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GRAPHITIC CARBON PARTICLES IN THE ATMOSPHERE

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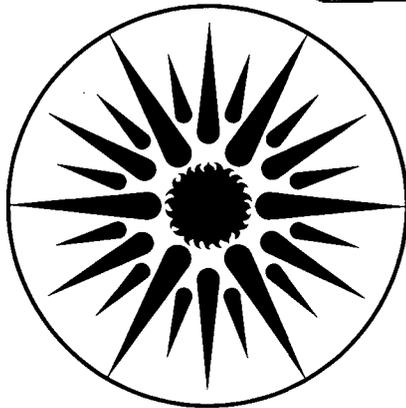
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GRAPHITIC CARBON PARTICLES IN THE ATMOSPHERE*

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Carbon particles can represent a major component of submicron aerosols in urban, rural, and remote atmospheres.[1-3] These particles can be formed directly from combustion processes (soot particles) or can be formed by gas-to-particle transformation processes in the atmosphere (secondary organics) as shown in Fig. 1. The soot particles can be further subdivided into a highly absorbing graphitic carbon component and into a wide range of weakly absorbing organics. The ratio of these two components can vary considerably as a function of combustion conditions and combustion sources. In this review, we will only consider the role of graphitic carbon in atmospheric absorption processes. The other components are important in radiative transfer since they do scatter light effectively but have minimal importance as far as the absorption of solar radiation.

Identification of Graphitic Carbon Particles in Urban Atmospheres

Raman scattering and infrared absorption spectroscopy are complementary techniques that measure the vibrational spectra of gases, liquids, and solids. Often vibrational modes that are infrared inactive are Raman active and vice versa. Graphitic structures in which trivalent carbon atoms occupy lattice sites in a two-dimensional hexagonal honeycomb network have intense Raman modes

but very weak infrared vibrational spectra. These Raman modes, which were first observed by Tuinstra and Koenig,[4] enable the identification of graphitic structures even in the presence of a complex mixture of substances. Solvent extraction, heat treatment, optical absorption, and morphology studies[5] can provide indirect evidence for a graphitic component; but Raman spectroscopy appears to be the only presently available method for making unambiguous identifications on a molecular level.

The Raman spectroscopy apparatus uses a Coherent Radiation argon ion laser producing 1 W of power at 514 nm. The laser beam is focused by a 75-mm focal length cylindrical lens to a spot 0.06 mm x 2 mm on the sample surface via a small mirror, and the backscattered radiation is collected and imaged by an f/1 lens onto the slit of a 1-m Jarrell Ashe double monochromator equipped with two 1180-grooves/mm gratings blazed at 5000 Å. The output of the spectrometer is detected by an FW130 photomultiplier cooled to $-20°C$ and used in a photon-counting mode. The pulses, after appropriate shaping, are counted and displayed on a multichannel analyzer. A computer-controlled grating drive made by RKB, Inc., allows a given spectral region to be scanned many times and added to the memory of the multichannel analyzer, greatly improving the SNR. In order to minimize heating effects, the highly absorbing samples used in these experiments are rotated at 1800 rpm by a motor, which increases the area illuminated by the laser beam by a large factor with almost no loss in signal level. The focal spot of the laser is located approximately 5 mm below the axis of rotation so that the effective illuminated area is an annulus of 5-mm radius and 2-mm width, resulting in the low power density of $\sim 1 \ W/cm^2$.

The Raman spectra are obtained directly from aerosol particles collected on various filter media without any pretreatment procedures. These spectra are observed on top of a large fluorescent background, which is due both to the filter media and the highly fluorescent material in the sample.

Irradiation of the sample with the argon laser for 24 hr reduced this background by about an order of magnitude.

The Raman scattering technique has been applied to identify substantial concentrations of graphitic particles in combustion effluents, urban air,[1] and the Alaskan Arctic.[3] These results are shown in Fig. 2, where the spectrum of a sample collected in December 1979 at the NOAA-GMCC observatory in the Alaskan Arctic is compared with spectra of urban particulates, various source emissions, carbon black, and polycrystalline graphite. All spectra show the presence of two intense Raman modes that have been attributed to phonons propagating within graphitic planes.[4] The Raman spectrum of a single crystal of graphite consists of a single band near 1575 cm^{-1}, which has been identified as an E_{2g} vibration of the hexagonal layers.[4] Polycrystalline graphite shows another band at 1355 cm^{-1}, which is not fully understood but has been attributed to the breakdown of selection rules.[4] A small shift in the frequency of the 1575 cm^{-1} Raman mode has also been observed, which apparently depends on the degree of order in the aromatic structures.[6] Such a shift is evident in comparing the spectra of polycrystalline graphite with the other spectra presented in Fig. 2. It is also evident from the figure that the frequency of the vibrational modes in carbon black and those in particles collected from various sources, urban air, and the Alaskan Arctic are coincident to $\pm$ 10 cm^{-1}, which is the estimated experimental error. This close correspondence has been used to show the presence of graphitic particles in urban air[1] and the Alaskan Arctic.[3]

Role of Graphitic Carbon in Aerosol Absorption

A laser transmission technique developed at Lawrence Berkeley Laboratory has been used extensively to determine the absorption coefficient and the graphitic carbon content of aerosols in the United States,[1,2] some areas of Europe, and the Arctic region.[3] The laser transmission apparatus compares

the transmission of a 632.8-nm He-Ne laser beam through a loaded filter relative to the transmission through a blank filter, as shown in Fig. 3. After multiple scattering through the filter medium, the forward scattered light is collected by low f-number optics and detected by a photomultiplier. The filters used in our method are almost perfect diffuse reflectors, and only a small fraction of the incident beam is transmitted through them.

This technique appears to be a direct measure of the absorbing component of aerosol particles and is insensitive to its scattering properties. This has been shown directly in a photoacoustic study[7] and indirectly by noting that most of the aerosol mass responsible for scattering can be removed by solvent extraction or heat treatment procedures without appreciably affecting the optical transmission measurement.[8] Furthermore, it has been shown that adding nonabsorbing particles to the filter substrate does not give an appreciable optical attenuation.[9] From a theoretical point of view, these results are not obvious, since it is unclear why the backscattered radiation from nonabsorbing particles should not make a significant contribution to the optical attenuation measurement. This is especially true where the absorbing component represents only a very small fraction of the aerosol mass. In this paper, we will present a simple theoretical model that accounts for all these observations and points out the critical role of the filter substrate as an almost perfect diffuse reflector in the technique. Similar considerations may also apply to the opal glass method developed by Lin et al.[10]

For this model calculation, we will assume that the particles and the filter media can be treated independently and consider the geometry shown in Fig. 4. A similar treatment, where the light beam is first incident on the particles, gives identical results. After the light beam passes through the filter medium, it is incident on the particles with an intensity, I_0. The

particles forward scatter a fraction of the incident light, backward scatter a fraction, and absorb a fraction. These components in the low loading limit are respectively given by $n_s \sigma_F I_0$, $n_s \sigma_B I_0$, and $n_A \sigma_A I_0$, where n_s is the number of scattering aerosol particles per unit area, n_A is the number of absorbing aerosols per unit area, σ_F is the forward scattering cross section, σ_B is the backward scattering cross section, and σ_A is the absorption cross section.

Since the optical attenuation technique only measures the forward scattering light, it would seem as if the backscattered light would be lost to the system and would contribute to the attenuation. However, the filter, in our method, is almost a perfect reflector. Under these circumstances, the backscattered light will be reflected in the forward direction and will again be incident on the particles. This process will continue until amost all the backscattered radiation is collected by the optics and therefore does not contribute to the optical attenuation. This result can be put in mathematical form, where I is the light detected by the collection optics and R_F is the relfectivity of the substrate.

$$I = I_0(1 - n_s \sigma_b - n_A \sigma_A) + I_0(1 - n_s \sigma_B - n_A \sigma_A)n_s \sigma_B R_F \qquad (1)$$

$$+ I_0(1 - n_s \sigma_B - n_A \sigma_A)n_s^2 \sigma_B^2 R_F^2$$

$$+ I_0(1 - n_s \sigma_B - n_A \sigma_A)n_s^n \sigma_B^n R_F^n$$

$$+ I_0 \frac{(1 - n_s \sigma_B - n_A \sigma_A)}{(1 - n_s \sigma_B R_F)} .$$

Consider several limits. Where $R_F \simeq 0$, which normally would be considered an ideal substrate, Eq. (1) reduces to

$$I = I_0(1 - n_s \sigma_B - n_A \sigma_A) .$$

Under these conditions, the backscattered radiation will contribute significantly

to the optical attenuation and make the technique unsuitable for exclusively measuring the absorbing properties of the aerosol. In our method, however, $R_F \simeq 1$ and Eq. (1) becomes

$$I = I_0 (1 - \frac{n_A \sigma_A}{1 - n_s \sigma_B}) \; .$$

From this expression it is clear that a nonabsorbing aerosol will not contribute to the optical attenuation; this is consistent with our experimental results. The magnitude of the optical attenuation is somewhat dependent on the scattering properties of the aerosol; however, in the low loading limit, this effect is small. For example, if the substrate has 50% coverage, the scattering cross section of the particles, σ_s, is twice the particle area, and σ_B is 20% of σ_s. Then

$$1 - n_s \sigma_B \simeq 0.8 \; .$$

This implies that even for these large scattering cross sections and rather high loading, the error in the absorption measurement due to scattering of the aerosol is only about 20%. This treatment should only be viewed as giving physical insight into why transmission measurements through aerosol particles collected on highly reflecting substrates selectively measure the absorbing component of the aerosol particles. It is clearly approximate since it assumes that the optical properties of the particles are not affected by the filter substrate and neglects penetration of the particles into the substrate, which can lead to enhanced absorption due to multiple scattering within the filter media. These effects could be substantial and require further investigation.

Particles collected from urban areas, the Arctic, and various combustion sources have a grey or black appearance. The graphitic species identified by Raman spectroscopy is the most likely candidate to explain this coloration.

In order to test this hypothesis, the optical absorption technique described above has been used to quantitatively study the properties of the absorbing species. We have determined the temperature stability and solubility of the absorbing species in ambient and source particulate samples. Our results show that these species have high temperature stability with only minimal oxidation up to 400°C and are essentially insoluble in a wide variety of solvents.[8] We have also shown, using a spectrophotometer, that to within 20% over the visible spectral region, the optical absorption has a $1/\lambda$ wavelength dependence characteristic of a constant imaginary index of refraction.

All these results strongly suggest that the absorbing substance in urban areas and in the Arctic is graphitic carbon. A direct substantiation of this hypothesis is provided by comparing the integrated intensity of the 1600 cm^{-1} Raman mode with the optical attenuation of the same filter sample. These measurements have been done on three types of samples: acetylene soot samples, which were essentially pure carbon with only trace amounts of metallic impurities; highway tunnel samples; and ambient samples collected in Berkeley and Fremont in the San Francisco air basin and Anaheim in the Los Angeles air basin. The results, shown in Fig. 5, indicate that within experimental error there is a direct correspondence between the optical attenuation and the Raman intensity or graphitic soot content for all samples studied, despite widely different chemical compositions (e.g., for a given optical attenuation, the Pb and Fe concentrations vary by more than a factor of 100). The only reasonable explanation is that the optical absorption is due to the graphitic carbon content of the collected particulates.

Long-Range Transport of Graphitic Carbon to the Arctic

Recent studies in the Alaskan Arctic[3,11,12] show the presence of substantial concentrations of carbon- and sulfur-containing particles that seem to be characteristic of the Arctic region as a whole.[13-15] These particles are effective scatterers and absorbers of visible radiation[3,16] and appear to be responsible for the phenomenon of Arctic haze first reported by Mitchell.[17] On the basis of trace element analyses, it has been suggested that these particles originate from anthropogenic sources at mid-latitudes.[11,13] Direct substantiation of combustion-generated particles in the Arctic atmosphere has been provided by the identification of large concentrations of graphitic carbon particles at the GMCC-NOAA observatory near Barrow, Alaska.[3] The concentrations of these particles during winter and spring is only about a factor of 4 less than typical urban concentrations in the United States,[3] as shown in Fig. 6. These graphitic particles, which can only be produced from high-temperature combustion processes, have been identified on a molecular level using Raman spectroscopy. If one excludes natural burning processes that are not expected to be a significant source term during winter and spring when the Arctic haze is at a maximum, then one can attribute these graphitic particles directly to anthropogenic activities. These particles, which have large absorption cross sections (~ 10 m^2/g) in the solar spectral region, can lead to significant heating effects over the high surface albedo polar icecap.[18-20] The magnitude of these effects largely depends on the vertical and horizontal distributions of the graphitic particles as well as their concentrations as a function of time of year.[19,20] In this paper, we report on an extension of our studies of carbon particles in the Alaskan Arctic to the Canadian Arctic and the Norwegian Arctic. These studies, using the Raman scattering technique, identify substantial concentrations of graphitic carbon particles at ground-level stations throughout the western Arctic.

Aerosol samples were obtained from six Arctic sites: Barrow in the Alaskan Arctic; Mould Bay, Igloolik, and Alert in the Canadian Arctic; and Bear Island and Spitzbergen in the Norwegian Arctic. The samples from the Alaskan Arctic were collected on prefired quartz-fiber filters (Pallflex 2500 QAO) with a sampler installed at the NOAA-GMCC observatory in cooperation with B.A. Bodhaine of the GMCC program. The samples from the Canadian and Norwegian Arctic were collected on Whatman 41 filters and were provided respectively by L.A. Barrie of the Canadian Atmospheric Environment Service and B. Ottar of the Norwegian Institute for Arctic Research.

In Fig. 7 Raman spectra of samples collected at the above sites are shown. These samples were collected at similar times of year; but due to sample availability, some samples are from 1980 and others from 1981. It is clear from the spectra that all sites show the presence of significant concentrations of graphitic particles. There are some differences in the relative intensities and line shapes of the two Raman modes, but these could be due to systematic errors in fluorescence subtraction for the 1350^{-1} mode, which is located on a highly sloping background. If one assumes fixed optical constants (Raman cross sections, absorption cross sections), one can use the integrated intensity of the 1600 cm^{-1} Raman mode as a measure of the relative concentrations of graphitic particles at these sites. These analyses indicate that the concentrations at all these sites are quite comparable with the largest and smallest within about a factor of 3 of each other. The relative ordering of these concentrations for Spitzbergen, Bear Island, Barrow, Mould Bay, Alert, and Igloolik are: 2.1/1.7/0.8/0.8/0.7. It should be emphasized that this analysis is for a particular time interval, and the relative contributions could vary considerably from one time period to the next.

In summary, these results show that the large concentrations of graphitic

particles found at the Barrow, Alaska, site that are not a local phenomenon but are characteristic of ground-level stations across the western Arctic. If these highly absorbing particles occur at substantial concentrations throughout the Arctic troposphere, then they may have a significant impact on the Arctic radiation balance and climate.

Acknowledgments

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Figure Captions

Figure 1. Schematic representation of various components of the carbonaceous aerosol.

Figure 2. Raman spectra of particles collected in the Alaskan Arctic compared with spectra of urban particles, various source emissions, carbon black, and polycrystalline graphite.
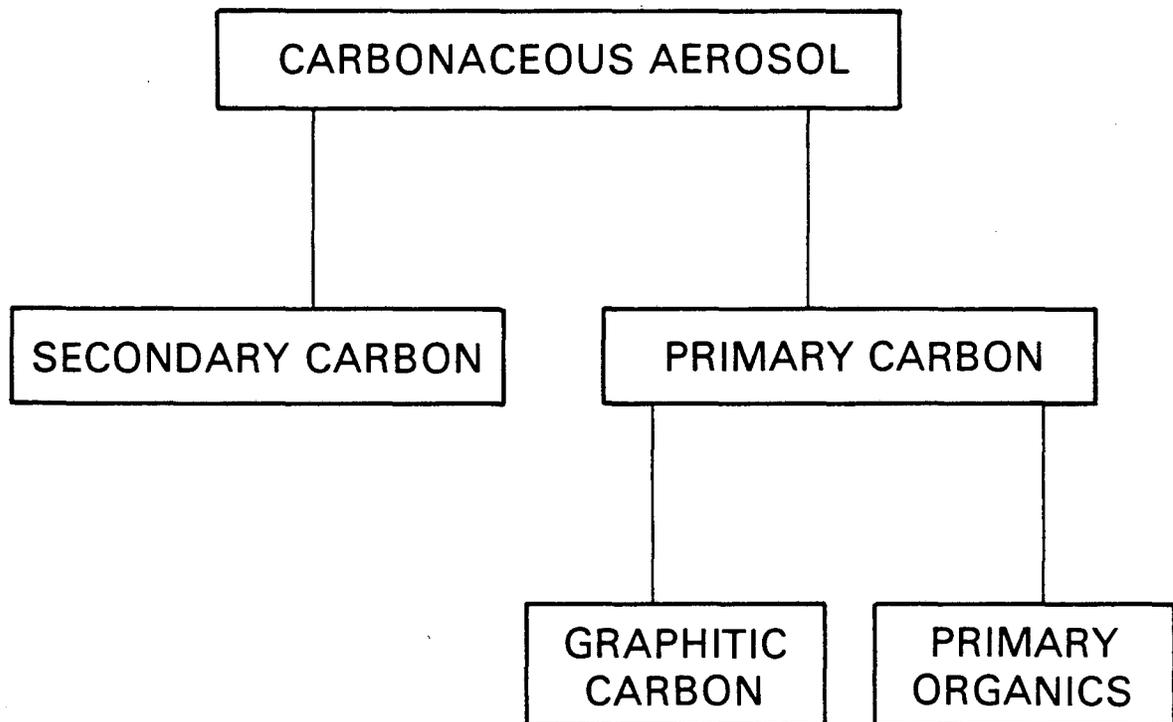
Figure 3. Schematic of the Lawrence Berkeley Laboratory laser transmission apparatus.

Figure 4. Schematic of the experimental arrangement used for the model calculation.

Figure 5. Comparison of the optical absorption of filter samples with the integrated intensity of the 1600 cm^{-1} Raman mode.
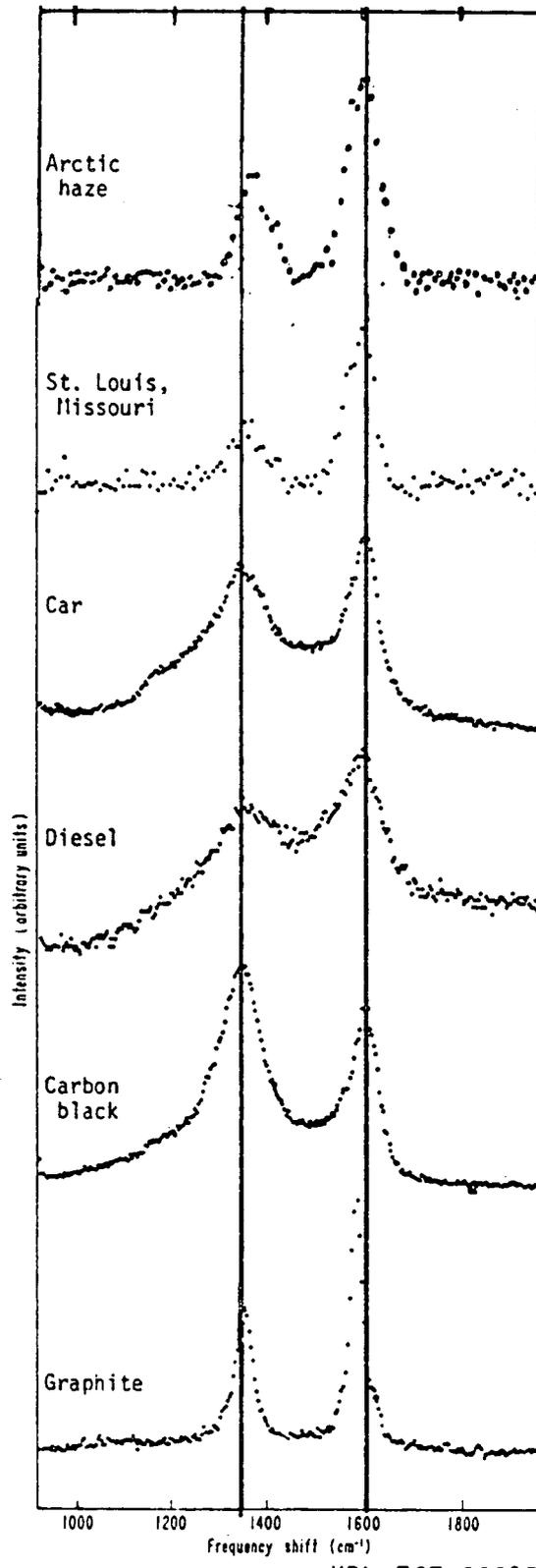
Figure 6. Comparison of the graphitic carbon concentration at Barrow, Alaska, with the concentrations at various urban locations in the United States.

Figure 7. Raman spectra of particles collected in the Alaskan Arctic (Barrow) compared with samples collected in the Canadian Arctic (Alert, Igloolik, Mould Bay) and the Norwegian Arctic (Spitzbergen, Bear Island).
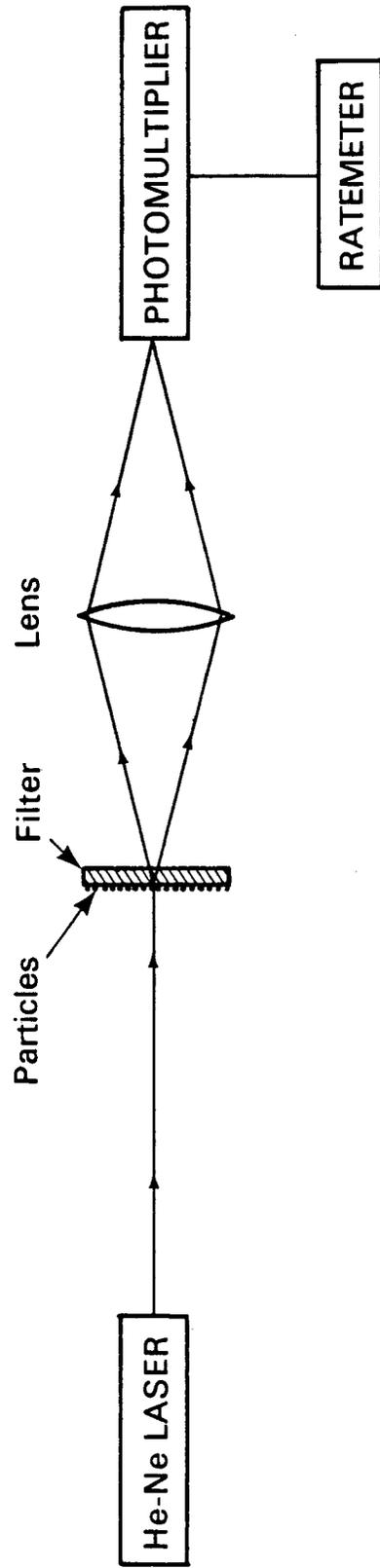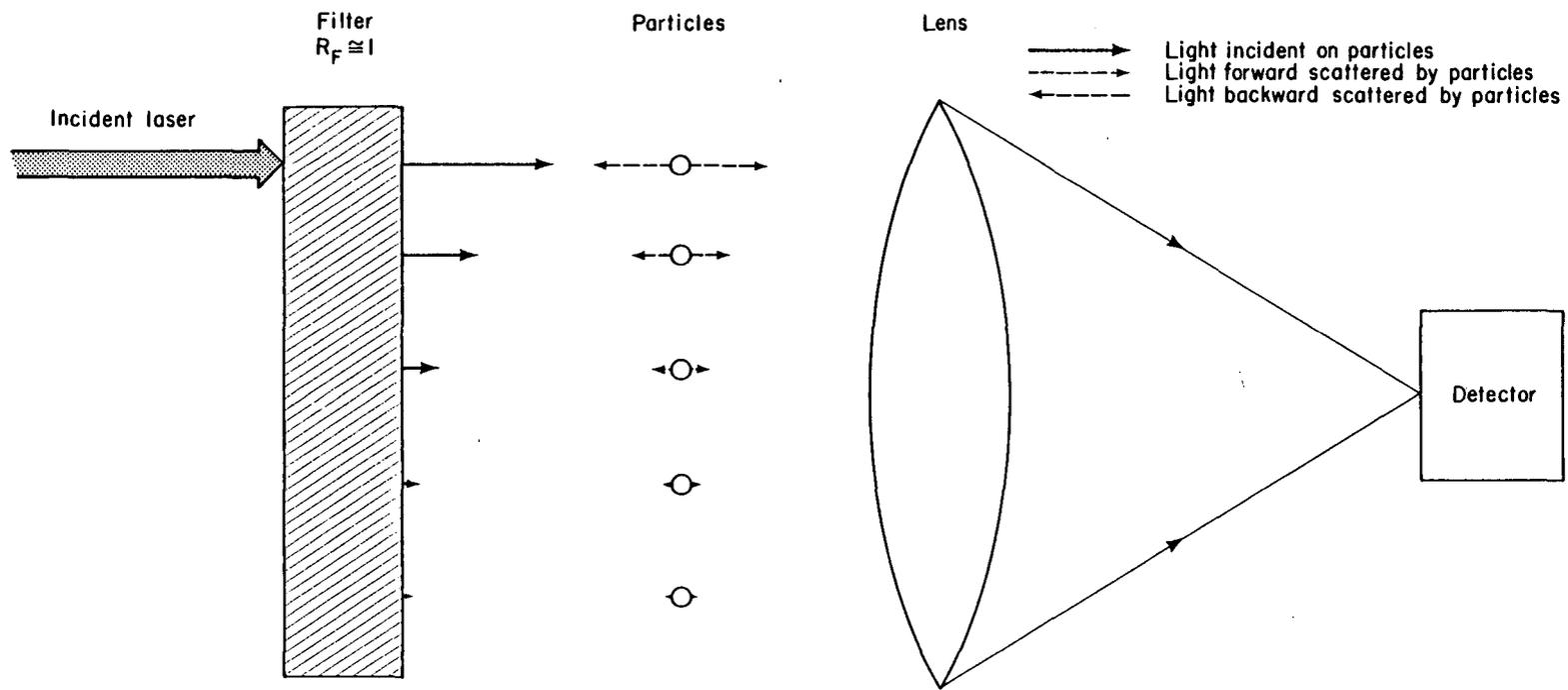
XBL 824-9115

Figure 1

XBL 767-3091B

Figure 2

Figure 3

XBL 787-1361

Filter
$R_F \cong 1$
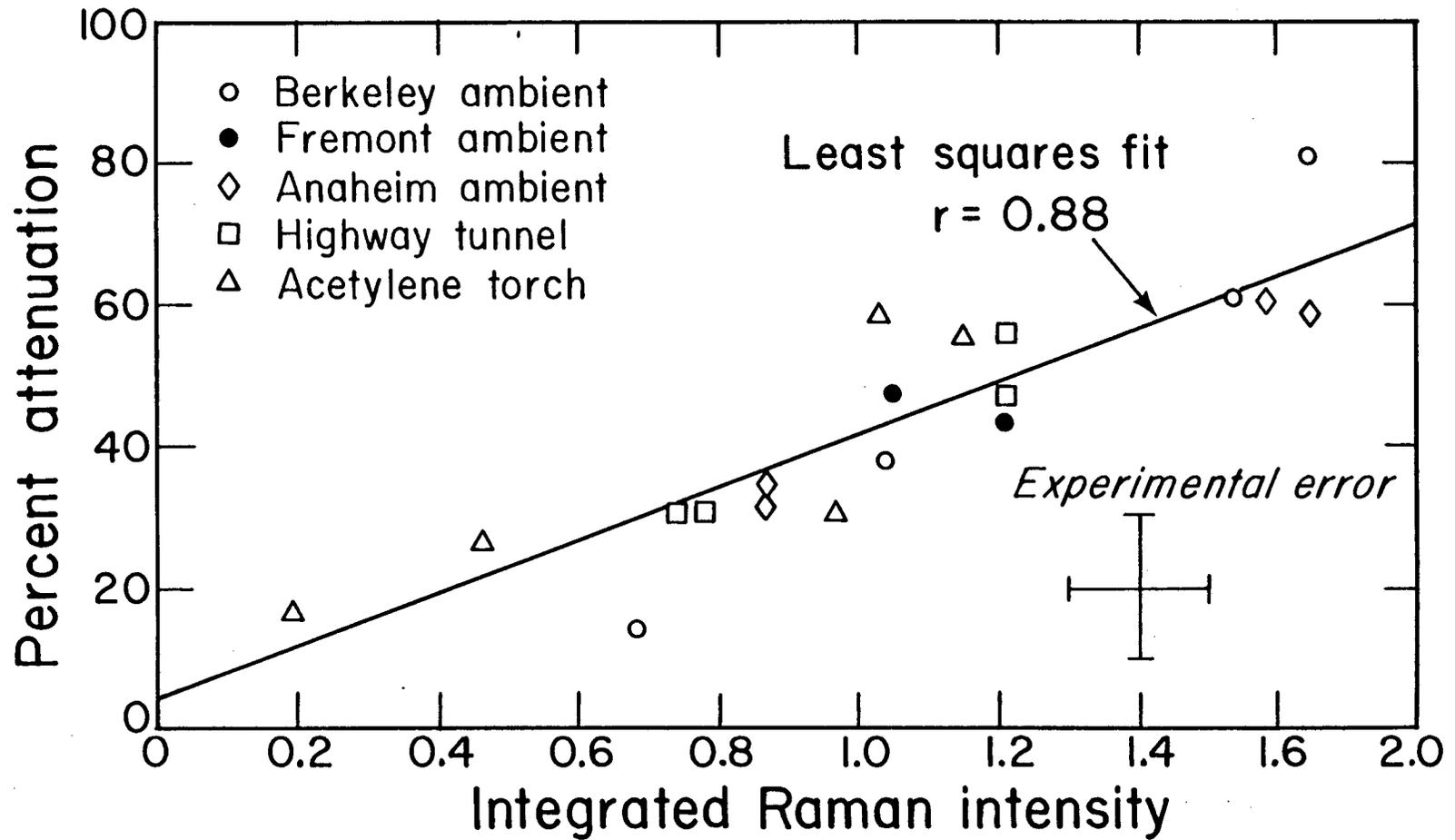
Particles

Lens

Incident laser

Light incident on particles
Light forward scattered by particles
Light backward scattered by particles

Detector

XBL 791-280

Figure 4

XBL 782-177

Figure 5

Figure showing a bar chart of Graphitic Carbon Concentrations at Barrow (1979-1980), with y-axis in $\mu g/m^3$ ranging from 0 to 0.50, and x-axis showing months from Oct to May.

Average Graphitic Carbon Concentration in Urban Areas

Argonne, Illinois	$1.8\ \mu g/m^3$
Gaithersburg, Maryland	$1.3\ \mu g/m^3$
Denver, Colorado	$1.6\ \mu g/m^3$
Anaheim, California	$3.2\ \mu g/m^3$
Fremont, California	$2.2\ \mu g/m^3$
Berkeley, California	$1.3\ \mu g/m^3$
New York, New York	$4.3\ \mu g/m^3$

XBL 822-135

Figure 6

Figure 7

XBL 822-137