Quantitative Measures of Carbon Microstructure

by

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ABSTRACT

The methodology for the characterization of the internal structure of carbonaceous materials is presented. It is based on High Resolution Transmission Electron Microscopy (HRTEM). Computational image analysis including pattern recognition techniques has been used to manipulate the HRTEM images. Quantitative information can be obtained on structural characteristics, e.g. inter-planar spacing, circularity, orientation, elongation and length distribution of lattice fringes as well as the fractional coverage of the extracted pattern.

To illustrate the capabilities of the methodology a series of study was performed to examine the evolution during oxidation of the internal structure of soot obtained from in-mine diesel engines operating under varying conditions, carbon black particles of different extent of burnout and graphitized anthracene.

Increasing ordering to the carbon structure with increasing oxidation is observed on both the diesel soot and the carbon black samples. Measures of the increased order are increases in the fractional coverage of a cross section of the particles with a layered structure, a decrease in the mean inter-layer spacing, and a decrease in the spread of the inter-layer spacing. The changing structure of the carbon black impacts its properties, such as the rate of oxidation.

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INTRODUCTION

There is considerable interest in the study of the structural changes of carbonaceous materials as a function of oxidation. Davis et al. (1) measured the variation of carbon dioxide surface area of various coals as a function of residence time in a flow reactor. X-ray measurements revealed that crystallite dimensions and inter-layer spacings are altered by combustion. Ishiguro et al. (2) showed that oxidation alters the structure of diesel soot. The aim of our current research is to develop a better understanding of the microstructural reordering of carbon blacks with implications to their properties. The carbon blacks used in this research have already been studied and their reactivity as a function of oxidation measured (3).

The methodology used in this work is described in detail in Appendix A. (4) The main body of this thesis presents an application to quantify the structural changes of carbon black particles as a function of oxidation and graphitization. Another application is presented in Appendix B. where Diesel soot samples were examined as a function of the operating conditions of the engine. The technique used is based on the use of HRTEM (High Resolution Transmission Electron Microscopy) and computational image analysis.

It is well known that carbonaceous materials like graphite, soots, coals, chars, etc. possess characteristic structural appearances which can vary from mostly random or amorphous to a perfectly ordered graphitic crystalline structure. The carbon structure has been variously described as turbostratic (5) or as crumpled sheets (6) to indicate that parallel layering, reminiscent of graphite, is observed over dimensions of nanometers but that these planes or crystallites show disorder over larger scales. The degree of order of such structures is strongly dependent on the thermal treatment of the material as well as the composition of the source of the carbonaceous material. The value of electron microscopy in studying the morphology of such materials has been well established (2; 7; 8) although only a few attempts toward quantification have been made.
MATERIALS

The sample observed was carbon black CB330 from Degussa. One set of carbon black samples were oxidized in a Thermo-Gravimetric Analyzer (TGA) in air atmosphere at 575 °C, so that the conversion varied from 0 to 96%. Another set of carbon black samples were graphitized and then oxidized in the TGA at 680 °C until 92% burnout was reached. The latter samples are called GB 0% and GB 92%, respectively.

For the HRTEM observation a small portion of each sample was ultrasonically dispersed in ethanol. The suspension was deposited dropwise on a copper TEM grid coated with a lacey carbon film. The examination of the samples was carried out on areas that extend over the holes in the supporting film in order to avoid interference from the amorphous carbon background film. An oriented gold crystal was used as a calibration standard and subjected to the same techniques as the carbon black samples.

Other materials examined include graphitized anthracene and Diesel soot. The results of these experiments are discussed in Appendix A and B.
METHODOLOGY

The detailed methodology is described in Appendix A., however it is summarized here briefly.

First, a high resolution transmission electron microscope, operated at 200 keV was used to record the images of each sample. These images were then digitized and stored as computer images (Figure 1a). A high-level language computer software (SEMPER6P®), developed specifically for use with high-resolution electron microscopy, was then used to manipulate the stored images in order to extract data which could characterize physically these soots.

![Image](image1.png)

Figure 1. Sequence of steps during image analysis (a) original HRTEM image, (b) power spectrum (c) extracted structure. (Carbon black)

From these digitized images computer generated diffraction patterns were produced (Figure 1b). The optical diffractogram is a power spectrum calculated from the modulus of the Fourier transform. The Fourier Transform (FT) of the TEM image can be used to find periodicities, and is also used to extract the significant structural data from the image while eliminating unwanted characteristics, e.g., noise. After filtration the resulting image is reverse transformed to yield a two color 'extracted structure' (Figure 1c). This is the pattern recognition phase of the technique. The extracted structure obtained in this way is
not only useful for improved visualization of the internal structure but is also the basis for the next step in the sequence which is statistical analysis.

The statistical analysis is aimed at identifying quantifiable structural parameters. At the current state of the research there are six parameters which can be divided into two major groups. The first three parameters are characteristic of the carbon fringes found in the transmission electron micrographs and they are called shape factors. These are:
circularity (C), elongation (E), and length of fringes (Lₜ).

The second set of parameters refers to the overall arrangement of the fringes. These are:
the orientation distribution of the fringes (αᵢ), the inter-layer spacing (d₀₀₂), and the fractional coverage of the extracted pattern (F).

The circularity, the elongation and the fractional coverage can be computed according to equations 1, 2 and 3, respectively:

\[ C = \frac{4 \cdot \pi \cdot \text{Area}}{(\text{Perimeter})^2} \]  
(1)

where

\( \text{Area} \) and \( \text{Perimeter} \) refer to the individual carbon fringes in pixel units.

\[ E = \sqrt{\frac{m_{\text{max}}}{m_{\text{min}}}} \]  
(2)

where

\( m \) is a principal second moment of area.

\[ F = \frac{\text{Area of fringes}}{\text{Area of view}} \]  
(3)

Some of the other geometrical factors, e.g., length of fringes, their distance, which is the inter-layer spacing and the orientation of their long axis are shown in Figure 2.
Figure 2. Explanation of the geometrical parameters of the extracted structure.

This methodology opens the possibility for the direct examination of individual soot clusters and particles as a function of oxidation. In order to be able to examine the very same soot cluster/particle, the sample have to be deposited on a grid which survives the oxidation environment. The technique to prepare an oxidizable/heat treatable grid has been elaborated and is described in Appendix E.

One simple way to perform the oxidation experiment is the use of a thermogravimetric analyzer (TGA) connected to a data collecting computer. The instructions for this equipment are outlined in Appendix F.
RESULTS

The different measures of the structures of carbon black particles as a function of the oxidation history of the particles are reported below.

INTER-LAYER SPACING

Earlier studies of other authors found that when examined with a transmission electron microscope (TEM), increasing oxidation of soots results in increased orderliness of structure (2). That is, partial oxidation allows the carbon atoms to relax toward the thermodynamically favored graphitic state. Buseck et al. showed that the structure of amorphous coke becomes more orderly with increasing annealing temperatures (7). Results from our experiments support this argument. Figure 3 shows a slight but monotonic decrease in the mean values of the characteristic inter-layer spacing of both the CB 330 and the GB sample as a function of burnout. The same trend can be observed in the standard deviation values. Both results show that the internal structure of the soot particles becomes more ordered as the oxidation proceeds.

![Graph showing inter-layer spacing and standard deviation](image)

Figure 3. Effect of oxidation on the mean inter-layer spacing and the standard deviation values of nongraphitized (CB 330) and graphitized (GB) carbon black.
Also, the graphitized carbon black has a significantly smaller mean inter-layer spacing and standard deviation values than those of the nongraphitized samples. These data confirm that there is substantial ordering in the microstructure as a result of the graphitization and the inter-layer spacing of the graphitized carbon black approaches that of pure graphite as the extent of oxidation increases.

It is essential to clarify whether the parameters obtained are true measures of the sample, or characteristics of only the particular area that was examined. In order to address this question multiple analyses have been performed on non-graphitized carbon black samples that were oxidized to different extents. Figures 4a and b show the mean and standard deviation values of the inter-layer spacing for the two extremes, i.e., those corresponding to the 0% and 96% burnout. Different bars represent different soot particles within the respective sample. The mean inter-layer spacings corresponding to the particles within the 0% burnout sample are greater than those of the 96% burnout in all cases except one, while the standard deviation values for 0% are always greater than those for 96%. These results show the internal consistency of data taken on a particular soot sample, and the difference in both the mean spacing and its variability in going from one sample to another.

![Figure 4](image.png)

Figure 4. Variations of the (a) mean inter-layer spacing and (b) its standard deviation within the 0% and the 96% burnout carbon black sample, respectively.
The HRTEM image analysis based technique has the ability to directly measure inter-layer spacing within individual soot or carbon black particles and this allows one to obtain the full distribution of that parameter within the samples. Figures 5a-d show that the discrete characteristic spacings can be found in this way. Although Figure 5a (showing the inter-layer spacing distribution for the 0% burnout CB 330 sample) seems to be noisy at first glance, careful comparison of the 38%, 78% and 96% burnout sample reveals that on each of the distributions the peaks are approximately at the same locations. This result confirms that one mean value for the inter-layer spacing does not describe well the material, the distribution is multimodal and there are several characteristic inter-layer spacing values.

Figure 5. Distribution of the inter-layer spacing of CB 330 carbon black.
FRAGMENTAL COVERAGE

Figure 6 shows the fractional coverage of the extracted pattern for the 38% burnout and the 96% burnout carbon black samples, respectively. Note that any particle of the 38% burnout sample has a considerably lower fractional coverage value than does the 96% burnout sample. Both results confirm the capability of HRTEM to pick up the small but definite ordering in carbon blacks.

Figure 6. Fractional coverage for carbon black. (a) Mean values as a function of oxidation (b) Values corresponding to different particles within the 38% burnout and the 96% burnout carbon black sample, respectively.
DISCUSSION

Previous studies have already shown that when soft carbonaceous materials are annealed at high temperature or when graphite is disordered by neutron irradiation or mechanical grinding, a graph of the inter-layer spacing versus the processing time shows a set of arrests or plateaus (9). Discrete inter-layer spacing values for a variety of carbonaceous sources were reported to be about 3.38Å, 3.40Å, 3.425Å, 3.44Å, 3.49Å, 3.55Å, 3.68Å, 3.87Å. (10-15) It has been hypothesized that a subset of the mentioned discrete values are unique in elemental carbons regardless of its origin. (16) The most commonly used technique is X-ray diffraction (XRD). While it is possible to obtain good data from highly ordered materials, e.g. graphite, using thin samples, the examination of samples with a large amorphous component requires a substantial amount of sample. Also the exact determination of d-spacings from the diffuse diffraction patterns using a diffractometer may require the separation of the weak pattern of coherent diffracted radiation from the total measured intensity. This total measured intensity can contain large contributions from Compton scattering and other incoherent scattering processes. No simple direct measurement of the 002 spacing is possible using this technique.

The major peaks in the size distribution values of the 0% burnout sample are marked with the letters A - F on Figure 5a. Figure 5b shows the distribution for the 38% burnout carbon black. The location of the first peak (characteristic value A) is 3.28 Å, exactly the same as on the 0% sample. The same relationship is true for peak B, C and F. Peak D of the 38% sample is shifted left as compared to the 0% sample; essentially this shift is responsible for the overall decrease of the mean inter-layer spacing. The same trend, although to a lesser extent, can be noticed by comparing the two E peaks. Note that Figure 5b shows a characteristic peak between B and C, but since this is not indicated on any of the other distributions, it might be a result of experimental error. Also between peaks A and B there is a shoulder in Figures 5a, c and d while in Figure 5b it is a smaller peak. These peaks do not seem to be as characteristic as the others therefore they are not marked at this stage of the study. This thesis does not target the correct description of all
possible characteristic inter-layer spacing, the aim here is to show that the technique presented is capable of yielding the full distribution of inter-layer spacings and thus can be a valuable tool in studying the microstructural reordering.

Figure 7 summarizes the characteristic inter-layer spacings and shows that the above mentioned trend is true regardless of which two samples are compared. The first peak corresponds to 3.28 Å in all cases. The same is true for the last peak (F), except in the 96% burnout sample where, because of the increased ordering of the structure that peak disappeared from the distributions. As far as peaks B, C and E are concerned, their locations are not changing or are slightly decreasing as oxidation increases. The biggest (monotonic) decrease is noticed on the location of peaks D.

![Location of the characteristic peaks](image)

**Figure 7.** Location of the peaks of the inter-layer spacing distribution of the carbon black samples shown in Figure 5.

The increased orderliness of the structure is highlighted in Figure 8 which shows the relative areas corresponding to the last two peaks. In Figure 5 a cut-off line indicating the area which is considered to belong to peaks E and F is shown. The monotonic decrease in the relative size of the areas shows that higher inter-layer spacing values are eliminated, hence the structure becomes more ordered.
The decrease in the mean inter-layer spacing is therefore a consequence of both the decrease in the spacing corresponding to peaks such as D and the decrease in the weighting given to peaks E and F.

![Relative areas corresponding to peaks E and F](image)

Figure 8. Relative areas corresponding to peaks E and F in Figure 5.

Figure 9 shows the inter-layer spacing distribution of the 92% burnout graphitized carbon black. By comparing it to Figure 5d (96%, nongraphitized sample) the result is not surprising. As expected from the results shown in Figure 3 the distribution is less wide (standard deviation is smaller) and the mean is shifted to the left. Also the inter-layer spacing is much more uniform, and the increased orderliness yields an essentially unimodal distribution.
Figure 9. Distribution of the inter-layer spacing of the graphitized carbon black at 92% conversion.

RELEVANCE

It is well known that graphites are less reactive than amorphous carbons. The HRTEM provides a means of quantifying the dependence of reactivity on structure. This has been attempted by Davis et al. who examined the burnout of various coals in a flow reactor. They found that reactivity decreases with conversion. They also found that the orderliness of the structure is increased, therefore there is strong qualitative evidence that the increase in crystallinity correlates with the observed decrease in reactivity (1).

The relationship between reactivity and ordering is not necessarily simple. For CB 330 the time rate of change, dX/dt, of carbon conversion X versus conversion is reported for a temperature of 550 °C and an oxygen partial pressure of 0.1 atm in Figure 10a. When the rate of reaction is expressed per unit of residual carbon (1-X) the corrected rate dX/dt/(1-X) is found to increase with conversion as shown in Figure 10b. This is contrary to the Davis et al. hypothesis that reactivity decreases with increases in fractional coverage. The relationship between reactivity and carbon structure is therefore more complex and yet to be determined.
The following are issues that need to be addressed. For a reaction catalyzed with a mobile carbon such as potassium (17) the catalyst concentration and hence reactivity will increase with increasing burnout. The carbon blacks, being produced from petroleum products, contain inorganic material the concentration of which will increase with conversion and therefore would explain the trend observed in Figure 10b. Other carbons with low ash content, also show a similar behavior; e. g., the reactivity of spherocarbons shows a trend similar that seen for the carbon blacks. Another factor to be considered is the relative number of edge versus face carbon sites, a measure of which is provided by the HRTEM. The carbon blacks have fewer edge carbons than the chars studied by Davis et al.

The use of HRTEM provides an important added dimension in trying to rationalize the variation of carbon reactivity with conversion. This thesis, in providing trend opposite to that reported by Davis et al. underlines the fact that the reactivity is governed by a multiplicity of factors.
CONCLUSIONS

The aim of this research is the development of an image analysis system that can provide verifiable and statistically significant results for the characterization of the internal structure of soot particles by the utilization of high-resolution transmission electron microscopy. This technique is believed to be an important and necessary step toward the understanding of the microstructure and its changes as a function of various parameters with implications to the material's properties. These measures of the fine structure of carbons can then be used to provide insight on the factors governing the physical and chemical properties of carbons.
REFERENCES


APPENDIX A.

SOOT MORPHOLOGY: AN APPLICATION OF IMAGE ANALYSIS IN HIGH-RESOLUTION TRANSMISSION ELECTRON MICROSCOPY

(Á. B. Palotás, L. C. Rainey, C. J. Feldermann, A. F. Sarofim and J. B. Vander Sande. Accepted for publication in Microscopy Research and Technique; 1995)

ABSTRACT

Interest in the fine structure of soots and carbon blacks is motivated by a variety of possible applications. The structure provides information on the origins of the particles and on their adsorptive and reactive properties.

This paper describes a method for quantification of the structure of soots and carbon blacks based on direct electron microscopic observation followed by image analysis of these materials. High-Resolution Transmission Electron Microscopy (HRTEM) provides a very detailed observation of the particle structure. The differences in soot structure, because of its complexity, may not be easily quantifiable with the human eye; therefore, high level computer software has been used to manipulate the HRTEM images. This technique involves the application of Fast Fourier Transforms (FFT) to single particles and the measurement of characteristic parameters such as inter-planar spacings and crystallite sizes from these particles.

The methodology and the application of this characterization technique is presented here. Results are shown for different samples obtained from soot and carbon black particles selected to illustrate the capabilities of the methodology. Quantitative information can be obtained on structural characteristics, e.g. inter-planar spacing, circularity, orientation, elongation and length distribution of lattice fringes as well as the fractional coverage of the extracted pattern.
INTRODUCTION

This paper presents a combination of techniques to recognize and classify different carbonaceous materials using their structural morphology. A new method to assess and quantify the parameters which define such structures is proposed and discussed. The technique is based on the use of HRTEM (High-Resolution Transmission Electron Microscopy) and computational image analysis.

It is well known that carbonaceous materials like graphite, soots, coals, cokes, chars, etc. possess characteristic structural appearances which can vary from mostly random or amorphous to a perfectly ordered graphitic crystalline structure (Buseck and Bo-Jun, 1985; Buseck et al., 1987). The carbon structure has been variously described as turbostratic (Oberlin, 1989) or as crumpled sheets (Rouzaud et al., 1991) to indicate that parallel layering, reminiscent of graphite, is observed over dimensions of nanometers but that these planes or crystallites show disorder over larger scales. The degree of order of such structures is strongly dependent on the thermal treatment of the material as well as the composition of the source of the carbonaceous material. The value of the electron microscope in studying the morphology of such materials has been well established and abundant information is available (Ishiguro et al, 1991; Lahaye and Prado, 1978; Buseck 1992).

The use of high-resolution TEM has brought further insight into this matter. Qualitative assessment of the structural order of such materials have been attempted over a long period of time in order to differentiate between various sources or treatments. There is to date no successful method available to quantify the structural characteristics of various carbonaceous materials. This paper presents a technique which is able to recognize different materials and to quantify the structural parameters of those materials using HRTEM and computational image analysis including pattern recognition techniques.

In the case of perfectly ordered graphitic crystals, electron diffraction is widely used for obtaining details on its structure. The analysis of the diffraction patterns can reveal parameters such as the inter-planar spacing, \( d_{002} \), crystallite size along the c-axis, \( L_c \), crystal size in the plane of the layers, \( L_a \), mean number of crystallites, \( N_c \), etc.
Complicated electron microscopy methods such as defocusing, tilted illumination, axial illumination, etc. often have to be used in order to characterize complex materials such as randomly oriented crystals in soots and carbons. Obtaining the right focus, contrast and phase settings is a subjective procedure and prone to errors. The thickness of the sample investigated is constrained by physical restrictions, which means that samples with layers oriented in different directions will present difficulties in focusing and will show an interference pattern difficult to interpret for more than a few layers. Additionally, the diffraction pattern will show the characteristics of the different layers observed. One way to overcome these problems was developed and refined after the appearance of the first laser sources (Taylor and Lipson, 1965; Ban, 1972). This method relies on the optical diffraction of a coherent light beam passing through a photographic image of the sample. The resulting optical diffraction pattern is basically the Fourier Transform of the image, the intensities are the Fraunhofer patterns (Hammond, 1992).

The technique presented here is a further development of this latter method and makes use of modern image analysis equipment and pattern recognition techniques. In contrast to the laser based technique, this new development allows for complete mathematical processing and filtering of the image. Much information is thus extractable from one single micrograph; many effects such as defocusing, variation of illumination, etc. can be simulated and tested. The method can be automated and the analysis of different structures made more objective and quantitative.
MATERIALS AND METHODS

The techniques referred to above are applicable to carbon samples thin enough to yield an image in a transmission electron microscope. Soots are convenient materials to study because they do not require any special sample preparation prior to observation. The method is also applicable to thicker samples of chars and carbons which can be comminuted to yield sections that are thin enough for TEM examinations (Davis et al., 1994).

Two soots, one generated by a Diesel engine and the other in the laboratory, and a partially oxidized carbon black were selected for the illustration of the methodology. The Diesel soot was generated by a D-916-6, 6 cylinder engine, 380 in$^3$ displacement, rated at 94 HP (at a speed of 2300 rpm) under a load of 106 ft-lb and it was collected on a 90 mm Palflex filter. The anthracene soot was formed in a drop-tube furnace by pyrolysing anthracene for 200 ms at 1200 °C and then subsequently graphitizing the collected solids for 3 hours at 2000 °C. The carbon black was a CB330 from DeGussa. It was oxidized in a Thermo-Gravimetric Analyzer (TGA) in air at 575 °C to an arbitrarily chosen 38% weight loss.

For the HRTEM observation a small portion of each sample was ultrasonically dispersed in ethanol. The suspension was deposited dropwise on a copper TEM grid coated with a lacey carbon film. The examination of the samples was carried out on areas that extended over the holes in the supporting film in order to avoid interference from the amorphous carbon background film. An oriented gold single crystal was used as a calibration standard and subjected to the same techniques as the soot samples.

An Akashi/TOPCON 002B transmission electron microscope, operated at 200 keV, with a LaB$_6$ filament was used to record high-resolution images of each sample. These images were then digitized with a VIDEK™ image acquisition system equipped with a Kodak MEGAPLUS™ Model 1400 camera and stored as 1024×1024 pixel computer images. A high-level language computer software, SEMPER6P® (Synoptics Ltd., Cambridge, UK), developed specifically for use with high-resolution electron microscopy, was then used to manipulate the stored images in order to extract data which could physically characterize
these soots. From these digitized images, optical diffraction patterns were generated. The optical diffractogram is a power spectrum calculated from the modulus of the Fourier Transform. Intensity profiles characteristic of the range of contrast of the diffractograms were then produced.

The Fourier Transform (FT) of the TEM image can be used to establish periodicities, and is also used to extract significant structural data from the image while eliminating noise. A direct relationship between the inverse space of the FT and the original image can be established by the use of an oriented gold single crystal as a calibration standard. Since the crystal is perfectly ordered, the distances of atoms within each plane are exactly the same regardless of the location. The Fourier Transform of the TEM image of this gold single crystal therefore shows pairs of spots corresponding to the repetition of the $d_{111}$, $d_{200}$, $d_{220}$, etc. distances. An example of the FT of this material is shown in Figure 1. The FT is symmetric by definition, each spot has a mirror pair, and the line connecting them goes through the center (origin) of the FT. Each spot can be described by the distance from the origin and this distance can be correlated with the corresponding repetition distance ($d_{111}$, $d_{200}$, $d_{220}$, etc.) of the original TEM image. Carbonaceous materials do not show such a high degree of order; therefore the characteristic repetition distance is spread over a $[d_1, d_2]$ range. The corresponding FT shows pairs of arcs with width $\Delta r$. (For purposes of comparison, the FT of the carbon black and the diesel soot can be found in Figure 5.) The relationship established using the oriented gold single crystal can be used to translate the $[d_1, d_2]$ range of interest, specified for pattern repetition, into an $[r_1, r_2]$ region in Fourier space. The FT of the original image is then masked for $r<r_1$ and $r>r_2$ ($r_2>r_1$). The remaining annulus is then reverse transformed\(^{\dagger}\). The resulting image is called the 'filtered' image of the original micrograph. This gray scale filtered image can be transformed to a two color 'extracted structure' by establishing an intensity threshold

\(^{\dagger}\) Theoretically the center peak (corresponding to infinite distance on the original image) in the Fourier space is always needed for the reverse Fourier Transformation, therefore an annulus would be insufficient. Our image analysis software retains the information content of the center peak, and even if the center is manually masked out the reverse transform can be performed.
value for the intensity of the pixels, separating the two colors (here selected as black and white). This is the pattern recognition phase of the technique.

Figure 1. Computer generated diffractogram (power spectrum) of an oriented gold single crystal. “Computer generated” in this context means that the image was digitized and then Fourier transformed. The power spectrum is simply the squared modulus (intensity) of the Fourier transform.

The resulting extracted structure then becomes the basis for statistical analysis of, in our case, the carbon lattice fringes. The parameters that can now be quantified are circularity, elongation, lateral extent, angular dependence or orientation of fringes, inter-planar spacing, and fractional coverage of the field of view by the extracted pattern, as defined below:

Circularity of fringes, measured on a scale of 0 to 1, is defined as

$$\frac{4 \cdot \pi \cdot Area}{(Perimeter)^2}$$

(1)
where *Area* and *Perimeter* refers to a single lattice fringe. A fringe, as far as the image analysis is concerned, is a continuous black area in the extracted pattern.

In Figure 2 a magnified region of the extracted pattern is shown to illustrate the fringes. Each individual fringe is considered to be an independent object and its area, perimeter, center of area, principal second moments, orientation, etc. can be determined.

![Figure 2. Magnified portion of the extracted pattern of a diesel soot sample.](image)

The elongation of fringes is defined as

$$\sqrt{\frac{m_{\text{max}}}{m_{\text{min}}}}$$

where $m$ is a principal second moment of the area. A second moment is a mean square distance of all pixels about a line through the center of the area of a structural element (fringe). The principal second moments are the second moments with respect to a pair of mutually perpendicular axes in directions that achieve maximum and minimum moments.

The lateral extent or length of fringes is defined as:

$$L_a = A \cdot B \cdot \sqrt{m_{\text{max}}}$$

$m_{\text{max}}$ is the maximum principal second moment and the value of $A$ is usually between 3 and 4 depending on the shape of the object in question. For carbon fringes the value of $A$ was determined experimentally and found to be 3.56 in pixel units. $B$ is a simple pixel to Ångström conversion factor. Given the magnification and resolution in our current setup:
\[ B = 0.4336 \frac{A}{\text{pixel}} \]

The orientation or angular dependence of a structural element (fringe) is the angle in degrees between a line connecting the center of the image to the center of area of the structural element and the axis giving the lowest second moment of area. In other words, the orientation of the fringe is the angle between the radius going through the center of the fringe and the long axis of the fringe.

None of the above parameters has a constant value over the area of interest; therefore a statistical analysis must be applied. The extracted structure of an area in the TEM image of approximately 25 nm diameter usually consists of several hundred fringes. The circularity, elongation, lateral extent, and orientation of each of these fringes are calculated by the image analysis software and the mean and the standard deviation values of the different parameter distributions are determined.

Inter-planar spacing is defined as the distance \((d_{002})\) between parallel fringes.

The best method to get the characteristic inter-planar spacing value for a sample proved to be the calculation of the distance within parallel fringe pairs. As a first step those fringes should be filtered out which have no parallel pair in a reasonable distance range (A meaningful inter-planar spacing for carbonaceous materials is between 3.2 and 4.0 Å. Any value outside this range is considered not to be physically realistic for an inter-planar spacing). For the purpose of the measurement of the inter-planar spacing each fringe \(i\) is characterized by the center of area \(P_i\) and the orientation of the long axis \(\alpha_i\). The actual calculation of the distances \(d_i\) of the parallel fringes \(i\) and \(i+1\) is then done by using the following formula:

\[
d_i = \frac{m_i \cdot (x_{i+1} - x_i) - (y_{i+1} - y_i)}{\sqrt{m_i^2 + 1}},
\]

\[
m_i = \tan \left( \frac{\alpha_i + \alpha_{i+1}}{2} \right),
\]
where \((x_i, y_i)\) and \((x_{i+1}, y_{i+1})\) are the coordinates of \(P_i\) and \(P_{i+1}\), respectively. This calculation should be repeated several times for as many pairs of fringes as possible in order to obtain statistically meaningful values. The inter-planar spacing can then be specified by the mean and the standard deviation values or as a distribution function which would show if there was more than one characteristic spacing.

The fractional coverage of the extracted pattern is defined by the following equation:

\[
C = \frac{\text{Area of fringes}}{\text{Area of view}}
\]  

(5)

It should be noted that the fractional coverage is very sensitive to the area chosen; therefore it can be used as a distinguishing parameter only in well defined situations. The conditions governing the choice of the area are given in the next section.
RESULTS

This paper presents the methodology and the application of a combination of techniques for the characterization of various soot particles. HRTEM is capable of providing detailed information on the crystalline structure of carbonaceous materials and allows one to distinguish individual graphitic layers oriented perpendicular to the image plane. Further, image analysis can provide the quantification of the micro-structure and can help distinguish between materials having similar structures. This technique involves the application of FFT to single particles and the measurement of characteristic parameters such as inter-planar spacings and crystallite sizes. Using the methodology described in the previous section, we were able to quantify the microstructure of soot particles by calculating the circularity, elongation, length and orientation distribution of fringes and the inter-planar spacing. An additional distinguishing parameter is the fractional coverage of the extracted patterns.

![High-resolution transmission electron micrographs of carbon black and diesel soot](image)

Figure 3. High-resolution transmission electron micrographs of carbon black and diesel soot: (a) carbon black; (b) diesel soot.

The electron micrographs in Figures 3a and b show the turbostratic lattice fringes of the carbon black and the diesel soot samples. These micrographs were digitized and stored as
a 1024×1024 pixel images. A circular portion (with 256 pixel radius) of each of these images was selected for further analysis, as seen on Figures 4a and b.

Figure 4. Selected area of the HRTEM images of the samples: (a) carbon black; (b) diesel soot. The center of magnification is indicated by arrows in Figures 3a and b, respectively.

The optical diffractogram (OD) or power spectrum (Figures 5a and b) generated from this circular section shows the periodicities present in this soot. The amount of diffusion in the brightest carbon ring (002) is indicative of the amount of ordering and the range of inter-planar spacings (d_{402}) present. The structural differences are also highlighted on the diffractogram. The fact that the OD pattern is almost a perfect circle shows that the lattice fringes are approximately evenly distributed over all possible directions (0...360°). The radius corresponding to the brightest point can be transformed to a distance on the original image which can be interpreted as the mean inter-planar spacing. The OD patterns of these samples have a wide range of radii where the intensity of the pixels are
approximately the same, which means that these materials have a wide range of inter-
planar spacings.

Figure 5. Computer generated power spectra of the samples shown in Figure 4:
(a) carbon black; (b) diesel soot.

Another series of manipulations which can be applied to the selected area of the original
images (Figures 4a and b) is that of 'filtering', or the use of a series of software
commands to extract only the significant structural data from the image while eliminating
any unwanted characteristics. Figures 6a and b show the extracted images of the carbon
black and the diesel soot particles, respectively. These images highlight the differences in
the morphology by eliminating the noise and still contain all of the necessary information
for the analysis of the structure.
Figure 6. Extracted patterns of the samples shown in Figure 4: (a) carbon black; (b) diesel soot. The extracted pattern is obtained from the digitized micrograph by Fourier transforming, filtering, reverse transforming and finally establishing a threshold value for the intensity of the pixels.

Table 1 shows the results of the statistical analysis.

<table>
<thead>
<tr>
<th></th>
<th>Carbon black</th>
<th>Diesel soot</th>
</tr>
</thead>
<tbody>
<tr>
<td>Circularity</td>
<td>0.35 ± 0.14</td>
<td>0.35 ± 0.15</td>
</tr>
<tr>
<td>Elongation</td>
<td>4.32 ± 1.96</td>
<td>4.29 ± 2.06</td>
</tr>
<tr>
<td>Length</td>
<td>11.76 ± 6.19 Å</td>
<td>12.47 ± 7.17 Å</td>
</tr>
<tr>
<td>Orientation</td>
<td>88.71° ± 40.65°</td>
<td>87.62° ± 34.44°</td>
</tr>
<tr>
<td>Inter-planar spacing</td>
<td>3.48 ± 0.12 Å</td>
<td>3.83 ± 0.25 Å</td>
</tr>
<tr>
<td>Fractional coverage</td>
<td>26.18 ± 0.47 %</td>
<td>29.46 ± 0.62 %</td>
</tr>
</tbody>
</table>

Table 1. Structural data of the samples
DISCUSSION

There are a number of software parameters which should be carefully chosen in order to be able to operate at conditions generally valid for most of the samples. These are:

The frequency band in Fourier space. Filtering was used in order to eliminate the maximum possible noise while retaining all possible fringe spacings.

In the realm of carbonaceous materials, the mean inter-planar spacing ($d_{002}$) varies from 3.35 Å up to more than 4.00 Å (Oberlin, 1989). Smith and Buseck (1981; 1982) found that, in carbon-rich residue of a meteorite, carbon consists of a tangled aggregate of fibrous crystallites, with a characteristic lattice-fringe spacing of 3.4 to 3.9 Å. The possible fringe spacings for carbon have been summarized by Aladekomo and Bragg (1990) and vary from the graphitic spacing of 3.35 Å to values for amorphous materials as high as 3.86 Å. For both vitrinite and inertinite extracts Lin and Guet (1990) found an average of 3.6 Å, approximately in the middle of the ranges quoted by other authors. On this basis filtering of the FT was used to retain those fringes only which show fringe spacings between 3.0 and 4.5 Å. As shown in Table B1, the results obtained are in good agreement with the literature values.

The threshold intensity. This is the minimum intensity of a pixel to be considered as a part of a fringe in the processed image (‘extracted structure’).

Figure 7 illustrates the effect of the intensity threshold value on a set of extracted patterns. In this set there are nine different “images” of the same carbon black particle. Along the vertical axis the intensity threshold value decreases, and it can be seen that the number of structure elements, as well as the fractional coverage, grows as lower intensity groups of pixels appear. Along the horizontal axis, the range in which repeated patterns are seen is narrowing around the inter-planar spacing of graphite (3.35 Å). These images were created in a way that the inner radius of the masked area of the Fourier Transform was increased while the outer radius was held constant. This produced a progressively narrower annulus in Fourier space which then was reverse transformed to yield the extracted pattern. Much of the structure is eliminated if we use too narrow a range, which
means that the inter-planar spacing of this carbon black is either different from that of graphite or the distribution of spacings is much wider.

<table>
<thead>
<tr>
<th></th>
<th>3.0 ... 5.0 Å</th>
<th>3.0 ... 4.2 Å</th>
<th>3.0 ... 3.7 Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I_1=3.0)</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td>(I_1=2.0)</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td>(I_1=1.0)</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
</tbody>
</table>

Figure 7. Effect of software parameters on the extracted pattern (carbon black). The horizontal axis shows the frequency window for the repeated pattern while the vertical axis is \(I_1\), the intensity threshold value for the filtered image.
By lowering the minimum intensity accepted as part of a fringe, the fringes become longer and thicker until the fringes begin to merge. As this happens the total number of fringes found increases as lower intensity groups of pixels appear. When the fringes begin to merge the number of identified fringes levels off and begin to decrease. The maximum is useful since it gives the largest and most realistic fringe length. (This technique will always underestimate the fringe length because of the twisting of the aromatic layers and the interference of amorphous material and other fringes).

![Fractional coverage vs. Intensity threshold](image)

Figure 8. Effect of the intensity threshold value on the fractional coverage and on the number of lattice fringes found (diesel soot). As the minimum intensity accepted as part of a fringe increases the fractional coverage decreases since fewer pixels satisfy the condition of having sufficiently high intensity. At low intensity threshold value the fringes are long and thick and they are merged. As the threshold value increases the fringes begin to separate and the total number of fringes increases. By increasing the threshold value even more the disappearance of the lower intensity group of pixels accelerates and the number of identified fringes levels off and begins to decrease.

Figure 8 shows these trends for the diesel soot sample. In addition the use of this well defined criterion also allows for consistent treatment of images which are taken from sections of varying thickness and potentially of varying contrast and brightness.
The importance of using the optimum intensity threshold values when determining the fractional coverage is illustrated by the next example. Figure 9 shows the extracted patterns of three particles of the same carbon black sample.

<table>
<thead>
<tr>
<th></th>
<th>Particle B</th>
<th>Particle D</th>
<th>Particle F</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I_t=2.1)</td>
<td>![Particle B Image]</td>
<td>![Particle D Image]</td>
<td>![Particle F Image]</td>
</tr>
<tr>
<td>Fractional coverage</td>
<td>26.7 %</td>
<td>13.6 %</td>
<td>3.3 %</td>
</tr>
</tbody>
</table>

Figure 9. Pictorial representation of the effect of the intensity threshold value on the fractional coverage (carbon black). The threshold value is optimized for particle B but not for particles D and F.

The intensity threshold value was held constant at the value of the optimum intensity threshold of the first particle (Particle B). Although the three particles were imaged using the same microscope, the microscopy work was done over a long period of time, and thus a number of microscope parameters had varied. The example illustrates well that using a constant value for the intensity threshold can falsify the fractional coverage. On the other hand, if the intensity threshold value is optimized as described above, the fractional coverage values for different particles of the same sample remain in a remarkably narrow band and this parameter seems to be a valuable one in distinguishing otherwise similar samples. Figure 10 shows the variation of the fractional coverage of the patterns extracted for different particles within the carbon black and the diesel soot samples. These images
show that the variation of this parameter between particles in a soot or carbon is small, of the order of plus or minus one percent.

Figure 10. Variation of the fractional coverage within the samples.

**Circularity and elongation.** Both parameters are the measure of the shape of the lattice fringes. The value of circularity ranges from 0 for an elongated shape of infinitesimal width to 1 for a circle. For the same shapes the value of the elongation is infinite and 1, respectively. This comparison may suggest that one parameter is just the reciprocal of the other, but this is not the case. Careful examination of the definitions reveal that they are two different parameters and they have the potential to distinguish otherwise similar structures.

**The minimum area of a fringe.** This is an additional filtering parameter for fringes to be considered in the extracted structure.

The minimum area used to define a fringe was determined by multiplying the length of one of the thinner fringes (approximately 1 Å) by the length of two aromatic units (approx. 5 Å). The elimination of noise to the maximum possible extent is vital, since it can falsify describing parameters, e.g., orientation or elongation distributions.
It should be noted that there can be other adjustable, filtering parameters (e.g., maximum circularity, maximum curvature, minimum length) but their effect on the characterization of the samples has not been determined.

Alternative methods for the quantification

Inter-planar spacing. The fundamentals of electron microscopy require that the lattice fringes that we have imaged are only those in the 002 plane that fulfill the Bragg condition (Edington, 1975). These lattice fringes are the aromatic layers seen edge-on. The interpretations of fringes in carbonaceous materials, as well as the decrease in order upon mesophase formation and the subsequent increase in order at higher temperatures, is supported by multi-slice calculations (Marsh and Craford, 1984; O'Keefe and Buseck, 1979). Since planes of carbon atoms can curl but still appear as fringes when viewed edge-on, rigorous interpretation of two dimensional images must be done with great caution. Fryer (1981) examined the micropore structure of turbostratic carbons as a function of accelerating potential of the TEM. Historically, inter-layer measurements have been made, since the early 1960's, by X-ray powder diffraction spectrometry. With this method, only averaged values are obtained, rather than the full range. The measurement of magnetoresistance on carbon black, coke and other carbonaceous materials that were well graphitized by heat or pressure has resulted in reliable values for inter-planar spacing; however, the method cannot be used for turbostratic structures such as non-graphitized carbon blacks, because the random orientation results in negative magnetoresistance values (Hishiyama et al., 1991).

By using the methodology described in the previous sections the distribution of the inter-planar spacings can be generated. It should be noted that this distribution has more than one peak; therefore in some cases instead of just quoting one characteristic value, it would be more appropriate to give the location and the width at half peak height of the other characteristic values as well. Figures 11a and b show the inter-planar spacing distributions for our samples. The characteristic values are given in Table 2. The use of microscope or computer generated diffractograms does not provide such detailed
information, but only a single mean and a standard deviation value of the inter-planar spacing.

![Graphs showing distributions of inter-planar spacing for carbon black and diesel soot.](image)

Figure 11. Distributions of the inter-planar spacing of the samples: (a) carbon black; (b) diesel soot.

<table>
<thead>
<tr>
<th>Peak no.</th>
<th>Carbon black</th>
<th>Diesel soot</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.31 ± 0.03 Å</td>
<td>3.54 ± 0.01 Å</td>
</tr>
<tr>
<td>2</td>
<td>3.42 ± 0.06 Å</td>
<td>3.75 ± 0.21 Å</td>
</tr>
<tr>
<td>3</td>
<td>3.48 ± 0.01 Å</td>
<td>3.85 ± 0.03 Å</td>
</tr>
<tr>
<td>4</td>
<td>3.58 ± 0.06 Å</td>
<td>4.06 ± 0.02 Å</td>
</tr>
<tr>
<td>5</td>
<td>3.74 ± 0.03 Å</td>
<td>4.23 ± 0.10 Å</td>
</tr>
</tbody>
</table>

Table 2. Characteristic inter-planar spacings for the samples

Another representation of the contrast transfer patterns is the radial intensity profile which has been generated from the power spectrum (Figures 5a and b). Figures 12a and b show the intensity profiles of the respective samples. The highest points of the profile, except for the center peak, are the characteristic values corresponding to the brightest part
of the diffractogram. One way of obtaining a value for the characteristic inter-planar spacing is to measure the radius corresponding to the peak on the intensity profile. The repeating distance (e.g. inter-planar spacing) on the original image is inversely proportional to the radius and can be calculated by using, for example, an oriented gold single crystal as a calibration standard. If the sample is not perfectly ordered (in which case the annulus of the OD pattern would shrink to a pair of dots) then interest is in the spread as well as the mean value of the inter-planar spacing (peak on the intensity profile). The difficulty with this method is that although a peak can be identified for any sample, the determination of the corresponding spread is far from trivial.

![Intensity profiles](image)

Figure 12. Intensity profiles of the computer generated diffractograms shown on Figure 5: (a) carbon black; (b) diesel soot. The sharp peaks at the center are reflecting the direct beam. Note that the intensity values are averaged over all the directions, that is why the shadowed cross, contained in Figure 5a, is not showing up.

**Orientation distribution**: The choice for quantification of this parameter is dependent on the structure of the material. For the case of highly turbostratic structures, like the carbon black and diesel soot presented in this paper, the best method is defined in the section ‘Materials and Method’. The methodology described in this paper, however, is not limited to these structures only; the method can be applied to non carbonaceous materials as well. If we were to examine a sample with a fairly ordered microstructure, we would
use a different approach to describe the orientation distribution. For the illustration of this idea let us examine a laboratory made and then graphitized anthracene soot. Figures 13a and b show the HRTEM image of this sample and the extracted pattern, respectively.

![HRTEM image and extracted pattern](image)

Figure 13. (a) HRTEM image and (b) extracted pattern of a graphitized anthracene sample.

It can be seen on the extracted pattern that there is a high degree of order in the orientation of the carbon fringes. Most of the fringes are more or less parallel; therefore the orientation distribution described earlier (Method 1) would yield a fairly constant value without an identifiable peak. If this is the case the quantification should be the following (Method 2): The orientation or angular dependence of a structural element is the angle in degrees clockwise from a reference axis to the axis giving the lowest second moment of area, i.e. the long axis of the structural element. The reference axis is chosen so that the statistical mean of the orientation of all structural elements is 90°. In other words the reference axis points along the mean of the normals to the fringes. Figures 14a and b show the comparison of the two methods in the case of the anthracene sample, while Figures 14c and d compare them using the diesel soot. It should be noted that Method 2 yields a peak in the case of a highly ordered structure, and therefore is more...
easily quantifiable than Method 1. The opposite is true for turbostratic structures: Method 1 gives a peak, while Method 2 yields a noisy distribution difficult to quantify.

**Distribution of the circularity, elongation and length of fringes.** Plots of these distributions (Figures 15a-c) show that they are essentially uni-modal, therefore the mean and the standard deviation values are reasonable measures of the data.

![Graphs](image)

**Figure 14.** Comparison of the two methods for the quantification of the orientation distribution: (a) anthracene, Method 1 (the orientation of the fringe is the angle between the radius going through the center of the fringe and the long axis of the fringe); (b) anthracene, Method 2 (the orientation of a structural element is the angle in degrees clockwise from a reference axis to the long axis of the structural element); (c) carbon black, Method 1; (d) carbon black, Method 2.
As a further test of our method and the reliability of the microscope conditions, the microscope was calibrated using an oriented gold crystal standard. The result showed virtually no change in pixel measurement over a six month period. The ability to reproduce consistent gold lattice images over a period of time is characteristic of a microscope with stable lens currents as well as invariable magnification, specimen height, and sample preparation.

Figure 15. Distributions for the following parameters: (a) circularity, (b) elongation and (c) the length of fringes (carbon black).
CONCLUDING COMMENTS

A combination of HRTEM and computational image analysis techniques has been used to recognize and classify the structural morphology of different carbonaceous materials. The quantification of the parameters which define such structures is proposed and discussed.

The quantification is based on several carefully defined geometrical parameters and it is apparent that the success or failure of this analysis technique relies on the choice of the above mentioned parameters. In addition to consistent microscopic techniques, the software parameters that are chosen must be those which are valid for most of the samples examined. Correct frequency band filtering of the Fourier Transform is necessary to obtain realistic parameter values, while eliminating 'noise' and retaining all possible inter-planar spacings. The optimum intensity threshold value must be found (by the method described in the previous section) in order to permit the most feasible and consistent analysis among particles of varying thickness. The applications of other filtering parameters may be potentially important in differentiating among samples of similar structure if proper restrictions are chosen.

We believe that the utilization of high-resolution microscopy and the development of an image analysis system that can provide verifiable and statistically significant results for the characterization of the internal structure of soot and other carbonaceous materials is an important and necessary step toward the quantification of the fine structure of carbons for a variety of applications. The methodology should also be applicable to other materials. Since the field is relatively unexplored there is obviously much scope for further developments.
ACKNOWLEDGMENTS

We are indebted to Prof. Ciambelli of the University of Salerno, Italy, for the carbon black samples, to Kevin Davis of Sandia National Laboratories, CA and to Richard C. Flagan of California Institute of Technology for valuable discussions.

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REFERENCES


APPENDIX B.

APPLICATION OF HIGH-RESOLUTION ELECTRON MICROSCOPY FOR THE CHARACTERIZATION AND SOURCE ASSIGNMENT OF DIESEL PARTICULATES

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ABSTRACT

The concern with the possible negative health effects of diesel exhaust in the mining environment has increased with the economic incentives for wider use of diesel-powered equipment in mining operations. The evidence derived primarily from inhalation studies has shown that diesel soot is a carcinogen for laboratory animals. Such results have led the National Institute for Occupational Safety and Health to recognize that diesel exhaust is a potential health hazard and that, although the risk for workers exposed to diesel exhaust has not yet been quantified, exposure to such exhausts should be minimized.

We have proposed, in this present work, to attempt to characterize and to allocate the source of various diesel soots. The differences in soot structure, because of the complexity of the soot lattice, may not be easily quantifiable with the human eye; therefore, high level computer software has been used to manipulate high resolution TEM images of in-mine diesel soots in order to extract pertinent information which can help identify the combustion, oxidation, and heat-treating history of these soots.

The first phase of this project has been the building of a data base for diesel soots which contains information that can be used to identify the physical and chemical history of these soots. Three diesel soot samples from a test diesel engine, operating under varying conditions, have been examined by TEM and high resolution image analysis computer software. The structural differences among these three soots have been quantified.

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INTRODUCTION

The standards for occupational safety and health in the workplace are becoming increasingly stringent. So too are the health and safety regulations in the coal mining environment. Diesel soot is one of several types of respirable particles to which miners may be exposed both in and outside of their workplace. The use of diesel-powered equipment has become more prevalent in the mining environment in recent years because of the economic incentives involved. The concern for the possible negative health effects of diesel exhausts is largely based on evidence from animal inhalation studies. There has been gathering evidence from animal inhalation studies in the laboratory in recent years to indicate that diesel soot is a carcinogen in animals.\(^\text{1-3}\) Such studies have prompted the National Institute of Occupational Safety and Health to state that whole diesel exhaust should be regarded as a potential carcinogen and that the probability of developing cancer may be decreased by minimizing exposure.\(^4\) Currently, diesel exhaust aerosol is regulated under the 2.0 mg/m\(^3\) respirable coal mine dust standard.; however, the U.S. Mine Safety and Health Administration has published an advanced notice for the establishment of a separate permissible exposure limit for diesel particulates.\(^5\)

The carcinogenic characteristics of diesel soots are largely attributed to the chemical compounds, polynuclear aromatic hydrocarbons (PAH), which are formed during combustion and are adsorbed onto the soot substrate particles.\(^7\) The release of PAH in the biological system may be controlled by the soot particle structure (size, morphology, porosity) as well as the overall mutagenic activity of the particle/adsorbate complex.\(^8-11\)

Diesel soot consists of spherical primary particles, approximately 30 nm in diameter, that are aggregated in grapelike clusters of 1-2 \(\mu\)m.\(^12\) In the diesel engine, soot usually forms in fuel-rich pockets and may undergo oxidation before being exhausted to the atmosphere. The extent of oxidation varies among engines\(^13\) and it has been found that when examined with a transmission electron microscope (TEM), increasing oxidation of soots results in increased orderliness of structure.\(^14\) That is, the partial oxidation allows the carbon atoms to relax toward the thermodynamically favored graphitic state. Buseck
et al. showed that the structure of amorphous coke, when imaged by TEM, becomes more orderly with increasing annealing temperatures.\(^{(15)}\)

In order to test the hypothesis that the internal structure of a diesel soot particle and its composition are related to the combustion conditions under which it was formed, and further that this structure may relate to the release of adsorbed compounds in the biological system, an in-depth study of the microstructures of diesel soots formed under various conditions is necessary. In this present work, we have begun the construction of a data base for diesel soots which contains information that can be used to identify the combustion history of these soots.
EXPERIMENTAL PROCEDURE

Diesel emissions, as noted above, are complex in structure and composition. High-resolution transmission electron microscopy (TEM) coupled with an image analysis technique, utilizing high level computer software, have been used to analyze the structure of three diesel soot samples obtained from a test diesel generator, an MWM engine approved for use in underground coal mines (courtesy of Winthrop Watts, U.S. Bureau of Mines, Minneapolis). These three samples were generated by a D-916-6, 6 cylinder engine, 380 in\(^3\) displacement, rated at 94 HP at 2300 rpm. The samples were collected on 90 mm Palflex filters, and were generated at steady state conditions to simulate the extremes and mid-point of engine load. The samples are called Idle, Medium and Heavy.

Sample Idle was generated at a speed of 800 rpm and a 20 ft-lb load. Sample Medium was generated at a speed of 2300 rpm and a 106 ft-lb load. Sample Heavy was generated at a speed of 2300 rpm and a 210 ft-lb load.

A small portion of each sample was ultrasonically suspended in ethanol and then deposited dropwise on lacey carbon TEM grids. An oriented gold crystal was used as a calibration standard and subjected to the same techniques as the diesel soot samples. The use of a specifically ‘oriented’ gold crystal allows only the lattice locations in one plane to be diffracted. Then precise measurements of the lattice distances may be made and compared to the experimental samples.

An Akashi/TOPCON 002B transmission electron microscope with an LaB\(_6\) filament was used to record high resolution images of each sample. These images were then digitized with a VIDEK\textsuperscript{TM} image acquisition system equipped with a Kodak MEGAPLUS\textsuperscript{TM} Model 1400 camera and stored as 1024×1024 pixel computer images. A high-level language computer software, SEMPER6P\textsuperscript{TM} (Synoptics LTD., Cambridge, UK), developed especially for use with high-resolution electron microscopy, was then used to manipulate the stored images in order to extract data which could physically characterize these soots. From these digitized images, optical diffraction patterns showing the periodicities present were generated. The optical diffractogram is a power spectrum calculated from the modulus of the Fourier transform. Intensity profiles characteristic of the range of contrast
of the diffractograms were then produced. A series of 'filters' was also applied to the
digitized soot images to extract only the significant structural data from the image while
eliminating unwanted characteristics. This then becomes the basis for statistical analysis
of the structures.

The parameters that can now be quantified are circularity of fringes, lateral extent of
fringes, angular dependence or orientation, and inter-layer spacing.

Circularity of fringes is measured on a scale of 0 to 1. It is defined as

$$\frac{4 \cdot \pi \cdot \text{Area}}{(\text{Perimeter})^2}. \tag{1}$$

The lateral extent of fringes is defined as

$$\sqrt{\frac{m_{\text{max}}}{m_{\text{min}}}}, \text{ where} \tag{2}$$

$m$ is a principal second moment of area. A second moment is a mean square distance of
all pixels about a line through the center of area of a structural element (fringe). The
principal second moments are the second moments with respect to a pair of mutually
perpendicular axes in directions that achieve maximum and minimum moments.

The orientation or angular dependence of a structural element is the angle in degrees
clockwise from a reference axis to the axis giving the lowest second moment of area, i.e.
the long axis of the structural element. The reference axis is chosen so that the statistical
mean of the orientation of all structural elements is zero. In other words the reference axis
points to the mean direction.

Inter-layer spacing is defined as the distance $(d)$ between parallel fringes.

None of the above parameters has a constant value over the area of interest, therefore
statistical analysis should be applied. The extracted structure of the TEM image usually
consists of several hundred fringes. The circularity, lateral extent and orientation of each
of these fringes are calculated by the image analysis software and then transferred to a
spreadsheet. Using statistical functions, the mean and the standard deviation values of the
different parameter distributions were determined. The Fourier Transform of the TEM image can be used to find periodicities, and it is also useful to eliminate some unwanted features. Using the Fourier Transform a range can be specified, in which repeated patterns are recorded. This is one method of so called filtering. To get the characteristic inter-layer spacing value for the sample, first the total area (OriginalArea) of fringes were determined with minimal filtering, i.e. eliminating repeated frequencies only below 2 Å and above 7 Å. Then this range was narrowed, and it was shifted to a position were the area of fringes showed a maximum. The final range was specified where the area of fringes was only 50% of the OriginalArea.
RESULTS

The electron micrographs in Figures 1a - c show the turbostratic lattice fringes of the Idle, Medium, and Heavy load diesel soots. Turbostratic structure is the random orientation of carbon atom layers in the soot lattice, in contrast to the highly oriented lattices of graphitic structures. These micrographs were digitized and stored as a 1024×1024 pixel images. In Figures 2 - 4 the digitized image of the Heavy diesel soot (2a) undergoes a series of manipulations. A circular portion of this image was masked off (2b) using the image analysis software. The optical diffractogram or power spectrum (Figure 3a) generated from this circular section shows the periodicities that are present in this soot. The amount of diffusion in the brightest carbon ring (002) is indicative of the amount of ordering and the range of inter-layer spacings (d_{002}) present. Another representation of this contrast transfer pattern is the intensity profile (Figure 3b) which has been generated from the power spectrum. The highest points of the profile, indicated by an arrow, are the characteristic value corresponding to the brightest part of the diffractogram.

Another series of manipulations which can be applied to the original digitized and masked images (Figure 2b) is that of ‘filtering’ or the use of a series of software commands to extract only the significant structural data from the image while eliminating any unwanted characteristics. Figure 4 shows the extracted image of this soot. Figure 5 shows the extracted patterns of the three diesel soot samples and of a graphitized anthracene soot. Also shown are the results of the statistical analysis of the data.
Figure 1  (a) Digitized TEM image of idle load diesel soot  
   (b) Digitized TEM image of medium load diesel soot  
   (c) Digitized TEM image of heavy load diesel soot
Figure 2. (a) Digitized TEM image of heavy load diesel soot
(b) Extracted circular portion of 2a
Figure 3. (a) Computer generated diffractogram of 2b
(b) Intensity profile generated from 3a

Figure 4. Extracted structural image of 2b
### Idle
- # of fringes: 301
- Area of fringes: 25800 (12.5%)
- Circularity: 0.35±0.11
- Lateral extent: 5.32±2.16
- Orientation: 0°±50°
- Inter layer spacing: 3.46±0.13 Å

### Medium
- # of fringes: 486
- Area of fringes: 51266 (24.9%)
- Circularity: 0.36±0.14
- Lateral extent: 4.73±2.03
- Orientation: 0°±51°
- Inter layer spacing: 3.51±0.14 Å

### Heavy
- # of fringes: 366
- Area of fringes: 32874 (16.0%)
- Circularity: 0.34±0.12
- Lateral extent: 5.23±2.25
- Orientation: 0°±57°
- Inter layer spacing: 3.49±0.16 Å

### Anthracene, graphitized
- # of fringes: 317
- Area of fringes: 41284 (20.1%)
- Circularity: 0.24±0.11
- Lateral extent: 12.03±7.58
- Orientation: 0°±8°
- Inter layer spacing: 3.34±0.08 Å

Figure 5. (a) Extracted structural image of idle load diesel soot and results
(b) Extracted structural image of medium load diesel soot and results
(c) Extracted structural image of heavy load diesel soot and results
(d) Extracted structural image of graphitized anthracene soot and results
DISCUSSION AND CONCLUSIONS

The fundamentals of electron microscopy require that the lattice fringes that we have imaged are only those of the 002 plane that fulfill the Bragg condition (16). These lattice fringes are the planes of carbon atoms that are randomly oriented in the diesel samples shown in Figures 1a-c. In the realm of carbonaceous materials, the mean inter-layer spacing varies from 3.35Å up to more than 4.00Å (17). Historically, inter-layer measurements have been made, since the early 1960's, by X-ray powder diffraction spectrometry. With this method, only the averaged values are obtained, rather than the full range. The measurement of magnetoresistance (change in the electrical resistivity of a conductor with magnetic field) on carbon black, coke and other carbonaceous materials that were well graphitized by heat or pressure has resulted in reliable values for inter-layer spacing; however, the method cannot be used for turbostratic structures such as diesel soots, because the random orientation results in negative magnetoresistance values (18).

The three soots that we examined showed some similarities and some differences. The average number and the total area of fringes measured within each particle was dependent on those areas that complied with the Bragg condition. The circularity and orientation of fringes, because of the large standard deviation, did not vary to any great extent. The lateral extent mean value of the fringes in the Medium load diesel soot is slightly less than those of the Idle and Heavy loads. The average value of the inter-layer spacings among the three samples showed the greatest variation. The reasons for the differences among these soots are not known at this time, but the results are potentially meaningful and may be explained through the expansion of our data base by means of more extensive testing of in-mine diesel soots that have different origins (fuel type, oxidation history, and temperature history).

As a test of this image analysis method, we applied the same techniques to an experimental anthracene soot that had been formed in a drop-tube furnace in 200 ms at 1200°C. This soot was subsequently graphitized for 3 hours @ 2000°C. The
characteristic inter-layer spacing, shown in Figure 3, is 3.6Å, within the range of characteristic spacings found in graphitized materials. It should also be noted that the graphitized anthracene soot has highly oriented, long fringes in comparison to the diesel values. As a further test of our method and the reliability of the microscope conditions, an oriented gold crystal standard showed virtually no change in pixel measurement over a six month period. The ability to reproduce consistent gold lattice images over a period of time is characteristic of a microscope with stable lens currents as well as invariable magnification, specimen height, and stable sample preparation.

The reader must be cautioned that the characteristic values given here for inter-layer spacing are not to be interpreted as inter-planar spacing or inter-lattice spacing. The characteristic values are the average values for the areas between observable fringes and crystallites that have been measured by this software system.

It must be emphasized that during the present research we have been creating and exploring a new technique that will be further refined in the future. This new tool that has been developed seems to be suitable for the characterization of the internal structure of soot particles. We will continue to expand our data base with additional diesel soots from the mining environment in order to correlate the structures to the effects of fuel type, effect of oxidation, graphitization, and other engine operating conditions. Other instrumentation applied to this problem will include scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) to further characterize the chemical structure of these soots. In conclusion, we feel the technique of utilizing high-resolution microscopy and image analysis to characterize diesel soots shows promise, and we will continue to refine and expand our knowledge of the subject.
REFERENCES


APPENDIX C.

HOW TO EXTRACT THE STRUCTURE FROM THE TEM IMAGE

copy 6800 3:1; cd=3; 1

________ This is the TEM image.

fourier 1 to 3; fullplane;

mask 3 radius 118; mask 3 inside radius 39;

\[ r = \frac{235.62}{\text{distance in Å}} \]

halfplane; image; mask 3 radius 256

---------- Masks out possible computational errors outside image after reverse Fourier.

analyse 3 5 le -3.0 area 30,10000 segment 4

The extracted pattern ("segmented image").

Maximum area to be considered as "particle" [pixels].

Minimum area for a "particle".

Intensity threshold: intensities above correspond to structure, pixels with intensities below this value are not element of the "structure" (do not form a "particle").

The Particle Parameter List (variable value: ppl=5).

pset count; TotalArea=0

_______ Count the particles, and the result is stored in variable n.

for index=1,n; pset area;

The area of the actual "particle" (in pixels) is stored in variable a.
TotalArea=a+TotalArea; loop;

Calculates Total Area of all the particles (if it is done more than once, it is important to annul it before the next loop).

Closes the loop "for" started in the previous line.

type TotalArea

Types the numerical value onto the screen.

copy 4 to 6737 byte; copy 5 to 6738;

Saves the Particle Parameter List. If you need to analyze it later, don't forget to define the variable ppl (i.e. give value to it, before using any command related to the ppl:
ppl=6738; pset count;...).

Saves the extracted pattern in byte format (byte requires less space on the hard drive).

calculate :4 >0 to 4; 4 to 1

Makes the segmented image ("extracted structure") black and white (originally it is multi gray level, each "particle" has an intensity value equal to its sequential number.)
APPENDIX D.

SEMPER PROGRAM FILES

(Accessible by the File/Open menu)

ANAL.TXT

6400
r=512 r2=512;
xwires;
extract @region to 3:1;
origin reset;
display;
mask outside radius 256;
display
   ps ln to 3:2;
   fullplane;
display;
ccd=3;
for CC=-1.0,-1.0,-1.0;
   for AA=3.4,4.0, 0.2;
      BB=AA+0.5;
      fourier 1 to 3;
      fullplane;
mask 3 radius 235.62/AA;
mask 3 inside radius 235.62/BB;
halfplane;
image;
mask 3 radius 256;
analyse 3 5 le CC area 80,10000 segment 4 noverify
pset count;
TotalArea=0;
for index=1,n;
pset area;
  TotalArea=a+TotalArea;
loop;
type 'Range: ',AA,' - ',BB,'
n=',n,
   '  Total Area=',TotalArea,' CC=',CC;
calculate :4 >0 to 4;
display 4 negate no letter
  loop;
loop
pset count if area>0;
for index=1,n;
  pset circularity;
  type c;
loop
for index=1,n;
  pset angle;
  type theta;
loop
for index=1,n;
  pset mmin;
  pset mmax;
  type root(m2)/root(m1);
loop
ANGLE.TXT

pset count;
TotalArea=0;
for index=1,n;
    pset area;
        TotalArea=a+TotalArea;
loop;
type n,' ',TotalArea
for index=1,n;
    pset xcen;
    pset ycen;
    pset angle;
    xl=xc;
    yl=yc;
    all=theta;
    al2=phase(yl/xl)
    type index,' ',xl,' ',yl,' ',deg(all),
         ' ',deg(al2);
loop
AREA.TXT

for ppl=11,351,10
    pset count if area>0;
    TotalArea=0
    for index=1,n;
        pset area;
            TotalArea=TotalArea+a;
    loop;
    type ppl, TotalArea
loop

BMP.TXT

display 6100 noborder noletter
CIRCLUL.TXT

copy 7101 3:1;
cd=3;
display 1
for AA=3.5,3.5, 0.1;
   BB=AA+1;
   fourier 1 to 3;
   fullplane;
   mask 3 radius 235.62/AA;
   mask 3 inside radius 235.62/BB;
   halfplane;
   image;
   mask 3 radius 256;
analyse 3 5 le -3.0 area 50,10000 segment 4 noverify
pset count;
TotalArea=0;
for index=1,n;
   pset area;
      TotalArea=a+TotalArea;
   loop;
type 'Range: ',AA,' - ',BB,'   n=',n,
      '   Total Area= ',TotalArea;
calculate :4 >0 to 4;display 4 negate noletter
loop
pset count if area>0;
for index=1,n;
   pset circularity;
   type c;
loop
for index=1,n;
   pset angle;
   type theta;
loop
for index=1,n;
   pset mmin;
   pset mmax;
   type root(m2)/root(m1);
loop

80
COPYRIGHT.TXT

copy 6084 3:1;
cd=3;
display 1
r=512 r2=512;
xwires;
extract &region to 3:1;
origin reset;
display;
mask outside radius 256;
display
AA=3.0;
BB=5.0;
for CC=-2.05,-2.1,-0.2
   fourier 1 to 3;
   fullplane;
   mask 3 radius 235.62/AA;
   mask 3 inside radius 235.62/BB;
   halfplane;
   image;
   mask 3 radius 256;
analyse 3 5 le CC area 50,100000 segment 4 noverify
pset count;
TotalArea=0;
for index=1,n;
   pset area;
   TotalArea=a+TotalArea;
loop;
type 'Intensity threshold= ',CC,'  n= ',n,
   '  Total Area= ',TotalArea;
calculate :4 >0 to 4;
display 4 negate noletter noborder
loop
CUT.TXT

fourier 1 to 3;
fullplane;
mask 3 radius 79;
mask 3 inside radius 56;
halfplane;
image;
display 3 to 2
fourier 1 to 3;
fullplane;
cut 3 4 size 2,2 position 0,0;
mask 4 radius 1 value 0;
mask 3 radius 79 val 0;
mask 3 inside radius 56 value 0;
paste 4 3 position 0,0
halfplane;
image
display 3 to 3
D002.TXT

copy 7251 to 3:1;
display;
cd=3
r=512 r2=512;
xwires;
extract @region to 3:1;
origin reset;
display 1
xwires curve closed to 51;
mask 1 to 2 with 51;
display 2;
xxx=1;
magnify 3:2;
xxx=2;
display;
r=512 r2=512;
xwires;
extract @region to 3:2;
origin reset;
display
CC=-3.0;
AA=3.0;
BB=AA+1.0;
fourier 2 to 3;
fullplane;
mask 3 radius 235.62/AA/xxx;
mask 3 inside radius 235.62/BB/xxx;
halfplane;
image;
mask 3 radius 256;
alalyse 3 5 le CC area 80,10000 segment 4 noverify
pset count;
TotalArea=0;
for index=1,n;
    pset area;
    TotalArea=a+TotalArea;
loop;

83
type 'Range: ',AA,' - ',BB,' n=',n,
   ' Total Area= ',TotalArea,' CC=',CC;
display 4 regate
pmark id
display 4 noletter
pmark id
nn=11
i1=36; i2=41; i3=47; i4=52; i5=57; i6=62; i7=67; i8=72;
i9=75; i10=77; i11=78; i12=24; i13=29; i14=35; i15=40;
i16=46; i17=51; i18=56; i19=61; i20=66; i21=71; i22=74;
i23=76; i24=44; i25=50; i26=54; i27=60; i28=20; i29=25;
i30=30;
for jj=1,nn-1;
   jk=jj+1;
   index=i#jj;
pset xcen;
pset ycen;
pset angle;
x1=xc;
y1=yc;
all=theta;
index=i#jk;
pset xcen;
pset ycen;
pset angle;
x2=xc;
y2=yc;
al2=theta;
m=tan((all+al2)/2)
d=(m*(x2-x1)-(y2-y1))/root(m*m+1)*0.4335/xxx;
type jj,' ','i#jj',' ','i#jk',' .deg((all+al2)/2),
   ',d;
loop
pmark cm
EXTRACT.TXT

copy 4211 to 3;
display 1;
cd=3;
display 1 to 2
fourier 1 to 3;
fullplane;
mask 3 radius 79;
mask 3 inside radius 56;
halfplane;
image
analyse 3 5 le -2.5 area 40,10000 segment 4;
calculate :4 >0 to 4;
display 4 to 4;
calculate to 6 (:4-min)/(max-min)*255;
display to 5
display noborder noletter
partition 1
IMPORT.TXT

examine device 6
dir device 6
inp 3:1 nam 'c:\lrainy\1516.pic' int;
display
copy 3:1 to 6700
title
6700
inp 6980 nam 'c:\lrainy\1525.pic' int;
display
examine device 6
3:1
r=512 r2=512
xwires
extract @region to 3:2;
origin reset;
display
mask outside radius 256;
display
delete 3:2
compress device 3
ps ln to 3:3;
fullplane;
display
delete 3:1,3:3
INTENSIT.TXT

copy 6084 3:1;
cd=3;
display 1
r=512 r2=512;
xwires;
extract &region to 3:1;
origin reset;
display;
mask outside radius 256;
display
AA=3.0;
BB=5.0;
for CC=-2.05,-2.1,-0.2
    fourier 1 to 3;
    fullplane;
    mask 3 radius 235.62/AA;
    mask 3 inside radius 235.62/BB;
    halfplane;
    image;
    mask 3 radius 256;
    analyse 3 5 le CC area 50,100000 segment 4 noverify
    pset count;
    TotalArea=0;
    for index=1,n;
        pset area;
        TotalArea=a+TotalArea;
    loop;
type 'Intensity threshold= ',CC,'   n= ',n,
    '   Total Area= ',TotalArea;
calculate :4 >0 to 4;
display 4 negate noletter noborder
loop
INT_PROF.TXT

display 6086
theta=0
section angle theta width pi mark yes to 3:2;
fullplane;
display to 1
examine device 3
write 3002 new format '(1F7.3)' name '3002' unlabelled
LENGTH.TXT

copy 6800 to 3:1;

cd=3;
display 1
fourier 1 to 3;
fullplane;
mask 3 radius 94;
mask 3 inside radius 52;
halfplane;
image;
mask 3 radius 256
for g=1,10
  analyse 3 5 le -3.0 area 0,300+50*g segment 4;
pset count if area>0;
TotalArea=0
for index=1,n;
  pset area;
  TotalArea=TotalArea+a;
loop;
type 300+50*11,TotalArea
gg=6930+11;
copy 5 to gg
loop
examine device 6
analyse 3 5 le -3.0 area 0,850 segment 4;
display 4
calculate :4 >0 to 4;
display 4
LENGTH2.TXT

pmark id
display 4;
ppl=5
pedit 5 to 15 segment 4,14 if id=3*round(id/3);
ppl=15;
pmark id
pmark cm if id =448
index=448;
pset mmin;
pset mmax;
type root(m2)/root(m1)
xwires line;
type r=0.04336
MEASURE.TXT

r=512 r2=512

xwires

extract @region to 3:1;

origin reset;

display

xwires line;

type r

6400
PPL-LOOP.TXT

rem 504, 506, 524, 528, 514, 516,
type ' # TotalArea AvgCirc MinMom MaxMom Elongation'
ppl=514
pset count if area>0;
TotalArea=0;
Circ=0;
Mol=0;
Mo2=0
for index=1,n;
    pset area;
    TotalArea=TotalArea+a
    pset circularity;
    Circ=Circ+c
    pset mmin;
    Mol=Mol+m1
    pset mmax;
    Mo2=Mo2+m2
loop;
type ppl,' ',TotalArea,' ',Circ/n,' ',Mol,' ',Mo2,
    ',root(mo2)/root(mol)
copy 6041 3:1;
cd=3;
display 1
for AA=3.1,3.3, 0.2;
    BB=AA+1.0;
    fourier 1 to 3;
    fullplane;
    mask 3 radius 235.62/AA;
    mask 3 inside radius 235.62/BB;
    halfplane;
    image;
    mask 3 radius 256;
    analyse 3 5 le -3.0 area 30,10000 segment 4 noverify
    pset count;
    TotalArea=0;
    for index=1,n;
        pset area;
            TotalArea=a+TotalArea;
    loop;
    type 'AA=',AA,'  BB=',BB,'  n=',n,
        '  Total Area=',TotalArea
    loop
rem copy 4 to 6737 byte;
rem copy 5 to 6738;
TEST.TXT

time reset


copy 9:1 to 3:1;

cd=3;

display 1 to 2

ps ln to 2;

fullplane;

display to 3

fourier 1 to 3;

fullplane;

mask 3 radius 79;

mask 3 inside radius 56;

halfplane;

image

analyse 3 5 le -3 area 20,10000 segment 4;

calculate :4 >0 to 4;

display 4 to 4;

calculate to 6 (:4-min)/(max-min)*255;

display to 5

time
APPENDIX E.

PRODUCTION OF A HEAT TREATABLE TEM GRID

In order to be able to examine the effect of oxidation of the very same soot cluster/particle, the sample have to be deposited on a grid which survives the oxidation environment. Lacey carbon TEM grids coated with aluminum are used in the experiment. These grids satisfy the following requirements:

- they should be able to support soot particles,
- to structurally withstand heat treatment and
- not become electrically charged under the electron beam.

In order to provide enough strength to withstand heat treatment and accumulation of electrical charge, the carbon grids were coated with 700 angstroms of aluminum on both sides. This layer of aluminum is thin enough to be transparent for the TEM and yet strong enough so that soot particles can easily be supported on the grids.

The aluminum is deposited on the carbon grids using a sputtering machine which deposits an even coatings using a vacuum system. Figure 1 shows the schematic of the experiment.

Figure 1. Layout of the sputtering experiment.
To determine the amount of aluminum needed for a 700 Ångström coating, the following equation was used:

\[ M = \frac{4 \cdot \pi \cdot R^2 \cdot \rho \cdot T \cdot t}{\cos \Theta}, \]  
where,

\( M = \) mass of evaporant [grams]
\( R = \) distance from source to specimen [cm]
\( \rho = \) density of evaporant [g/cm³]
\( T = \) thickness of evaporative coating [cm]
\( \Theta = \) angle between normal to the specimen and the evaporative direction

Data for the experiment:

\( \rho = 2.7 \text{ g/cm}^3 \) (Aluminum),
\( R = 7.9 \text{ cm}, \)
\( T = 7.0 \cdot 10^{-6} \text{ cm}, \) and
\( \Theta = 16.3. \)

Performing the calculations the result is the following, 0.05 grams of aluminum are required for a 700 Ångström coating.

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APPENDIX F.

INSTRUCTIONS FOR THE THERMOGRAVIMETRIC ANALYZER AND FOR THE DATA COLLECTION

PROGRAMMING THE TGA, CAHN 2000, AND THE COMPUTER

Instructions for programming the initial startup and temperature profile for the TGA are in the instructions manual in the orange binder (pp. 8-21). In order to reprogram a temperature profile, the yellow [Manual] button must be pressed and then [Enter]. From then on, the TGA will accept changes in the program.

The computer must be set up to record data. Following are instructions for the computer and the CAHN 2000:

The "Recorder Range" on the CAHN 2000 depends on the weight of the sample. For example, if a 0.8 mg sample is to be used, the "Recorder Range" should be put on 1 mg.

Once the recorder range is selected, on the computer:

- type cd nb [enter]
- type nb [enter]
- select setup
- select save/recall
- select recall
- type meters [enter]
- push the [esc] button twice
- select go

After the screen changes, hit [enter]; in the top screen the temperature should be between 0.0400 and 0.0500 -- if not, check the connection between the CAHN and the TGA which
gives the temperature signal; in the bottom screen, the weight should be about 0.04 -- if not, unlock and use the "Zero" knobs on the CAHN to adjust the weight signal.

push the [esc] button twice
select setup
select save/recall
select recall
type zero4 [enter]
push the [esc] button twice
select go
push [enter]

A graph will form showing the "zero" values. The graph points can be varied using the zero suppression control on the CAHN 2000. In these experiments, the graph points should be positioned as close to actual zero while showing all fluctuations (so that no points are negative). Once the zero suppression is set, run zero4 again for the full 60-second duration at the constant zero suppression value (a file containing this data will be copied onto a floppy disk later).

Select setup
select save/recall
select recall
type tpd4 [enter]
press [esc]
select blocks
select normal
change Stage Duration to the number of seconds that the computer should record during the experiment
press [enter]
go up to Current Block and type 2
change Stage Duration to the same number of seconds typed above [enter]
go up to Current Block and type 3
change Stage Duration to the same number of seconds typed above [enter]
press [esc] twice

98
select go

Reset the furnace by pushing the black button on the right top side of the TGA, turn the furnace on, and check the flow rate of gas. For these experiments, flow rate has been set at approximately 100 according to the flow meter.
STARTING THE TGA

Once the TGA has been programmed and is ready to run (the display reads "**** Run at 001"), press [enter] on the computer and enter on the TGA at the same time. The computer screen will show two graphs -- one of the temperature profile and the other of the weight of the sample with time.

In order to see the setpoint of the temperature, press [Setpoint] on the TGA. Press [Load Top Display] and then press [Process Variable]. This will show you the programmed temperature at the top of display and the actual temperature at the bottom of the display.

Once the experiment is done, turn off the furnace and allow the sample to cool down before opening the furnace. The alarm will go off once the process variable is 100 degrees above the setpoint, and the program will stop on its own.

Now that the data is in a file, copy the file with the zero values (named zero_.prn) and the file with the weight and temperature profile values (named tpd_.*) onto a floppy disk. The next step is to go to Athena to print out the graphs on matlab.
PRINTING OUT THE GRAPHS ON ATHENA

Insert the floppy disk and type dosdir. Then type dosread tpd_* tpd_* (this copies the data in tpd_* onto the hard drive). Type emacs tga.m. In tga.m, if the format of the graph is to be the same as it usually is, the only data to be changed in the program are the title of the graph and the recorder range. Save tga.m.

rmheader is a program that removes the header in tga.m. In order to remove the header, type rmheader tpd_* tpd.mat. Then open matlab. Once in matlab, type clear tga.m. Then type tga. The graph should show up on the screen and simultaneously print on the machine specified on the last line of tga.m (currently, it is pandora).
APPENDIX G.

MEDIA ATTENTION TOWARDS THE PROJECT

- *Business Week*, October 3, 1994, p. 121; "How the pollution patrol can fingerprint hydrocarbons"

- *MIT Tech Talk*, October 26, 1994, p. 5; "Soot structures show history"

- *New Scientist*, October 22, 1994, p.25; Polluters' signature is written in soot

- *Science Update #1095* of the American Association for the Advancement of Science (Radio interview with Professor Sarofim on November 23, 1994)


- *BBC "World News Hour"* (Interview with Professor J. B. Vander Sande in March 1995)


- *Tiede 2000; 4/95* (Finland); “Nokeajat esiin”