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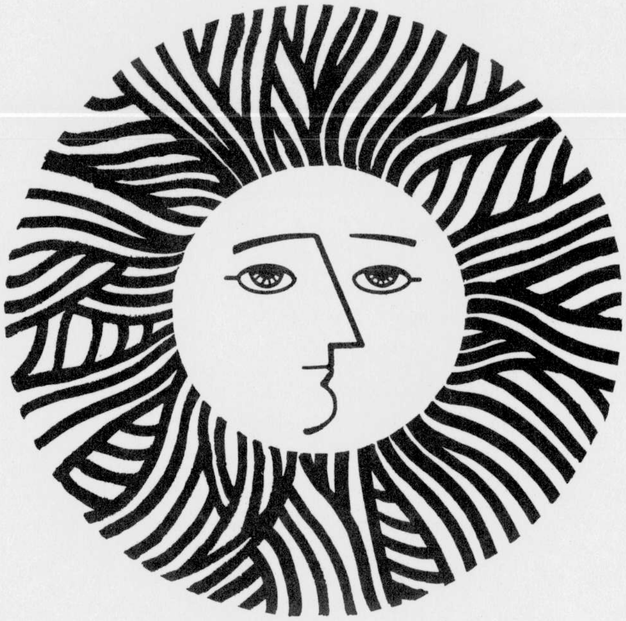
MICROCHEMICAL CHARACTERIZATION OF AEROSOLS

T. Novakov

October 1980



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MICROCHEMICAL CHARACTERIZATION OF AEROSOLS*

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Introduction

The main purpose of chemical characterization of aerosol particles is to provide information about their chemical composition. This information should ultimately help in identifying their sources, formation mechanisms, and fate in the atmosphere.

Carbon-, sulfur-, and nitrogen-containing particles account for most of the anthropogenically generated particulate burden in urban areas. Considerable attention has been given to understanding the origin and speciation of the sulfur and nitrogen components, but until recently relatively little effort has been directed toward the carbonaceous aerosol, which is often the single most important contributor to the submicron aerosol mass. The objective of ~~this paper is to outline~~ a methodology developed in our laboratory to quantitate the amounts of different classes of carbonaceous particulates collected at various urban locations in the United States. The analysis of the results provides an assessment of the relative amounts of primary and secondary particulate carbon at these locations.

Carbonaceous particles in the atmosphere consist of two major components — graphitic or black carbon (sometimes referred to as elemental or free carbon) and organic material. The latter can be either directly emitted from sources (primary organics) or produced by atmospheric reactions from gaseous precursors (secondary organics). For the sake of clarity, we define soot as the total primary carbonaceous material, i.e., the sum of graphitic carbon and primary organics.

Black carbon can be produced only in a combustion process and is therefore definitely primary. Because of this, black carbon can be used as a tracer for primary carbonaceous particles. The problem of differentiating the primary and secondary components would be simple if black carbon were the only primary component. However, because many sources besides black carbon produce substantial amounts of primary organic material, the differentiation of these two components can be achieved only by a systematic study of large numbers of samples collected directly from sources, source-dominated environments, and well-aged ambient air. The ambient samples should also be collected in areas with widely different atmospheric chemical characteristics (e.g., degree of photochemical activity).

Two approaches have been used in our studies. The first essentially involves a systematic study of 24-hr average black carbon to total carbon ratios, since measurements of this ratio from a number of source samples give insights into the relative black to total carbon ratio of primary emissions and the source variabilities. Secondary material will not contain the black component, but it will increase the total mass of carbon and will therefore reduce the black to total carbon fraction.

For example, photochemical gas to particle conversion reactions should be most pronounced in the summer in the Los Angeles air basin, while in the winter these reactions should play a much smaller role and the primary component should be much more important. These different photochemical conditions should manifest themselves in the ratio of the black carbon to total carbon of these particles. That is, under high photochemical conditions one would expect this ratio to be significantly smaller than under conditions obviously heavily influenced by sources.

This approach to the identification and quantitation of primary and secondary carbonaceous aerosols involves a systematic comparison of particulates collected from a wide range of ambient sites as well as combustion sources. Ambient particulates are sampled at sites that differ significantly in meteorology, photochemical activity, and source composition. Source samples have been obtained at a tunnel and a parking garage, and from direct source samplings.

The second approach in our studies relies on the evolved gas (CO_2) thermal analysis method as a means of "fingerprinting" the organic and black carbon components of source emissions, source-enriched samples, and ambient particles. The differences between these should correspond to the secondary component.

Methods

In our field experiments the samples are collected in parallel on prefired quartz fiber and Millipore filter membranes. The Millipore filter is used for X-ray fluorescence (XRF) elemental analysis and for the LBL laser transmission technique [1]. The latter technique gives a measurement that is proportional to the amount of light-absorbing (black) carbon present on the filter. The quartz filter is used for total carbon determination by a combustion method similar to that described by Mueller et al. [2].

A schematic representation of the LBL laser transmission (optical attenuation) apparatus is shown in Fig. 1. This apparatus compares the transmission of a 633-nm He-Ne laser beam through a loaded filter relative to that of a blank filter. The loaded filters are placed in the beam with the loaded side towards the laser; after multiple scattering through the filter substrate, the light is collected by an f/1 lens and focused on a photomultiplier tube. The data presented in this paper were obtained from particles collected on Millipore filters. This technique is based on a principle similar to that of the opal glass method used by Weiss et al. [3] and measures the absorbing, rather than the scattering, properties of the aerosol. The relationship between the optical attenuation and the black carbon content can be written as:

$$[C_{black}] = (1/K) \times ATN \text{ ,} \tag{1}$$

where ATN = -100 $\ln(I/I_0)$. I and I_0 are the transmitted light intensities for the loaded filter and for the filter blank.

Besides the black carbon, particulate material also contains organic material which is not optically absorbing. The total amount of particulate carbon is then:

$$[C_{tot}] = [C_{black}] + [C_{org}] \text{ .} \tag{2}$$

We define specific attenuation (σ) as the attenuation per unit mass of total carbon:

$$\sigma \equiv \frac{ATN}{[C_{tot}]} = K \times [C_{black}]/[C_{tot}] \text{ .} \tag{3}$$

The determination of specific attenuation therefore gives an estimate of black carbon as a fraction of total carbon.

The proportionality constant K, which is equal to the specific attenuation of black carbon alone, was recently shown to have an average value of 20 [4]. In principle the percentage of soot (i.e., primary carbonaceous material) in ambient particles can be determined from the ratio of ambient specific attenuation and an average specific attenuation of major primary sources:

$$[Soot]/C = \sigma_{ambient}/\sigma_{source} \text{ .} \tag{4}$$

The thermal analysis method used in our studies is a modified version of the apparatus originally developed by Malissa et al. [5]. Our version [6] enables measurement of optical attenuation simultaneously with the evolution of CO_2. Thermal analysis is used to obtain total carbon, black carbon, organic carbon, and carbonate carbon. A schematic representation of the thermal analysis apparatus used in our studies is shown in Fig. 2. The main components of this apparatus are a quartz tube and a temperature-programmed furnace. The tube is mounted axially inside the furnace. The particulate sample, collected on a prefired quartz filter, is placed in the quartz tube so its surface is perpendicular to the tube axis. The tube is constantly supplied with pure oxygen. The excess oxygen escapes through an axial opening at the end of the tube, while the remainder of the oxygen (and other gases evolved during analysis) passes through a nondispersive infrared analyzer at a constant flow. In addition to the variable temperature furnace, the apparatus also contains a constant temperature furance, usually kept at about 850°C. The segment of quartz tube inside the constant temperature furnace is filled with a copper oxide catalyst to ensure that carbon-containing gases evolved from the sample are completely converted to CO_2. This is especially important at relatively low temperatures when complete oxidation to CO_2 does not occur.

The actual measurement consists in monitoring the CO_2 concentration as a function of the sample temperature. The result is a "thermogram" — a plot of the CO_2 concentration vs. temperature. The area under the thermogram is proportional to the carbon content of the sample. The carbon content is quantitated by calibrating with a calibration gas (CO_2 in oxygen) and by measuring the flow rate through the system. This calibration is crosschecked by analyzing samples of known carbon content. The thermograms of ambient and source aerosol samples reveal distinct features in the form of peaks or groups of peaks that correspond to volatilization, pyrolysis, oxidation, and decomposition of the carbonaceous material.

To determine which of the thermogram peaks corresponds to black graphitic carbon, the intensity of the light beam produced by a He-Ne laser is monitored by a photomultiplier and displayed by the second pen of the chart recorder, simultaneously with the measurement of the CO_2 concentration [6]. In actual experiments the light penetrating the filter is collected by a quartz light guide and filtered by a narrow band interference filter to eliminate the effect of the glow of the furnaces. An examination of the CO_2 and light intensity traces enables the assignment of the peak or peaks in the thermograms corresponding to the black carbon because they appear concomitantly with the decrease in sample absorptivity.

In Fig. 3, a complete thermogram of an ambient sample is shown. The lower trace represents the CO_2 concentration vs. the sample temperature, while the upper curve corresponds to the light intensity of the laser light beam that reaches the detector during the temperature scan. Inspection of the thermogram shows that a sudden change in the light intensity occurs concomitantly with the evolution of the CO_2 peak at about 470°C. The light intensity I_0, after the 470°C peak has evolved, corresponds to that of a blank filter. This demonstrates that the light-absorbing species in the sample are combustible and carbonaceous. We refer to these species as black carbon. The carbonate peak evolves at about 600°C; and as carbonate is not light absorbing, it does not change the optical attenuation of the sample. In addition to black carbon and carbonate, the thermogram in Fig. 3 also shows several distinct groups of peaks at temperatures below $\sim$ 400°C that correspond to various organics.

The thermogram in Fig. 3 was obtained with a 1.46-cm-diameter disc cut out of a sample collected on prefired quartz fiber filters. The temperature ramp rate was 10°C/minute. The integrated area under the CO_2 trace is proportional to the total carbon concentration. For this sample the total carbon concentration, determined by thermal analysis, was 17.9 $\mu g\ (C)/cm^2$. The black carbon, determined from the thermogram, composes 14% of the total carbon. This value can be crosschecked by using the optical attenuation and total carbon data. The specific attenuation for this sample, determined in a separate measurement, is $\sigma \equiv ATN/C = 3.00$. The estimated percentage of black carbon (as a percent of total C), determined from measurement of optical attenuation and total carbon only, is $100 \times 3.0/20.0 = 15\%$. This value is in excellent agreement with the percentage of black carbon determined directly from the CO_2 thermogram.

Results and Discussion

The data presented in this paper consist of information obtained from analyses of 24-hr samples (collected weekdays) and multi-day samples (collected over weekends) [4]. Table I lists the routine sampling sites with the beginning date of sampling. In this section we present data on total average 24-hr concentrations of total carbon, specific attenuation, and estimated black carbon concentrations for ambient and source samples. By determining an average specific attenuation value for sources, the soot (total primary carbon) fraction can be estimated from Eq. 4.

Figure 4 shows the variations of 24-hr total carbon (weekends excluded) at the Fremont, California, site. These data cover the period from July 1977 to January 1980. The 24-hr histogram superimposed on the bar diagram represents the monthly averages. It is evident that there are significant day-to-day variations in total carbon. The maximum and minimum daily concentrations differ by an order of magnitude. The monthly averages are at peak values during the November-December periods of each year. The variations in optical attenuation for the same samples are represented in Fig. 5. The pattern of ATN values resembles that of total carbon and shows similar seasonal variations. The specific attenuation (ATN/C) variations represented in Fig. 6 are much less pronounced and show no clear seasonal variations. Similar features of total C, ATN, and ATN/C are also observed at other sites.

The data on total carbon, black carbon (from Eq. 3), and specific attenuation are presented in Tables II and III. These results imply that there is a correlation between the black carbon and the total carbon content at every site studied. Furthermore, a study of a number of source samples shows that there is also a strong correlation between optical attenuation and total carbon for these samples. The correlations between optical attenuation and total carbon for the three California sites, Argonne, and source samples are shown in Fig. 7 (a-e) [7].

Results obtained from ambient samples imply that the fraction of graphitic soot to total particulate carbon is approximately constant under the wide range of conditions occurring at a given site. On specific days, however, there can be large variations in the ratio, reflecting the variations in the relative amounts of organic and black carbon. The least squares fit of the data shows regional differences which are related to the fraction of black carbon due to primary emissions. These differences suggest an increase in the relative importance of the primary component for samples collected at Berkeley, Fremont, Anaheim, and Argonne.

Soot contains not only black carbon but also various organic material. Because the organic soot component does not absorb light, the specific attenuation of soot is much less than 20, the σ value of pure black carbon. Table IV lists the average and extreme values of specific attenuation and the black carbon fraction of a number of source samples.

The percentage of soot in ambient carbonaceous particulates can be estimated by comparing the σ of sources with that of ambient samples. The fraction of soot is given in Eq. 4. Table V lists the mean specific attenuation of ambient samples (weekends excluded) in order of decreasing σ and soot fractions obtained by using Eq. 4 and $\sigma_{source} = 5.85$.

Based on this estimate, the New York City carbonaceous aerosol is essentially primary soot. A different value of σ_{source} would certainly change the estimated soot percentage. However, New York City's average soot content would nevertheless remain the highest, irrespective of the actual numerical value of σ_{source}. It is logical that samples from this location have the highest soot content because the site represents a heavily traveled street canyon. Fremont and Anaheim samples have on the average the smallest soot content, as may be expected, because both sites represent receptor sites. According to the above estimate, Denver has the smallest specific attenuation value. It is possible that high-altitude combustion results in increased emissions of primary organics; however, we note that the number of samples from this location is small compared to that from other sites, so the results should be taken with caution.

It is instructive to present the specific attenuation data in the form of histograms representing their frequency of occurrence. Histograms for New York and Fremont (Fig. 8) show that the occurrence of high specific attenuation samples is much greater for New York than for Fremont. In Fig. 9 the histogram of specific attenuations of a number of source samples is shown together with those for New York and Fremont. The distribution for sources looks similar to the distribution for New York. This supports the inference that the New York samples, on the average, consist almost entirely of primary carbonaceous material. Histograms for other sampling sites are shown in Figs. 10 and 11.

It is clear from the results described so far that the ratio of black carbon to total carbon may vary on specific days. However, no large systematic differences are found as a function of the ozone concentration, which is viewed as an indicator of the photochemical activity [7]. This is graphically demonstrated in Fig. 12, which shows the distribution of the ratios of the optical attenuation to total carbon content for ambient samples from all the California sites taken together, subdivided according to peak hour ozone concentration. Clearly there is no trend for high-ozone days to be characterized by aerosols which have a significantly reduced black carbon fraction. This places a low limit on the importance of secondary organic particulates formed in correlation with the ozone concentration.

Results in Table V suggest that the California sites have an organic component that occurs in excess of sources of source-dominated organics. This excess should be equal to the secondary organic material, which can be conveniently identified by the thermal analysis method.

We have already described how thermal analysis can be used to obtain the total carbon, black carbon, organic carbon, and carbonate carbon. The greatest strength of this method, however, is its ability to "fingerprint" source-produced carbonaceous particles and their contribution to the ambient aerosols. As an illustration, in Figs. 13 and 14 we show the thermograms of a sample collected in Manhattan (high σ) and one collected in Berkeley (low σ). The common features of both thermograms are the black carbon peak, the peak at ∿ 340°C, and the peaks occurring below ∿ 250°C which correspond to the volatile organics. The Berkeley sample clearly shows the presence of a prominent peak at ∿ 380°C which is absent in the thermogram of the New York sample. This peak (or possibly group of peaks) may correspond to secondary organic species.

To check this hypothesis, we have performed solvent extractions on some of the ambient samples and obtained thermograms of the insoluble filter residues [8], since according to an operational definition of Appel et al. [9], "primary" organic carbon is cyclohexane-extracted carbon; "secondary" carbon is the difference between the total carbon extracted by the benzene, methanol-chloroform sequence and the cyclohexane-extracted carbon. The thermograms of sequentially extracted filters should thus show which peaks can be identified with primary and secondary organics.

The result of one such experiment with a sample collected in Berkeley is shown in Fig. 15. Cyclohexane extraction has removed practically the entire volatile organics, which — according to the above definition — should be primary species. The peak at ∿ 380°C is removed only with the polar benzene-methanol-chloroform solvent. This is consistent with our preliminary assignment — that this peak is due to secondary species. The black carbon peak, as expected, was not removed by solvent extraction.

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b. B.R. Appel, E.M. Hoffer, E.L. Kothny, S.M. Wall, M. Haik, and R.L. Knights, "Analysis of carbonaceous material in southern California atmospheric aerosols," Environ. Sci. Technol. 13, 98 (1979).

Table I. LBL aerosol sampling sites.

Site	Location	Date of first sample
Lawrence Berkeley Laboratory	Berkeley, California	1 June 1977
BAAQMD monitoring station	Fremont, California	15 July 1977
SCAQMD monitoring station	Anaheim, California	19 August 1977
Argonne National Laboratory	Argonne, Illinois	22 January 1979
DOE Environmental Measurements Laboratory	Manhattan, New York	22 November 1978
National Bureau of Standards	Gaithersburg, Maryland	23 January 1979
Denver Research Institute	Denver, Colorado	15 November 1978

Table II. Carbon concentrations ($\mu g/m^3$).

Site	Average		Highest		Lowest	
	C	BC	C	BC	C	BC
New York	15.2	4.2	53.1	12.6	3.4	0.6
Argonne	8.1	1.7	25.1	5.2	3.1	0.2
Gaithersburg	6.1	1.4	17.6	5.6	2.3	0.3
Denver	9.8	1.6	30.8	5.3	4.1	0.2
Anaheim	16.6	3.1	112.9	17.4	3.1	0.3
Fremont	12.0	2.1	75.6	9.2	3.4	0.3
Berkeley	6.7	1.3	31.7	5.2	3.0	0.3

Table III. Specific attenuation (σ) and black carbon (BC)(% of total C) from ambient samples.

			Average		Highest		Lowest	
Site	Dates on file	# samples	σ	% BC	σ	% BC	σ	% BC
New York	Nov 78 - Apr 80	439	5.44	27%	11.1	56%	2.8	14%
Argonne	Jan 79 - Mar 80	438	4.30	22%	9.1	46%	1.1	6%
Gaithersburg	Jan 79 - Mar 80	381	4.33	22%	8.0	40%	1.8	9%
Denver	Nov 78 - May 79	141	3.23	16%	5.7	29%	1.4	7%
Anaheim	Aug 77 - Jan 80	852	3.70	19%	9.6	48%	0.8	4%
Fremont	Jul 77 - Mar 80	924	3.55	18%	8.3	42%	1.6	8%
Berkeley	Jun 77 - Apr 80	998	4.09	20%	9.2	46%	1.2	6%

Table IV. Specific attenuation (σ) and black carbon (BC)(% of total C) of source samples.

Source	# samples	Average		Highest		Lowest	
		σ	% BC	σ	% BC	σ	% BC
Parking garage	12	5.4	27%	7.7	39%	2.25	11%
Diesel	6	5.6	28%	5.7	29%	3.5	18%
Scooter	9	5.1	26%	6.1	31%	4.2	21%
Tunnel	63	6.3	32%	12.5	63%	3.7	19%
Natural gas	6	2.6	13%	3.3	17%	1.9	10%
Garage and tunnel		5.85	29%				

Table V. Mean specific attenuation of ambient samples.

Site	# samples	$\bar{\sigma}$	SDEV	Soot (%)
New York	211	5.69	1.34	97
Gaithersburg	155	4.72	1.51	81
Argonne	221	4.35	1.64	74
Berkeley	513	4.28	1.47	73
Anaheim	444	3.99	1.71	68
Fremont	461	3.74	1.25	64
Denver	42	3.47	1.49	59

Figure Captions

Figure 1. Schematic representation of the optical attenuation (laser transmission) apparatus (from Ref. 1).

Figure 2. Schematic representation of the thermal analysis apparatus.

Figure 3. Thermogram of an ambient sample showing carbonate, black carbon, and several forms of organic material.

Figure 4. Variations in the daily total carbon concentration at the Fremont, California, site (from Ref. 4).

Figure 5. Variations in the optical attenuation at the Fremont, California, site (from Ref. 4).

Figure 6. Variations in the specific attenuation at the Fremont, California, site (from Ref. 4).

Figure 7. Plots of optical attenuation versus carbon loading in $\mu g/cm^2$ for particulate samples collected at Berkeley, Fremont, Anaheim, and Argonne, and from various combustion sources. The solid line represents the least squares fit of the data points (from Ref. 7).

Figure 8. Distribution of specific attenuation for the New York and Fremont sites (from Ref. 4).

Figure 9. Distribution of specific attenuation for source, New York, and Fremont samples (from Ref. 4).

Figure 10. Distribution of specific attenuation for Anaheim, California, and Berkeley, California, sites (from Ref. 4).

Figure 11. Distribution of specific attenuation for Denver, Colorado; Argonne, Illinois; and Gaithersburg, Maryland, sites (from Ref. 4).

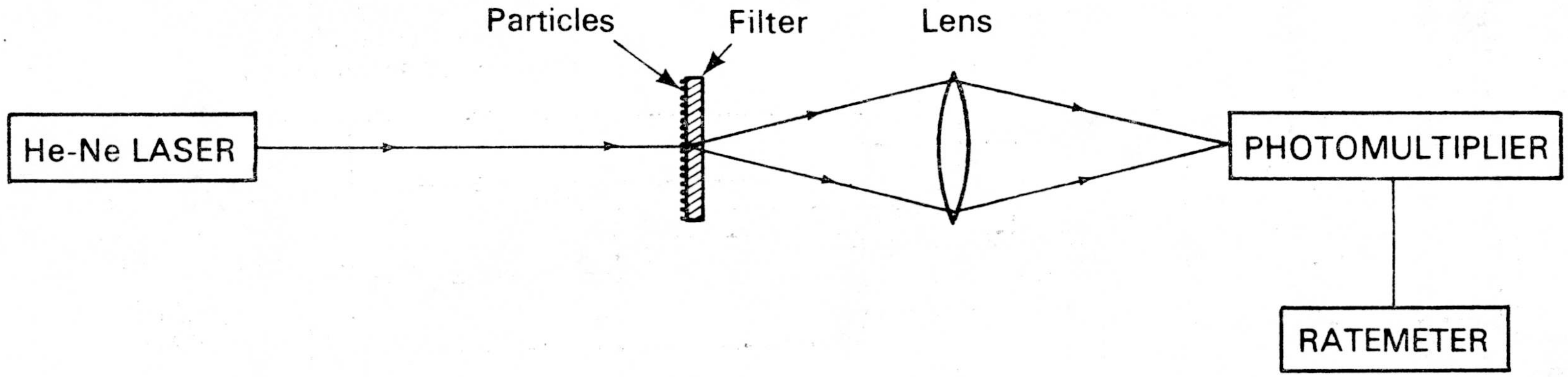
Figure 12. Distribution of the ratios of specific attenuation subdivided according to the peak ozone concentration. Note that the means of the distributions are only marginally smaller at larger ozone concentrations,

which puts a rather low limit on secondary organics produced in correlation with ozone (from Ref. 7).

Figure 13. Thermogram of a New York sample with high specific attenuation.

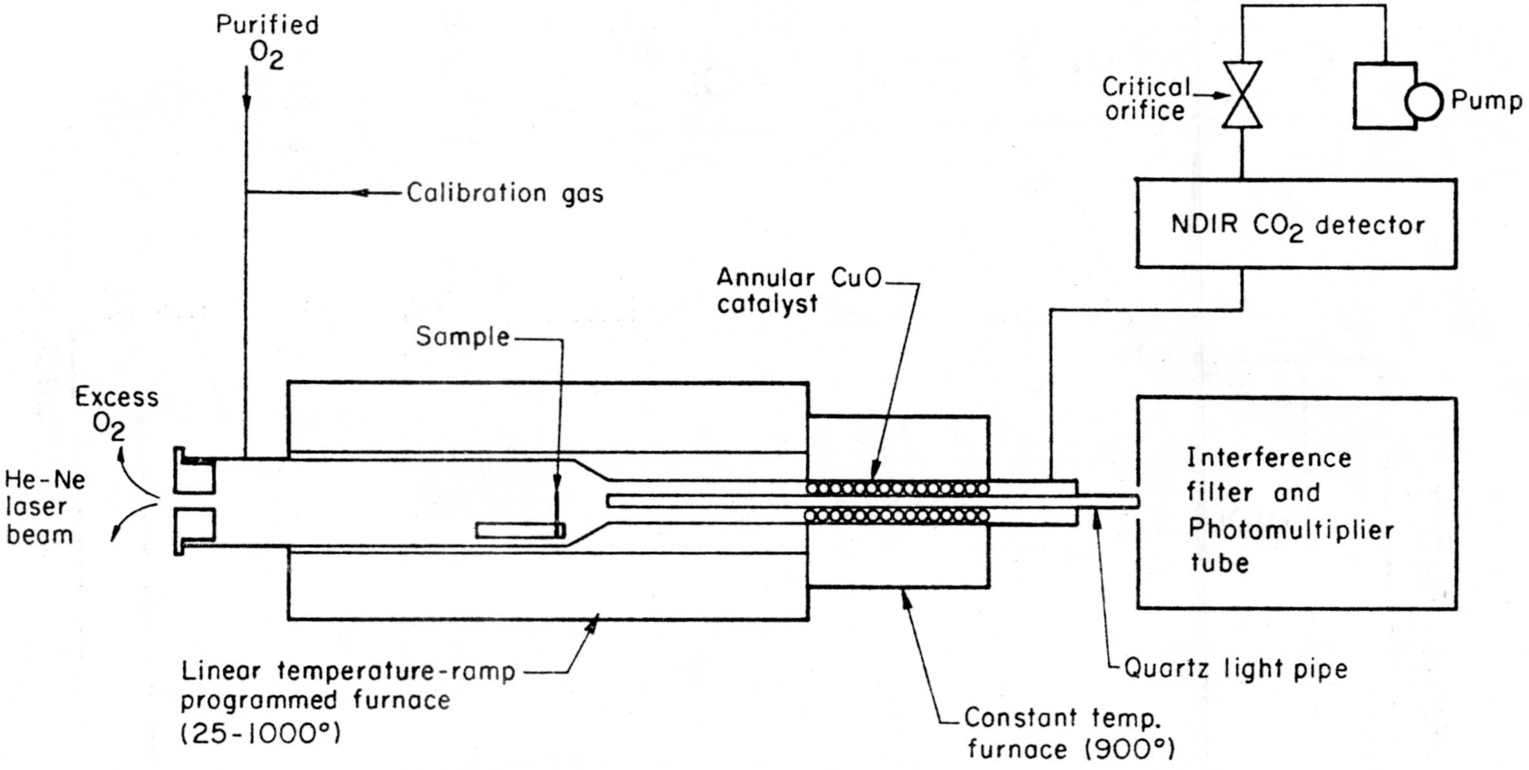
Figure 14. Thermogram of a Berkeley, California, sample with low specific attenuation.

Figure 15. Thermograms of a sequentially extracted ambient (Berkeley) sample.



XBL 787-1361

Figure 1



COMBUSTION OPTICO-THERMAL ANALYSIS (EGA-CO_2)

XBL 8012-13504

Figure 2

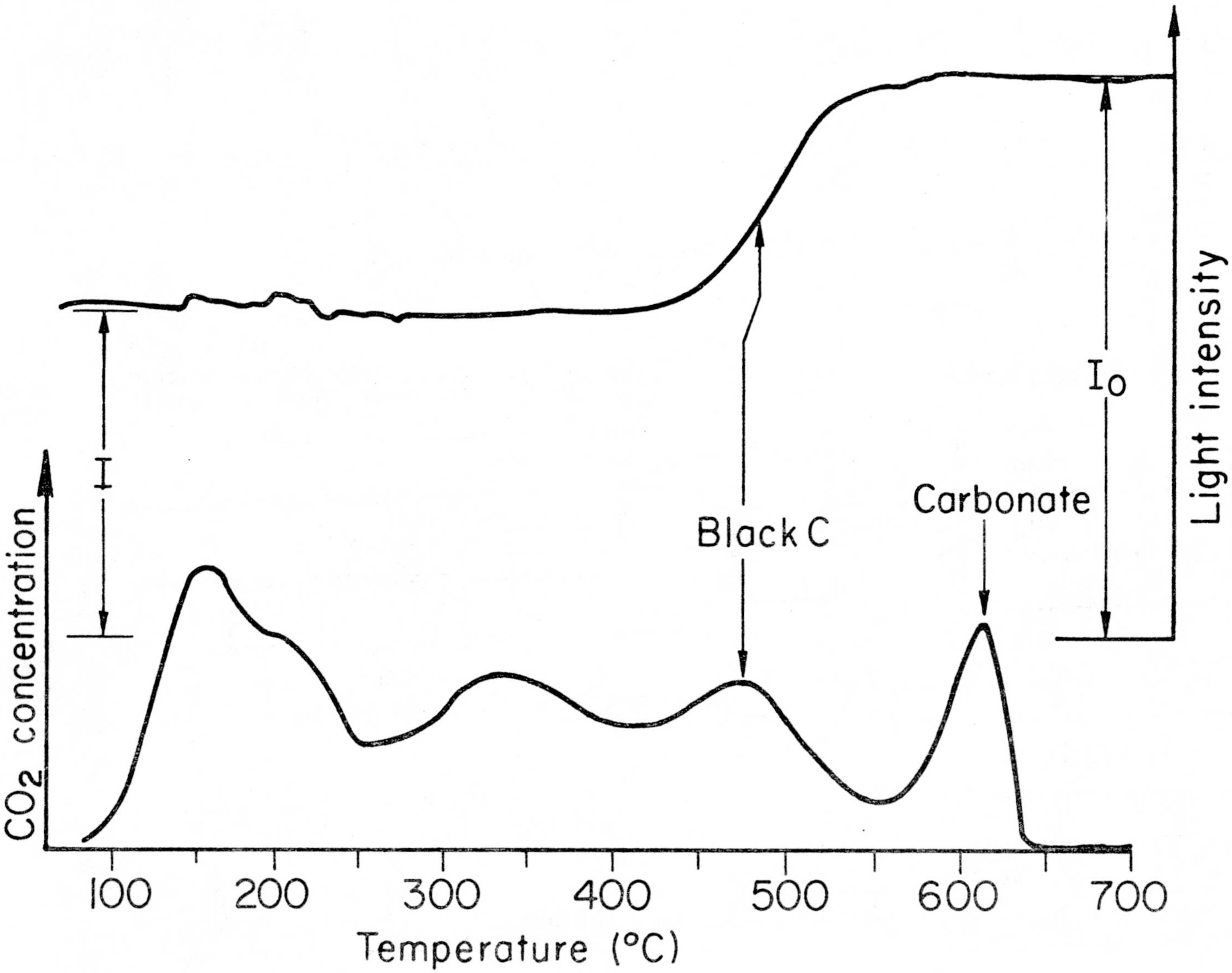


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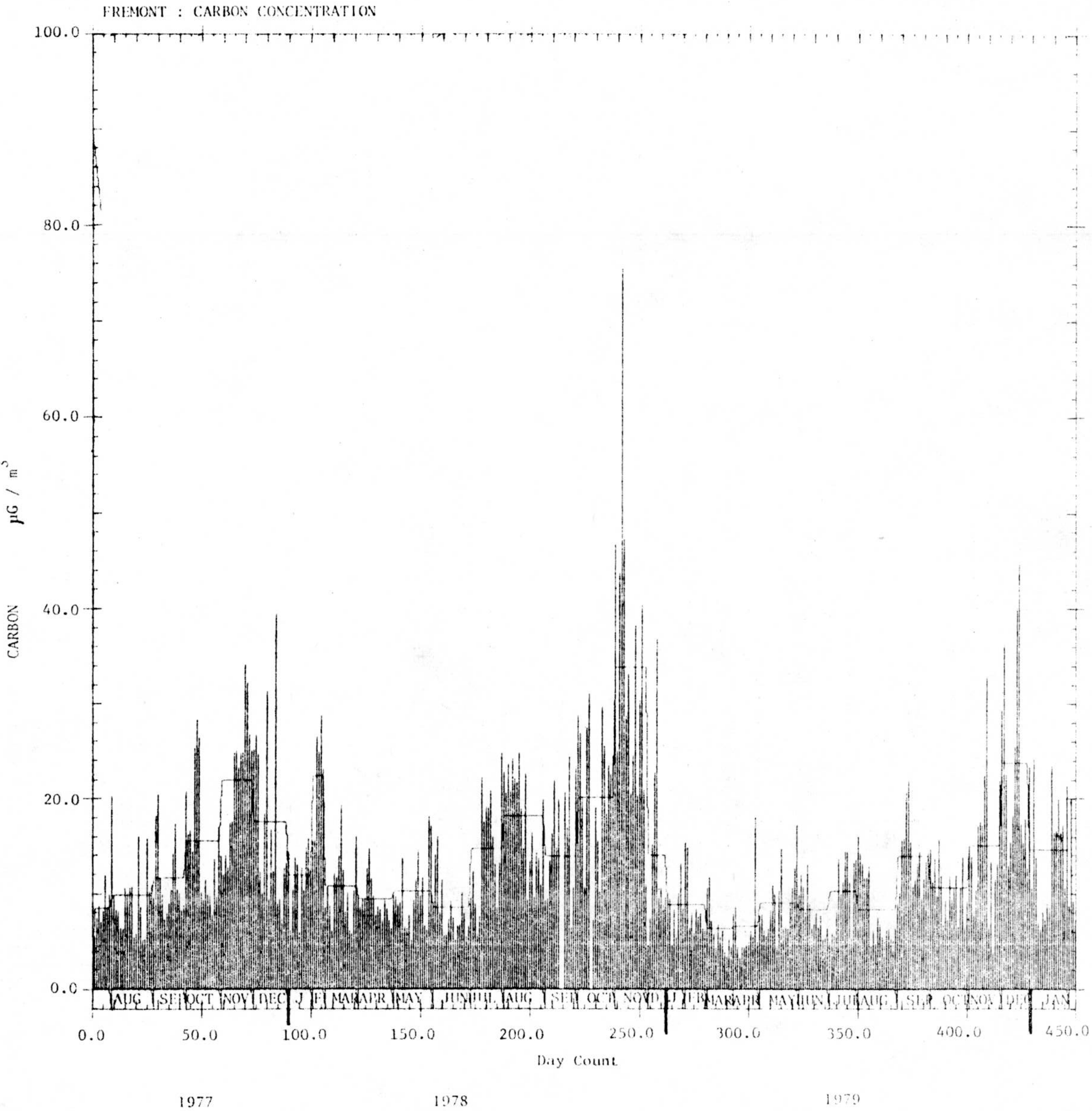
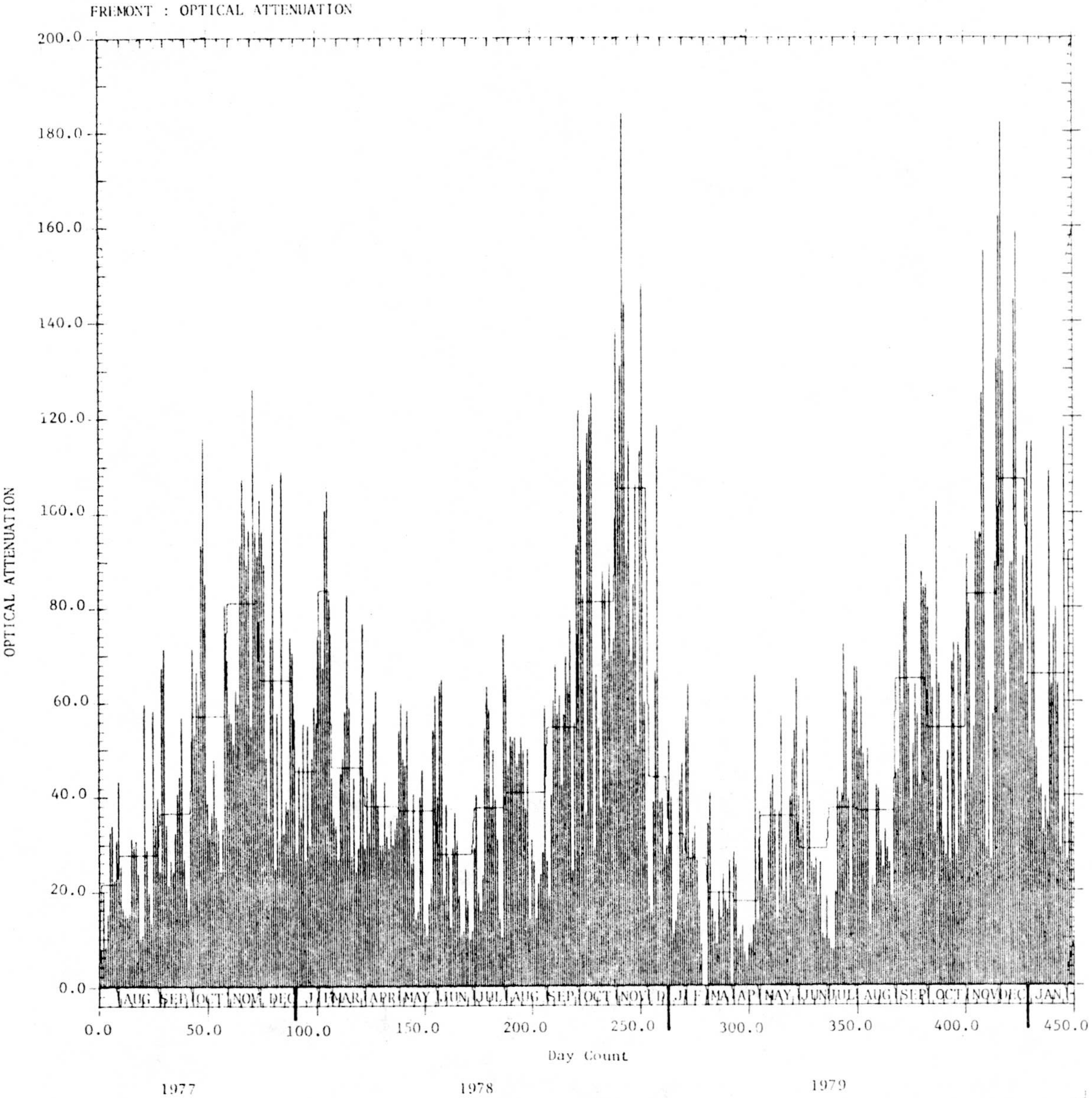
Figure 3



XBL 806-10534

Figure 4



XBL 806-10536

Figure 5

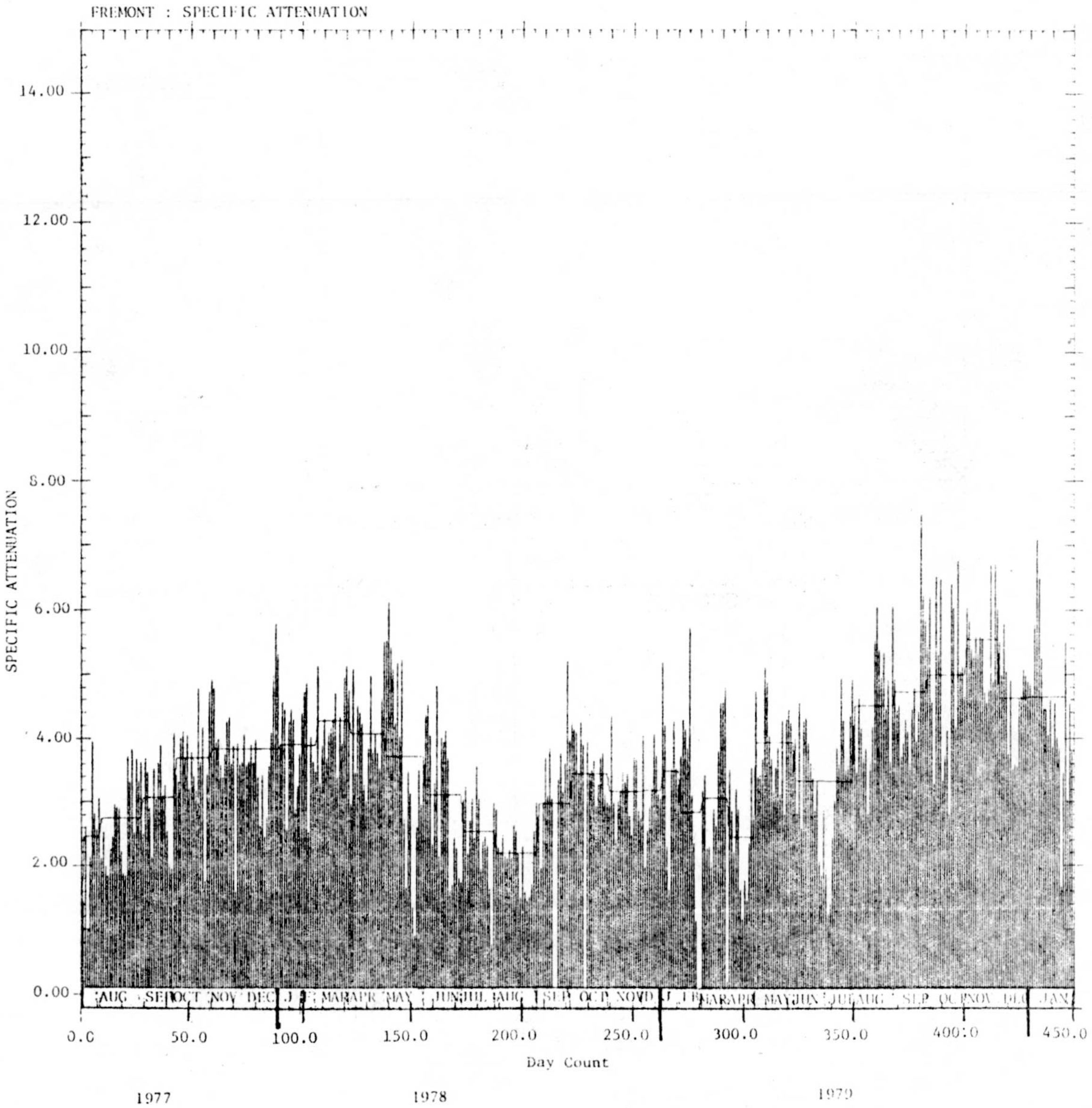


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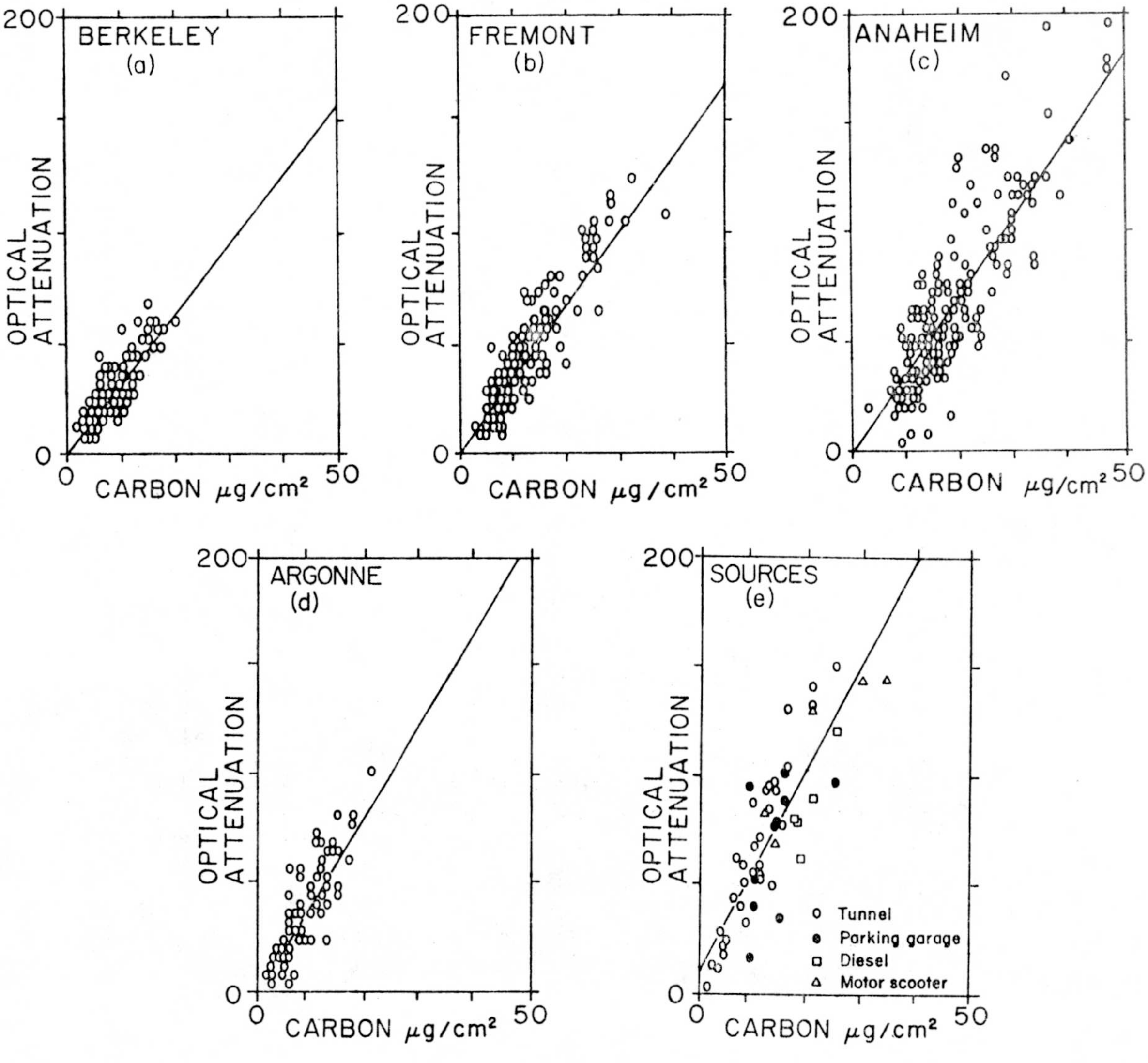
Figure 6



XBL 796-1920A

Figure 7

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HISTOGRAM OF ATN/  C FOR SITES NYC
FOR DATES 27 NOV 78 TO 14 APR 80
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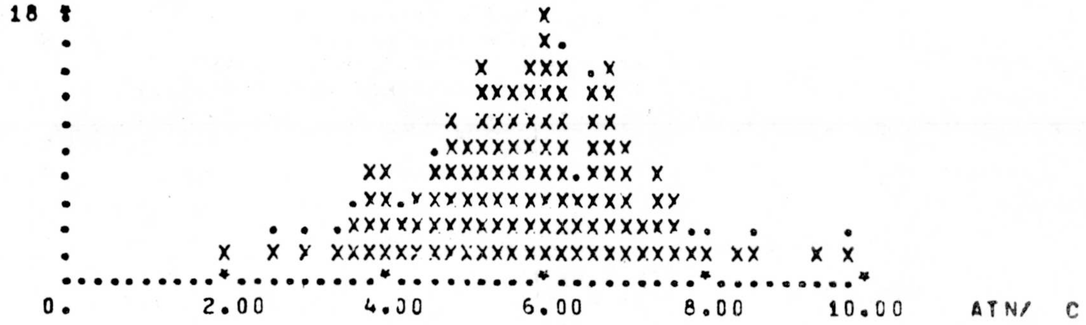

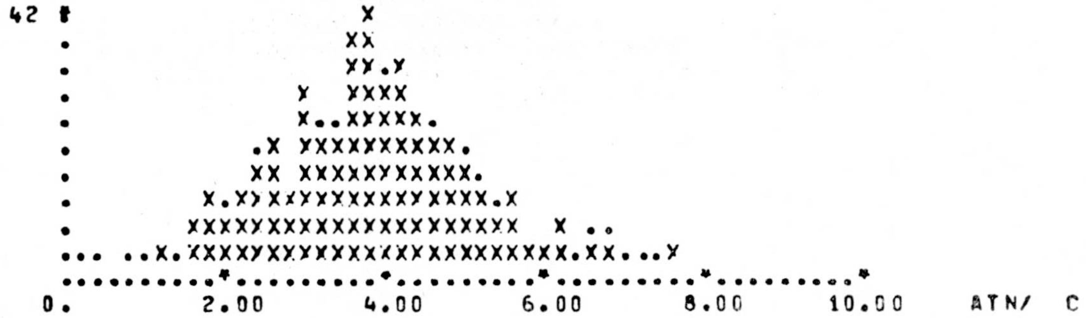

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HISTOGRAM OF ATN/  C FOR SITES FRE
FOR DATES 18 JUL 77 TO 12 MAR 80
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XBL 8010-12695

Figure 8

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HISTOGRAM OF ATN/  C FOR SITES GRG TUN SCT OSL NGS
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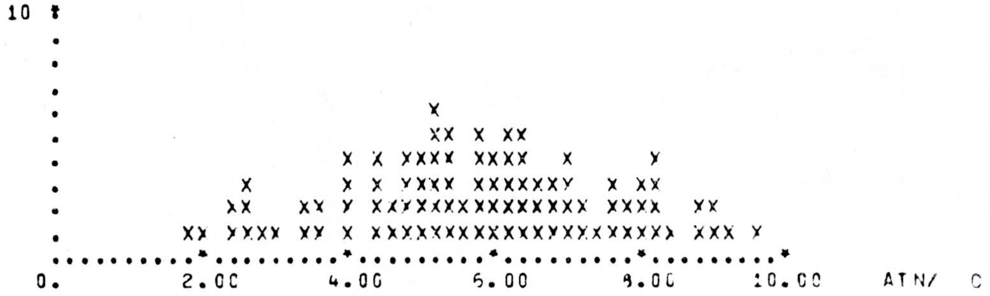

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HISTOGRAM OF ATN/  C FOR SITES NYC
FOR DATES 27 NOV 78 TO 14 APR 80
NPOINTS = 211     MEAN =  5.69     SDEV =  1.34     NO WKENDS
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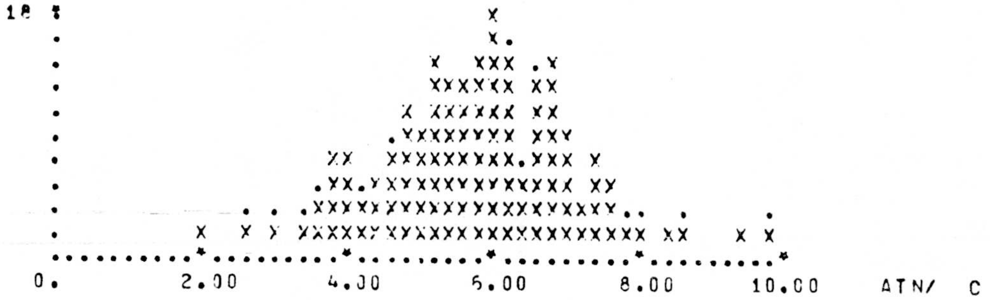

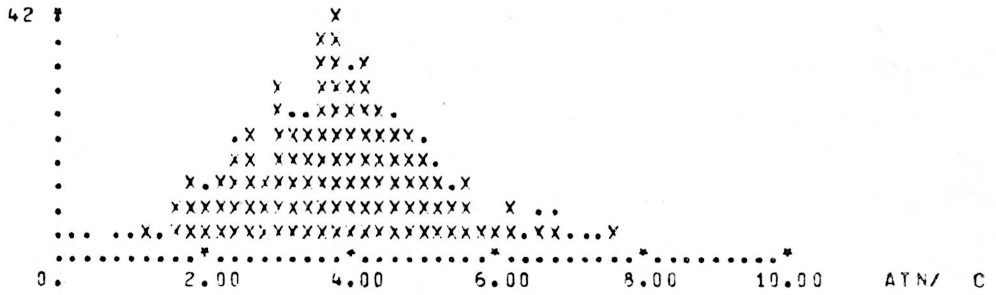

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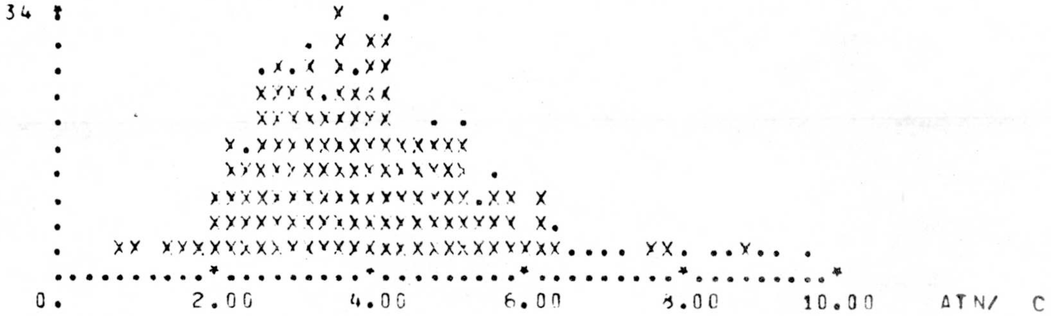
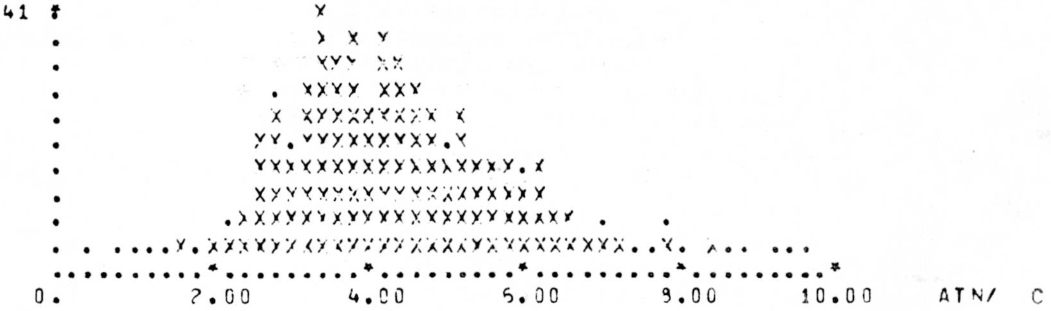
HISTOGRAM OF ATN/  C FOR SITES FRE
FOR DATES 18 JUL 77 TO 12 MAR 80
NPOINTS = 461     MEAN =  3.74     SDEV =  1.25     NO WKENDS
```

XBL 8010-12697

Figure 9

HISTOGRAM OF ATN/ C FOR SITES ANA
FOR DATES 22 AUG 77 TO 29 JAN 80
NPOINTS = 444 MEAN = 3.93 SDEV = 1.71 NO WKENDS



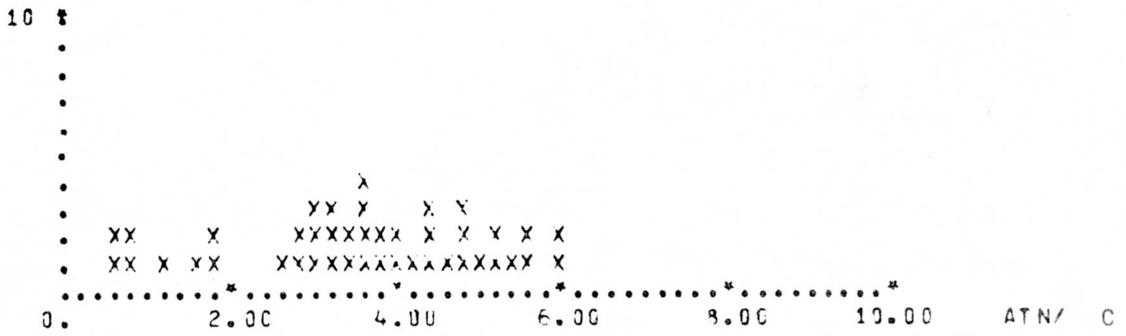


HISTOGRAM OF ATN/ C FOR SITES BRK
FOR DATES 1 JUN 77 TO 17 APR 80
NPOINTS = 513 MEAN = 4.28 SDEV = 1.47 NO WKENDS

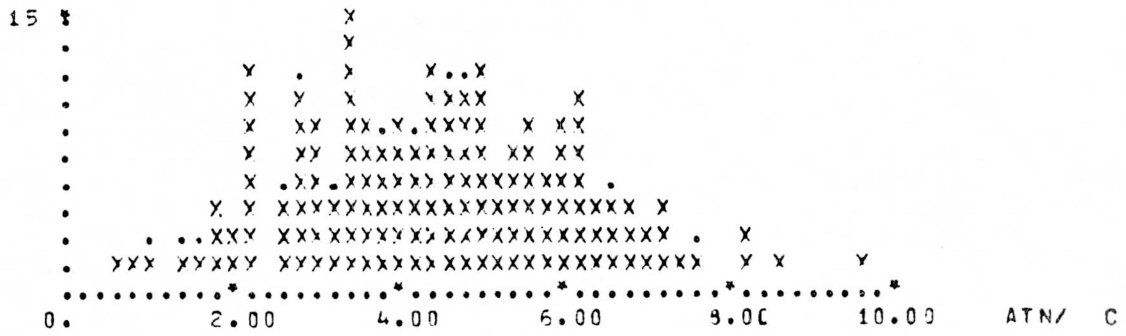
XBL 8010-12696

Figure 10

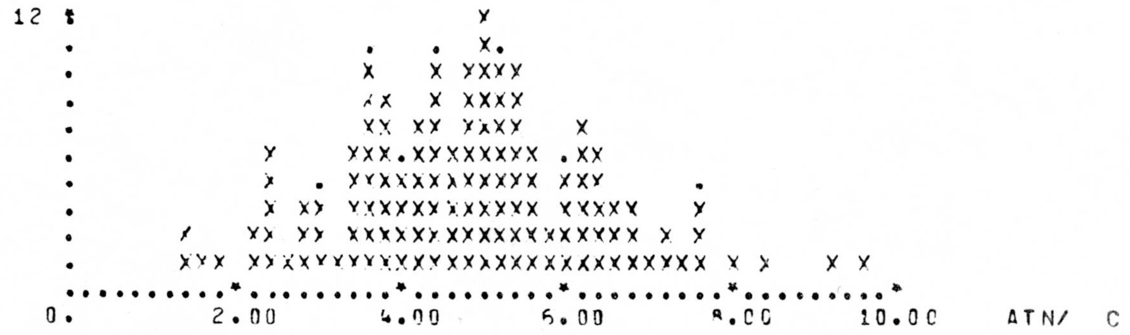
```
HISTOGRAM OF ATN/  C FOR SITES DNV
FOR DATES 16 NOV 78 TO 22 MAY 79
NPOINTS =  42     MEAN =   3.47     SDEV =   1.49      NO WKENDS
```



```
HISTOGRAM OF ATN/  C FOR SITES CHI
FOR DATES 23 MAR 78 TO 27 MAR 80
NPOINTS = 221     MEAN =   4.35     SDEV =   1.64      NO WKENDS
```

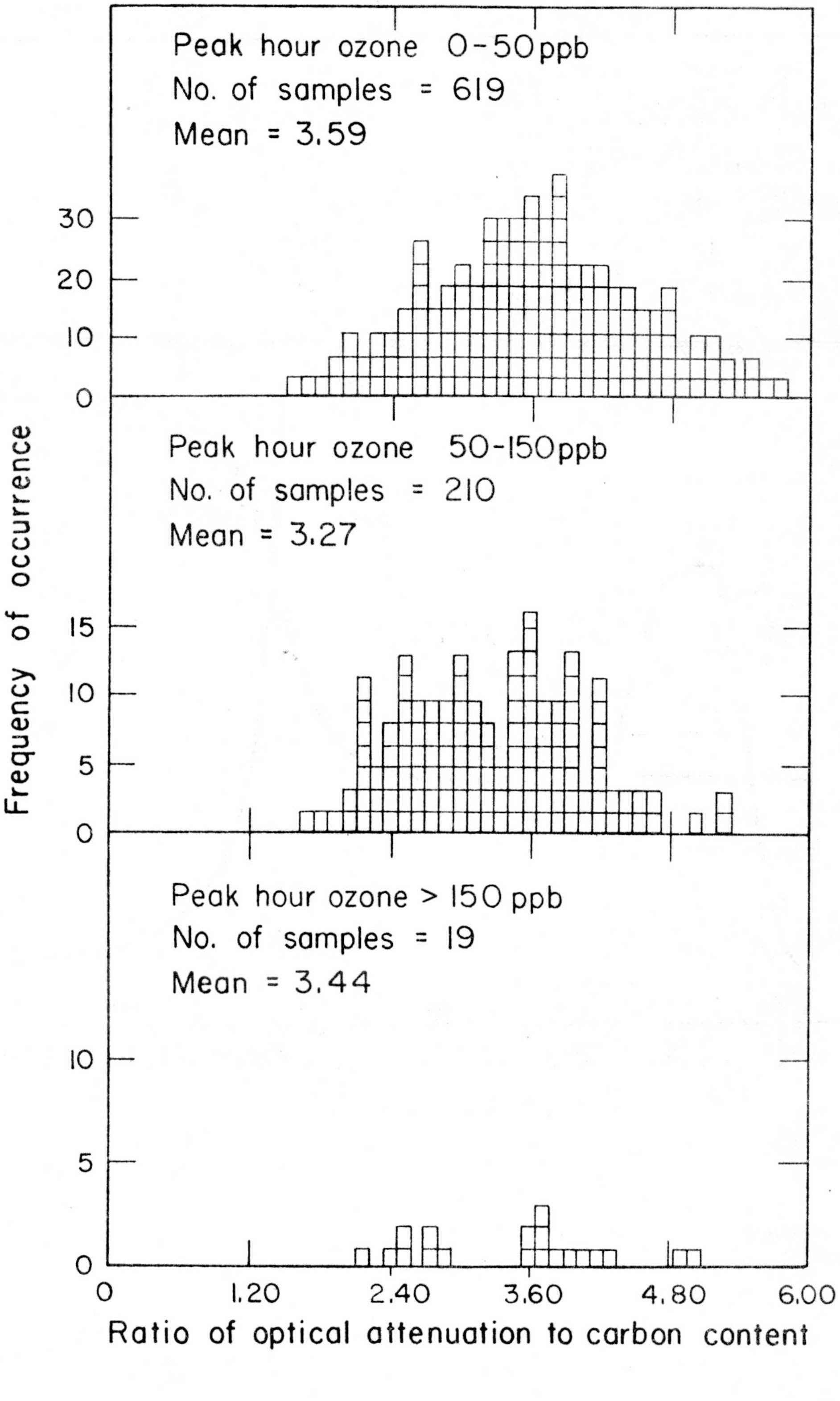


```
HISTOGRAM OF ATN/  C FOR SITES WDC
FOR DATES 23 JAN 79 TO  5 MAR 80
NPOINTS = 155     MEAN =   4.72     SDEV =   1.51      NO WKENDS
```



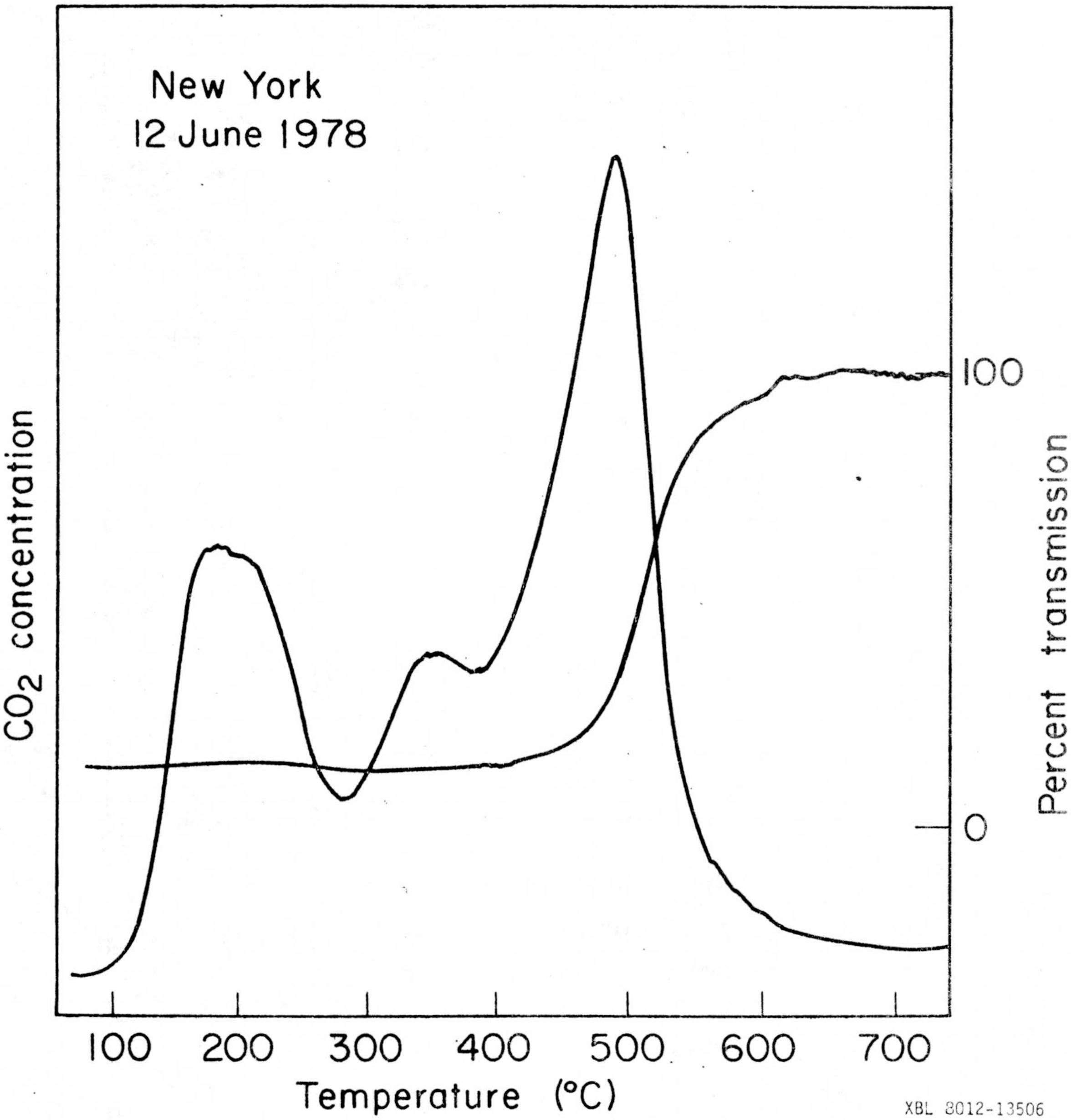
XBL 8010-12698

Figure 11



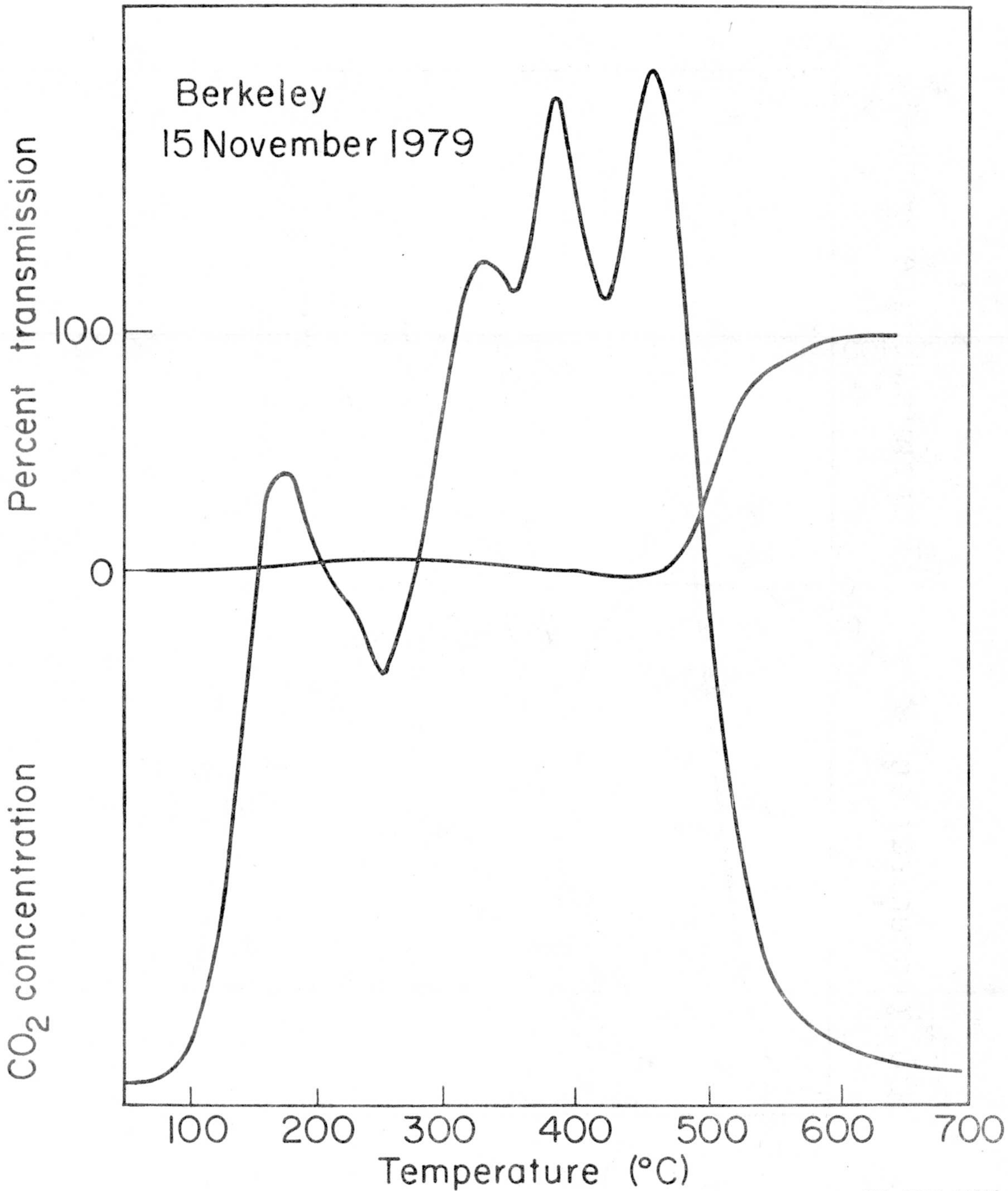
XBL 798-2704

Figure 12



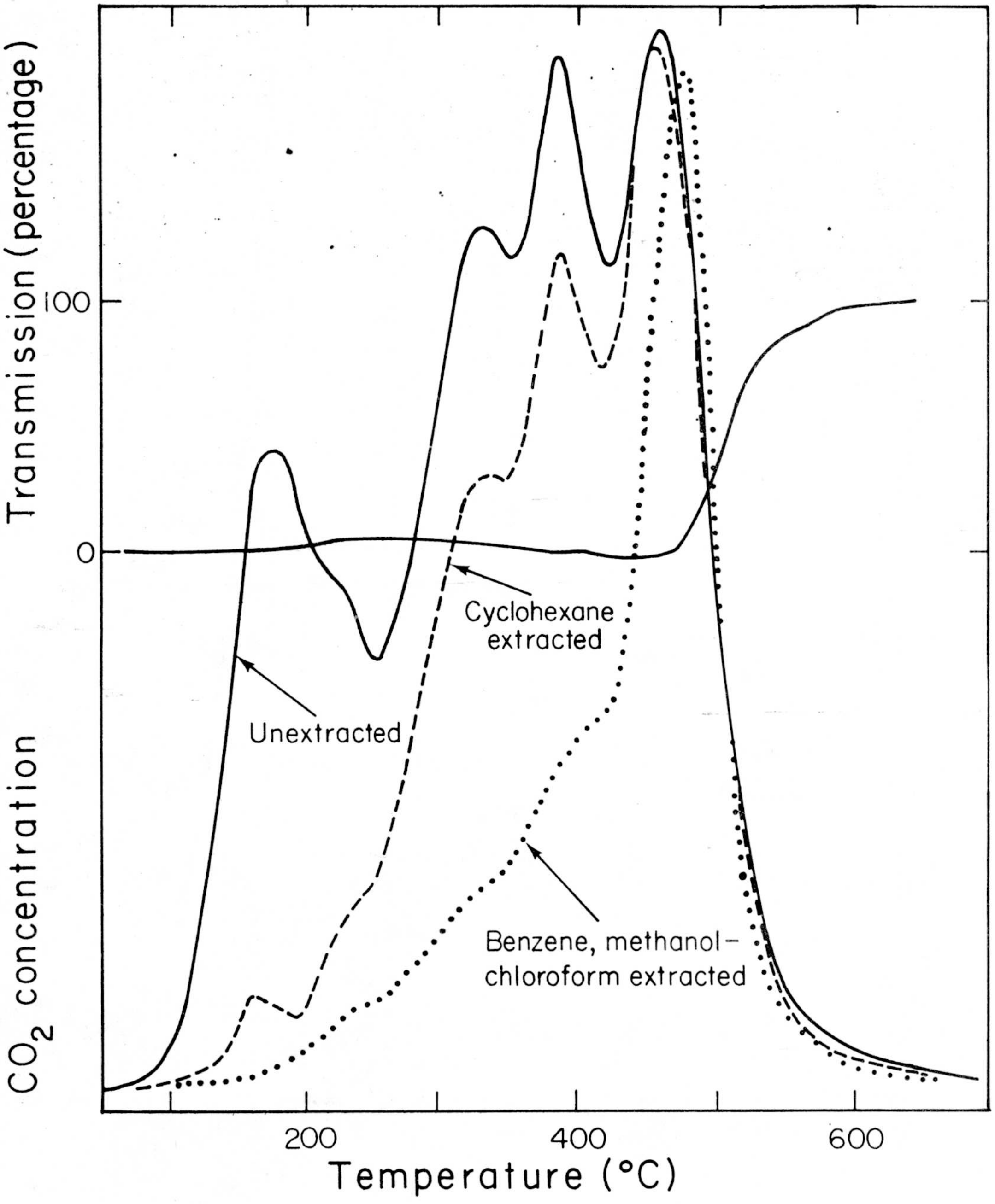
XBL 8012-13506

Figure 13



XBL 8012-13503

Figure 14



XBL8012-2568

Figure 15

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