 8061	20/08/86	1200-2000

} combined samples

Figure XIII-5

%Modern Carbon: Hydrocarbon vs. Residual Fractions

Total samples collected at city of Glendora



Key

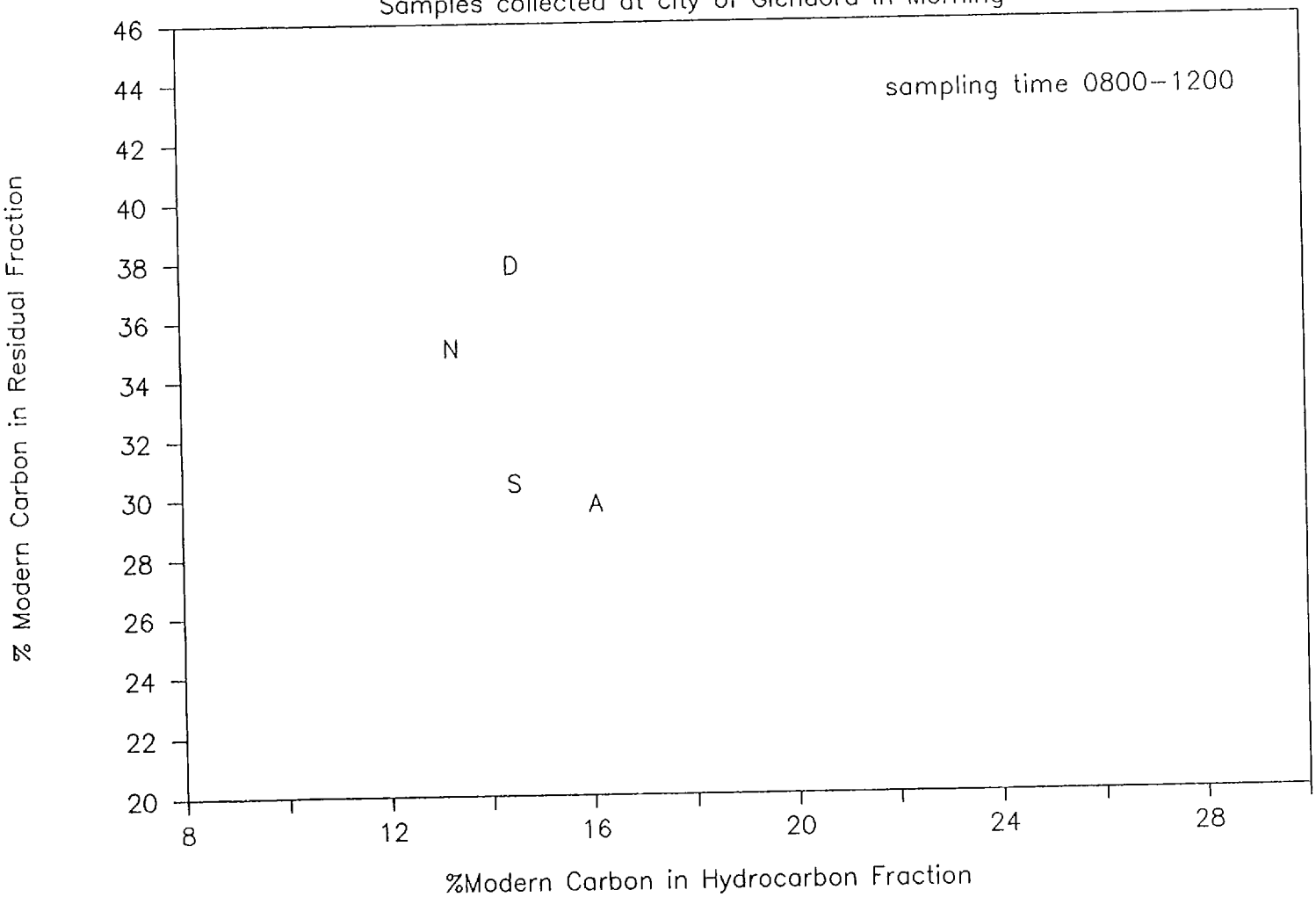
	Filter No.	Sampling Date	Sampling Time
A	8007	13/08/86	0800-1200
A	8008	13/08/86	0800-1200
B	8009	13/08/86	1200-2000
C	8013	13/08/86	2000-0800
C	8014	13/08/86	2000-0800
D	8017	14/08/86	0800-1200
D	8027	15/08/86	0800-1200
E	8019	14/08/86	1200-2000
F	8020	14/08/86	1200-2000
G	8024	14/08/86	2000-0800
H	8026	15/08/86	1200-2000
H	8029	15/08/86	1200-2000
I	8031	15/08/86	2005-0800
J	8033	16/08/86	1205-2000
J	8036	16/08/86	1205-2000
K	8037	16/08/86	2000-0720
L	8043	17/08/86	1200-2000
L	8044	17/08/86	1200-2000
M	8045	17/08/86	2000-0800
N	8047	18/08/86	0800-1200
N	8051	19/08/86	0800-1200
O	8048	18/08/86	1200-2000
O	8049	18/08/86	1200-2000
P	8050	18/08/86	2000-0800
Q	8054	19/08/86	1200-2000
Q	8055	19/08/86	1200-2000
R	8056	19/08/86	2020-0800
S	8057	20/08/86	0800-1200
S	8058	20/08/86	0800-1200
T	8060	20/08/86	1200-2000
T	8061	20/08/86	1200-2000

} combined samples

Figure XIII-6

%Modern Carbon: Hydrocarbon vs. Residual Fractions

Samples collected at city of Glendora in Morning



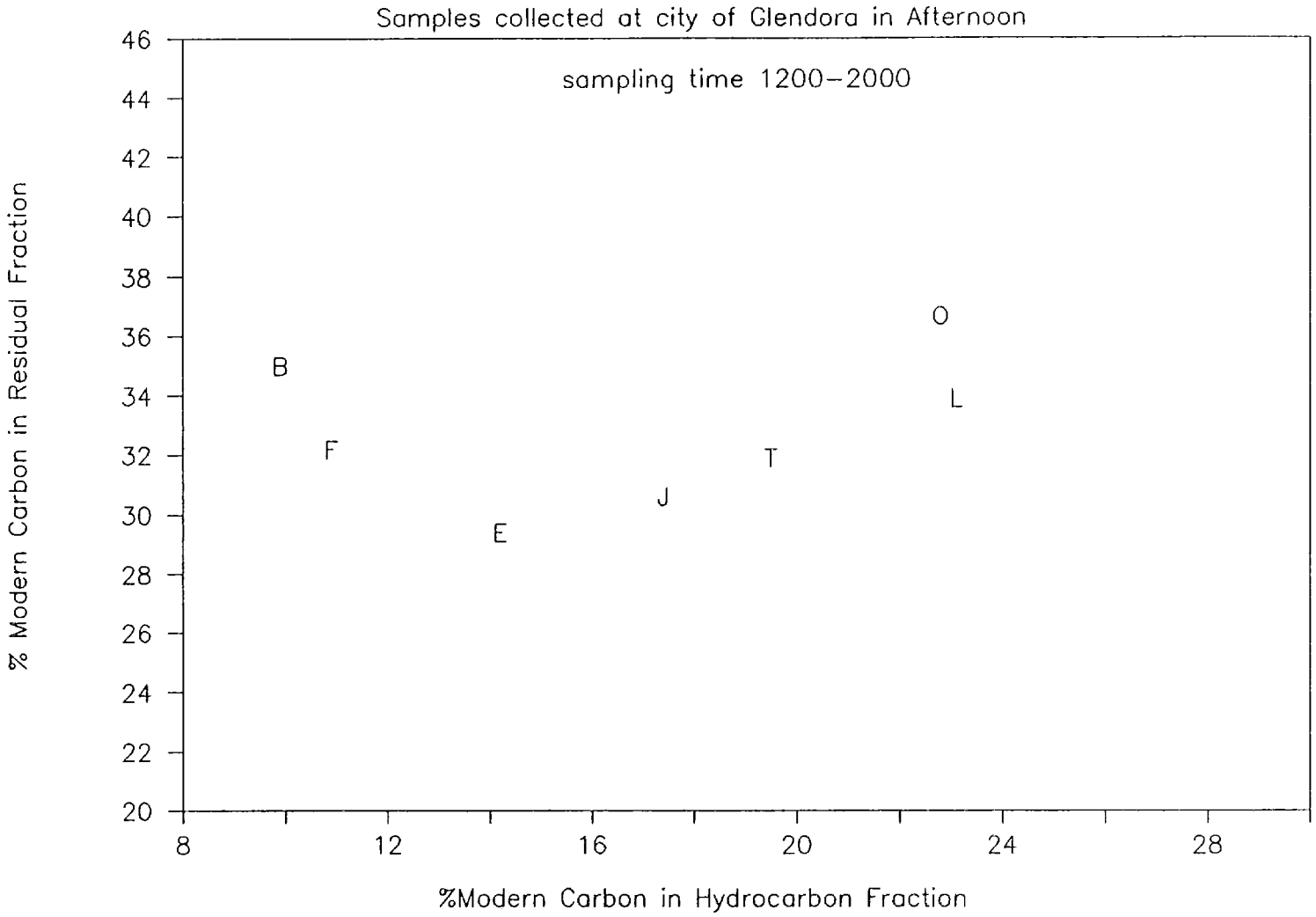
Key

	Filter No.	Sampling Date	Sampling Time
A	8007	13/08/86	0800-1200
A	8008	13/08/86	0800-1200
B	8009	13/08/86	1200-2000
C	8013	13/08/86	2000-0800
C	8014	13/08/86	2000-0800
D	8017	14/08/86	0800-1200
D	8027	15/08/86	0800-1200
E	8019	14/08/86	1200-2000
F	8020	14/08/86	1200-2000
G	8024	14/08/86	2000-0800
H	8026	15/08/86	1200-2000
H	8029	15/08/86	1200-2000
I	8031	15/08/86	2005-0800
J	8033	16/08/86	1205-2000
J	8036	16/08/86	1205-2000
K	8037	16/08/86	2000-0720
L	8043	17/08/86	1200-2000
L	8044	17/08/86	1200-2000
M	8045	17/08/86	2000-0800
N	8047	18/08/86	0800-1200
N	8051	19/08/86	0800-1200
O	8048	18/08/86	1200-2000
O	8049	18/08/86	1200-2000
P	8050	18/08/86	2000-0800
Q	8054	19/08/86	1200-2000
Q	8055	19/08/86	1200-2000
R	8056	19/08/86	2020-0800
S	8057	20/08/86	0800-1200
S	8058	20/08/86	0800-1200
T	8060	20/08/86	1200-2000
T	8061	20/08/86	1200-2000

} combined samples

Figure XIII-7

%Modern Carbon: Hydrocarbon vs. Residual Fractions



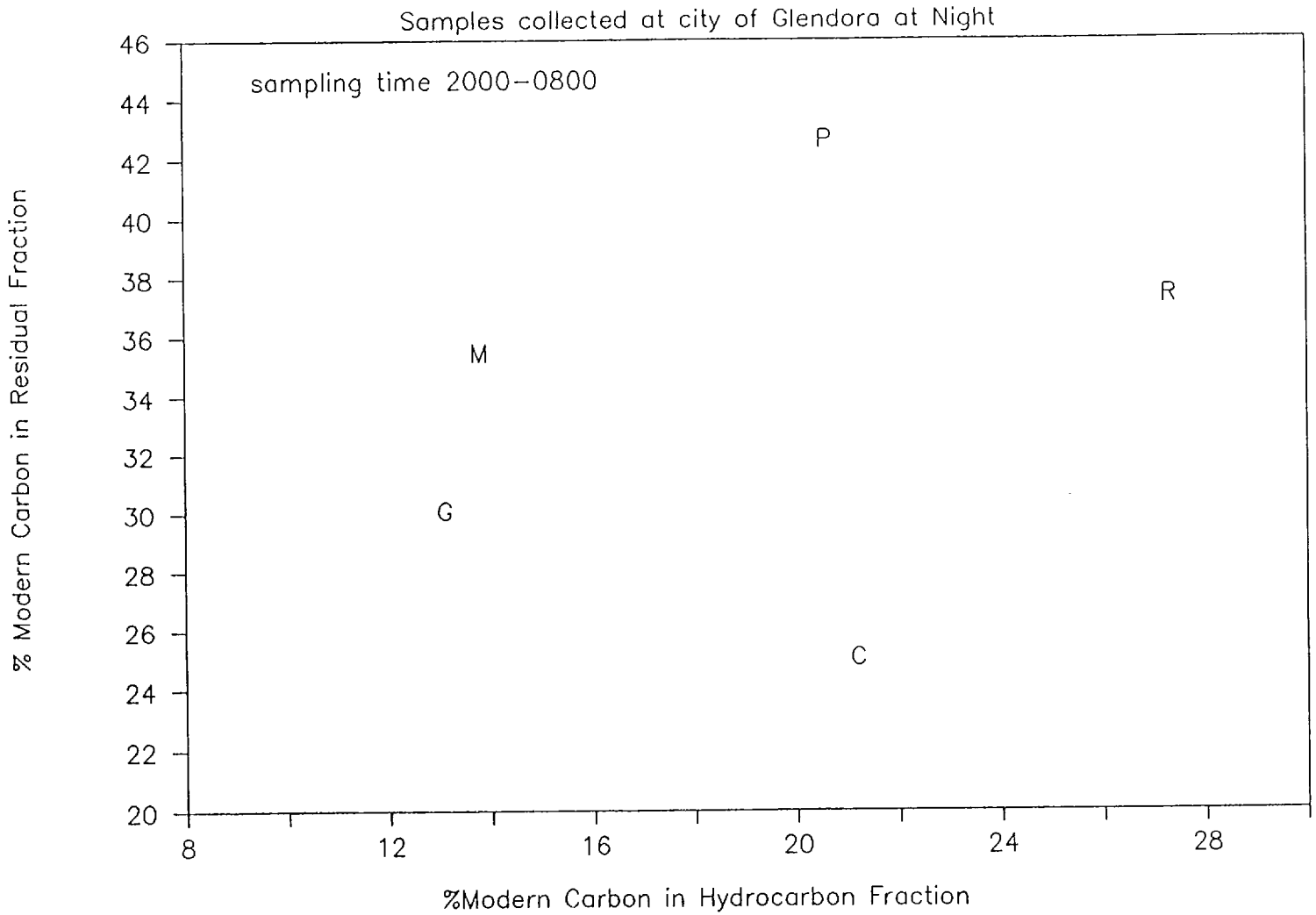
Key

Filter No.	Sampling Date	Sampling Time
A 8007	13/08/86	0800-1200
A 8008	13/08/86	0800-1200
B 8009	13/08/86	1200-2000
C 8013	13/08/86	2000-0800
C 8014	13/08/86	2000-0800
D 8017	14/08/86	0800-1200
D 8027	15/08/86	0800-1200
E 8019	14/08/86	1200-2000
F 8020	14/08/86	1200-2000
G 8024	14/08/86	2000-0800
H 8026	15/08/86	1200-2000
H 8029	15/08/86	1200-2000
I 8031	15/08/86	2005-0800
J 8033	16/08/86	1205-2000
J 8036	16/08/86	1205-2000
K 8037	16/08/86	2000-0720
L 8043	17/08/86	1200-2000
L 8044	17/08/86	1200-2000
M 8045	17/08/86	2000-0800
N 8047	18/08/86	0800-1200
N 8051	19/08/86	0800-1200
O 8048	18/08/86	1200-2000
O 8049	18/08/86	1200-2000
P 8050	18/08/86	2000-0800
Q 8054	19/08/86	1200-2000
Q 8055	19/08/86	1200-2000
R 8056	19/08/86	2020-0800
S 8057	20/08/86	0800-1200
S 8058	20/08/86	0800-1200
T 8060	20/08/86	1200-2000
T 8061	20/08/86	1200-2000

} combined samples

Figure XIII-8

%Modern Carbon: Hydrocarbon vs. Residual Fractions



Key

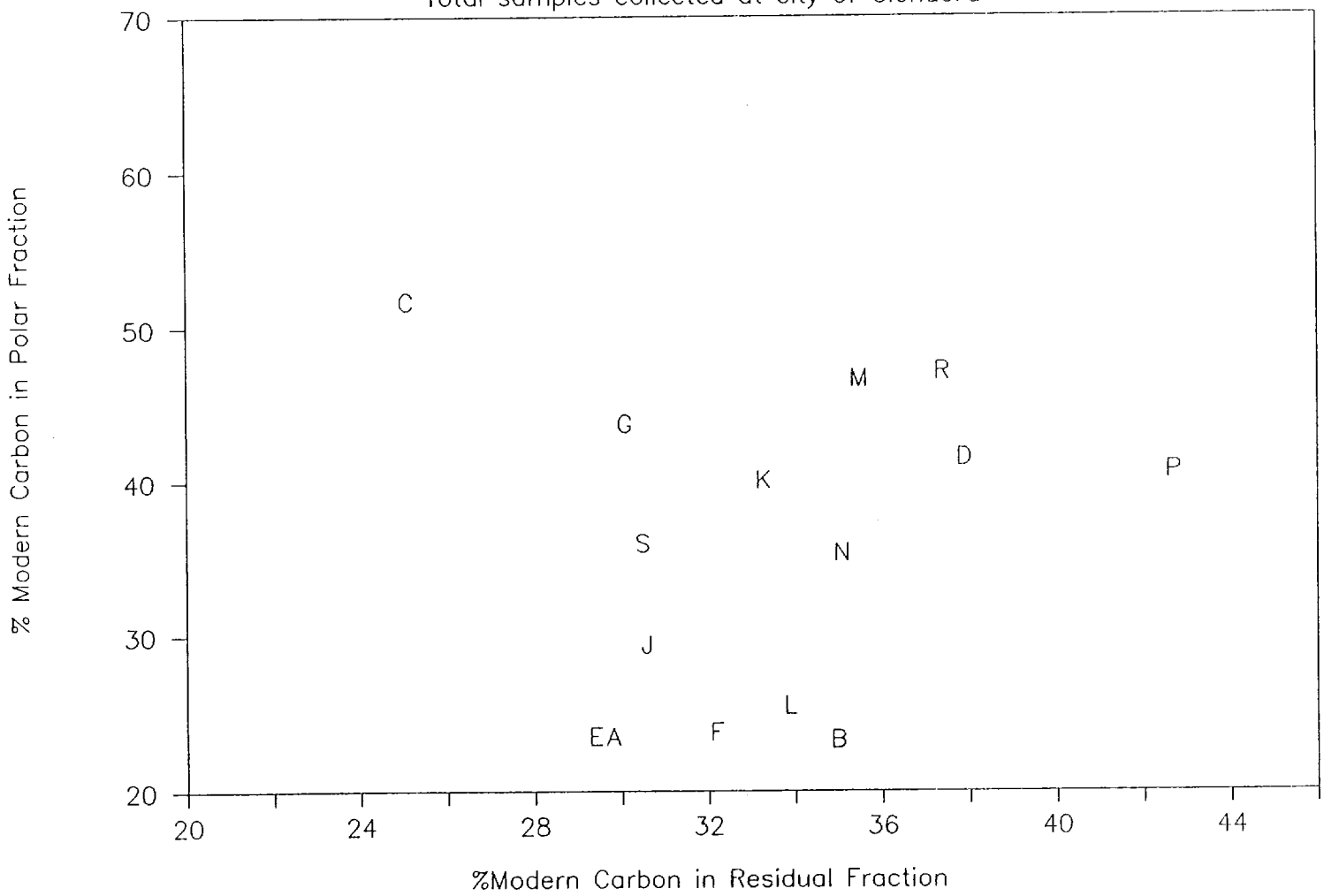
Filter No.	Sampling Date	Sampling Time
A 8007	13/08/86	0800-1200
A 8008	13/08/86	0800-1200
B 8009	13/08/86	1200-2000
C 8013	13/08/86	2000-0800
C 8014	13/08/86	2000-0800
D 8017	14/08/86	0800-1200
D 8027	15/08/86	0800-1200
E 8019	14/08/86	1200-2000
F 8020	14/08/86	1200-2000
G 8024	14/08/86	2000-0800
H 8026	15/08/86	1200-2000
H 8029	15/08/86	1200-2000
I 8031	15/08/86	2005-0800
J 8033	16/08/86	1205-2000
J 8036	16/08/86	1205-2000
K 8037	16/08/86	2000-0720
L 8043	17/08/86	1200-2000
L 8044	17/08/86	1200-2000
M 8045	17/08/86	2000-0800
N 8047	18/08/86	0800-1200
N 8051	19/08/86	0800-1200
O 8048	18/08/86	1200-2000
O 8049	18/08/86	1200-2000
P 8050	18/08/86	2000-0800
Q 8054	19/08/86	1200-2000
Q 8055	19/08/86	1200-2000
R 8056	19/08/86	2020-0800
S 8057	20/08/86	0800-1200
S 8058	20/08/86	0800-1200
T 8060	20/08/86	1200-2000
T 8061	20/08/86	1200-2000

} combined samples

Figure XIII–9

%Modern Carbon: Residual vs. Polar Fractions

Total samples collected at city of Glendora

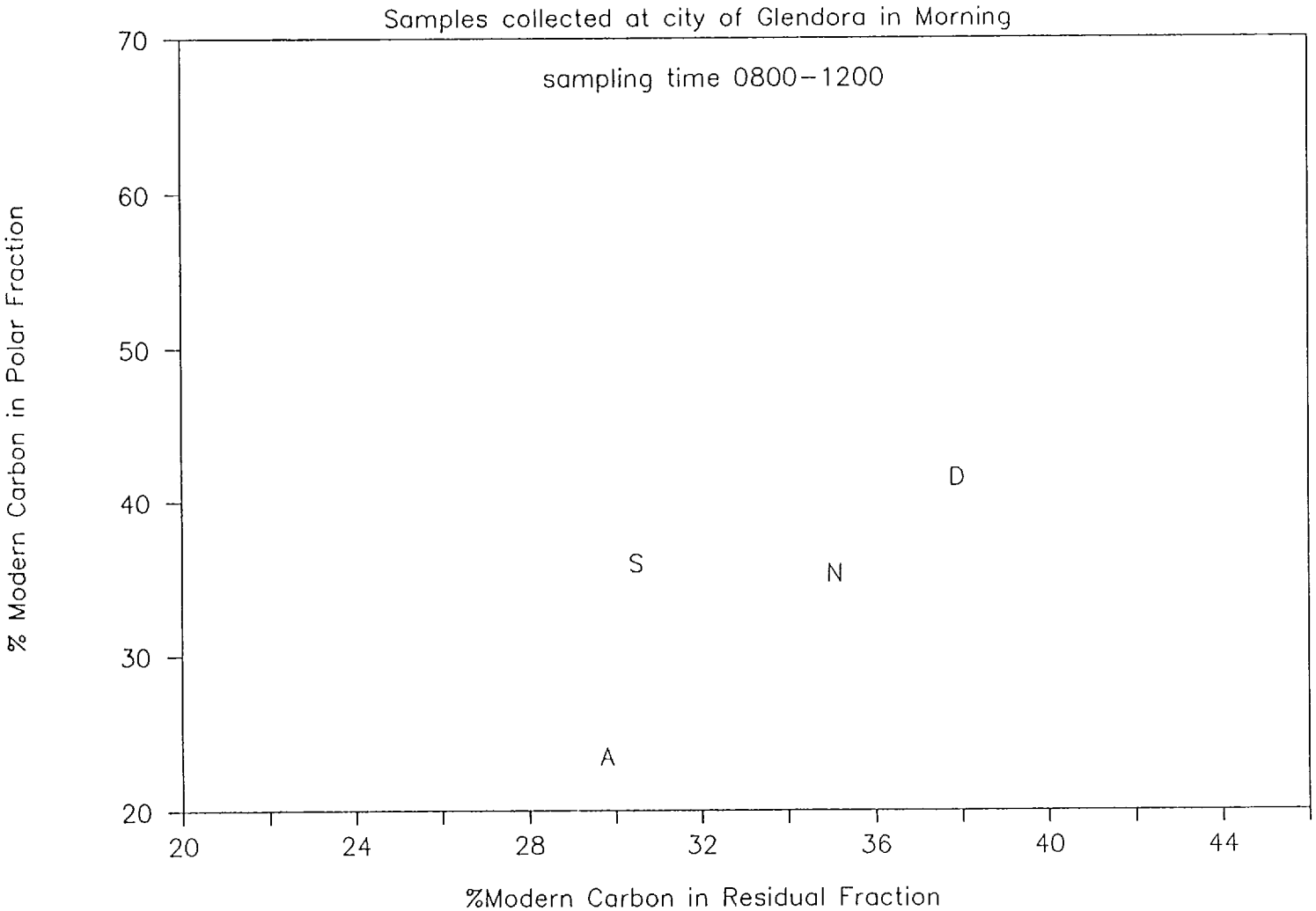


	Filter No.	Sampling Date	Sampling Time
A	8007	13/08/86	0800-1200
A	8008	13/08/86	0800-1200
B	8009	13/08/86	1200-2000
C	8013	13/08/86	2000-0800
C	8014	13/08/86	2000-0800
D	8017	14/08/86	0800-1200
D	8027	15/08/86	0800-1200
E	8019	14/08/86	1200-2000
F	8020	14/08/86	1200-2000
G	8024	14/08/86	2000-0800
H	8026	15/08/86	1200-2000
H	8029	15/08/86	1200-2000
I	8031	15/08/86	2005-0800
J	8033	16/08/86	1205-2000
J	8036	16/08/86	1205-2000
K	8037	16/08/86	2000-0720
L	8043	17/08/86	1200-2000
L	8044	17/08/86	1200-2000
M	8045	17/08/86	2000-0800
N	8047	18/08/86	0800-1200
N	8051	19/08/86	0800-1200
O	8048	18/08/86	1200-2000
O	8049	18/08/86	1200-2000
P	8050	18/08/86	2000-0800
Q	8054	19/08/86	1200-2000
Q	8055	19/08/86	1200-2000
R	8056	19/08/86	2020-0800
S	8057	20/08/86	0800-1200
S	8058	20/08/86	0800-1200
T	8060	20/08/86	1200-2000
T	8061	20/08/86	1200-2000

} combined samples

Figure XIII-10

%Modern Carbon : Residual vs. Polar Fractions



Key

Filter No.	Sampling Date	Sampling Time
A 8007	13/08/86	0800-1200
A 8008	13/08/86	0800-1200
B 8009	13/08/86	1200-2000
C 8013	13/08/86	2000-0800
C 8014	13/08/86	2000-0800
D 8017	14/08/86	0800-1200
D 8027	15/08/86	0800-1200
E 8019	14/08/86	1200-2000
F 8020	14/08/86	1200-2000
G 8024	14/08/86	2000-0800
H 8026	15/08/86	1200-2000
H 8029	15/08/86	1200-2000
I 8031	15/08/86	2005-0800
J 8033	16/08/86	1205-2000
J 8036	16/08/86	1205-2000
K 8037	16/08/86	2000-0720
L 8043	17/08/86	1200-2000
L 8044	17/08/86	1200-2000
M 8045	17/08/86	2000-0800
N 8047	18/08/86	0800-1200
N 8051	19/08/86	0800-1200
O 8048	18/08/86	1200-2000
O 8049	18/08/86	1200-2000
P 8050	18/08/86	2000-0800
Q 8054	19/08/86	1200-2000
Q 8055	19/08/86	1200-2000
R 8056	19/08/86	2020-0800
S 8057	20/08/86	0800-1200
S 8058	20/08/86	0800-1200
T 8060	20/08/86	1200-2000
T 8061	20/08/86	1200-2000

} combined samples

Figure XIII-11

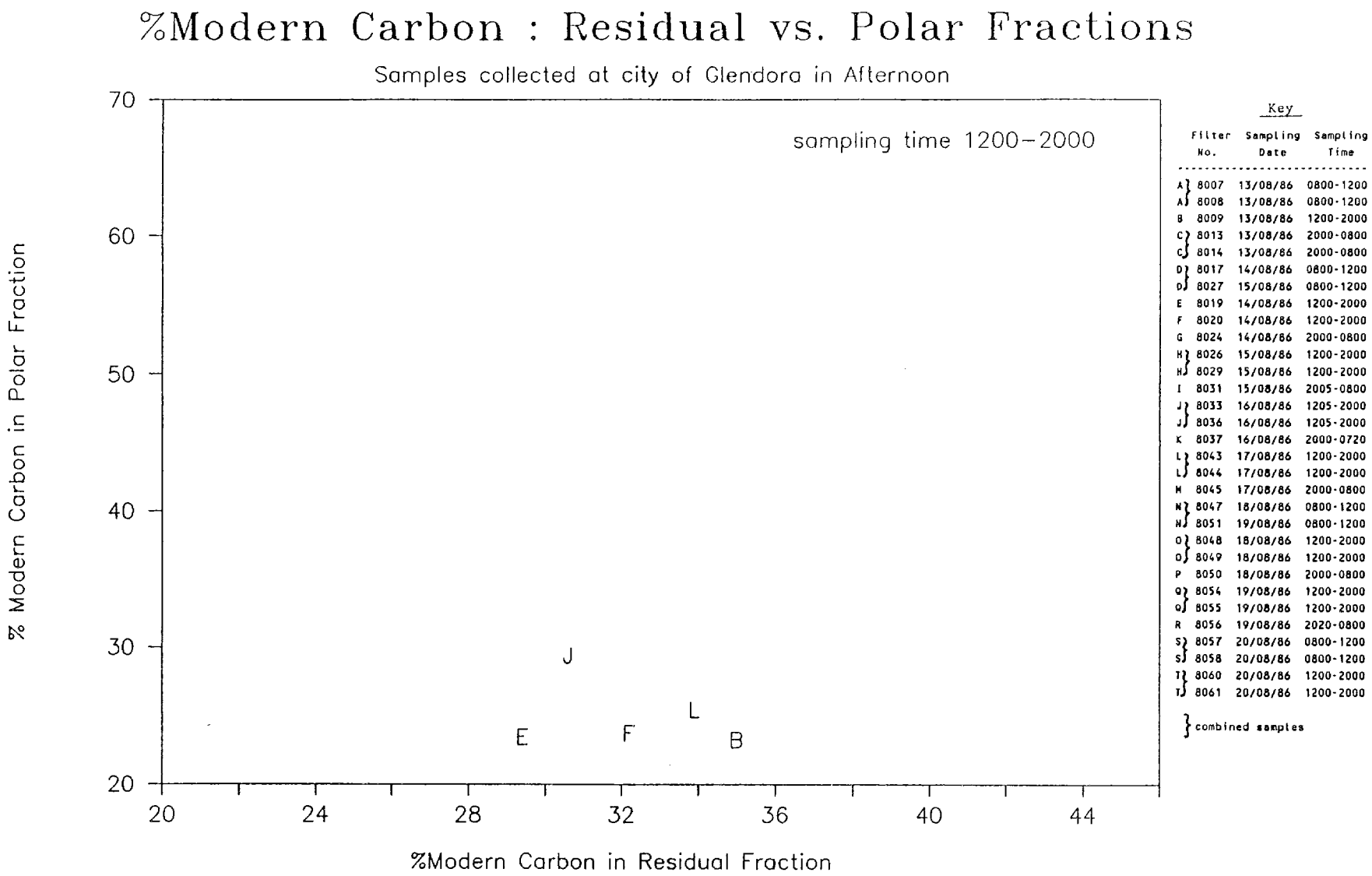
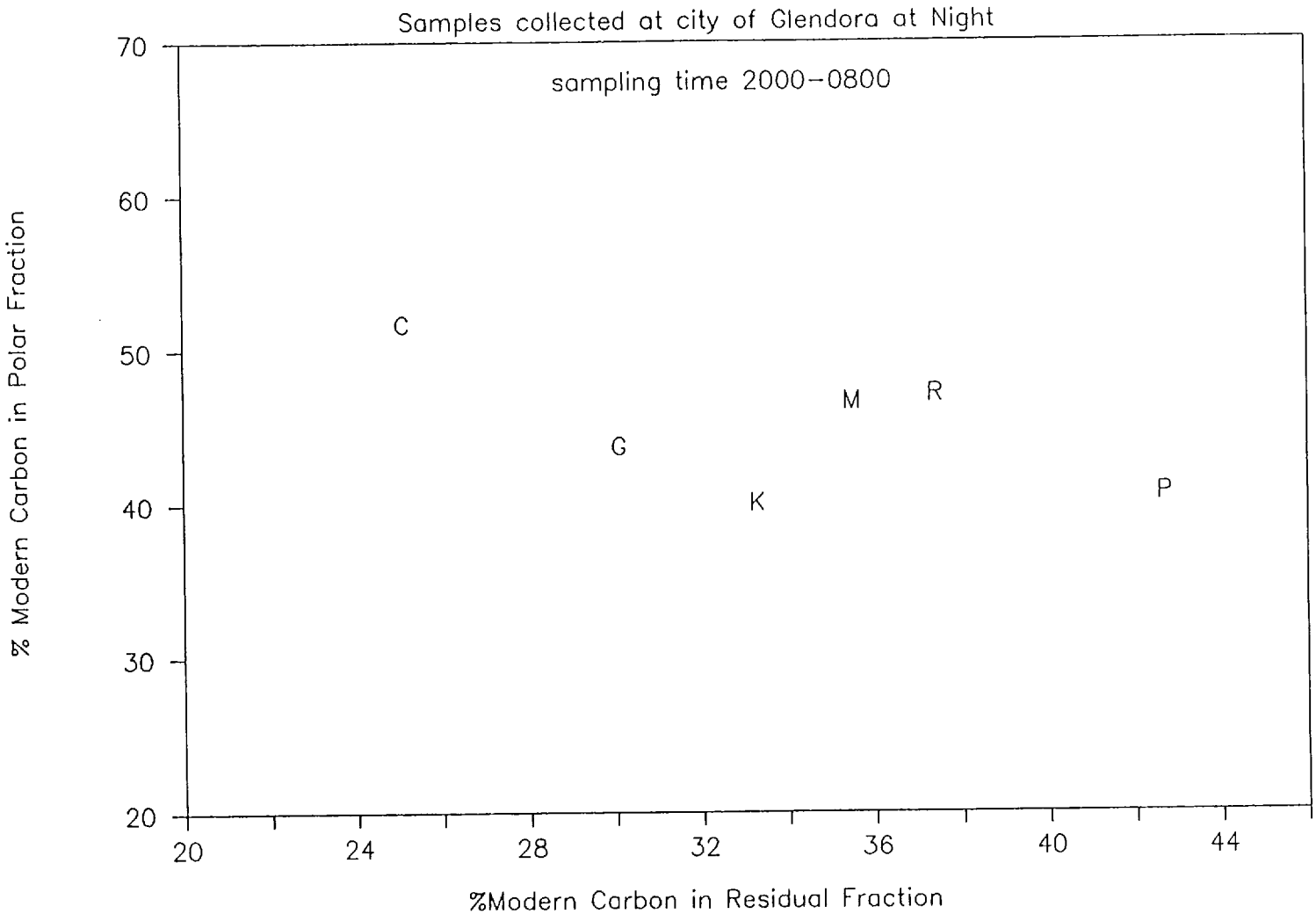


Figure XIII-12

%Modern Carbon : Residual vs. Polar Fractions



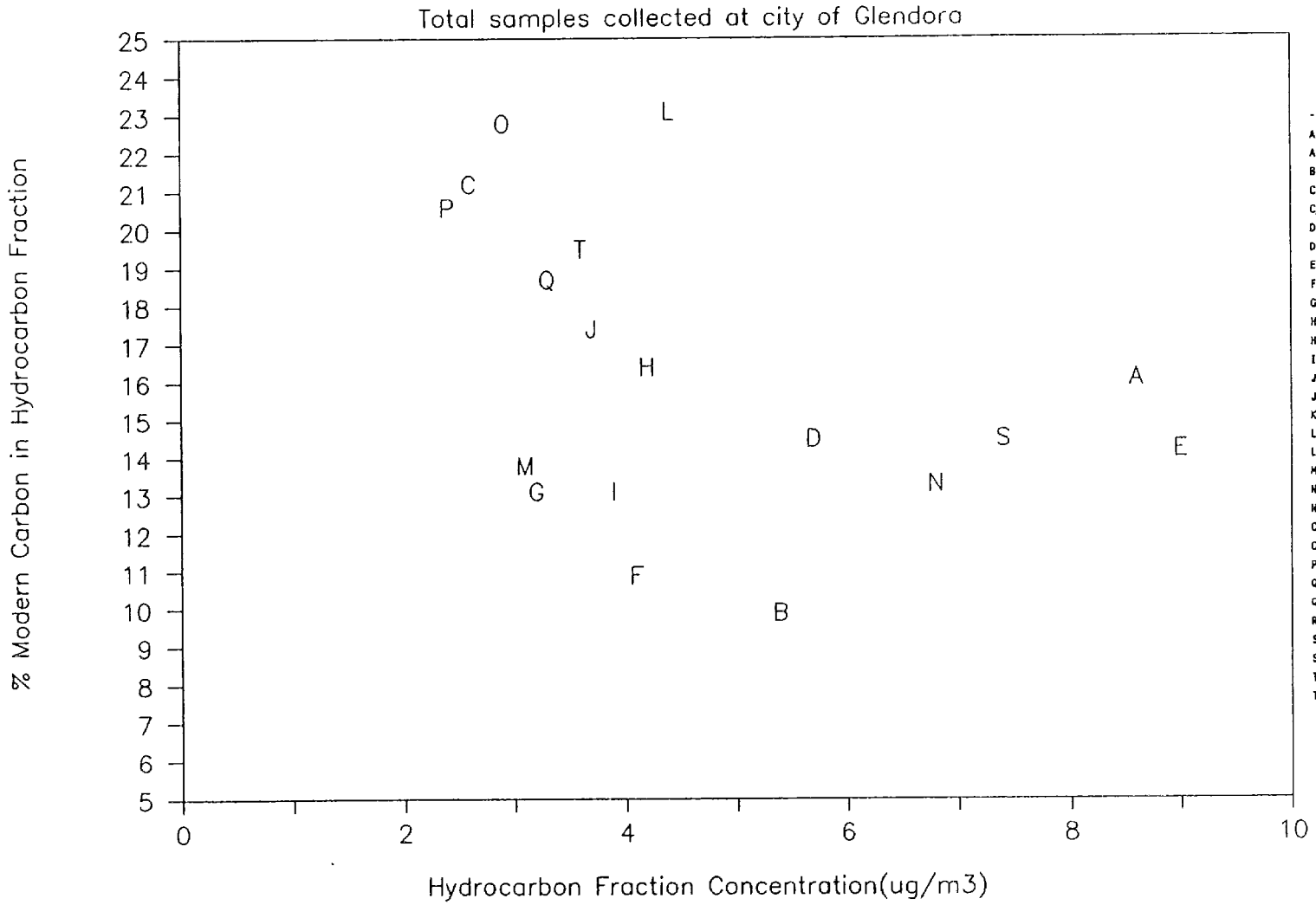
Key

Filter No.	Sampling Date	Sampling Time
A } 8007	13/08/86	0800-1200
A } 8008	13/08/86	0800-1200
B 8009	13/08/86	1200-2000
C } 8013	13/08/86	2000-0800
C } 8014	13/08/86	2000-0800
D } 8017	14/08/86	0800-1200
D } 8027	15/08/86	0800-1200
E 8019	14/08/86	1200-2000
F 8020	14/08/86	1200-2000
G 8024	14/08/86	2000-0800
H } 8026	15/08/86	1200-2000
H } 8029	15/08/86	1200-2000
I 8031	15/08/86	2005-0800
J } 8033	16/08/86	1205-2000
J } 8036	16/08/86	1205-2000
K 8037	16/08/86	2000-0720
L } 8043	17/08/86	1200-2000
L } 8044	17/08/86	1200-2000
M 8045	17/08/86	2000-0800
N } 8047	18/08/86	0800-1200
N } 8051	19/08/86	0800-1200
O } 8048	18/08/86	1200-2000
O } 8049	18/08/86	1200-2000
P 8050	18/08/86	2000-0800
Q } 8054	19/08/86	1200-2000
Q } 8055	19/08/86	1200-2000
R 8056	19/08/86	2020-0800
S } 8057	20/08/86	0800-1200
S } 8058	20/08/86	0800-1200
T } 8060	20/08/86	1200-2000
T } 8061	20/08/86	1200-2000

} combined samples

Figure XIII-13

Hydrocarbon Fraction Concentration vs. % Modern Carbon



Key

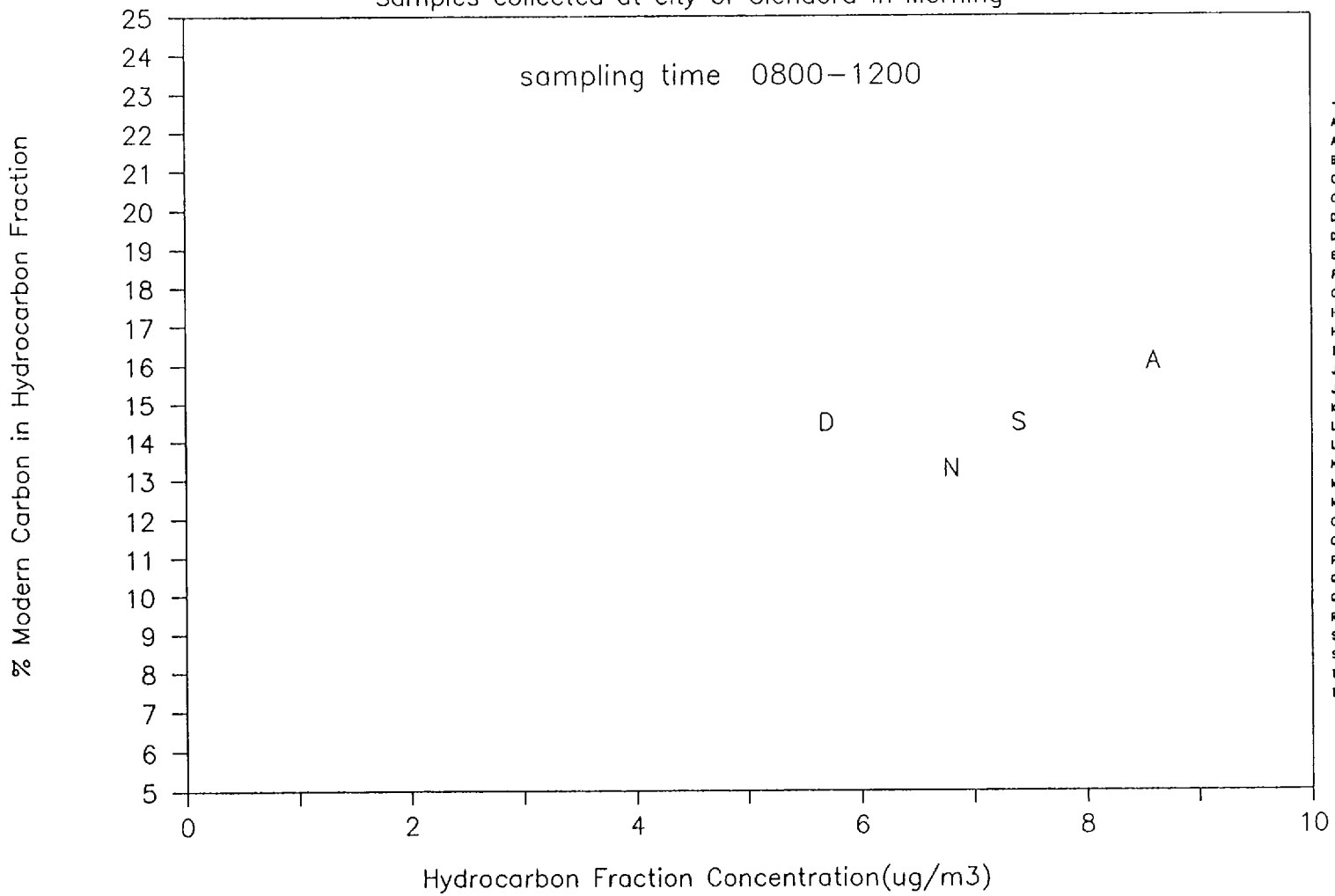
Filter No.	Sampling Date	Sampling Time
A 8007	13/08/86	0800-1200
A 8008	13/08/86	0800-1200
B 8009	13/08/86	1200-2000
C 8013	13/08/86	2000-0800
C 8014	13/08/86	2000-0800
D 8017	14/08/86	0800-1200
D 8027	15/08/86	0800-1200
E 8019	14/08/86	1200-2000
F 8020	14/08/86	1200-2000
G 8024	14/08/86	2000-0800
H 8026	15/08/86	1200-2000
H 8029	15/08/86	1200-2000
I 8031	15/08/86	2005-0800
J 8033	16/08/86	1205-2000
J 8036	16/08/86	1205-2000
K 8037	16/08/86	2000-0720
L 8043	17/08/86	1200-2000
L 8044	17/08/86	1200-2000
M 8045	17/08/86	2000-0800
N 8047	18/08/86	0800-1200
N 8051	19/08/86	0800-1200
O 8048	18/08/86	1200-2000
O 8049	18/08/86	1200-2000
P 8050	18/08/86	2000-0800
Q 8054	19/08/86	1200-2000
Q 8055	19/08/86	1200-2000
R 8056	19/08/86	2020-0800
S 8057	20/08/86	0800-1200
S 8058	20/08/86	0800-1200
T 8060	20/08/86	1200-2000
T 8061	20/08/86	1200-2000

} combined samples

Figure XIII-14

Hydrocarbon Fraction Concentration vs.% Modern Carbon

Samples collected at city of Glendora in Morning



Key

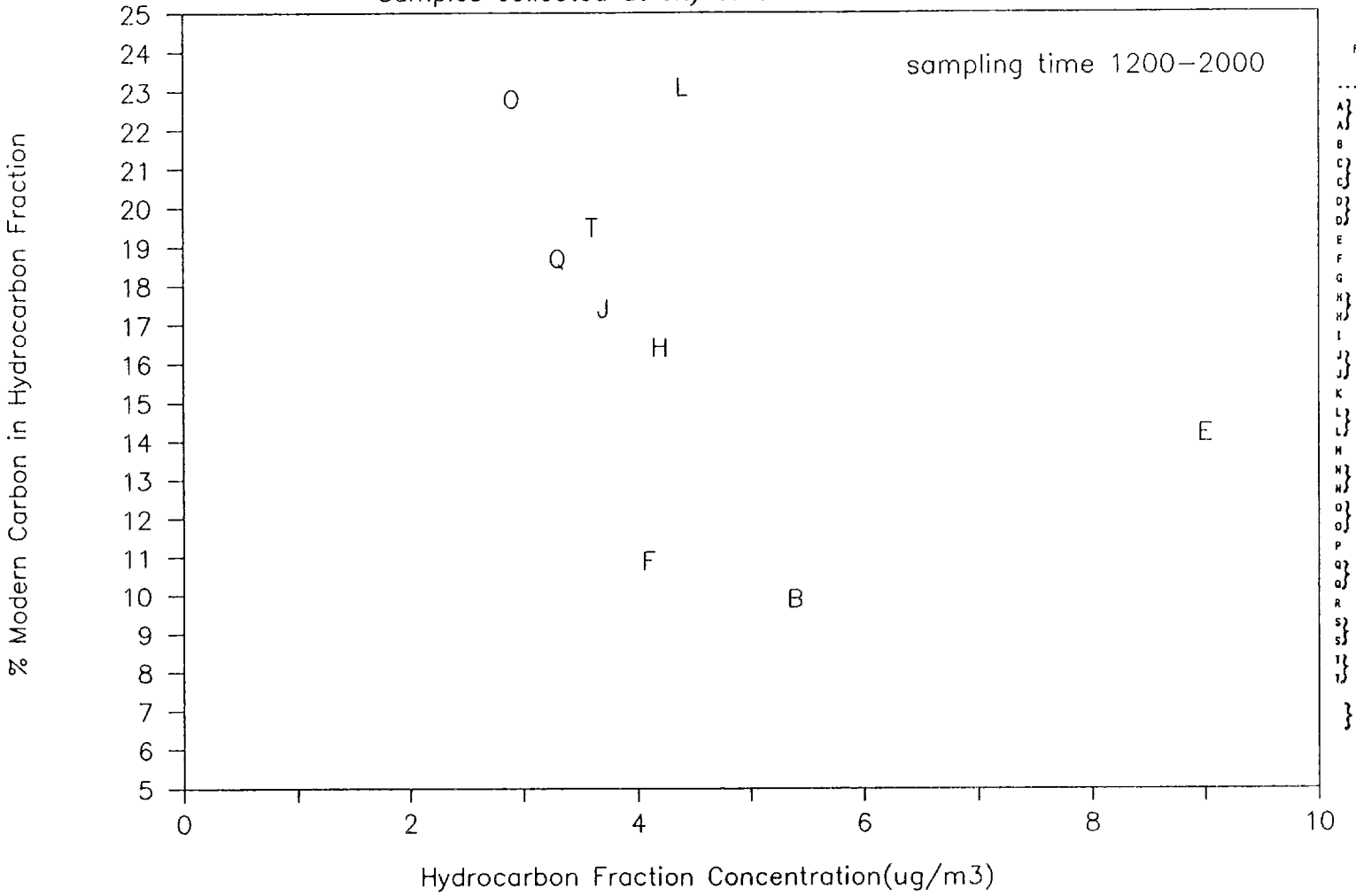
Filter No.	Sampling Date	Sampling Time
A 8007	13/08/86	0800-1200
A 8008	13/08/86	0800-1200
B 8009	13/08/86	1200-2000
C 8013	13/08/86	2000-0800
C 8014	13/08/86	2000-0800
D 8017	14/08/86	0800-1200
D 8027	15/08/86	0800-1200
E 8019	14/08/86	1200-2000
F 8020	14/08/86	1200-2000
G 8024	14/08/86	2000-0800
H 8026	15/08/86	1200-2000
H 8029	15/08/86	1200-2000
I 8031	15/08/86	2005-0800
J 8033	16/08/86	1205-2000
J 8036	16/08/86	1205-2000
K 8037	16/08/86	2000-0720
L 8043	17/08/86	1200-2000
L 8044	17/08/86	1200-2000
M 8045	17/08/86	2000-0800
N 8047	18/08/86	0800-1200
N 8051	19/08/86	0800-1200
O 8048	18/08/86	1200-2000
O 8049	18/08/86	1200-2000
P 8050	18/08/86	2000-0800
Q 8054	19/08/86	1200-2000
Q 8055	19/08/86	1200-2000
R 8056	19/08/86	2020-0800
S 8057	20/08/86	0800-1200
S 8058	20/08/86	0800-1200
T 8060	20/08/86	1200-2000
T 8061	20/08/86	1200-2000

} combined samples

Figure XIII-15

Hydrocarbon Fraction Concentration vs. % Modern Carbon

Samples collected at city of Glendora in Afternoon



Key

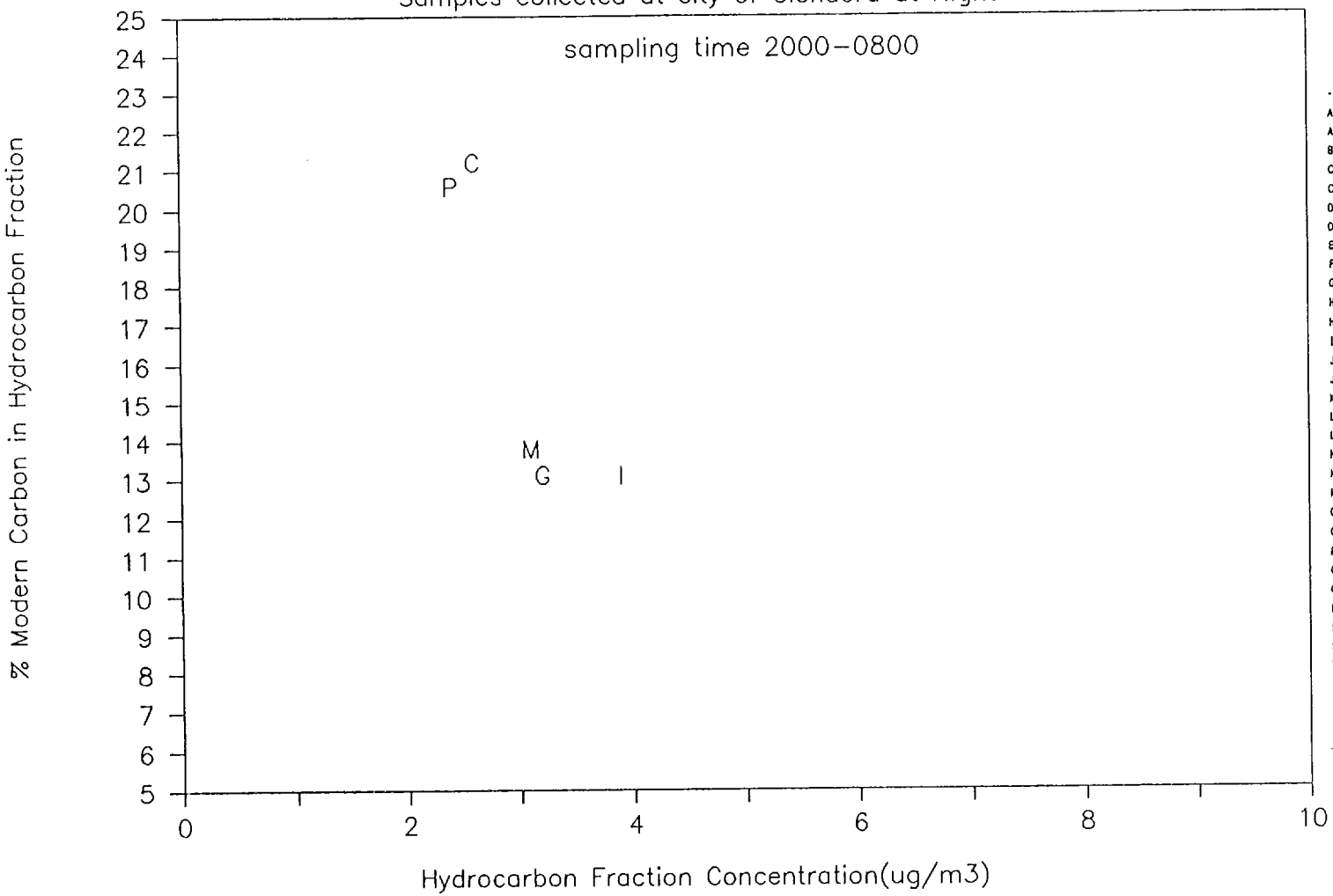
Filter No.	Sampling Date	Sampling Time
A 8007	13/08/86	0800-1200
A 8008	13/08/86	0800-1200
B 8009	13/08/86	1200-2000
C 8013	13/08/86	2000-0800
C 8014	13/08/86	2000-0800
D 8017	14/08/86	0800-1200
D 8027	15/08/86	0800-1200
E 8019	14/08/86	1200-2000
F 8020	14/08/86	1200-2000
G 8024	14/08/86	2000-0800
H 8026	15/08/86	1200-2000
H 8029	15/08/86	1200-2000
I 8031	15/08/86	2005-0800
J 8033	16/08/86	1205-2000
J 8036	16/08/86	1205-2000
K 8037	16/08/86	2000-0720
L 8043	17/08/86	1200-2000
L 8044	17/08/86	1200-2000
M 8045	17/08/86	2000-0800
N 8047	18/08/86	0800-1200
N 8051	19/08/86	0800-1200
O 8048	18/08/86	1200-2000
O 8049	18/08/86	1200-2000
P 8050	18/08/86	2000-0800
Q 8054	19/08/86	1200-2000
Q 8055	19/08/86	1200-2000
R 8056	19/08/86	2020-0800
S 8057	20/08/86	0800-1200
S 8058	20/08/86	0800-1200
T 8060	20/08/86	1200-2000
T 8061	20/08/86	1200-2000

} combined samples

Figure XIII-16

Hydrocarbon Fraction Concentration vs. % Modern Carbon

Samples collected at city of Glendora at Night



Key

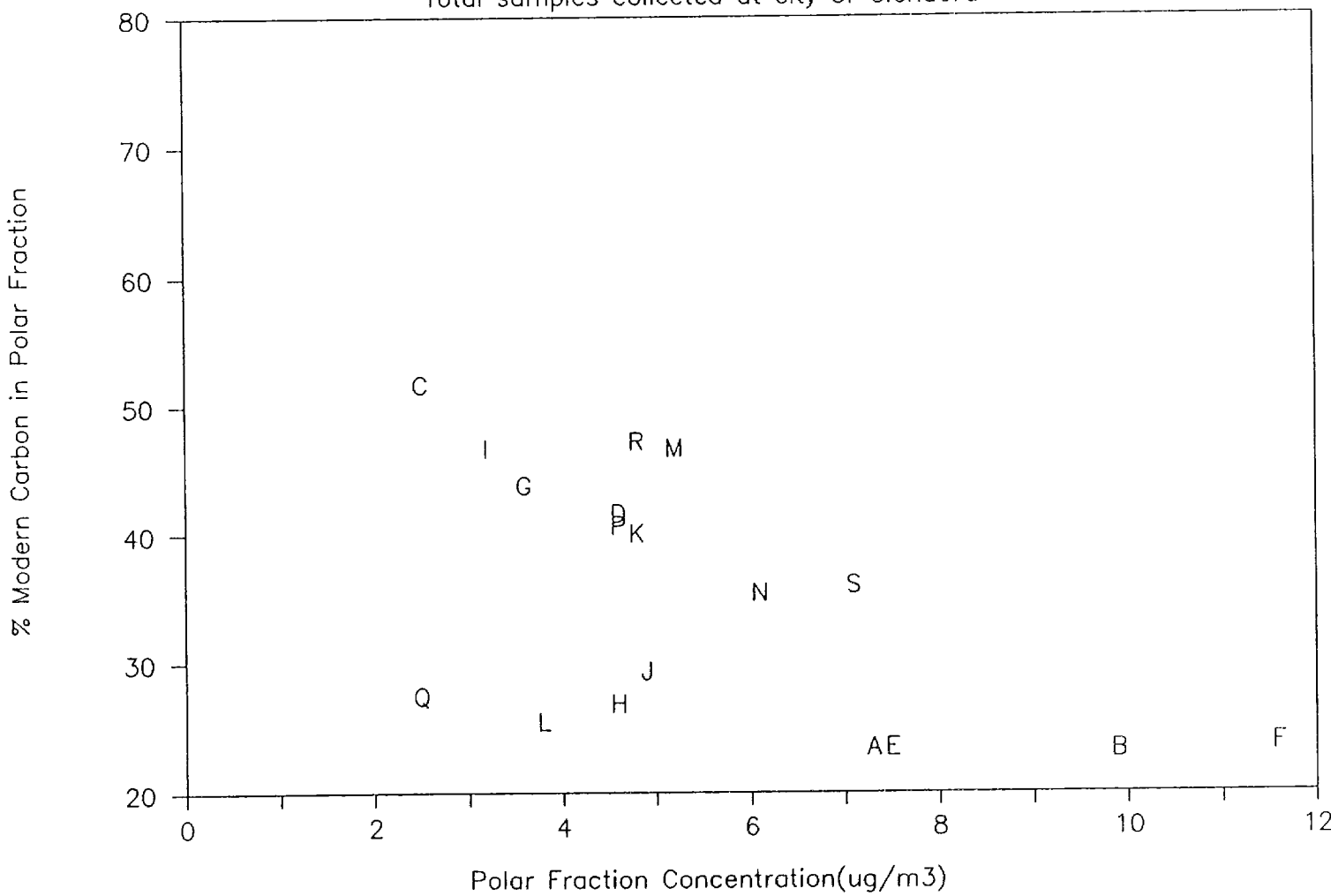
Filter No.	Sampling Date	Sampling Time
A 8007	13/08/86	0800-1200
A 8008	13/08/86	0800-1200
B 8009	13/08/86	1200-2000
C 8013	13/08/86	2000-0800
C 8014	13/08/86	2000-0800
O 8017	14/08/86	0800-1200
O 8027	15/08/86	0800-1200
E 8019	14/08/86	1200-2000
F 8020	14/08/86	1200-2000
G 8024	14/08/86	2000-0800
H 8026	15/08/86	1200-2000
H 8029	15/08/86	1200-2000
I 8031	15/08/86	2005-0800
J 8033	16/08/86	1205-2000
J 8036	16/08/86	1205-2000
K 8037	16/08/86	2000-0720
L 8043	17/08/86	1200-2000
L 8044	17/08/86	1200-2000
M 8045	17/08/86	2000-0800
N 8047	18/08/86	0800-1200
N 8051	19/08/86	0800-1200
O 8048	18/08/86	1200-2000
O 8049	18/08/86	1200-2000
P 8050	18/08/86	2000-0800
Q 8054	19/08/86	1200-2000
Q 8055	19/08/86	1200-2000
R 8056	19/08/86	2020-0800
S 8057	20/08/86	0800-1200
S 8058	20/08/86	0800-1200
T 8060	20/08/86	1200-2000
T 8061	20/08/86	1200-2000

} combined samples

Figure XIII-17

Polar Fraction Concentration vs. % Modern Carbon

Total samples collected at city of Glendora



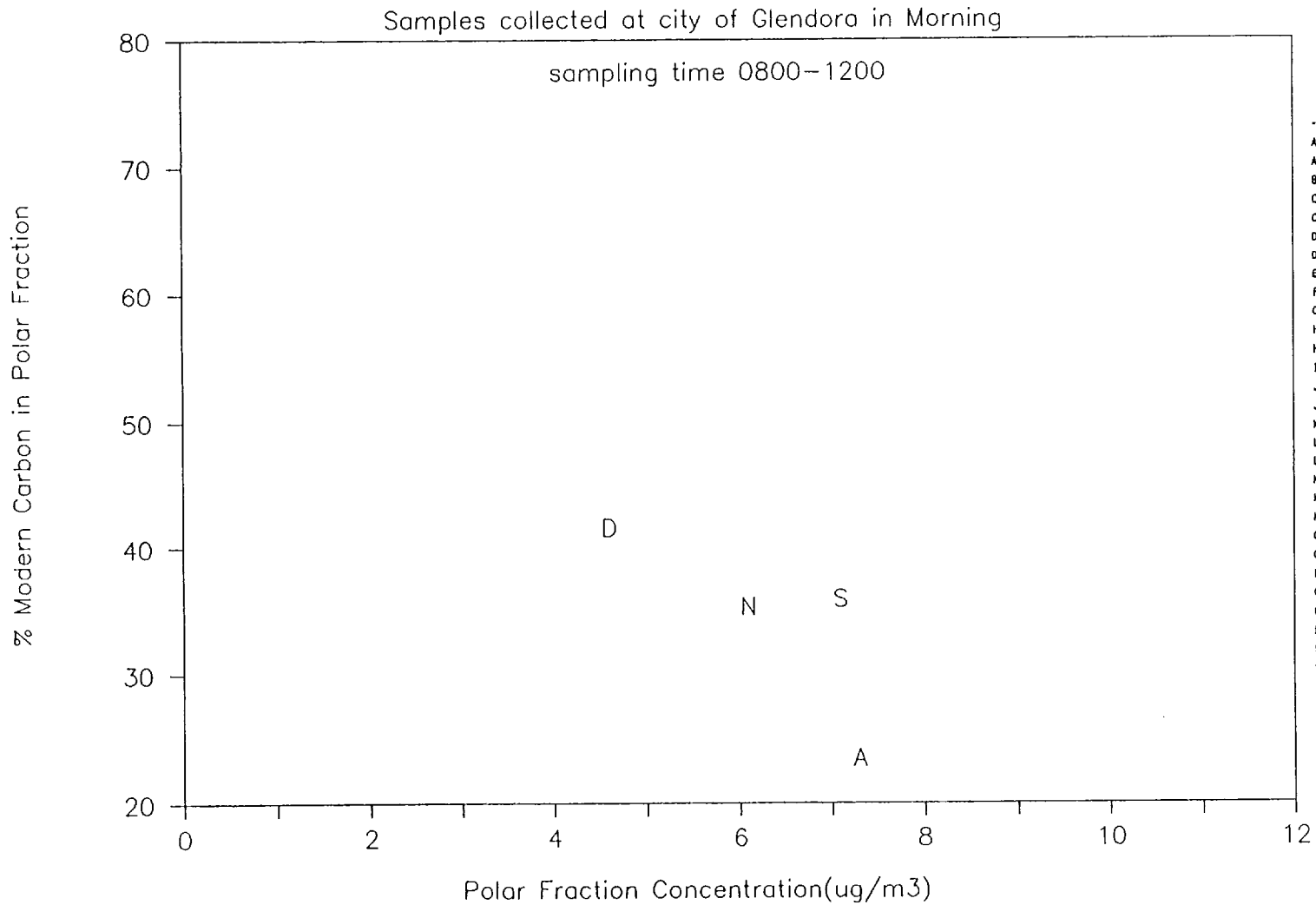
Key

Filter No.	Sampling Date	Sampling Time
A 8007	13/08/86	0800-1200
A 8008	13/08/86	0800-1200
B 8009	13/08/86	1200-2000
C 8013	13/08/86	2000-0800
C 8014	13/08/86	2000-0800
D 8017	14/08/86	0800-1200
D 8027	15/08/86	0800-1200
E 8019	14/08/86	1200-2000
F 8020	14/08/86	1200-2000
G 8024	14/08/86	2000-0800
H 8026	15/08/86	1200-2000
H 8029	15/08/86	1200-2000
I 8031	15/08/86	2005-0800
J 8033	16/08/86	1205-2000
J 8036	16/08/86	1205-2000
K 8037	16/08/86	2000-0720
L 8043	17/08/86	1200-2000
L 8044	17/08/86	1200-2000
M 8045	17/08/86	2000-0800
N 8047	18/08/86	0800-1200
N 8051	19/08/86	0800-1200
O 8048	18/08/86	1200-2000
O 8049	18/08/86	1200-2000
P 8050	18/08/86	2000-0800
Q 8054	19/08/86	1200-2000
Q 8055	19/08/86	1200-2000
R 8056	19/08/86	2020-0800
S 8057	20/08/86	0800-1200
S 8058	20/08/86	0800-1200
T 8060	20/08/86	1200-2000
T 8061	20/08/86	1200-2000

} combined samples

Figure XIII-18

Polar Fraction Concentration vs. %Modern Carbon



Key

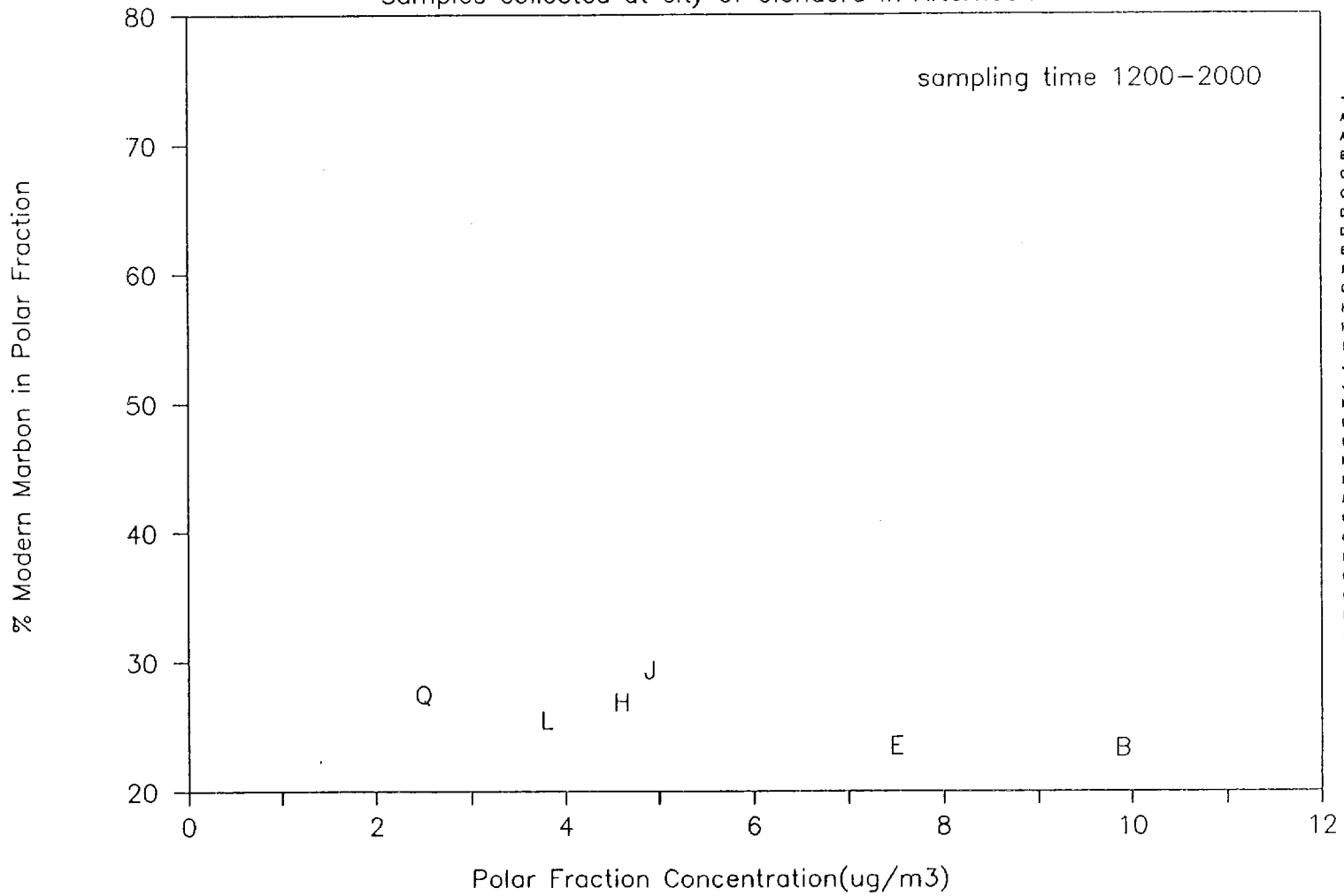
	Filter No.	Sampling Date	Sampling Time
A	8007	13/08/86	0800-1200
A	8008	13/08/86	0800-1200
B	8009	13/08/86	1200-2000
C	8013	13/08/86	2000-0800
C	8014	13/08/86	2000-0800
D	8017	14/08/86	0800-1200
D	8027	15/08/86	0800-1200
E	8019	14/08/86	1200-2000
F	8020	14/08/86	1200-2000
G	8024	14/08/86	2000-0800
H	8026	15/08/86	1200-2000
H	8029	15/08/86	1200-2000
I	8031	15/08/86	2005-0800
J	8033	16/08/86	1205-2000
J	8036	16/08/86	1205-2000
K	8037	16/08/86	2000-0720
L	8043	17/08/86	1200-2000
L	8044	17/08/86	1200-2000
M	8045	17/08/86	2000-0800
N	8047	18/08/86	0800-1200
N	8051	19/08/86	0800-1200
O	8048	18/08/86	1200-2000
O	8049	18/08/86	1200-2000
P	8050	18/08/86	2000-0800
Q	8054	19/08/86	1200-2000
Q	8055	19/08/86	1200-2000
R	8056	19/08/86	2020-0800
S	8057	20/08/86	0800-1200
S	8058	20/08/86	0800-1200
T	8060	20/08/86	1200-2000
T	8061	20/08/86	1200-2000

} combined samples

Figure XIII-19

Polar Fraction Concentration vs. % Modern Carbon

Samples collected at city of Glendora in Afternoon



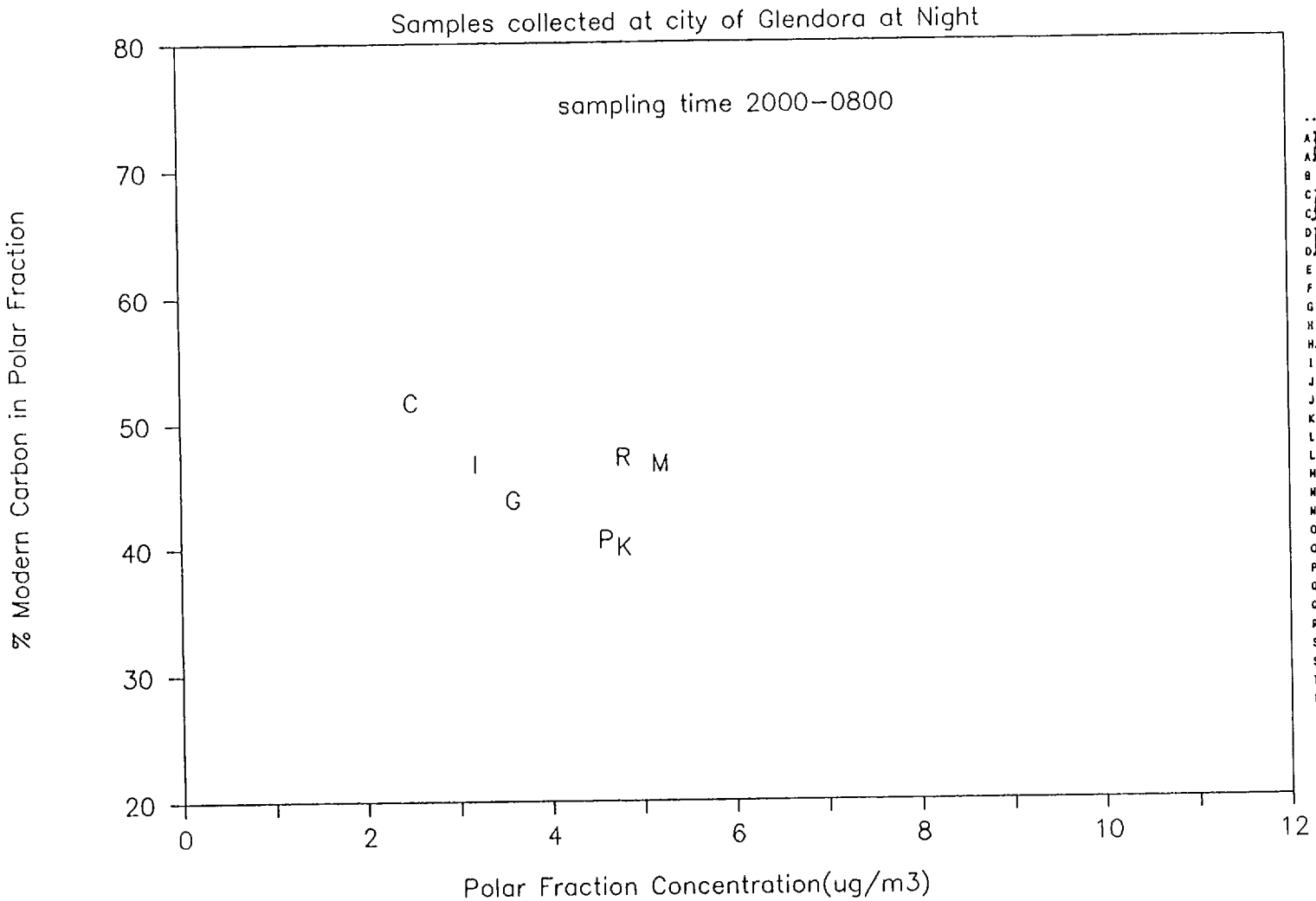
Key

	Filter No.	Sampling Date	Sampling Time
A	8007	13/08/86	0800-1200
A	8008	13/08/86	0800-1200
B	8009	13/08/86	1200-2000
C	8013	13/08/86	2000-0800
C	8014	13/08/86	2000-0800
D	8017	14/08/86	0800-1200
D	8027	15/08/86	0800-1200
E	8019	14/08/86	1200-2000
F	8020	14/08/86	1200-2000
G	8024	14/08/86	2000-0800
H	8026	15/08/86	1200-2000
H	8029	15/08/86	1200-2000
I	8031	15/08/86	2005-0800
J	8033	16/08/86	1205-2000
J	8036	16/08/86	1205-2000
K	8037	16/08/86	2000-0720
L	8043	17/08/86	1200-2000
L	8044	17/08/86	1200-2000
M	8045	17/08/86	2000-0800
N	8047	18/08/86	0800-1200
N	8051	19/08/86	0800-1200
O	8048	18/08/86	1200-2000
O	8049	18/08/86	1200-2000
P	8050	18/08/86	2000-0800
Q	8054	19/08/86	1200-2000
Q	8055	19/08/86	1200-2000
R	8056	19/08/86	2020-0800
S	8057	20/08/86	0800-1200
S	8058	20/08/86	0800-1200
T	8060	20/08/86	1200-2000
T	8061	20/08/86	1200-2000

} combined samples

Figure XIII-20

Polar Fraction Concentration vs. % Modern Carbon



Key

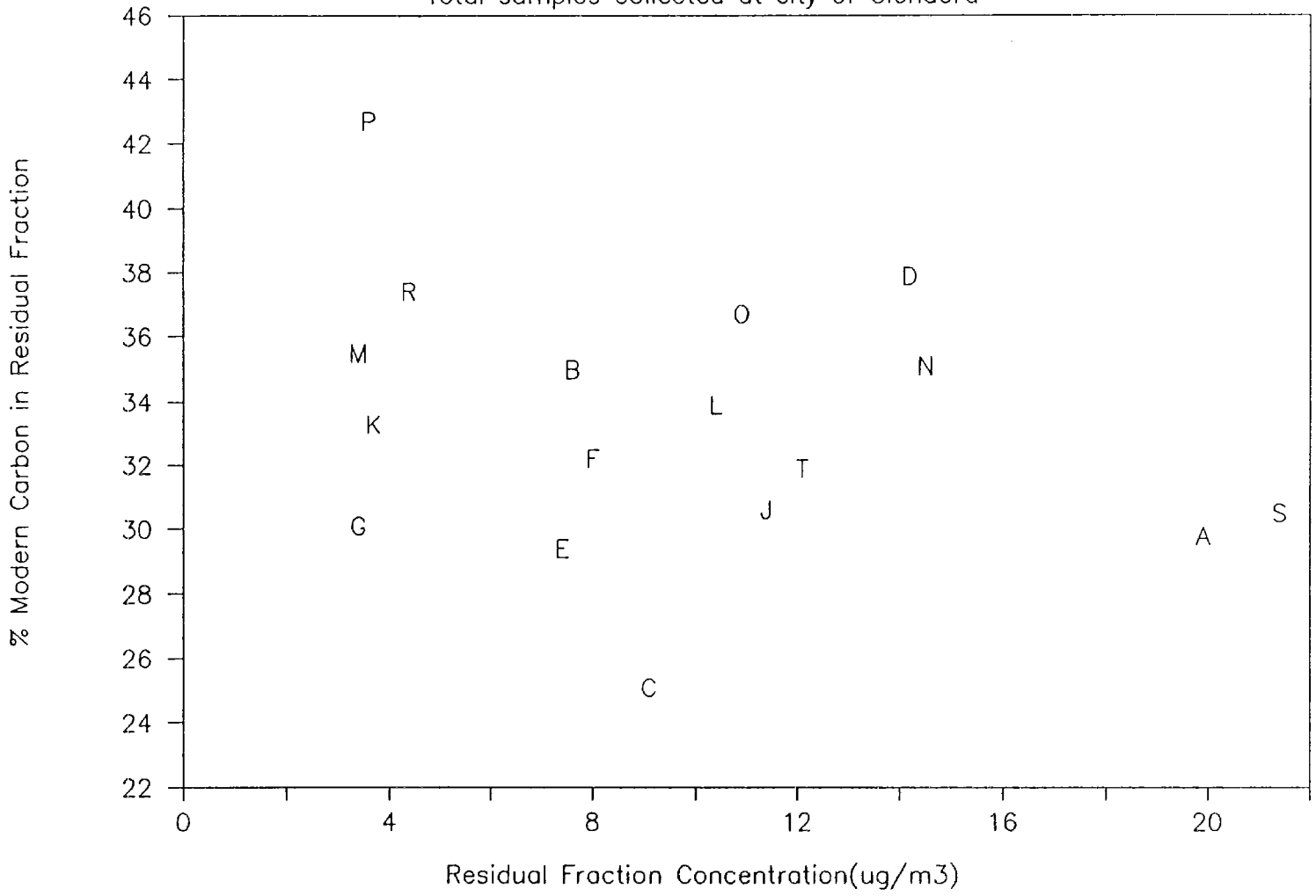
Filter No.	Sampling Date	Sampling Time
A 8007	13/08/86	0800-1200
A 8008	13/08/86	0800-1200
B 8009	13/08/86	1200-2000
C 8013	13/08/86	2000-0800
C 8014	13/08/86	2000-0800
D 8017	14/08/86	0800-1200
D 8027	15/08/86	0800-1200
E 8019	14/08/86	1200-2000
F 8020	14/08/86	1200-2000
G 8024	14/08/86	2000-0800
H 8026	15/08/86	1200-2000
H 8029	15/08/86	1200-2000
I 8031	15/08/86	2005-0800
J 8033	16/08/86	1205-2000
J 8036	16/08/86	1205-2000
K 8037	16/08/86	2000-0720
L 8043	17/08/86	1200-2000
L 8044	17/08/86	1200-2000
M 8045	17/08/86	2000-0800
N 8047	18/08/86	0800-1200
N 8051	19/08/86	0800-1200
O 8048	18/08/86	1200-2000
O 8049	18/08/86	1200-2000
P 8050	18/08/86	2000-0800
Q 8054	19/08/86	1200-2000
Q 8055	19/08/86	1200-2000
R 8056	19/08/86	2020-0800
S 8057	20/08/86	0800-1200
S 8058	20/08/86	0800-1200
T 8060	20/08/86	1200-2000
T 8061	20/08/86	1200-2000

} combined samples

Figure XIII-21

Residual Fraction Concentration vs. % Modern Carbon

Total samples collected at city of Glendora



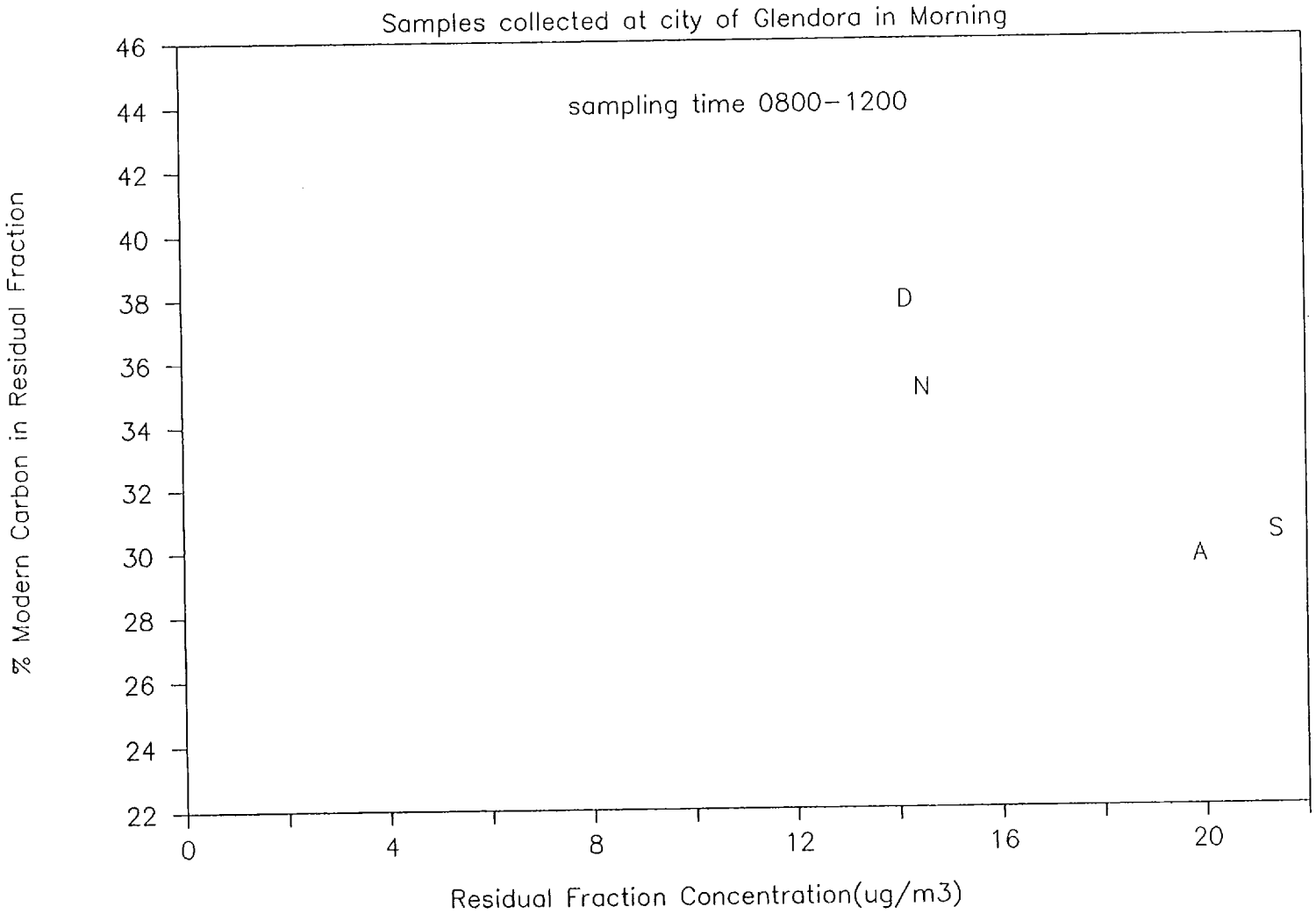
Key

	Filter No.	Sampling Date	Sampling Time
A	8007	13/08/86	0800-1200
A	8008	13/08/86	0800-1200
B	8009	13/08/86	1200-2000
C	8013	13/08/86	2000-0800
C	8014	13/08/86	2000-0800
D	8017	14/08/86	0800-1200
D	8027	15/08/86	0800-1200
E	8019	14/08/86	1200-2000
F	8020	14/08/86	1200-2000
G	8024	14/08/86	2000-0800
H	8026	15/08/86	1200-2000
H	8029	15/08/86	1200-2000
I	8031	15/08/86	2005-0800
J	8033	16/08/86	1205-2000
J	8036	16/08/86	1205-2000
K	8037	16/08/86	2000-0720
L	8043	17/08/86	1200-2000
L	8044	17/08/86	1200-2000
M	8045	17/08/86	2000-0800
N	8047	18/08/86	0800-1200
N	8051	19/08/86	0800-1200
O	8048	18/08/86	1200-2000
O	8049	18/08/86	1200-2000
P	8050	18/08/86	2000-0800
Q	8054	19/08/86	1200-2000
Q	8055	19/08/86	1200-2000
R	8056	19/08/86	2020-0800
S	8057	20/08/86	0800-1200
S	8058	20/08/86	0800-1200
T	8060	20/08/86	1200-2000
T	8061	20/08/86	1200-2000

} combined samples

Figure XIII-22

Residual Fraction Concentration vs. % Modern Carbon



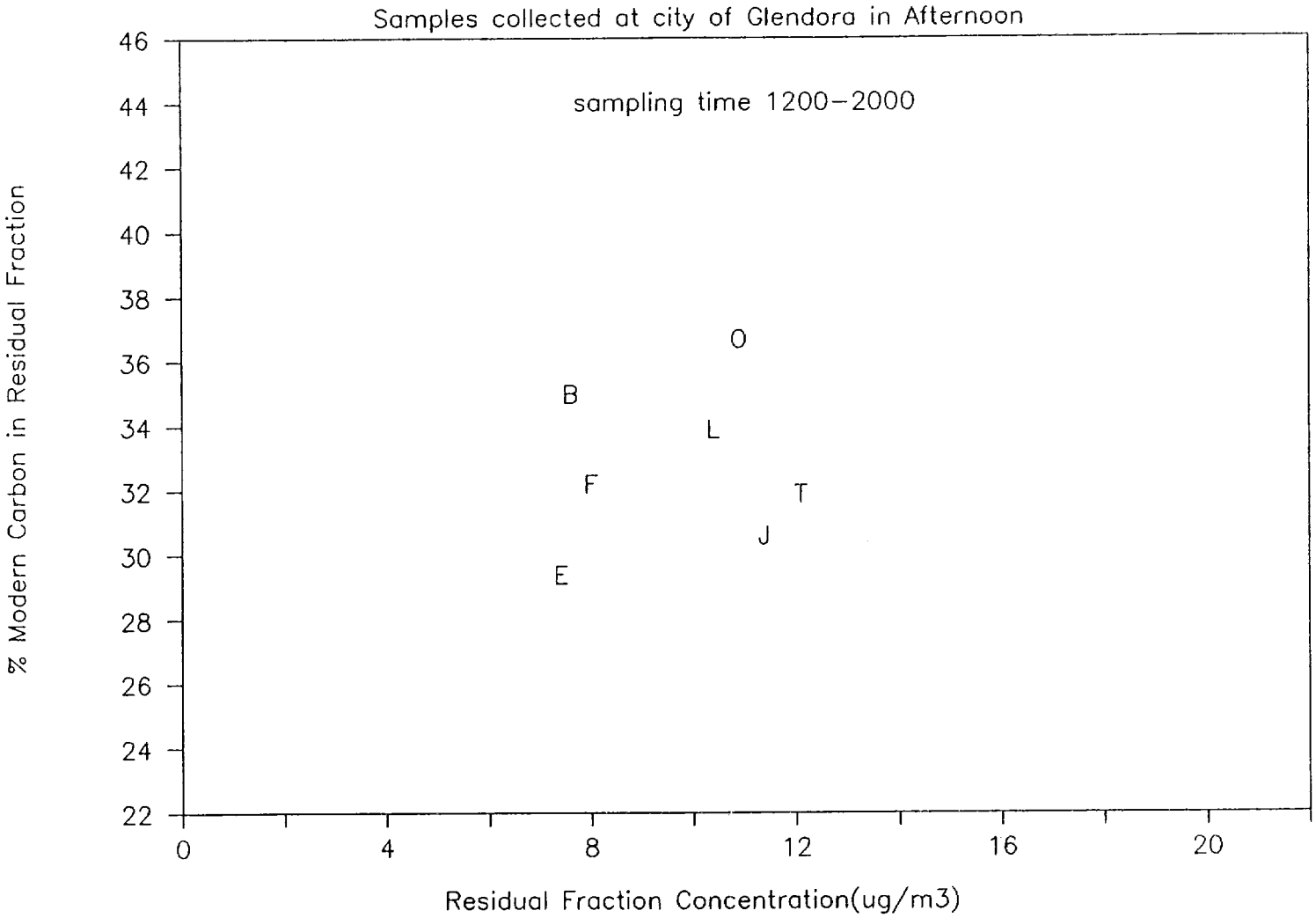
Key

Filter No.	Sampling Date	Sampling Time
A 8007	13/08/86	0800-1200
A 8008	13/08/86	0800-1200
B 8009	13/08/86	1200-2000
C 8013	13/08/86	2000-0800
C 8014	13/08/86	2000-0800
D 8017	14/08/86	0800-1200
D 8027	15/08/86	0800-1200
E 8019	14/08/86	1200-2000
F 8020	14/08/86	1200-2000
G 8024	14/08/86	2000-0800
H 8026	15/08/86	1200-2000
H 8029	15/08/86	1200-2000
I 8031	15/08/86	2005-0800
J 8033	16/08/86	1205-2000
J 8036	16/08/86	1205-2000
K 8037	16/08/86	2000-0720
L 8043	17/08/86	1200-2000
L 8044	17/08/86	1200-2000
M 8045	17/08/86	2000-0800
N 8047	18/08/86	0800-1200
N 8051	19/08/86	0800-1200
O 8048	18/08/86	1200-2000
O 8049	18/08/86	1200-2000
P 8050	18/08/86	2000-0800
Q 8054	19/08/86	1200-2000
Q 8055	19/08/86	1200-2000
R 8056	19/08/86	2020-0800
S 8057	20/08/86	0800-1200
S 8058	20/08/86	0800-1200
T 8060	20/08/86	1200-2000
T 8061	20/08/86	1200-2000

} combined samples

Figure XIII-23

Residual Fraction Concentration vs. % Modern Carbon



Key

Filter No.	Sampling Date	Sampling Time
A 8007	13/08/86	0800-1200
A 8008	13/08/86	0800-1200
B 8009	13/08/86	1200-2000
C 8013	13/08/86	2000-0800
C 8014	13/08/86	2000-0800
D 8017	14/08/86	0800-1200
D 8027	15/08/86	0800-1200
E 8019	14/08/86	1200-2000
F 8020	14/08/86	1200-2000
G 8024	14/08/86	2000-0800
H 8026	15/08/86	1200-2000
H 8029	15/08/86	1200-2000
I 8031	15/08/86	2005-0800
J 8033	16/08/86	1205-2000
J 8036	16/08/86	1205-2000
K 8037	16/08/86	2000-0720
L 8043	17/08/86	1200-2000
L 8044	17/08/86	1200-2000
M 8045	17/08/86	2000-0800
N 8047	18/08/86	0800-1200
N 8051	19/08/86	0800-1200
O 8048	18/08/86	1200-2000
O 8049	18/08/86	1200-2000
P 8050	18/08/86	2000-0800
Q 8054	19/08/86	1200-2000
Q 8055	19/08/86	1200-2000
R 8056	19/08/86	2020-0800
S 8057	20/08/86	0800-1200
S 8058	20/08/86	0800-1200
T 8060	20/08/86	1200-2000
T 8061	20/08/86	1200-2000

} combined samples

Figure XIII-24

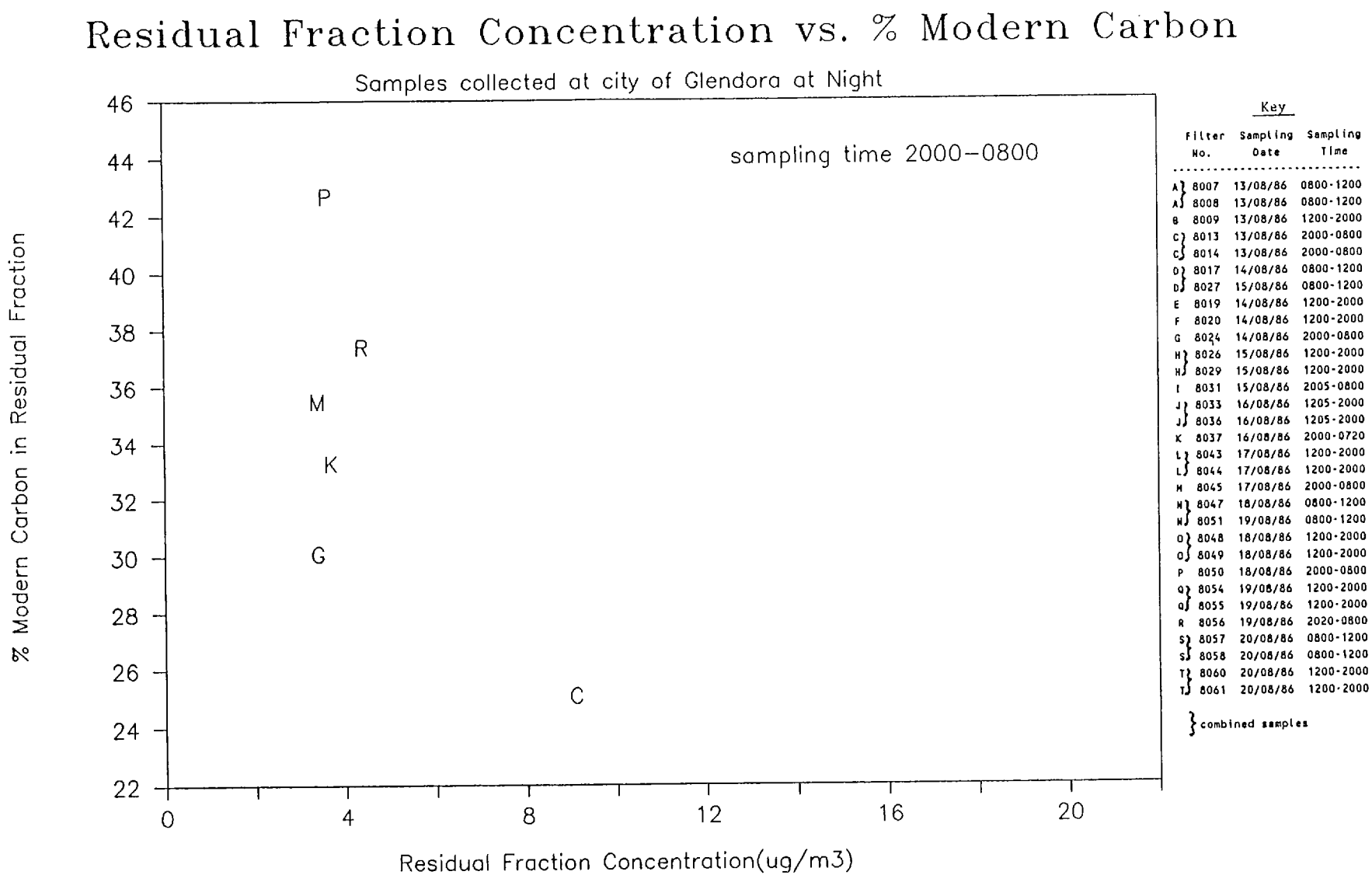
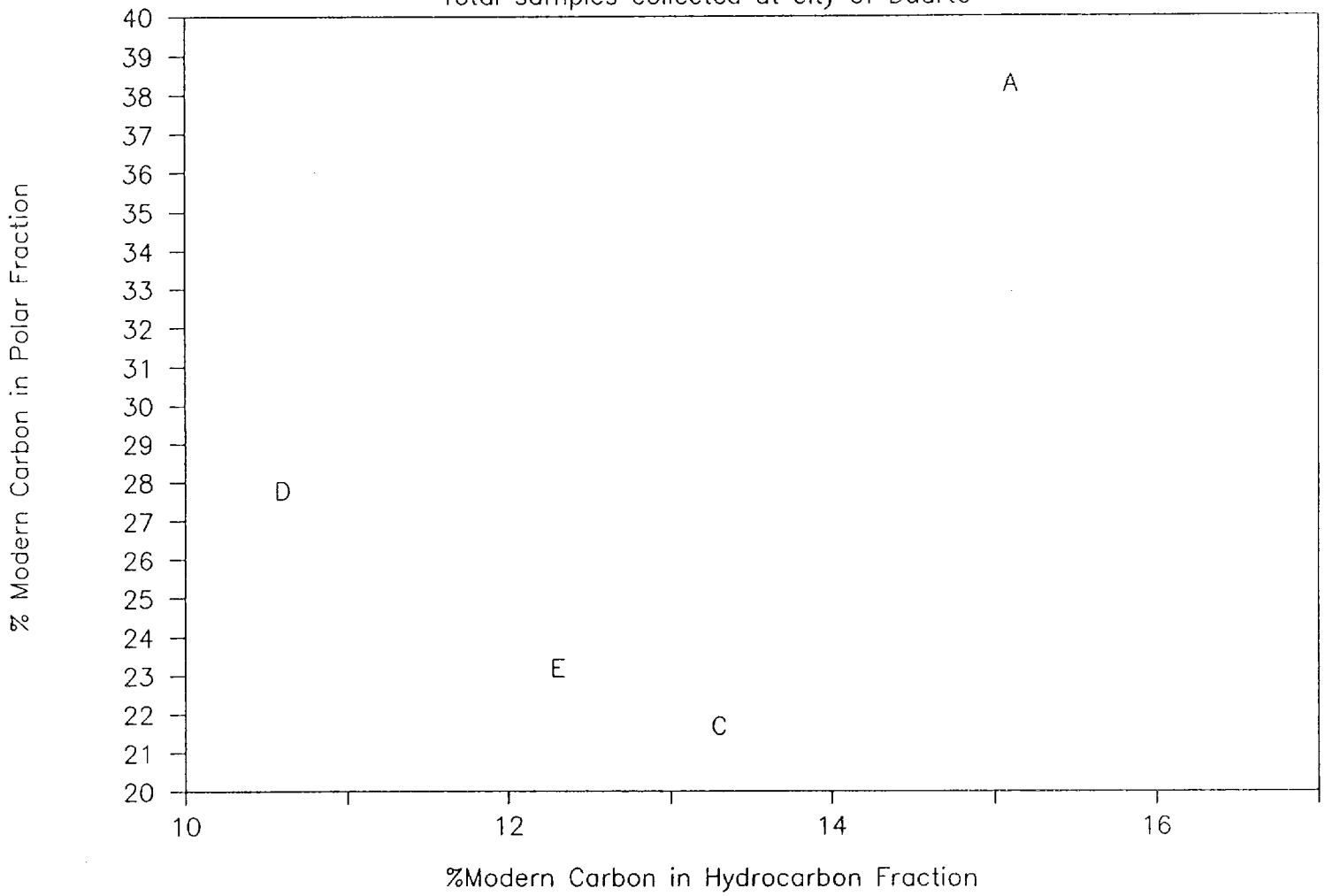


Figure XIII-25

%Modern Carbon : Hydrocarbon v Polar Fractions

Total samples collected at city of Duarte



Key

Filter No.	Sampling Date	Sampling Time
A 8006	13/08/86	0830-1230
A 8018	14/08/86	0830-1230
B 8015	13/08/86	2030-0830
C 8010	13/08/86	1230-2030
C 8025	15/08/86	1230-2030
D 8041	17/08/86	1200-2000
E 8053	19/08/86	1200-2000
E 8059	20/08/86	1200-2000

} combined samples

Figure XIII-26

%Modern Carbon : Hydrocarbon vs. Residual Fractions

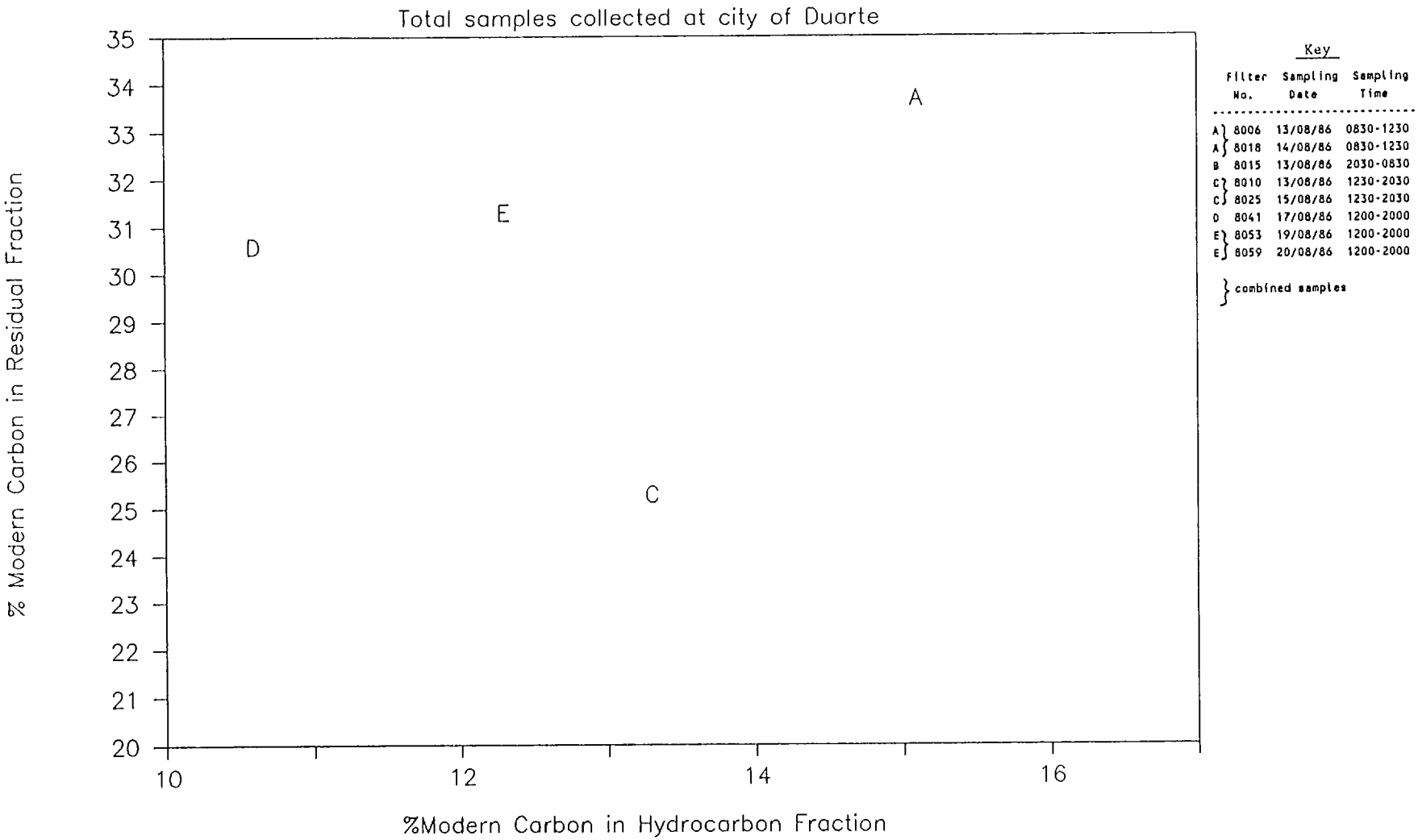


Figure XIII-27

%Modern Carbon : Residual vs. Polar Fractions

Total samples collected at city of Duarte

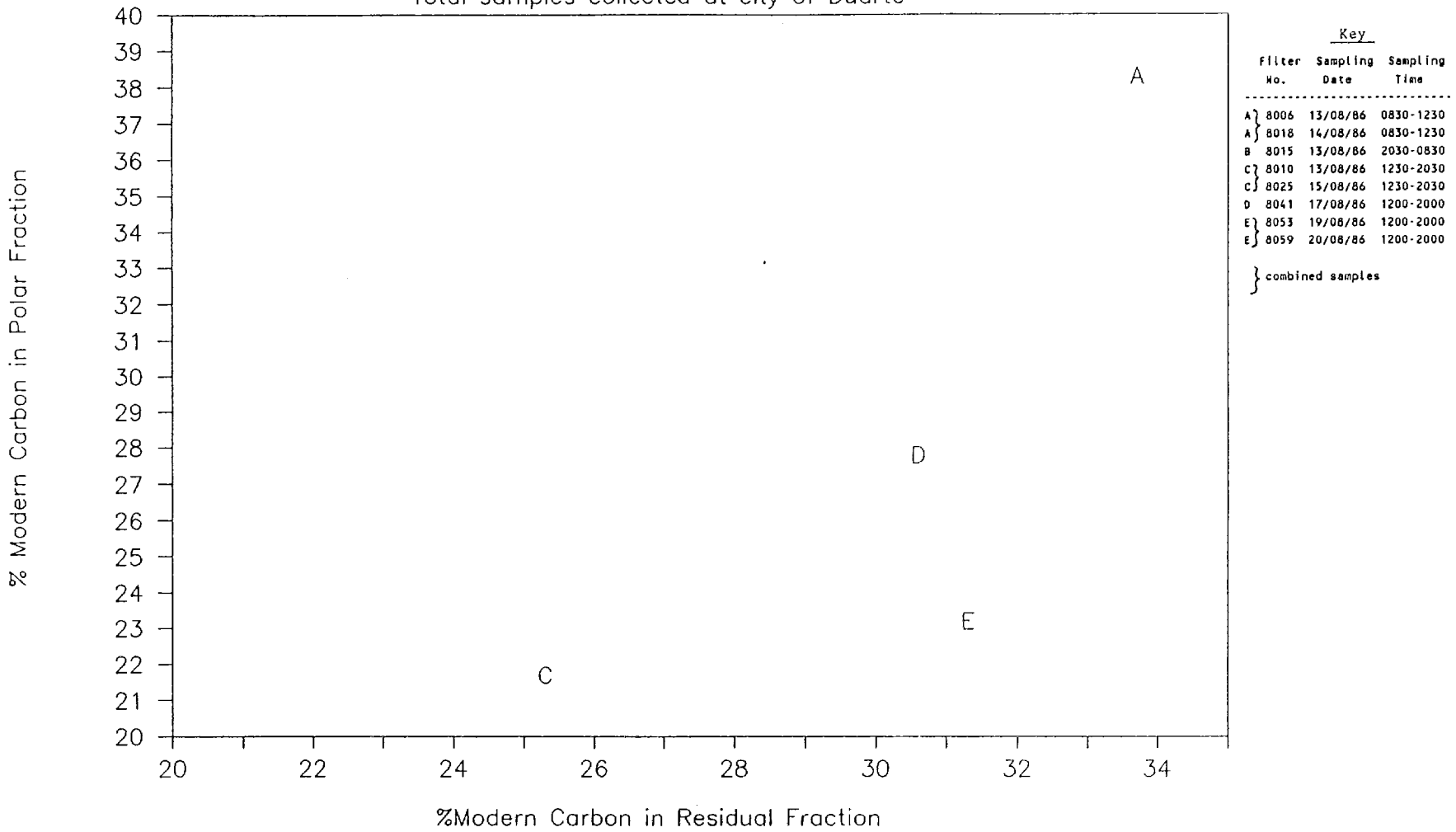


Figure XIII-28

Hydrocarbon Fraction Concentration vs. % Modern Carbon

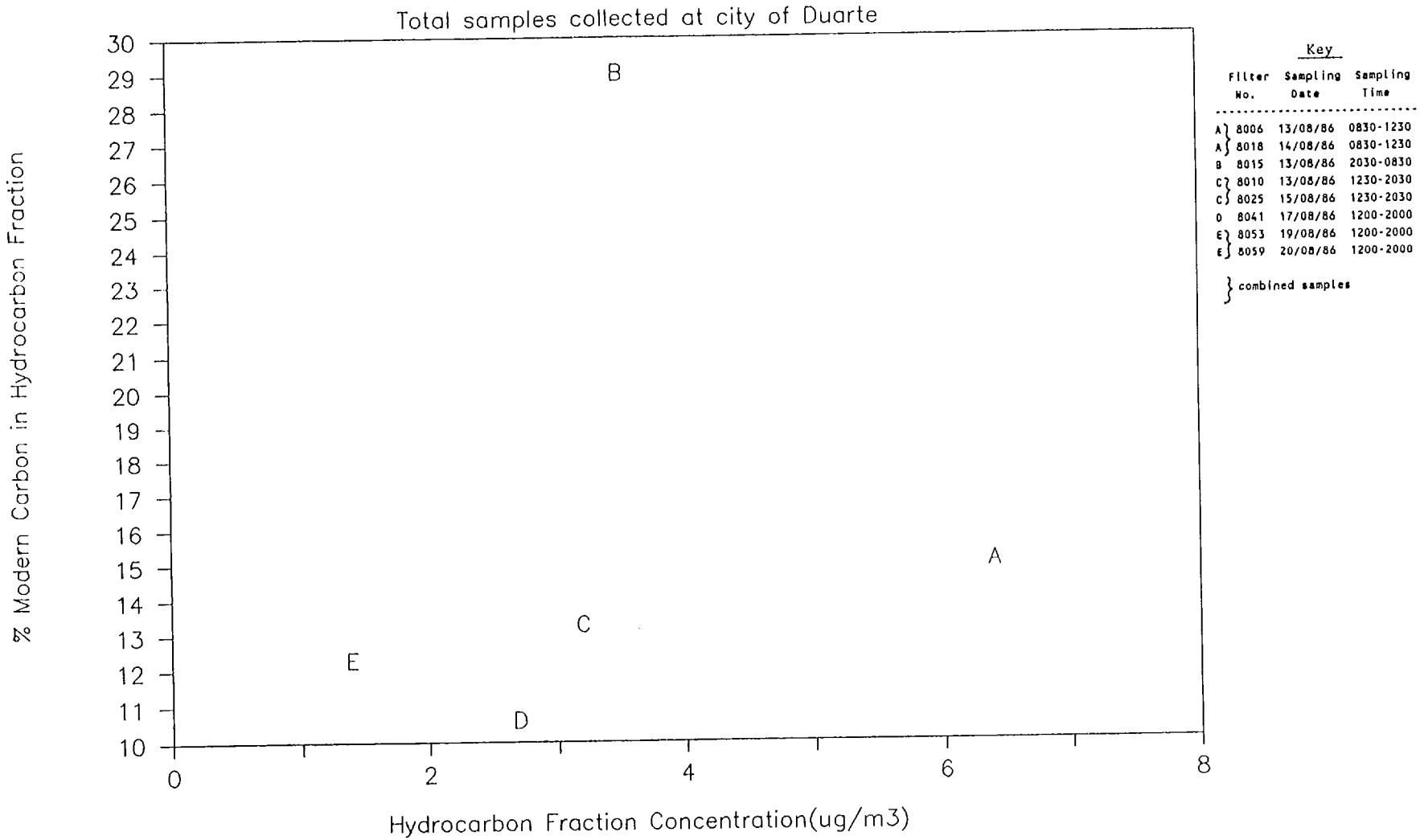


Figure XIII-29

Hydrocarbon Fraction Concentration vs.% Modern Carbon

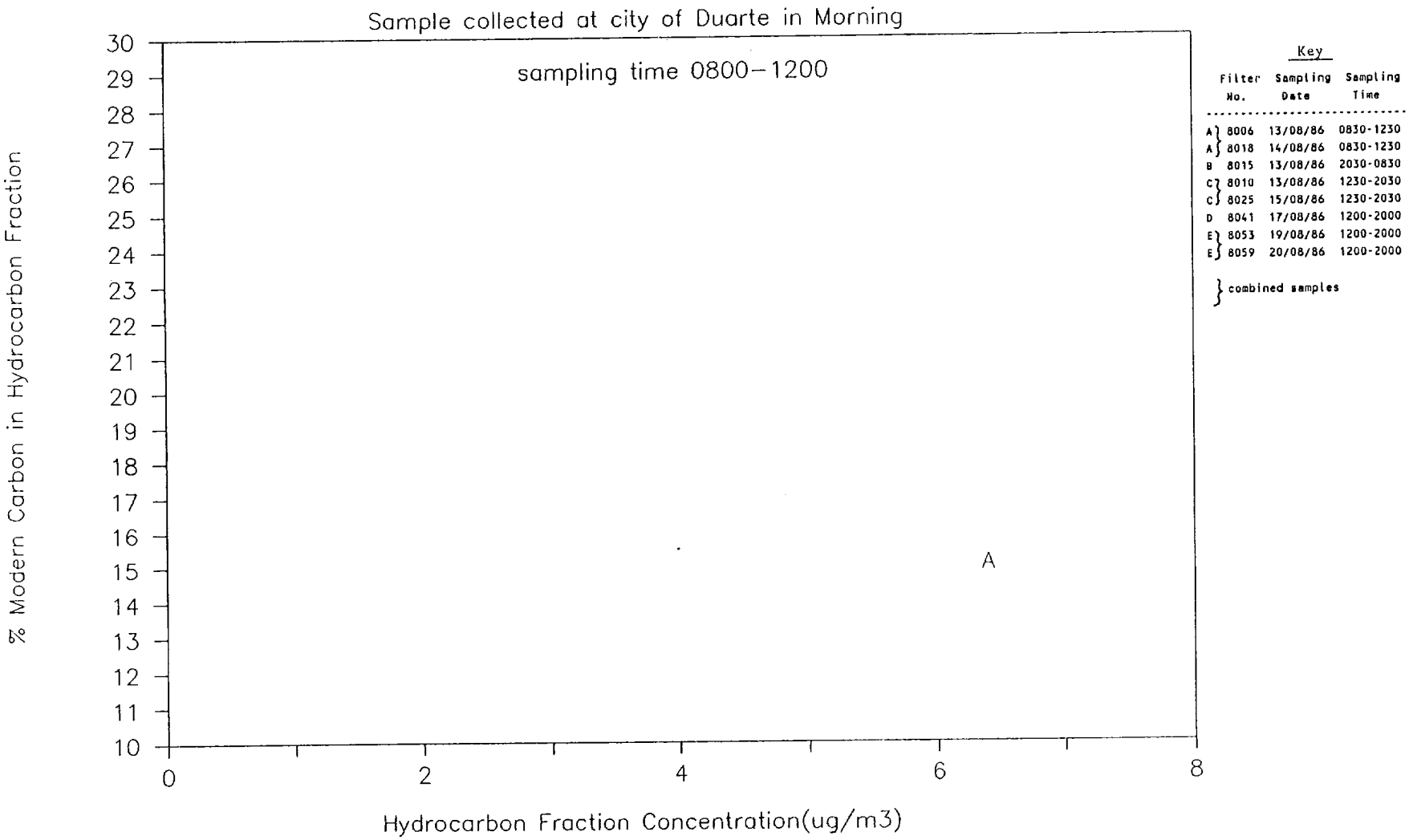
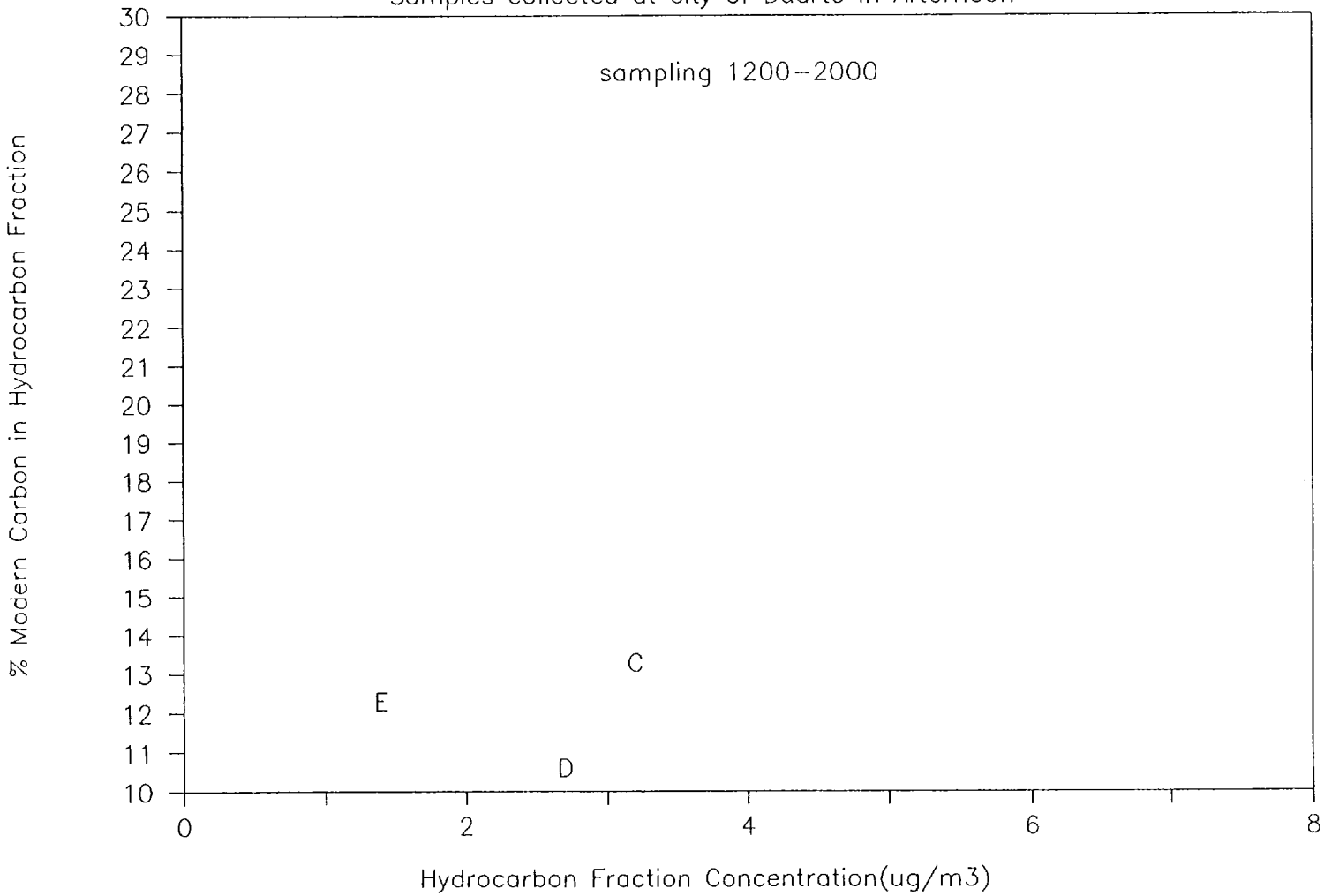


Figure XIII-30

Hydrocarbon Fraction Concentration vs. % Modern Carbon

Samples collected at city of Duarte in Afternoon



Key

	Filter No.	Sampling Date	Sampling Time
A	8006	13/08/86	0830-1230
A	8018	14/08/86	0830-1230
B	8015	13/08/86	2030-0830
C	8010	13/08/86	1230-2030
C	8025	15/08/86	1230-2030
D	8041	17/08/86	1200-2000
E	8053	19/08/86	1200-2000
E	8059	20/08/86	1200-2000

} combined samples

Figure XIII-31

Polar Fraction Concentration vs. % Modern Carbon

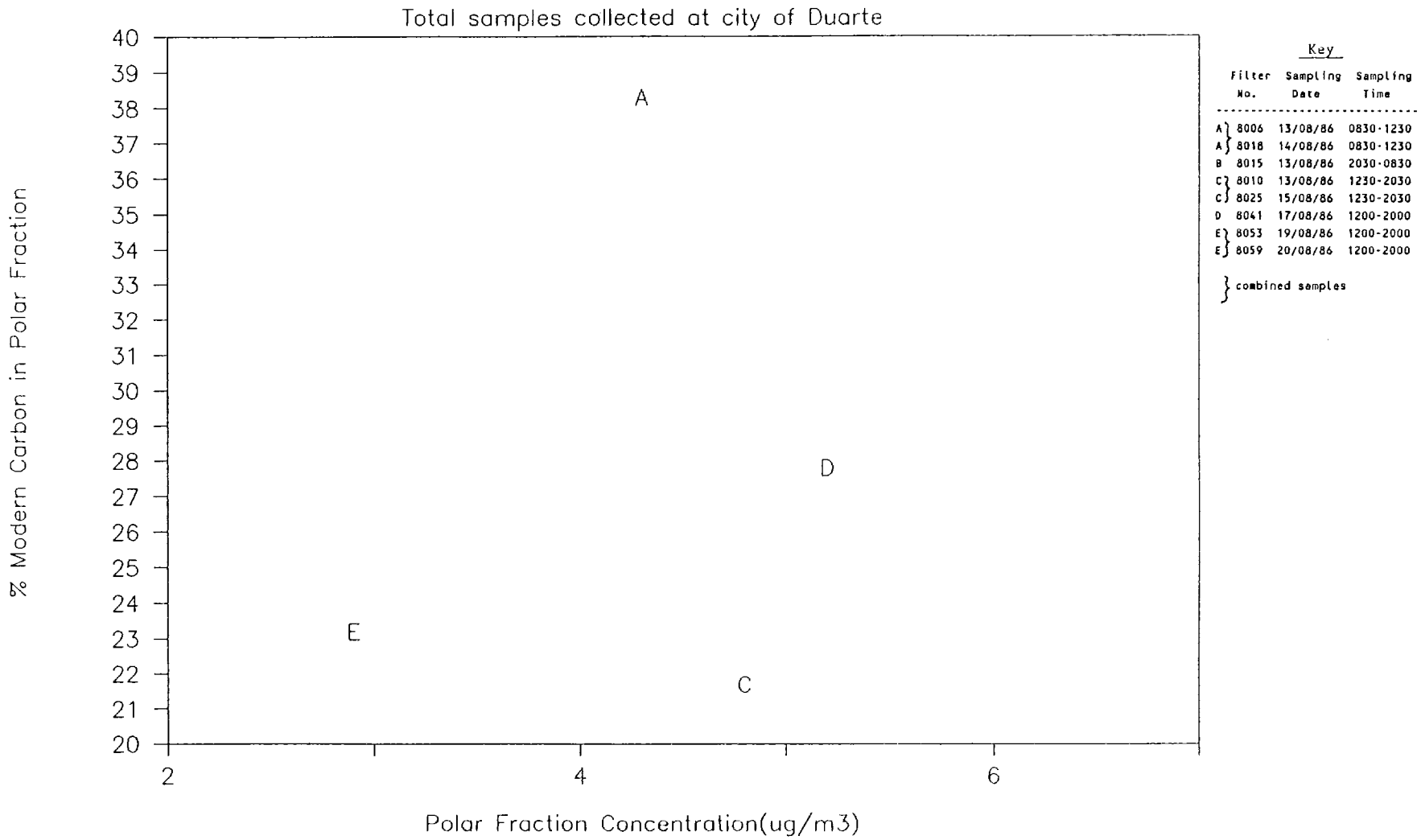


Figure XIII-32

Polar Fraction Concentration vs. % Modern Carbon

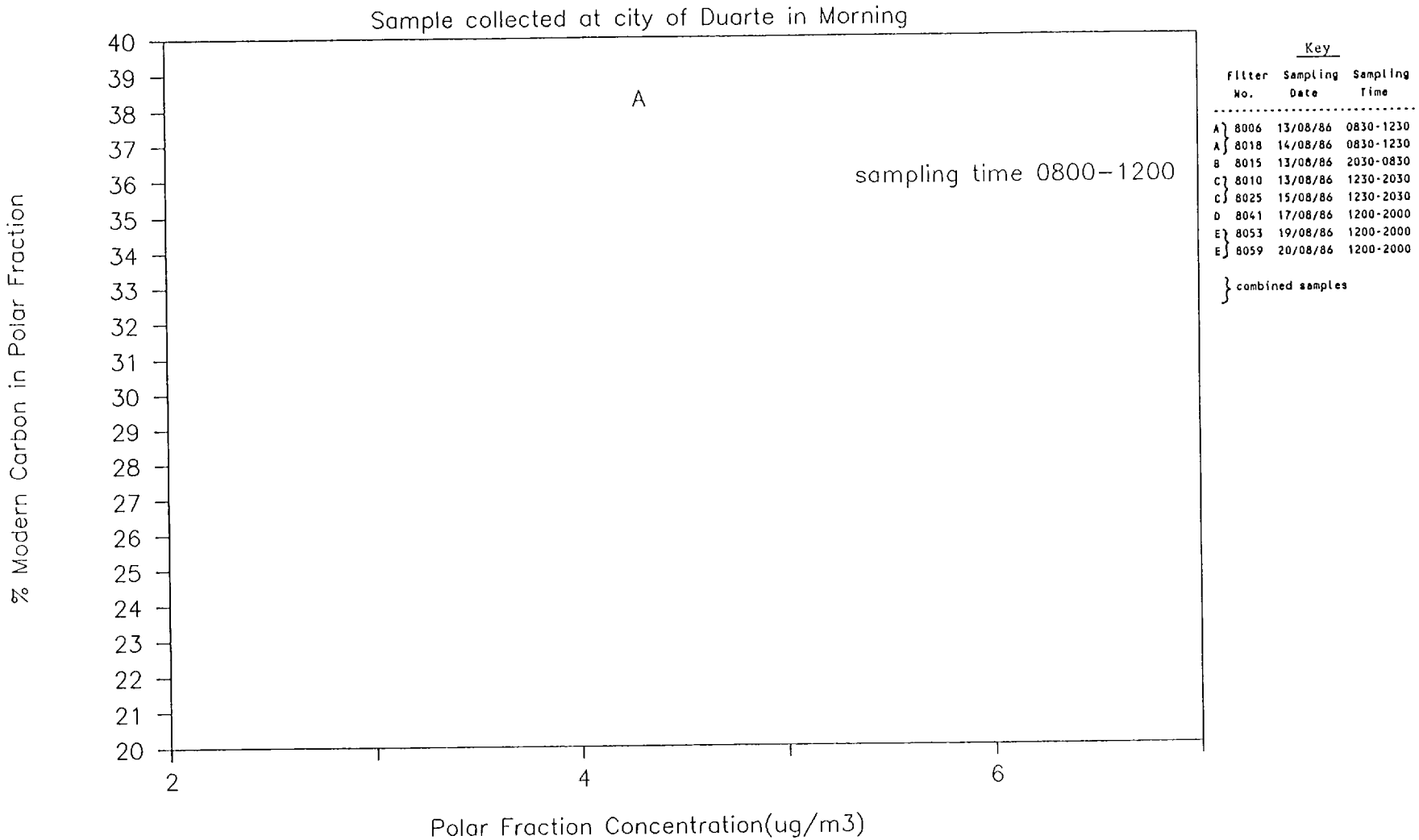


Figure XIII-33

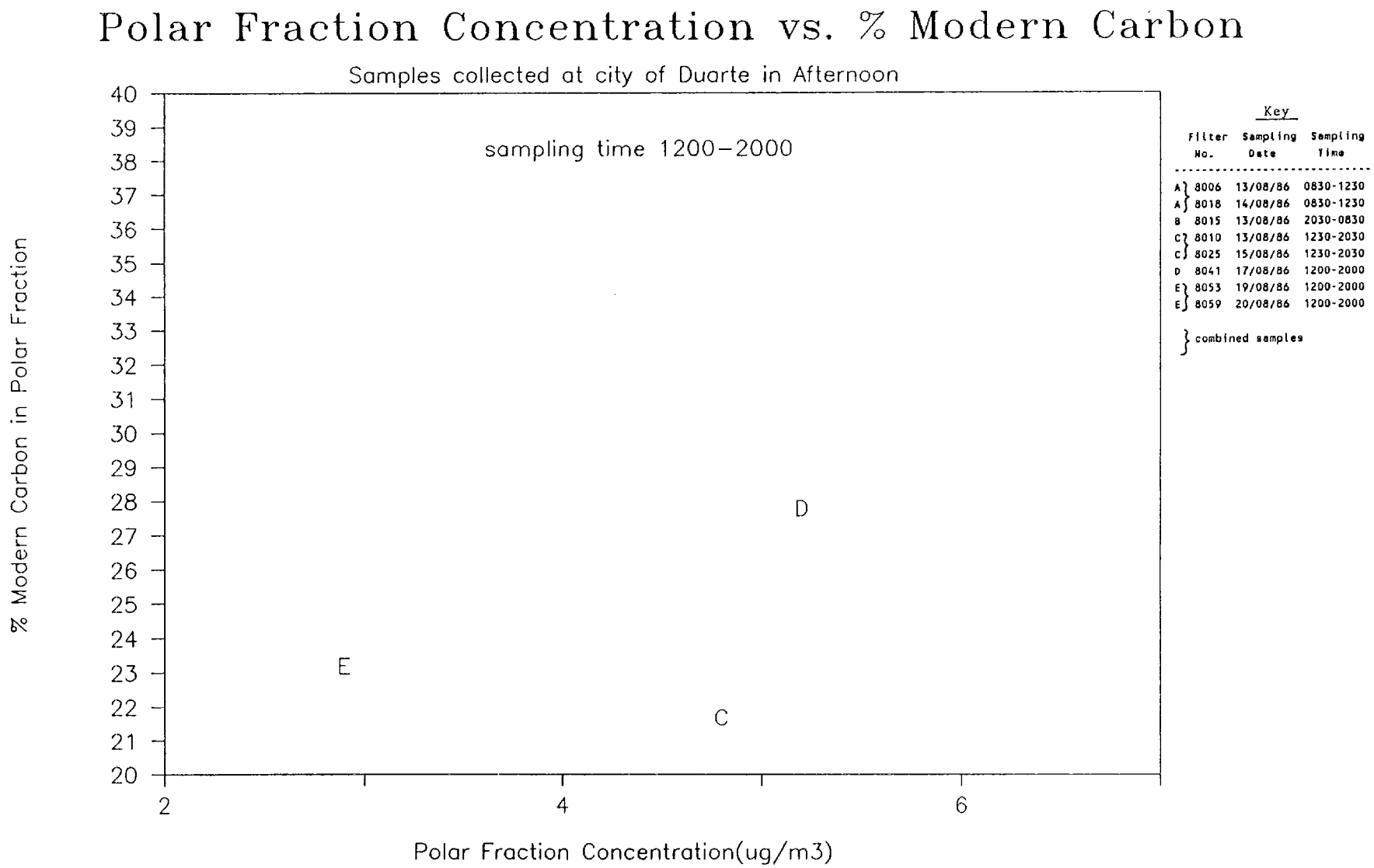


Figure XIII-34

Residual Fraction Concentration vs. % Modern Carbon

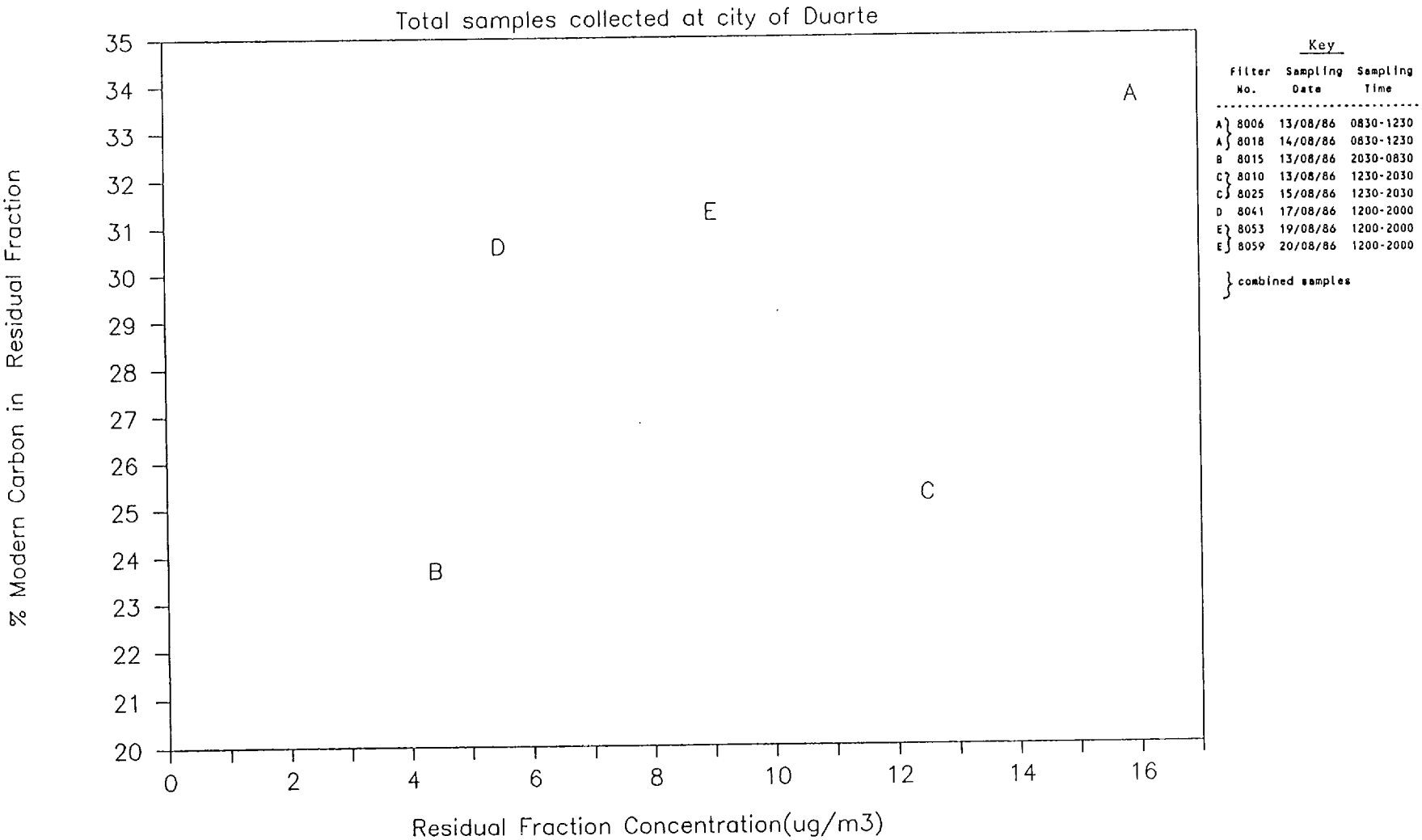
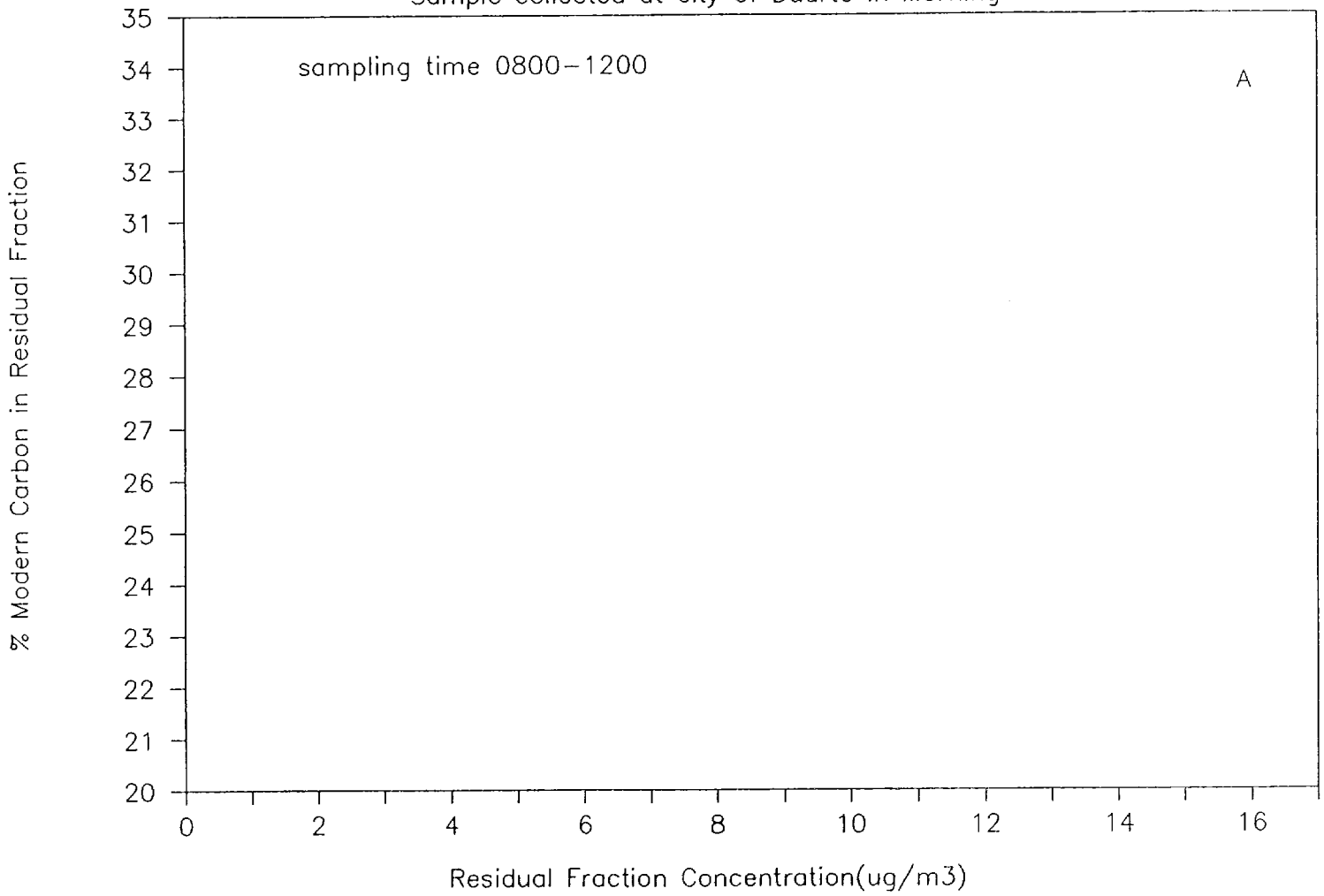


Figure XIII-35

Residual Fraction Concentration vs. % Modern Carbon

Sample collected at city of Duarte in Morning



Key

	Filter No.	Sampling Date	Sampling Time
A	8006	13/08/86	0830-1230
A	8018	14/08/86	0830-1230
B	8015	13/08/86	2030-0830
C	8010	13/08/86	1230-2030
C	8025	15/08/86	1230-2030
D	8041	17/08/86	1200-2000
E	8053	19/08/86	1200-2000
E	8059	20/08/86	1200-2000

} combined samples

Figure XIII-36

Residual Fraction Concentration vs. % Modern Carbon

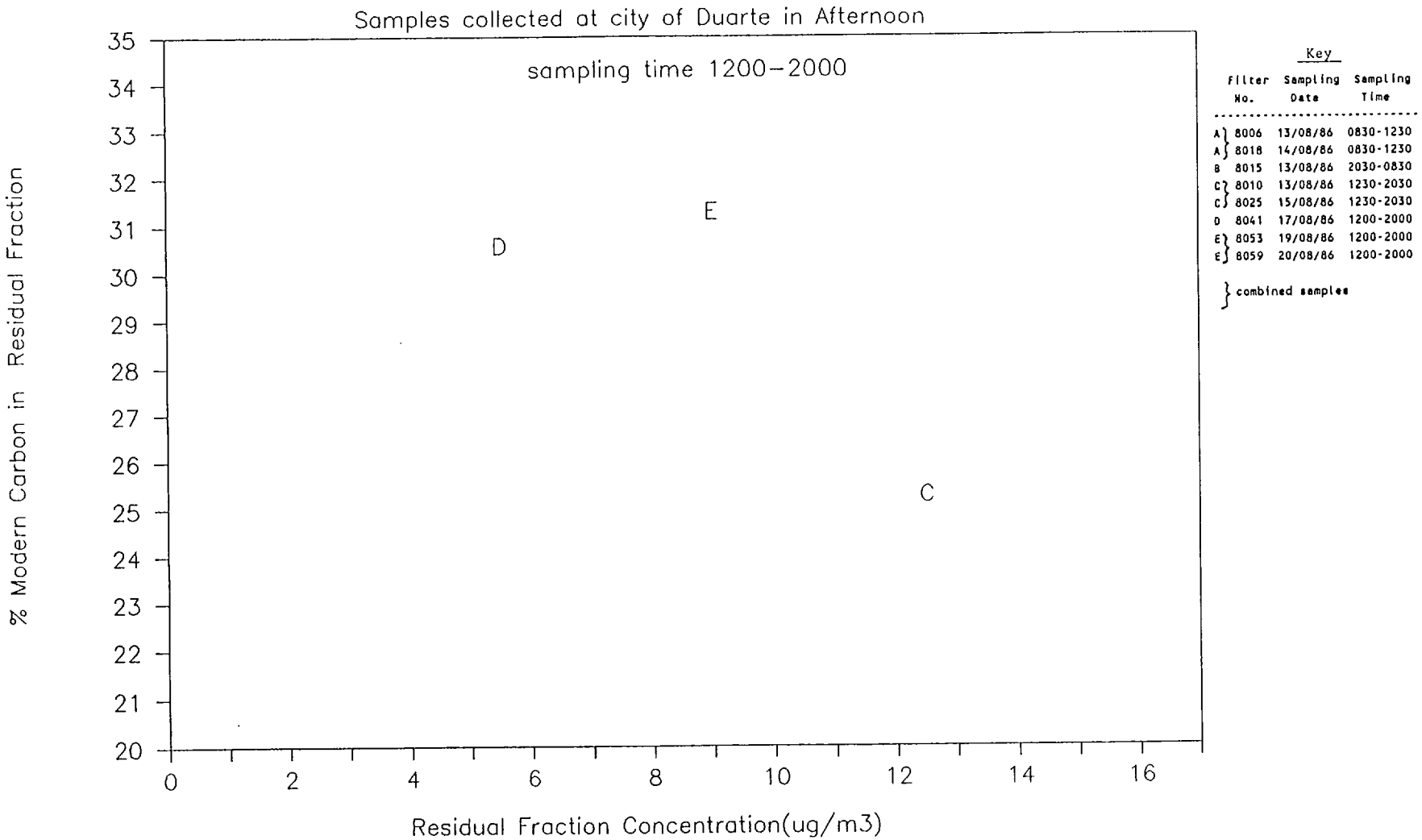


Figure XIII-37

%Modern Carbon:Hydrocarbon vs Polar Fractions

Samples collected at Coldecott Tunnel

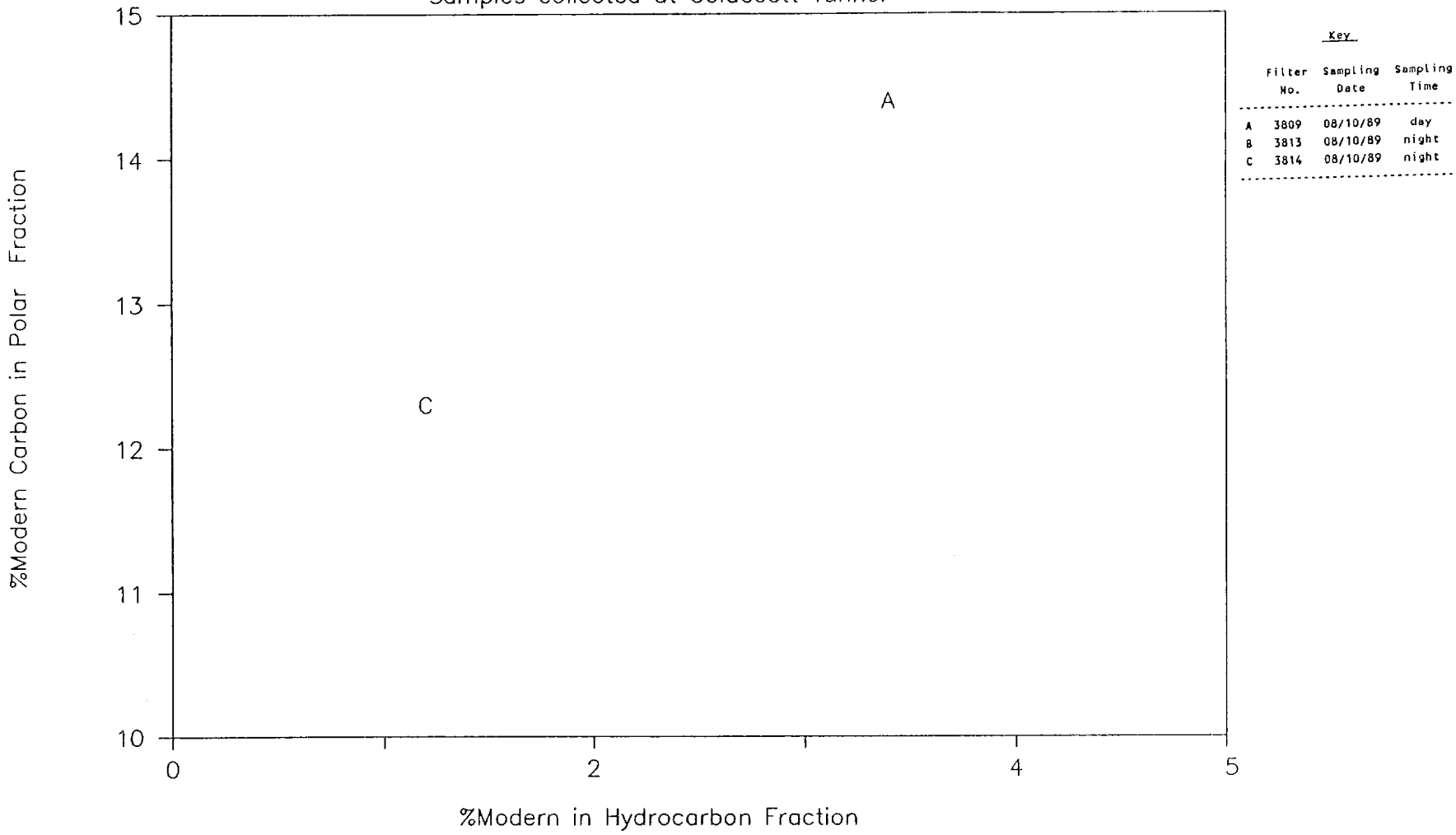


Figure XIII-38

%Modern Carbon: Hydrocarbon vs. Residual Fractions

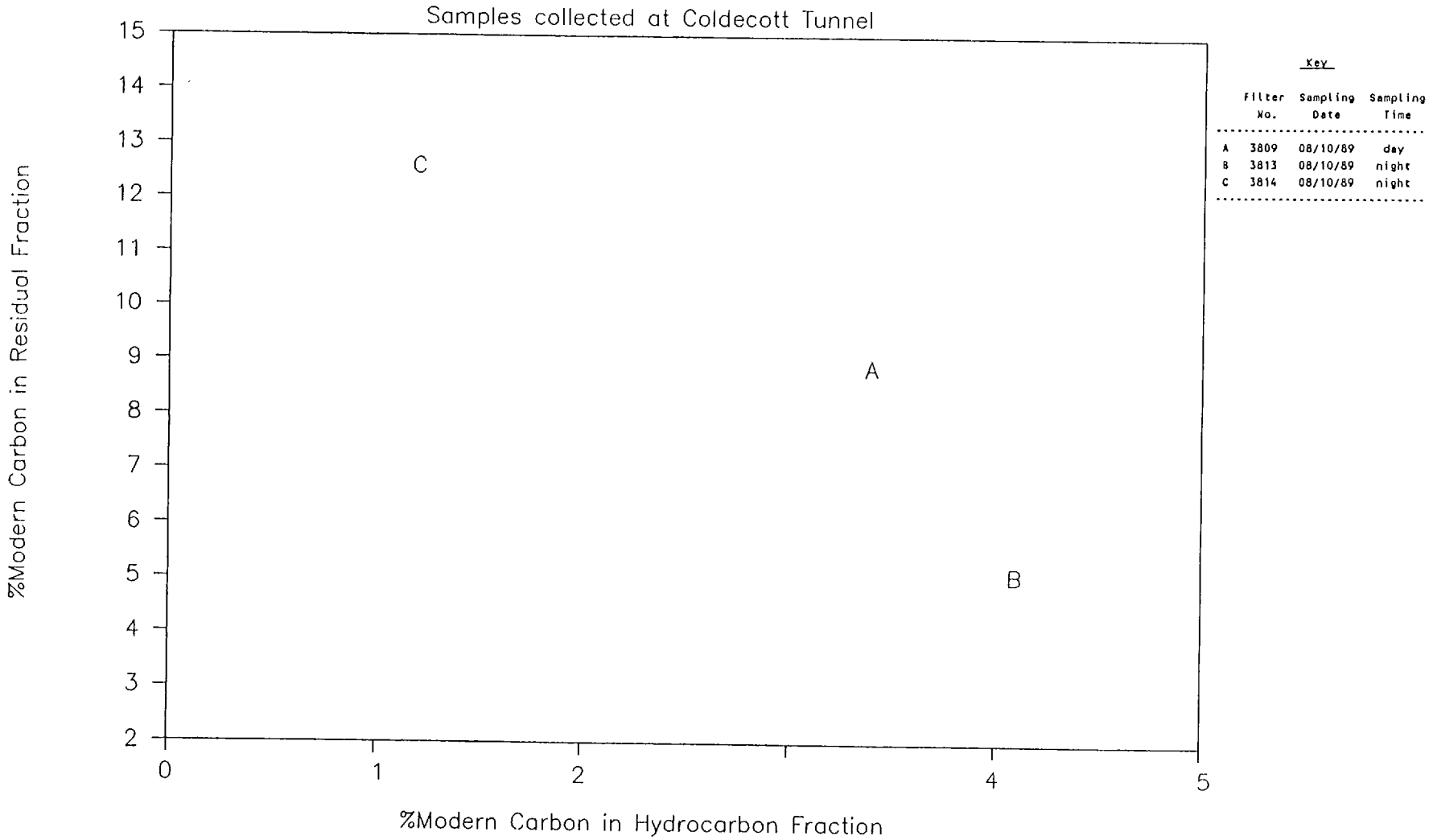


Figure XIII-39

%Modern Carbon:Polar vs. Residual Fractions

Samples collected at Coldecott Tunnel

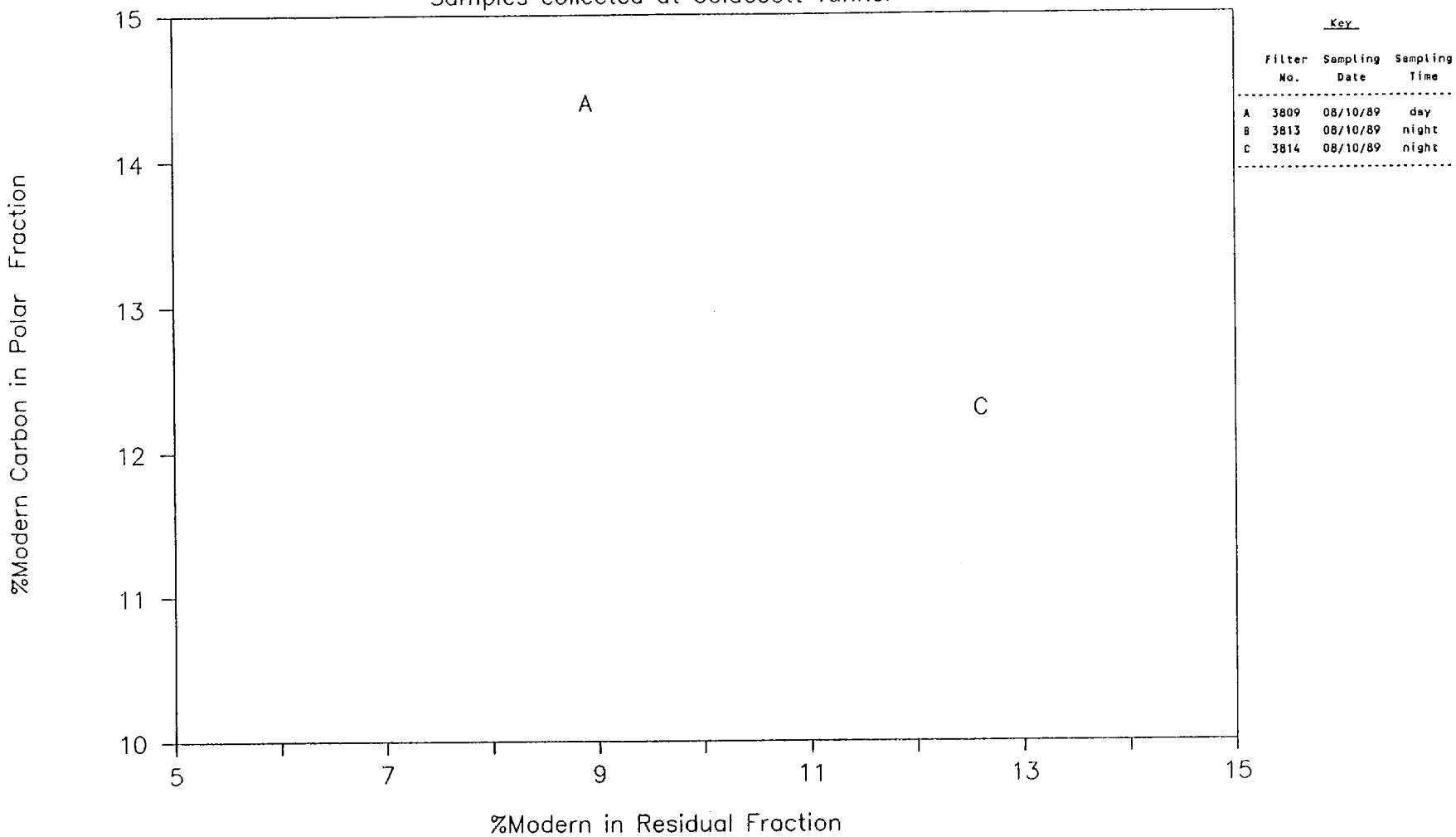
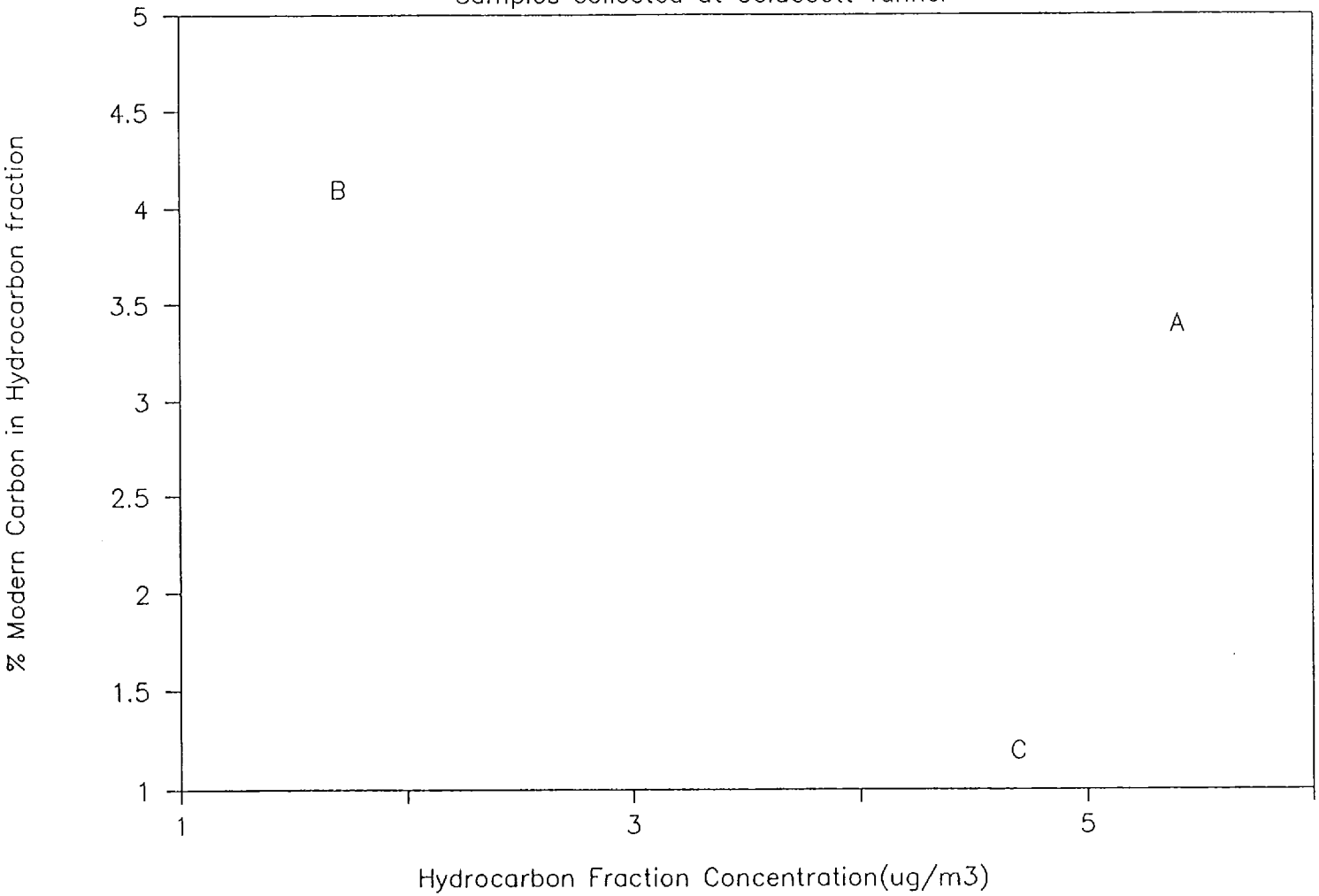


Figure XIII-40

Hydrocarbon Fraction Concentration vs. % Modern Carbon

Samples collected at Coldecott Tunnel



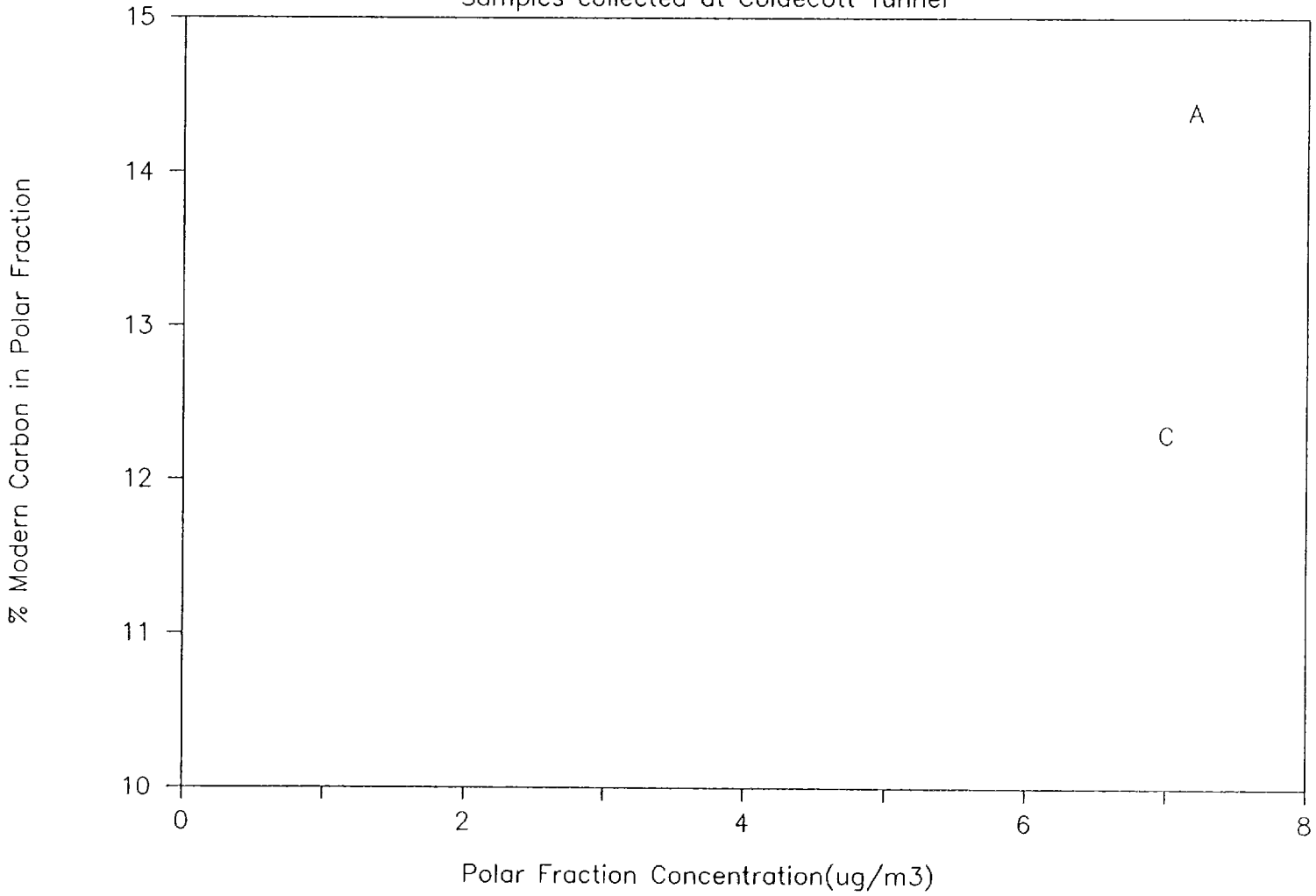
Key

	Filter No.	Sampling Date	Sampling Time
A	3809	08/10/89	day
B	3813	08/10/89	night
C	3814	08/10/89	night

Figure XIII-41

Polar Fraction Concentration vs. % Modern Carbon

Samples collected at Coldecott Tunnel

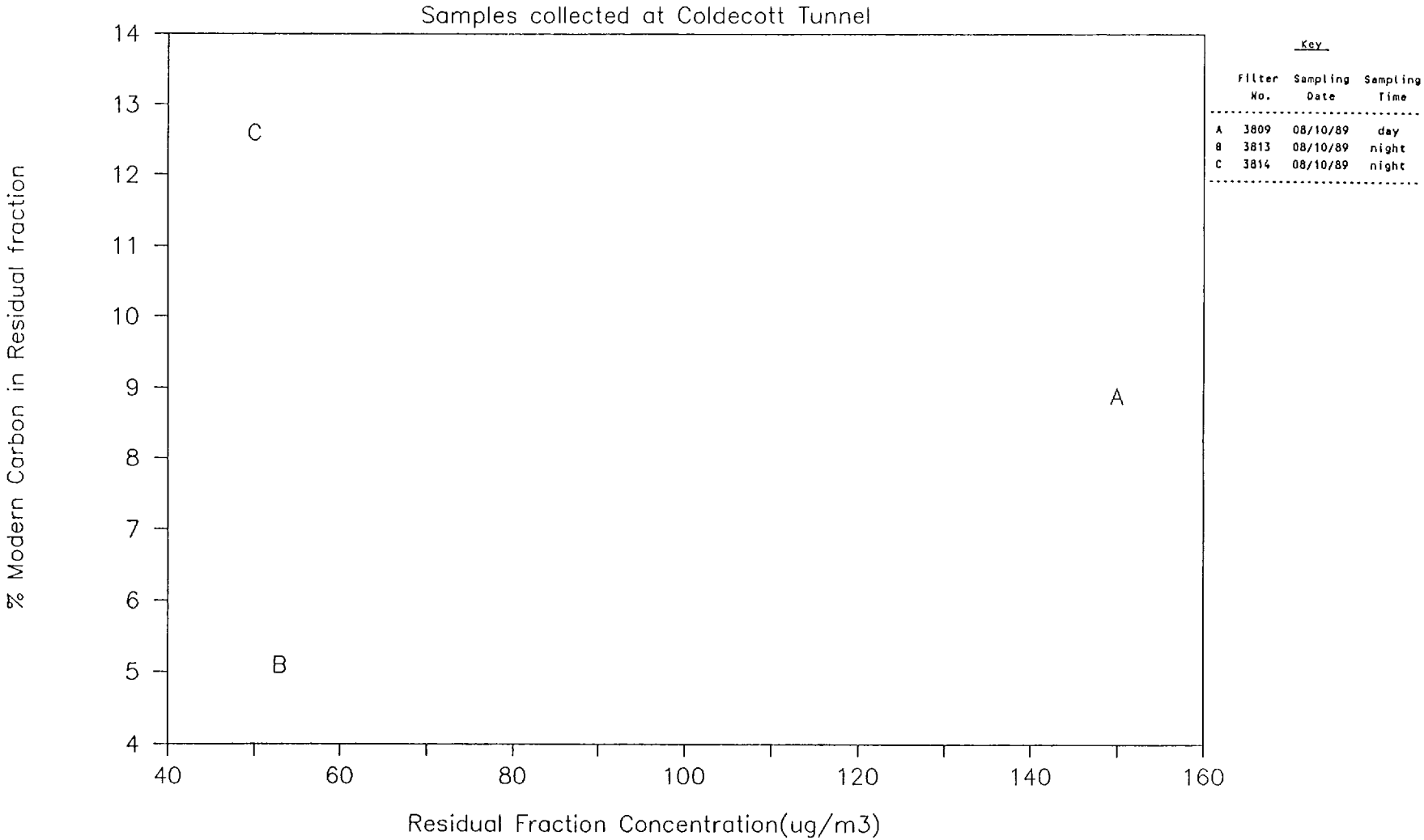


Key

	Filter No.	Sampling Date	Sampling Time
A	3809	08/10/89	day
B	3813	08/10/89	night
C	3814	08/10/89	night

Figure XIII-42

Residual Fraction Concentration vs. % Modern Carbon



of the hydrocarbon fraction (Fraction 1).

The correction was made by multiplying the percent contamination in each fraction (Table XIII-1) with the modern carbon content (38%). The factor was then applied to correct the measured value of ^{14}C modern carbon content (MC) to the corrected modern carbon content (CMC) as follows.

$$MC = (1 - y) \times CMC + f$$

or

$$CMC = \frac{MC - f}{(1 - y)}$$

In doing this, new data were generated for the corrected ^{14}C modern carbon contents of Glendora, Duarte and Caldecott Tunnel samples and are shown in Tables XIII-2 to XIII-4 and as plots in Figures XIII-43 to XIII-45. The net result of this process is to lower the modern carbon content of the hydrocarbon fraction and the polar fraction of the Glendora and Duarte day samples and slightly raise the modern carbon content of the Glendora night samples. The correction further lowers the modern carbon content of the Caldecott Tunnel samples hydrocarbon fraction to show 0% modern carbon (or 100% fossil fuel derived carbons). However, although the modern carbon content of the polar fraction was reduced to ~9.5% by applying the factor, it nevertheless still shows a significant modern carbon content which calculates out to be very close to the average uncorrected content of residual (elemental carbon) with a modern carbon content of 8.9% (Table ES-1).

Subsequent to performing this correction, new data for the compiled filter blanks (Table XII-14) were performed, showing that the blank corrections could be negligible for the hydrocarbon fraction and small for the polar fraction.

Table XIII-2. Determination of modern carbon content from D14C measurements on samples collected at city of Glendora.

Collection Date AUG 1986	Filter No.	D/N*	GGCID	Aliphatic + Aromatic		Polar		Residual
				% Modern (uncorrected)	%Modern (corrected)	% Modern (uncorrected)	%Modern (corrected)	% Modern (uncorrected)
13	8007, 8008	D	4672-20	16.1	14.2	23.5	21.7	29.8
13	8009	D	4672-12	9.9	7.5	23.3	21.5	35.0
14/15	8017, 8027	D	4672-19	14.5	12.5	41.6	42.1	37.9
14	8019	D	4672-2	14.2	12.2	23.5	21.7	29.4
14	8020	D	4672-7	10.9	8.6	23.8	22.1	31.8
15	8026,8029	D	4672-18	16.4	14.5	26.9	25.6	----**
16	8033,8036	D	4672-15	17.4	15.6	29.4	28.4	30.6
17	8043,8044	D	4672-14	23.1	21.8	25.5	24.0	33.9
18/19	8047,8051	D	4672-30	13.3	11.2	35.4	35.1	35.1
18	8048,8049	D	4672-17	22.9	21.6	Lost	----	36.7
19	8054,8055	D	4672-28	18.7	17.0	27.5	26.2	Lost
20	8057,8058	D	4672-29	14.5	12.5	36.0	35.8	30.5
20	8060,8061	D	4672-27	19.5	17.9	----*	----	31.9
13	8013,8014	N	4672-21	21.3	19.9	51.7	53.4	24.8
14	8024	N	4672-8	13.1	11.0	48.3	49.6	30.1
15	8031	N	4672-10	13.1	11.0	46.7	47.8	Lost
16	8037	N	4672-11	Lost	----	40.1	40.4	33.3
17	8045	N	4672-9	13.8	11.7	46.7	47.8	35.5
18	8050	N	4672-4	20.6	19.1	40.7	41.1	42.7
19	8056	N	4672-3	27.3	26.4	47.2	48.4	37.4

* D = day, N - night

** Removed by statistical screening

Table XIII-3. Determination of modern carbon content from D14C measurements on samples collected at city of Duarte.

Collection Date (AUG 1986)	Filter No.	D/N*	GGC ID	Aliphatic + Aromatic		Polar		Residual
				% Modern (uncorrected)	% Modern (corrected)	% Modern (uncorrected)	% Modern (corrected)	% Modern (uncorrected)
13/14	8006,8018	D	4672-22	15.1	13.1	38.3	38.4	33.7
13/15	8010,8025	D	4672-32	13.3	11.2	21.7	19.7	25.3
17	8041	D	4672-24	10.6	8.2	27.8	26.6	30.6
19/20	8053,8059	D	4672-23	12.3	10.1	23.2	21.4	31.3
13	8015	N	4672-31	29.0	28.2	Lost	----	23.7

Table XIII-4. Determination of modern carbon content from D14C measurements on samples collected at Caldecott Tunnel.

Collection Date (AUG 1986)	Filter No.	D/N*	GGC ID	Aliphatic + Aromatic		Polar		Residual
				% Modern (uncorrected)	%Modern (corrected)	% Modern (uncorrected)	%Modern (corrected)	% Modern (uncorrected)
10	3809	D	4672-1	3.4	0	14.4	9.5	8.9
10	3813	N	4672-6	4.1	0	Lost	---	5.1
10	3814	N	4672-41	1.2	0	12.3	9.4	12.6

* D = day; N = night

Figure XIII-43

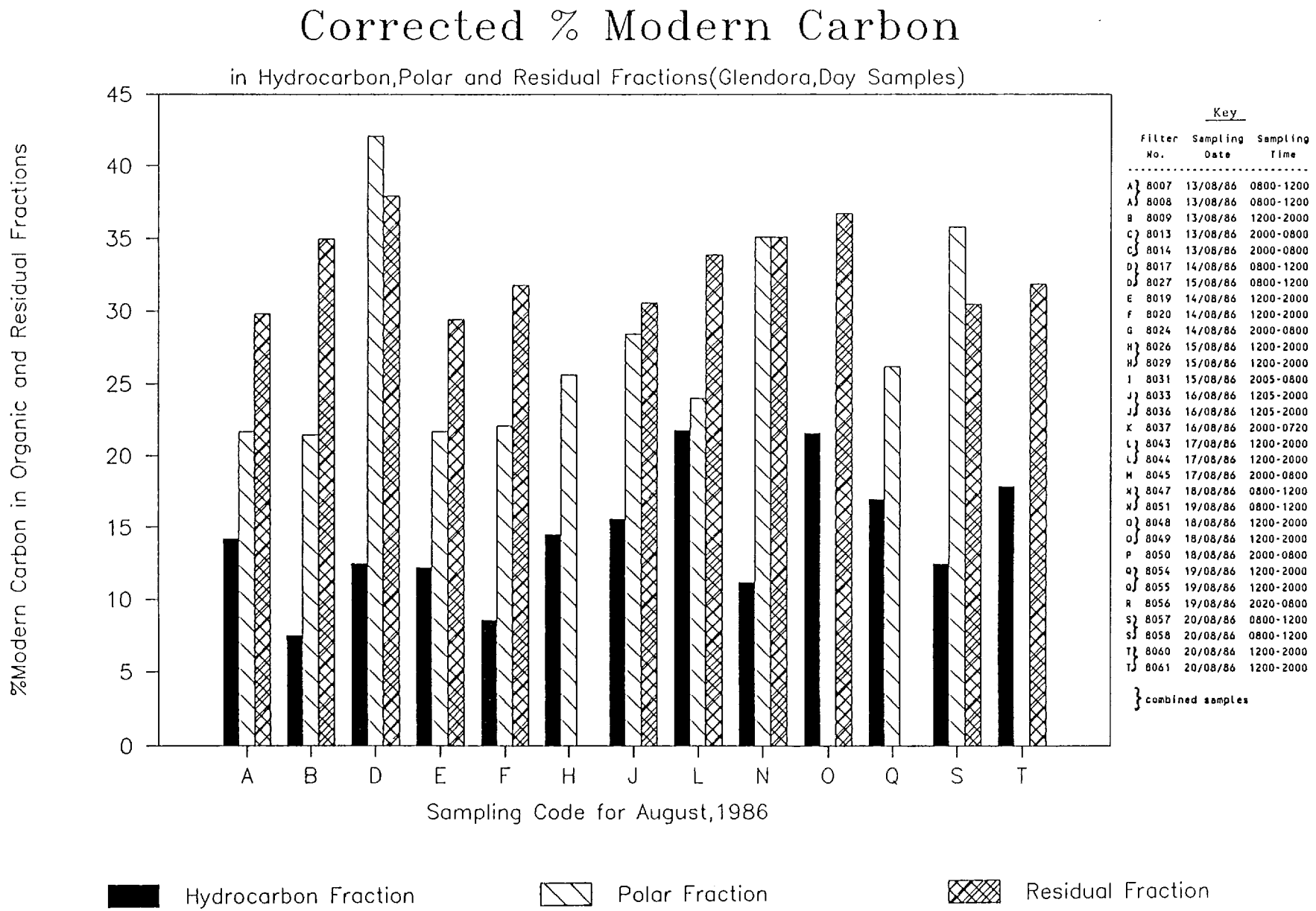


Figure XIII-44

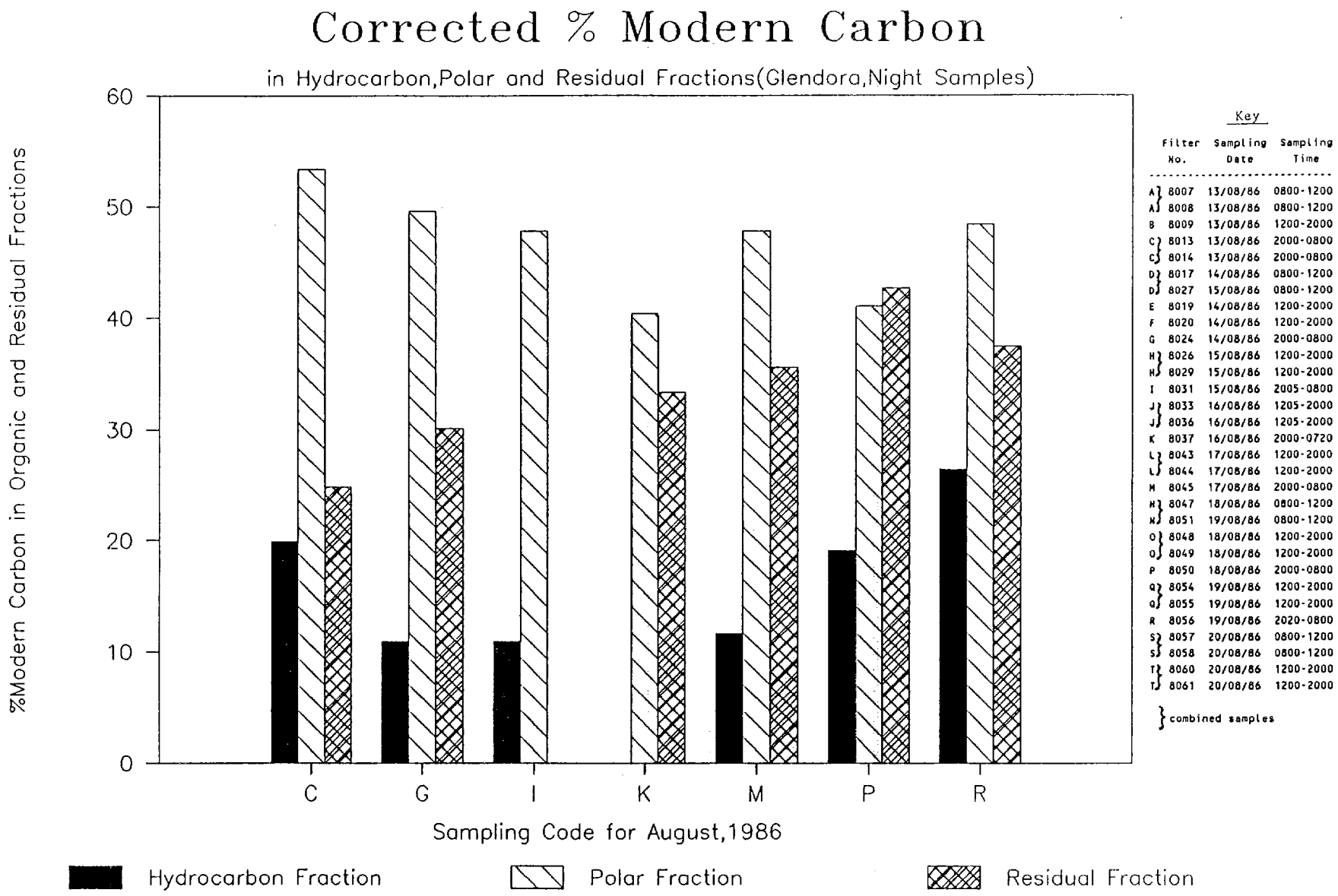
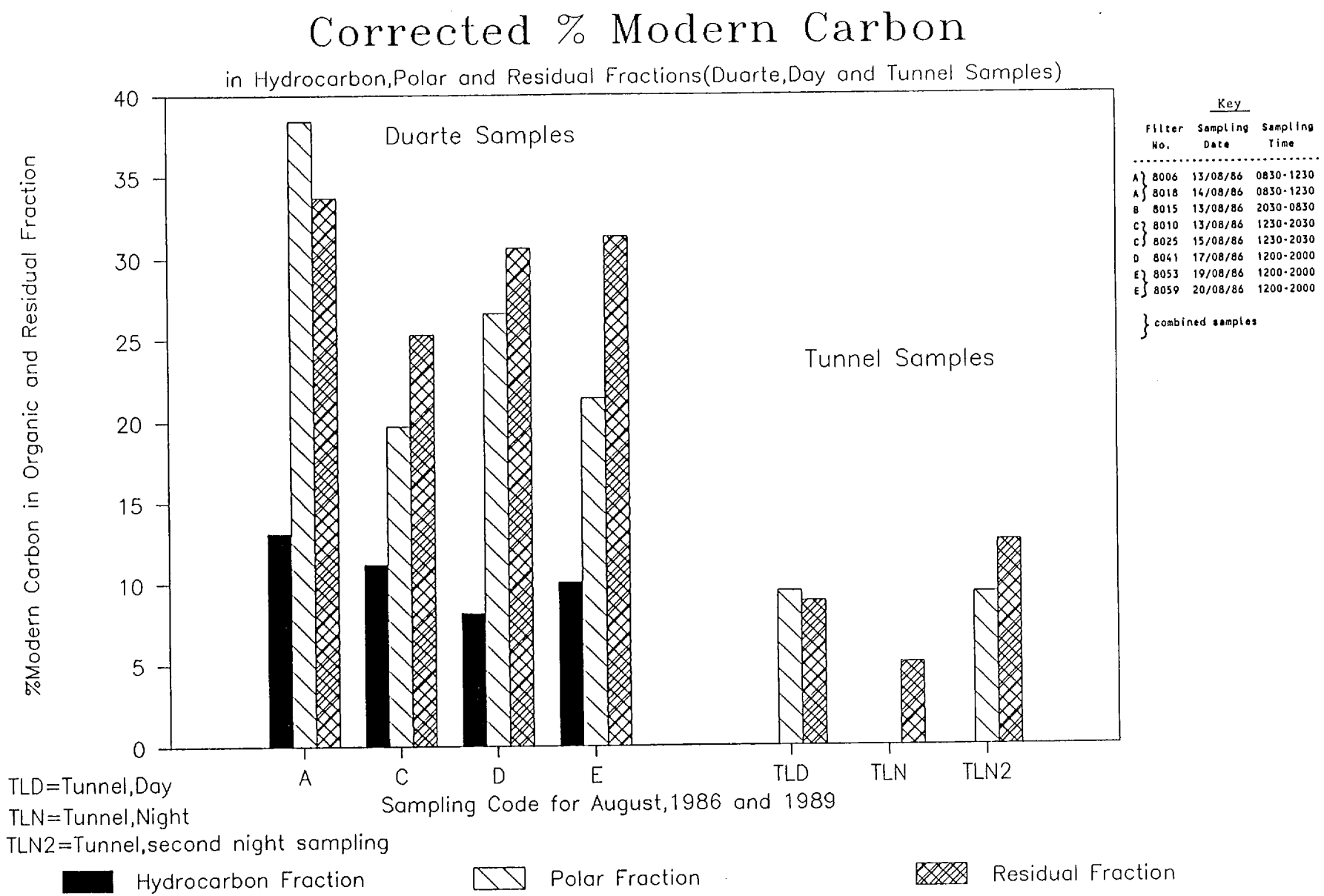


Figure XIII-45



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