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Particle Size Analysis of Prepared Solutions and Fingerprint Deposits of High Explosive Materials

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**Particle Size Analysis of Prepared Solutions and Fingerprint Deposits of
High Explosive Materials**

**William J. Carmack
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Published March 1998

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SUMMARY

The Idaho National Engineering and Environmental Laboratory (INEEL) managed and operated by Lockheed Martin Idaho Technologies Company (LMITCO) was tasked via the Federal Aviation Administration (FAA) and U.S. Department of Energy (DOE) to conduct various studies involving the detection and measurement of explosive materials and their associated residues. This report details the results of an investigation to determine the particle size characteristics of the explosive materials used in the design, development, and testing of trace explosives detection systems. These materials, in the form of water suspensions of plastic explosives, are used to provide a quantitative means of monitoring the performance characteristics of the detection systems. The purpose of this investigation is to provide data that allows a comparison between the particles deposited using the suspension standards and the particles deposited from fingerprints. This information may support the development of quality control aids, measurement methods, or performance criteria specifications for the use of trace explosives detection systems.

For this report, particle size analyses were completed on explosives standard suspensions/solutions for Composition C-4, Semtex-H, and Detasheet and fingerprints for C-4, Detasheet, and Pentolite. Because of the difficulty in collecting microscopic images of the particles in the suspensions from test protocol surfaces, this paper discusses the characteristics of the particles as they are found on metal, glass, and paper.

The results of the particle characterization analyses indicate that the water suspensions contain particulate composed of binder materials and dissolved portions of the explosive compounds. Upon drying of the water suspensions, significant particle nucleation and growth is observed. The nucleated particulate is comparable to the particulate deposited by fingerprints.

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1.0 Introduction

The Idaho National Engineering and Environmental Laboratory (INEEL) managed and operated by Lockheed Martin Idaho Technologies Company (LMITCO) is tasked by the Federal Aviation Administration (FAA) via the FAA/Department of Energy (DOE) interagency agreement #DRFA03-94-X-00012 to conduct various studies involving the detection and measurement of explosive materials and their associated residues.

This report details the results of an investigation to determine the particle size characteristics of the explosive materials used in the design, development, and testing of trace explosives detection systems. These materials, in the form of water suspensions of plastic explosives, are used to provide a quantitative means of monitoring the performance characteristics of the detection systems. The purpose of this investigation is to provide data that allows a comparison between the particles deposited using the suspension standards and the particles deposited from fingerprints. This information may support the development of quality control aids, measurement methods, or performance criteria specifications for the use of trace explosives detection systems.

For this report, particle size analyses were completed on explosives standard suspensions/solutions (Miller, C. J. et al., 1997) for Composition C-4, Semtex-H, and Detasheet and fingerprints of C-4, Detasheet, and Pentolite. When used to evaluate explosive detection systems, the suspensions are normally placed on surfaces that simulate luggage and air passenger carry-on items (e.g., floppy disks, luggage handles, and zippers). Because of the difficulty in collecting microscopic images of the particles in the suspensions from the test surfaces, this paper discusses the characteristics of the particles as they are found on metal, glass, and paper.

The results of the particle characterization analyses are presented as: 1) a description of the collection and sample preparation methods; 2) a description of the particle size representation and distribution data; and 3) a description of the observations and conclusions.

2.0 Particle Collection and Sample Preparation Methods

This section presents a description of the methods used in this study to prepare samples of particle deposits, methods used to prepare the samples for analysis, and a description of the specific analytical instruments used. One of the goals of this study was to determine how fingerprint deposits compare with the prepared suspension standards. Clearly, dry deposits of explosives found from fingerprints will differ dramatically from the particles found in water suspensions. Although, if the suspensions are placed on a surface and the water allowed to evaporate, the resulting distribution of particles may be similar to fingerprints.

2.1 Sample/Deposit Preparation

We performed two sample preparation methods during this study. Standard solutions of C-4 (a M112 Block of Composition C-4 RDX based high explosive), Detasheet (a PETN high explosive formulation), and Semtex-H (a RDX and PETN high explosive formulation) were prepared in concentrations ranging between 4 and 72 ng/ μ l of the suspected explosive component. The solution concentrations generally are dependent upon the source of explosive material used to manufacture the solutions. We also prepared fingerprint samples of C-4, Detasheet, and Pentolite (a PETN-TNT alloy high explosive formulation) on glass slides by applying finger pressure to the bulk explosive and then to the glass cover slip.

Explosive standard solutions were prepared by methods detailed in (Miller, C. J. et al., 1997). The samples were either frozen or refrigerated as needed. The samples were transferred to the particle measurement laboratory and allowed to reach room temperature and placed on a stirring plate for mixing. A 10 ml drop was extracted from the center of the mixing region and placed on a glass slide for viewing under the optical microscope.

After the optical microscope analysis, the remaining solution was placed in the small volume analysis cell (containing 10 ml of nanopure water) of the Microtrac FRA analyzer for volumetric particle size analysis. Since only a very small quantity of suspension was used for optical analysis, approximately 10 to 20 ml of solution was used for the volumetric analysis.

2.2 Particle Characterization Methods

We have used two general methods for determining the particle size distributions of the prepared explosive samples. We used an optical microscope with a maximum magnification of 1000 X and a minimum magnification of 50 X. Analysis results obtained with the optical microscope method take the form of a count based projected area particle size distribution. The second method of particle size analysis yielded a volumetric based particle size distribution. The two methods are fundamentally different and care must be used when comparing results from the two methods. For example, a count based microscope analysis of a standard solution will yield a median particle size much smaller than a volume based analysis of the same sample. This is because large particles have large volumes compared to small particles, i.e. $4/3\pi r^3$, and will tend to skew volumetric analyses to larger particle sizes. While it takes only a few large particles to skew a volumetric analysis to large diameters, there are usually many more smaller particles (100's or 1000's) compared to a few large particles. This will tend to skew count based distributions to smaller particle sizes. These two results are not in conflict rather they should be considered as different characteristics of the same material. The two methods used in this study were applied to three different sample preparations, suspended particulate, particulate nucleated as water solvent evaporated, and fingerprint deposits.

2.2.1 Optical Microscope Count Distribution Measurement

The Nikon Optiphot 100 optical microscope provides a means for photographing magnified views of substrates at 50X, 100X, 200X, 500X, and 1000X. The photographs are digital images stored to a Macintosh computer through a Hitachi high resolution black and white digital camera. A full description of the analysis technique is given in Section 3.0.

2.2.2 Microtrac FRA Volumetric Distribution Measurement

The Microtrac 9200 Particle Size Analyzer provides an analysis of particle size distribution in wet suspension. The analyzer uses the principle of measuring forward scattered light from a laser beam projected through a stream of particles. The amount and direction of light scattered by the particles is measured by an optical detector array and analyzed by a microcomputer that calculates the volume based size distribution of the particles in the sample stream. Since the Microtrac measures a volume of particle and then calculates the diameter of a sphere having the measured volume, the resulting particle size distribution is termed a volume based distribution.

3.0 Data Analysis

This section provides a description of general particle sizing considerations and basics. Following this discussion a detailed description of the count based particle sizing technique used in this study is described. The purpose of this section is to familiarize the reader with general particle sizing knowledge needed to understand the appropriate use and implications of the data generated in this study. Information is provided in this section in reference to aerodynamic particle size distributions and particle shape factors. These two pieces of information have not been determined for this study but are provided for completeness as some discussion of these measurements will be made in the conclusions of this paper.

3.1 General Particle Sizing Considerations

A number of techniques exist for the measurement of particle size distributions. Each measurement relies upon some characteristic parameter of a particle in a gas based on an equivalent diameter. Generally, when a particle size distribution is determined, it is based upon segregation of particles by measuring the number of particles, volume of particles, mass of particles, or surface area of particles falling within defined size classifications. Basic histograms can then be determined based upon fractions, total number, or frequency of occurrence within those classifications. The measurement technique chosen to determine the particle size distribution should be consistent with the intended use of the particle size distribution data. For example, count or number based distributions are generally used to indicate or impact process system performance such as in the design of high efficiency filtration systems. Mass distributions are generally used when the end use of the data is to determine effects upon the human body. For example, mine dust is usually quantified as a mass distribution because it usually is used to determine worker exposure limits.

3.1.1 Equivalent Particle Diameters

There are a number of different characteristic diameters of particles. Stokes diameter, aerodynamic diameter, and projected area diameter are three expressions for particle diameters that are commonly used in aerosol and particulate characterization technology. For any particle they are defined as:

- **Stokes' diameter d_s** , the diameter of the sphere that has the same density and settling velocity as the particle of interest.
- **Aerodynamic diameter d_a** , the diameter of unit density (1 g/cm^3) sphere that has the same settling velocity as the particle of interest.
- **Projected area diameter d_{pA}** , the diameter of an irregular particle calculated by measuring the projected (or viewed) area corresponding to a circle having an equivalent area.

Figure 1 shows the relationship between physical, Stokes' equivalent, and aerodynamic equivalent diameters (Hinds, p. 50). If a particle of interest has an aerodynamic diameter, d_a , of $1 \mu\text{m}$, it behaves aerodynamically like a $1 \mu\text{m}$ water droplet regardless of its shape or density. It is aerodynamically indistinguishable from other particles of different size, shape, and density having an aerodynamic diameter of $1 \mu\text{m}$.

The Stokes' diameter is usually defined in terms of the theoretical density of the bulk material of the particle of interest. This eliminates the problem of defining the true density of the particle, which may be less than the theoretical density due to porosity, occlusions, or agglomerated structure.

Figure 1. Comparison of equivalent diameter spheres and particles. V_{ts} is the terminal settling velocity of a particle as defined by the Stokes' diameter.

When measuring particle size with a microscope, it is necessary to assign to each particle a size based on its two-dimensional projected image or silhouette. For spheres this is simply the diameter of the circular silhouette observed in the microscope, but for the more common case of irregular particles we must use equivalent diameters such as those shown in Figure 2. These equivalent diameters are based solely on the geometry of the silhouette as contrasted to the equivalent diameters which are based on the aerodynamic behavior of the particles. The smallest diameter shown is Martin's diameter d_M , the length of the line parallel to a given reference line that divides the projected area (silhouette) of the particle into two equal areas. This diameter is often referred to as a "statistical" diameter, because its value depends on particle orientation, and only its mean value for all particle orientations is unique for a given particle. In practice this orientation averaging is rarely done, and it is more common when sizing particles to measure a single Martin's diameter for each of many particles randomly oriented with respect to the reference line. This has the practical effect of averaging over all orientations. Martin's diameter always passes through the centroid of the particle silhouette, and the average Martin's diameter of a particle represents the mean of all cords through the particle silhouette.

Another "statistical" diameter is Feret's diameter d_F , shown in Figure 2. It is defined as the length of the projection of a particle along a given reference line or the distance between left and right tangents that are perpendicular to a reference line. It is most convenient to use Feret's diameter when a scale along a given axis is available, such as a microscope equipped with a filar micrometer.

The most commonly used equivalent diameter is the projected area diameter d_{PA} , shown in Figure 2. It is defined as the diameter of the circle that has the same projected area as the particle silhouette. It has the advantage of providing a unique size for a given silhouette regardless of its orientation. It is widely used because it allows a simple visual comparison between particle area and standard circles of known area. Such comparisons allow particles to be grouped rapidly into size intervals based on their projected area and the size distribution determined.

In general, $d_M < d_{PA} < d_F$, with the equality holding only for spheres. For irregular particles of most crushed materials, d_M is only slightly less than d_{PA} ($< 10\%$ difference), and they are often assumed to be equal. Feret's diameter is generally about 20% larger than d_{PA} for such materials.

3.1.2 Particle Shape

Particles also have a variety of shapes. The shape of a particle is determined by a number of factors including such processes as, production, handling, erosion, and chemical reaction. A number of different shape factors can be defined depending on the intended use. Here we will discuss dynamic shape factors, volumetric shape factors, and surface area shape factors (also known as k-factors).

Figure 2. Martin's, projected area, and Feret's diameter for an irregular particle.

The dynamic shape factor is defined by,

$$X = \frac{F_D}{3\pi\eta d_e} \quad (1)$$

where,

X	=	dynamic shape factor,
F_D	=	Stokes drag force,
η	=	fluid viscosity,
V	=	velocity,
d_e	=	equivalent volume diameter.

The dynamic shape factor, X , shown in Figure 1 is used to account for the effect of shape on the settling behavior of a particle. The equivalent volume diameter, d_e , is the diameter of a sphere having the same volume as the irregular particle of interest. The d_e can be thought of as the diameter of the sphere that would result if the irregular particle were melted to form a droplet. Using the equivalent volume diameter and the dynamic shape factor, the Stokes diameter and the aerodynamic diameter can be calculated using:

$$d_e^2 = d_s^2 X \quad (2)$$

$$d_e^2 = d_a^2 X / \rho_p \quad (3)$$

Dynamic shape factors have been measured for a number of materials and generally ranges from 1.0 to 1.5 for different geometries and different materials. For coal dust the shape factor ranges from 1.05 to 1.11. Larger values might be expected for chain-agglomerates or long fibers.

The calculation of d_e from optical microscope data is made by measuring the projected area diameter, d_{pa} , and using a volumetric shape factor a_v to yield;

$$d_e = d_{pa} (6a_v/\pi)^{1/3} \quad (4)$$

Hinds [1] lists volume shape factors for a variety of geometric shapes and mineral dusts all in the range of 0.16 to 0.52. The value 0.52 is $(\pi/6)$ for a sphere. The volume shape factor can be calculated for regular geometric shapes. For irregular shapes an empirical approach using a combination of measurement methods is required. Except for fibers and platelets, equivalent volume diameter and projected area diameter should not differ by more than a factor of 2.

In some applications (e.g., powder metallurgy), it is important to know about the specific surface area of an aerosol or powder. In powder metallurgy, the specific surface area affects the packing, flow, and compressibility of the powder. For a monodisperse spherical aerosol, the specific surface area, S , is given by

$$S = 6/(\rho d) \quad (5)$$

where

S = specific surface area (m^2/g)

ρ = density of material (g/m^3)

d = size of aerosol (m)

For a polydisperse aerosol, the specific surface area is given by Hinds [1]:

$$S = 6(d_{sa})^2 / (\rho (d_m)^3) = 6/(\rho d_{msv}) \quad (5)$$

where

d_m = diameter of average mass of the aerosol

d_{sa} = diameter of average surface area of the aerosol

d_{msv} = mean surface volume diameter of the aerosol

Definitions of these quantities for a log normal distribution are discussed in Section 3.2.

For the case where a polydisperse aerosol has an irregular shape, a general form of equation [5] is used:

$$S = k/(\rho d_{msv}) \quad (6)$$

where k is termed a surface area shape factor. Thus, for a sphere $k = 6$. This k -factor can be calculated for a number of different geometrical shapes as shown in the table below from German, p. 41. As the particle shape deviated from spherical the k -factor increases from the value of 6. For a very large flake that is rather thin, the k -factor is 24, four times that of a sphere. The k -factor value of particles can be determined using the results of the particle characterization presented here and a BET (Brunauer, Emmett and Teller) specific surface area measurement of a particle sample.

Table 1. Surface area shape factors (k-factors) for different shapes (Hinds, p. 58).

Shape	Axial Ratio	k-factor
sphere	1:1:1	6
ellipsoid	1:2:4	7.57
cylinder	1:1:1	6.86
cylinder	1:1:2	7.21
cube	1:1:1	7.44
parallelepiped	1:4:4	9.38
flake	1:10:10	24.00

3.2 Particle Size Distributions and Statistics

Once a particle size distribution has been measured it must be presented in a clear graphical manner and analyzed statistically for mathematical description. A variety of mathematical relationships are used in particle or aerosol physics to describe particle size distributions. Many aerosols are adequately described mathematically by the log normal distribution. An example of a log normal distribution with particle diameter plotted on a linear scale is shown in Figure 3. This distribution is taken from Hinds, 1982 and has a count median diameter, CMD, of 9.0 μm and a geometric standard deviation, GSD, of 1.89. The figure also shows the graphical relationship between various average diameters. Figure 4 is a graph of the same data with diameter plotted on a logarithmic scale. A log normal distribution can be calculated and fit to Frequency/ $(\Delta \ln(d_p))$ versus diameter data as in Figure 3 by using the following equation:

$$\frac{\text{Fraction}}{\Delta \ln(d_p)} = \frac{1}{\sqrt{2\pi} \ln \sigma_g} \exp \left[-\frac{(\ln d_p - \ln \text{CMD})^2}{2(\ln \sigma_g)^2} \right] \quad (7)$$

Four averages used to describe particle size distributions are the count median diameter, CMD, the mass median diameter, MMD, the diameter of average mass, d_m , and the diameter of average surface area, d_{sa} . The count median diameter is the diameter in the distribution below which half of the total number of particles are smaller and above which half the total number of particles are larger. The mass median diameter is the corresponding diameter below which half of the total mass of particles are smaller and half the total mass of particles are larger. The MMD will always be larger than the CMD because the mass per particle scales as the particle diameter cubed. Thus, 1000 0.1 μm particles have the same total mass as one 1.0 μm particle. All distributions in this study are based upon the count median diameter. The diameter of average mass is the diameter that provides a link between the number and total mass of aerosol particles in a sample. The diameter of average surface area provides the link between the total number of particles and the total surface area of the aerosol, assuming spherical particles with full density. The graphical relationship of these averages is shown in Figure 3.

Figure 3. Arithmetic plot of data showing various average diameters (Hinds, p. 93).

As a simple illustration of different weighted distributions, consider an aerosol composed of equal numbers of two particle sizes, one in which 50 particles are 1 μm in diameter and 50 particles are 10 μm in diameter. While one-half the number are in each size category, most of the mass is represented by the 10 μm particles. Each 10 μm particle weighs 1000 times that of a 1 μm particle. Since the 10 μm particles contribute 50,000 units of mass to the total mass whereas the 1 μm particles contribute only 50 units of mass, the mass is distributed with 99.9% in the 10 μm particles and only 0.1% in the 1 μm particles. A similar analysis for surface area gives 99% of the surface area attributable to the 10 μm particles and 1 % to the 1 μm particles. The distinction between count and mass distributions can be put in even simpler terms; a bowl containing nine grapes and one apple is 90% grapes by count and 90% apple by weight (Hinds, p. 78).

Figure 5 is a plot of a log normal particle distribution on a log probability scale. The CMD and the σ_g are determined from this log probability plot. The axis in Figure 5 is the logarithm (base 10) of the particle size expressed in microns. The abscissa is the cumulative fraction on a log probability scale. For a log normal distribution, the data fit a straight line. Particle count median diameter and geometric standard deviation can be obtained directly from a straight-line curve fit of the log probability data. The value of $\log(D_p)$ at a cumulative fraction of 50% yields the count median diameter, $d_{50\%}$. The ratio $d_{84\%}/d_{50\%}$ provides the geometric standard deviation. For a log normal distribution, specification of the mean diameter and the geometric standard deviation is sufficient to fully characterize the size distribution.

Figure 4. Logarithmic plot of data shown in Figure 3.

Figure 5. Cumulative probability plot of data shown in Figures 3 and 4.

If a particle size distribution is log normal, then many other important diameters can be calculated based on the count based median diameter and the GSD using the Hatch-Choate transformation equations. can be calculated from the measured count median diameter, CMD, and the GSD obtained from the log normal distribution. The technique for converting count based distributions to mass based distributions is

described fully in Hinds, 1982. Equations for calculating the diameter of average mass (Equation 8), the mass median diameter (Equation 9), the diameter of average surface area (Equation 10), and the mean surface volume diameter [Equation 11] are given below:

$$d_m = \text{CMD} * \exp [1.5 * \ln^2 \text{GSD}] \quad (8)$$

$$\text{MMD} = \text{CMD} * \exp [3.0 * \ln^2 \text{GSD}] \quad (9)$$

$$d_{sa} = \text{CMD} * \exp [1.0 * \ln^2 \text{GSD}] \quad (10)$$

$$d_{msv} = \text{CMD} * \exp [2.5 * \ln^2 \text{GSD}] \quad (11)$$

where;

d_m = diameter of average mass, μm ,

MMD = mass median diameter, μm ,

d_{sa} = diameter of average surface area, μm ,

d_{msv} = mean surface volume diameter, μm ,

CMD = count median diameter, μm ,

GSD = geometric standard deviation.

It should be pointed out that the use of count based particle size distributions to calculate aerodynamic properties of an aerosol can be problematic depending on the amount of particle size data that have been measured at the tails of the distribution. Because of the exponential nature of the Hatch-Choate equations, small uncertainty in the GSD could cause large errors in the calculated diameters, especially the MMD because of the factor of 3 in the exponent. As a result, gravimetric measurements (e.g. measurement of settling velocity in a liquid, cascade or virtual impactor measurements) are traditionally used to determine aerodynamic properties of the aerosol. Such gravimetric measurements were not performed as part of this characterization but in principal could be done if needed.

3.3 Particle Size Distribution Construction - Processing Explosive Samples

The procedure used to construct a particle size distribution from data obtained with the optical microscope is multi-step and has been developed for this type of research. The following is a step by step procedure used to construct a particle size distribution using the Nikon optical microscope, NIH-Image software, and spreadsheet software. Figure 6 is a flow-chart depiction of the procedure used to construct the distributions.

Figure 6. Flow chart schematic of particle size distribution construction.

Four distinct areas of the samples were each photographed with an optical microscope at five magnifications. Each photograph taken of the sample was analyzed on a computer using the public domain image analysis software named NIH Image program. NIH-Image is a software package developed by the National Institute of Health for image analysis of magnetic resonance image analysis based on the pixel density. The technique can be applied to resolving particles on a substrate and counting the number of pixels representing the particle to determine a total area for the particle. The software package can only relate the number of pixels to the physical size of the particle by a scaling factor supplied by the user of the software. This value is used as a conversion from pixels to physical size. To do this, a calibrated micrometer with a 1 millimeter scale with 100 divisions was used. Each division corresponds to 10 micrometers. Scaling factors were then obtained for each magnification.

Pictured below in Figures 7 through 11 are photographs of the micrometer at the five magnifications used during this study, 50X, 100X, 200X, 500X, and 1000X. Table 2 shows the pixel per micron scaling used in the NIH-Image software package as determined using these micrometer photographs.

Figure 7. 5 X magnification photograph of an Olympus 1 mm micrometer (100 division).

Figure 8. 10 X magnification photograph of an Olympus 1 mm micrometer (100 division).

Figure 9. 20 X magnification photograph of an Olympus 1 mm micrometer (100 division).

Figure 10. 50 X magnification photograph of an Olympus 1 mm micrometer (100 division).

Figure 11. 100 X magnification photograph of an Olympus 1 mm micrometer (100 division).

Table 2. Pixel to micron scaling values determined from above photographs and NIH-Image.

Magnification	Scaling Conversion (pixels/ μm)
50 X	0.3625
100 X	0.7250
200 X	1.4500
500 X	3.625
1000 X	7.250

Diameter data obtained from NIH-Image analysis of photographs in this study are generated as a projected area diameter. This projected area is converted into a diameter by assuming a spherical particle and using $\text{Area} = (\pi d^2)/4$. Spreadsheet software is then used to determine the projected area diameter, D_{PA} , of the particles from the measured particle area data using:

$$D_{PA} = 2 \sqrt{\frac{\text{Area}_{PA}}{\pi}} \quad (12)$$

This equation converts particle areas to diameters assuming spherical geometry. After the data generated from NIH-Image have been converted to particle diameters, the data at a specific magnification from each of the four areas are compared using a Kruskal-Wallis test (Hollander and Wolfe, 1973) to determine if the data represent the same sample. This test allows us to discard data that are not representative of the entire population. Following the Kruskal-Wallis test of the individual magnification data, cumulative distributions are constructed for each magnification by summing the count histograms from each photograph.

The distribution is characterized by calculating three parameters of the particle size distribution: the $d_{50\%}$, $d_{84\%}$ and the geometric standard deviation, GSD. The $d_{50\%}$ corresponds to the particle size at which 50% of the counted particles have smaller diameters and 50% have larger diameters. A similar value can be found for the $d_{84\%}$. The GSD is simply the $d_{84\%}$ divided by the $d_{50\%}$. At this point in the procedure, we have combined particle size histograms at each of the different magnifications. The next step in the process is to determine how to develop a cumulative distribution across the entire size spectrum for the underlying particle population recognizing that (a) the size range that can be identified by the various magnifications of the optical microscope overlap and (b) the different magnifications correspond to different amounts of filter surface examined.

To ensure that there is no double counting of particles due to overlap in size ranges, the portion of the distribution within generally one standard deviation of the count mean is identified for each magnification.^a The diameter range associated with that portion is selected for inclusion in the final overall distribution for the substrate and hence the sample location.

The contributions from each magnification are combined with the use of an area scaling factor. This factor is the area viewed in a low magnification 50 X photograph divided by the area viewed in either a 100 X, 200 X, 500 X, or 1000 X photograph. This scales the data so that contributions from the high magnification photographs can be combined on the same scale as the low magnification 50 X photograph. Without this factor, the distribution would be biased toward larger sizes since the lower magnification photographs cover more surface area and hence more particles than a higher magnification photograph. The scaling factors applied to the data obtained at the various magnifications are shown in Table 3.

^a To determine the influence of selected diameter on the overall distribution some data sets were processed using different ranges. The overall results, $d_{50\%}$, R value, and GSD changed by less than 3 percent. This result was consistent across range selections as long as the range selection was within one sigma of the mean of the distribution.

Table 3. Various Values of Interest for Optical Microscope Data Analysis.

Objective Magnification	Approximate Analysis Size	Area μm^2	Area Multiplication
1000	0 to 1.5	5600.96	400
500	1.5 to 3.4	22403.80	100
200	3.4 to 6.4	140023.78	16
100	6.4 to 10.0	560095.12	4
50	10.0 and up	2240380.5	1

*NA is used because the particle size data obtained from the SEM are not used in construction of the overall particle size distributions. These area values are included only to show comparison with the optical microscope photographs.

The overall combined distribution for the sample is calculated and the 95% confidence intervals associated with the data determined. The 95% confidence intervals are calculated using statistical technique described in Appendix A. The log normal parameters are then determined from this graph and a calculated log normal distribution generated according to Equation 8 as described above. The result is plotted along with a histogram representing the frequency per micron of the above overall distribution. This graph is shown in Figure 18.

Recall that the microscope method is capable of counting particles with diameters in the range of 0.15 microns to 300 microns. Particles larger than 300 μm begin to exceed the viewable area of the microscope and particles smaller than 0.15 μm are not resolvable because they are too small to be seen within the magnification capability of the microscope.

The particle size distribution technique has also been applied to BCR quartz reference material obtained from Duke Scientific Inc to determine its validity. The results of this analysis are generally good and are presented in Appendix B.

3.4 Microtrac FRA Analysis

Data obtained from the Microtrac FRA analysis are generated in the form of volume percent in a channel where each channel corresponds to a particle diameter. Two limitations were experienced using the Microtrac instrument. First the instrument cannot resolve particles smaller than approximately 1 micron. Secondly, the instrument often mistakes bubbles in the solution as very large particles. The bubble data must be separated from actual particle data prior to comparison to data taken with other methods. This measurement is relatively automatic and further details can be found in the manufacturer's operation handbook. Information can also be obtained from the manufacturer, Leeds&Northrup, 351 Sumneytown, PA 19454, (310) 594-8525.

4.0 Results and Discussion

This section presents results of particle analyses conducted on fingerprint samples of C-4, Detasheet, and Pentolite. In addition particle analysis results of solution standards prepared at the INEEL are compared to the particle analyses of the respective fingerprint sample. We seek to provide answers to four questions of interest.

- a. How do fingerprint deposits compare with solution standards?
- b. What is the size distribution of particles found in the solution suspensions?
- c. What is the particle size distribution resulting from allowing the water in the solution suspensions to evaporate on a glass slide?
- d. What is the effect of placing the suspension on substrates of metals, glass, airline boarding pass paper, and gloss magazine paper?

In answering the above four questions we identified two areas of variability. First, at the concentrations used in preparing the standard solutions (4 to 30 ng/ μ l), some fraction of explosive is dissolved in the water. The remaining particles found in the suspensions are large portions of binder material. Secondly, upon placing a drop of suspension on a glass slide, particles are nucleated as the water evaporates from the droplet.

4.1 Standard Solution Deposits

Optical analysis results of the standard explosive solutions are presented below in two distinct areas. First the count based particle size distribution of binder particles found suspended in the water solutions is presented as CMD and GSD. Second, the count based particle size distribution of particles found following water evaporation is presented as CMD and GSD.

4.1.1 Suspended Particulate

Particles found suspended in solution and those found following water evaporation originate from the same solution standard. The particle size distribution and characteristics of these particles are fundamentally different. The particles found suspended in solution are presumably either above the solubility limit for the compound or are insoluble in water. Prior to this work the assumption was that the solutions contained concentration levels of explosive chemicals above the solubility limit and these compounds existed in water as suspended particles. Following further analysis the solutions were found to have concentrations of 30 to 35 ng/ μ l, close to or below the solubility limit in water. One of the final C-4 samples was prepared with a concentration of 72 ng/ μ l. This sample concentration is above the solubility limit for C-4 in water but there was not a significant quantity of additional particles found in the water solution. It did however exhibit very quick nucleation and readily formed particles upon evaporation of the water from the droplet.

Optical analyses were carried out on samples from Semtex-H and Detasheet standard solutions. No solutions of Pentolite were tested as no solutions were available for these tests. Figure 12 shows a 200 x magnification photograph of the edge of a droplet of C-4 standard solution. Figures 13 and 14 show similar photographs of Semtex-H and Detasheet solutions. The particles seen in the photograph have migrated to the edge of the droplet. Table 4 presents a summary of the measured CMDs and GSDs determined from photographs similar to Figure 12, 13, and 14. Some key statistics are also shown in Table 4. Of particular interest is the number of particles found suspended in each of the droplets.

Generally, the particles found suspended in solution ranged between 4 and 25 microns in diameter. These particles generally had appearances similar to those seen in Figure 12, 13, and 14.

Figure 12. Photograph of particles found floating in water solution of C-4.

Figure 13. Photograph of particles found floating in water solution of Semtex-H.

Table 4. Summary of results from optical particle counts of particles found in suspension.

Particles Found In Suspension						
Sample	HPLC Concentration (ng/μl)	CMD (μm)	GSD	# Particles	-95% Confidence (μm)	+95% Confidence (μm)
DS-1	3.3	8.02	1.55	78	7.26	8.86
DS-2	4.3	10.4	1.41	16	8.76	12.35
DS-3	4.4	16.5	4.6	110	12.33	22.07
C-4-72	72.0	5.27	3.55	21	3.03	9.16
C-4-(1)	30.3	No Particles Found				
C-4-(2)	30.3	4.92	2.71	11	2.70	8.98
C-4-(3)	30.3	No Particles Found				
C-4-(4)	36.4	25.8	2.2	8	14.77	45.06
C-4-(5)	36.4	No Particles Found				
C-4-(6)	36.4	5.27	1.36	6	4.10	6.77
Semtex-H H-1	11.1	6.2	2.7	322	5.55	6.93
Semtex-H H-2	11.1	22.3	1.79	7	14.36	34.63
Semtex-H H-3	11.1	No Particles Found				
Particles Found Following Evaporation						
DS-1	3.3	5.29	2.40	261	4.75	5.90
DS-2	4.3	No Particles Found				
DS-3	4.4	2.17	2.28	331	1.98	2.38
C-4-72	72.0	1.38	1.88	1080	1.33	1.43
C-4-(1)	30.3	1.4	2.46	223	1.24	1.58
C-4-(2)	30.3	0.55	2.52	257	0.49	0.62
C-4-(3)	30.3	1.83	1.4	527	1.78	1.88
C-4-(4)	36.4	1.67	1.71	1829	1.63	1.71
C-4-(5)	36.4	No Particles Found				
C-4-(6)	36.4	1.47	1.91	1535	1.42	1.52
Semtex-H H-1	11.1	1.13	2.35	927	1.07	1.20
Semtex-H H-2	11.1	1.6	2.33	3627	1.56	1.65
Semtex-H H-3	11.1	1.38	1.46	940	1.35	1.41
Fingerprint Deposition Particle Size						
C-4 7.2		2.06	1.38	392	1.99	2.13
		7.50	1.75	1321	7.27	7.73
C-4 8.2		1.50	1.74	729	1.44	1.56
		4.80	2.37	2728	4.64	4.96
C-4 9.2		1.65	2.33	932	1.56	1.74
DS 7.3		1.81	1.16	2379	1.80	1.82
DS 8.3		1.93	1.30	299	1.87	1.99
DS 9.3		1.00	1.58	754	0.97	1.03
P 7.1		2.47	1.18	1487	2.45	2.49
P 8.1		1.96	1.65	729	1.89	2.03
P 9.1		1.77	2.02	1812	1.71	1.83

Figure 14. Photograph of particles found floating in water solution of Detasheet.

4.1.2 Particles Nucleated following Water Evaporation from Solution

Analyses using the Nikon optical microscope yielded data indicating that the solution standards contained a mixture of particles (primarily binder) and dissolved explosive chemicals. This was determined primarily by observation of a drop of solution on a glass slide. As the water evaporated from the drop of solution fine particles nucleated at various sites along the edge of the drying droplet. As the droplet completely dried, a very fine distribution of particles was nucleated and remained deposited on the glass slide.

Table 4, above, shows a summary of the particle size distribution results determined for particles nucleated from drying standard solutions. The results are shown in the same table as the particles found floating in solution to allow comparison. Generally, the particle median diameters ranged between 1.0 and 2.0 microns in diameter. More particles were formed during evaporation than were found suspended in solution. Figure 15 shows a 200 x photograph of nucleated particles formed following evaporation of water from a C-4 solution. Figures 16 and 17 show similar evaporation and nucleation of particles from water-Semtex-H and water-Detasheet solutions.

Figures 18 through 21 show a series of 200 x photographs illustrating the growth of a large particle structure at the edge of an evaporating drop of C-4 solution. This was a common phenomena observed during most of the analyses. Also observed during this analyses was the fine nucleation of particles as a solution droplet dried. Figures 22 through 24 show a series of 200 x photographs taken as a droplet of C-4 solution dried on a glass slide. The particles generated can be seen evenly distributed in the dry area of the slide.

Figure 15. Photograph of particles nucleated following evaporation of water-C-4 solution.

Figure 16. Photograph of particles nucleated following evaporation of water-Semtex-H solution.

Figure 17. Photograph of particles nucleated following evaporation of water-Detasheet solution.

Figure 18. C-4 solution, nucleation of a particle in right-hand corner of droplet (0:29:26).

Figure 19. C-4 solution, nucleation of a particle in right-hand corner of droplet (0:29:50).

Figure 20. C-4 solution, nucleation of a particle in right-hand corner of droplet (0:30:59).

Figure 21. C-4 solution, nucleation of a particle in right-hand corner of droplet (0:32:49).

Figure 22. Nucleation of particles from a C-4 solution drying on a glass slide (1:37:43).

Figure 23. Nucleation of particles from a C-4 solution drying on a glass slide (1:37:58).

Figure 24. Nucleation of particles from a C-4 solution drying on a glass slide (1:38:21).

4.2 Optical Analysis of Fingerprint Deposits

Detection of explosive articles depends largely on the amount and type of contamination on exterior surfaces of the article. One primary source of exterior contamination is by fingerprint deposits of explosive. Simple fingerprint samples were deposited on glass slides by three different people. The slides were then examined under the optical microscope and the particles analyzed for size distribution. Figure 25 shows a 200 x magnification photograph of a fingerprint deposit of C-4 on a glass slide. Table 4 presents a summary of the analyses of fingerprint deposits of explosives on glass slides. Analyses were completed for C-4, Detasheet, and Pentolite explosives. Figures 26 and 27 show photographs of fingerprint deposits of Pentolite and Detasheet, respectively.

Figure 25. Photograph of fingerprint deposit of C-4.

Figure 26. Photograph of fingerprint deposit of Pentolite.

Figure 27. Photograph of fingerprint deposit of Detasheet.

4.3. Standard Solution Microtrac FRA

Following analyses of solution standards using the optical microscope, the remaining solution was used for analysis in the Microtrac FRA particle sizing instrument. The photographs in Figure 16 show the growth of a particle at the water-glass interface as well as a particle floating in the water solution. Particles found suspended in the water solution can be analyzed using the Microtrac FRA laser diffraction particle sizing method. Following analysis of solutions under the optical microscope, the solutions were placed in the analysis volume of the Microtrac FRA. The Microtrac FRA measures the volumetric particle size distribution of the sample. Table 5 presents a summary of the key particle size analysis results obtained using the Microtrac FRA particle sizer. MMD refers to the mass median diameter explained in Section 3.0 and the GSD refers to the geometric standard deviation. Primary, Secondary, and Tertiary refer to multiple size peaks found during the analysis. Primary is always the smallest particle found and Tertiary is always the largest, with secondary falling in a middle range. The significance of these separate peaks is an indication of multiple particle sources within the same sample. This is expected with high explosives due to the many components found in the manufacturing process.

Table 5. Summary of Results of Microtrac Volumetric Analysis of standard solutions.

C-4 Samples	MMD (μm)	GSD
C-4-72	56.40	1.63
C-4-(1)	206.00	1.49
C-4-(2)	No Particles Found	
C-4-(3)	No Particles Found	
C-4-(4)	76.60	1.26
C-4-(5)	No Particles Found	
C-4-(6)	152.30	1.81
C-4-1-FR	53.70	1.67
	61.50	1.61
C-4-2-FR	142.00	1.20
C-4-3-FR	148.30	1.37
C-4-4-REF	152.00	1.30
C-4-5-REF	170.00	1.20
C-4-6-REF	256.00	1.16

Detasheet Samples	MMD (μm)	GSD
DS-1	20.70	1.58
	73.00	1.18
	213.50	1.11
DS-1-FR	3.09	1.19
	10.18	1.19
DS-2-REF	25 - 100 μm	
DS-3	64.80	2.29
	59.80	2.37
	53.40	2.53

Semtex-H Samples		MMD (μm)	GSD
H-1		25.50	1.53
		29.90	1.29
		25.50	1.45
		28.40	1.41
H-2		37.80	1.10
H-3		34.20	2.78
		27.40	2.99
1-FR	Primary	6.20	2.43
		6.94	2.50
		6.99	2.39
	Secondary	97.01	1.20
		97.01	1.20
		97.19	1.20
	Tertiary	306.30	1.18
		306.00	1.18
		310.00	1.19
2-FR	Primary	6.96	1.81
		6.94	1.86
		6.87	1.78
	Secondary	42.60	1.32
		39.90	1.24
		43.10	1.27
3-FR		365.00	1.17
		364.00	1.17
4-REF	Primary	10.80	2.54
		9.04	3.14
		10.00	3.34
	Secondary	174.50	1.29
		184.90	1.29
		184.60	1.29
5-REF	No Particles Found		
6-REF	Primary	71.70	1.56
		58.90	1.51
	Secondary		
		220.40	1.21

4.4. Deposition of Prepared Standard Solution on Absorbent Material.

Limited studies were conducted investigating the behavior of explosive particulate when deposited on airline ticket paper, filtration media, and on high gloss magazine paper. Similar to preparation of samples for analysis of suspended particulate, a 10 ml drop of prepared solution was placed on sections of airline ticket paper, filtration media, and on high gloss magazine paper. In all cases the droplet was absorbed into the fibers of the substrate material. No particles could be identified once the solution was absorbed. We believe explosive is dissolved in the water solution and easily absorbed into fibrous material where it is unavailable for particle analysis.

5.0 Conclusion and Future Work

This report presents the sample preparation and sample analysis conducted for the purpose of determining the particle size characteristics of standard calibration solutions and fingerprint deposits of explosive materials. The primary objective of this study was to provide the explosive detection community with information on the particle size characteristics of standard explosive solutions made at the Idaho National Engineering and Environmental Laboratory (INEEL). In addition the standard solution particle size characteristics have been compared to the particle size characteristics of simple fingerprint deposits of explosives onto a flat surface.

Three general procedures were performed during these analyses. Standard solutions ranging in concentrations between 4 and 71 ng/ μ l of C-4, Semtex-H, and Detasheet explosives were prepared. These solutions were analyzed for both suspended particle size distribution and "evaporated solvent" particle size distribution using an optical count fraction technique. The solutions were then analyzed for suspended particle size distribution by volumetric laser diffraction analysis.

To compare the above results with fingerprint transferred particles, simple fingerprint depositions of C-4, Detasheet, and Pentolite were placed on glass slides and analyzed using the optical count fractionation techniques used above. The particle size characteristics of fingerprint deposits from actual fingerprints compare reasonably well with the particles nucleated following evaporation of the water from the prepared solutions. It is not clear however, why fingerprint transferred particles compare reasonably well with particles nucleated from dried prepared suspensions. A possible explanation is that the materials found in explosive compounds seek a minimum energy state generally resulting in 1 to 4 μ m particles regardless of the production path. This has not yet been confirmed.

We recommend that further studies be conducted to fully determine the effect solution concentration has upon both the suspended particle size characteristics and compositions and the nucleated particle size characteristics and compositions. In addition, the aerodynamic particle size distribution should be determined. An aerodynamic size distribution measurement could then be compared to predictions using the measurements from this study and estimates for particle shape factors and the theoretical density of the components of the explosive mixture.

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Appendix A: Statistical Modeling and Analysis of Particle-size Data

Max Engelhardt

Statistical Modeling and Analysis of Particle-size Data

This appendix is concerned with statistical analyses that are performed with sets of particle-size data. It is assumed that data are collected at two or more magnifications of the microscope. For example, some microscopes are designed to observe the substrate at five magnifications such as 5X, 10X, 20X, 50X and 100X, and we will discuss the methods in that context. However, the methods discussed here can be applied with any number of magnifications. The size is represented in terms of a "projected diameter" which is computed as the diameter of a circle with the same area as seen by the microscope for a given particle.

It is necessary to consider different magnifications, because smaller particles are not detected at lower magnifications such as 5X or 10X. Each magnification is best at detecting particles in some associated size range, and thus, it is necessary to combine results of the data analysis from different size ranges and magnifications to obtain an estimate of the overall distribution.

One complicating factor is that the observed areas are smaller when viewed at higher magnifications, so even though smaller particles are more visible at high resolutions, the number of particles observed also tends to be smaller. Thus, the number of particle counted at different magnifications are not directly comparable without some sort of adjustment or weighting. For example, the surface area observed at magnification 5X is 400 times the surface area observed at magnification 100X. Thus, a weighting factor must be used to put counts taken at different magnifications on a common basis.

If weights associated with all observed areas are scaled to the 5X magnification, then the weighting factors for frequencies corresponding to magnifications 100X, 50X, 20X, 10X and 5X are $w(1) = (100/5)^2 = 400$, $w(2) = (50/5)^2 = 100$, $w(3) = (20/5)^2 = 16$, $w(4) = (10/5)^2 = 4$ and $w(5) = (5/5)^2 = 1$, respectively. On the other hand, if the surface areas are scaled to 100X magnification, then the appropriate weights are $v(1) = 400/w(1) = 1$, $v(2) = 400/w(2) = 4$, $v(3) = 400/w(3) = 25$, $v(4) = 400/w(4) = 100$ and $v(5) = 400/w(5) = 400$. For example, if the particles are counted at magnification 100X on a surface of area A , then to compare to a count at magnification 5X on a surface of area $400A$, the 100X count should be multiplied by $w(1) = 400$ to adjust for the differences in surface area.

Another approach would be to do more counts at 100X and add the results. For example, if 400 independent counts could be obtained at 100X, and the results added, then it would not be necessary to rescale the count when comparing to a 5X count. In general, if K independent counts are taken at 100X, then the total surface area observed is $K \times A$, and the appropriate scaling factor would be $w(1) = 400/K$. For example, if $K = 4$ counts are taken at 100X, then the weighting factor for comparing the total count with a single 5X count would be $w(1) = 100$.

It is assumed that the number of particles on a surface is a Poisson Process with mean occurrence rate λ . Specifically, the number of particles counted on a surface of area A is Poisson distributed with mean λA , where λ is the mean number per unit area. Furthermore, the numbers of particles counted in non-overlapping surfaces are independent. Under this assumption, it can be shown that conditional on the number of particles on a rectangular surface, the coordinates of particles are uniformly distributed over the surface.

Suppose further that the particles are of different sizes, and that the size is modeled as a random variable X with cumulative distribution function, (CDF), $F(x) = P[X \leq x]$. For example, for a given interval $I_j = (a_{j-1}, a_j]$ of positive numbers, the probability that the size of a randomly selected particle will lie in the interval is $p_j = F(a_j) - F(a_{j-1})$. We assume also that the size of a particle is independent of its location (i.e. its coordinate).

It can be shown, under these assumptions, that the number of particles on a surface of area A whose sizes are in the interval I_j is also Poisson distributed with mean $\lambda A p_j$. In other words, for each particle on the surface, there is a probability p_j that it will be included in the count for particles in the size range $(a_{j-1}, a_j]$. The resulting count is also Poisson, but with reduced mean rate of λp_j occurrences per unit area. This is sometimes referred to as a "filtered" Poisson process. For the sake of discussion, we will assume that the

positive x -axis is divided into 5 disjoint subintervals, I_1 (with $a_0 = 0$) through I_5 , and the particle size for each magnification are sorted into a different interval, 100X into I_1 , 50X into I_2 , etc.

Denote by N_j the number of particles observed with sizes contained in the j th subinterval, so that the total for all subintervals is

$$N = \sum_{j=1}^5 N_j. \quad (\text{A-1})$$

As noted previously, the counts at different magnifications cannot be compared directly, but need to be adjusted in some way to make the comparison. The approach considered here is to adjust the counts for the higher magnifications with the weights $w(j)$. Of course, if the number of magnifications used is less than 5, then the sum would be over the corresponding smaller set of indices, and the number of intervals would be reduced accordingly.

If A is the area of the surface observed at 100X magnification, then N_1 = the number observed over this surface which are in the interval $I_1 = (0, a_1]$ is Poisson distributed with mean $\lambda A p_1 = \lambda A \times [F(a_1) - F(0)]$. Similarly, for the j th subinterval, N_j = the number observed over the smaller surface which are in the interval $I_j = (a_{j-1}, a_j]$ is Poisson distributed with mean $\lambda A v(j) p_j = \lambda A v(j) \times [F(a_j) - F(a_{j-1})]$. Thus, the total number of particles observed, N , is Poisson with mean $\lambda A \sum_{j=1}^5 v(j) p_j$. This follows from the well known property that the sum of independent Poisson random variables is Poisson distributed, and the mean of the sum is the sum of the means of the individual variates. Furthermore, conditional on $N = n$, the counts $N_1, N_2, \dots, N_5$ have a multinomial distribution with parameters n and $\phi_1, \phi_2, \dots, \phi_5$, where

$$\phi_k = \lambda A v(k) p_k / \sum_{j=1}^5 \lambda A v(j) p_j = v(k) p_k / \sum_{j=1}^5 v(j) p_j. \quad (\text{A-2})$$

Notice also that this also implies that

$$p_k = \left[\sum_{j=1}^5 v(j) p_j \right] \frac{\phi_k}{v(k)}, \quad (\text{A-3})$$

and because $w(j) = 400/v(j)$ and $\sum_{j=1}^5 p_j = 1$,

it follows that

$$p_k = w(k) \phi_k / \sum_{j=1}^5 w(j) \phi_j. \quad (\text{A-4})$$

The Maximum Likelihood Estimate (MLE) for a multinomial parameter ϕ_k is $\hat{\phi}_k = N_k/N$ and consequently, by the invariance property for MLEs, the MLE of p_k is

$$\hat{p}_k = w(k) \hat{\phi}_k / \sum_{j=1}^5 w(j) \hat{\phi}_j. \quad (\text{A-5})$$

It is also possible, by a similar construction, to derive the MLE, $\hat{F}(x)$, of the CDF $F(x)$. If x is an arbitrary positive number, then let j be the integer such that $x \in I_j = (a_{j-1}, a_j]$. Then we can divide N_j into two terms, $N_{1,j}$ = the number of observations in the lower subinterval $(a_{j-1}, x]$ and $N_{2,j}$ = the number of observations in the upper subinterval $(x, a_j]$. The probability that a particles size is in the lower interval is $p_{1,j} = F(x) - F(a_{j-1})$. The probability it is in the upper interval is $p_{2,j} = F(a_j) - F(x)$. Conditional on $N = n$, the variables $N_{1,j}$, $N_{2,j}$ and the four variables N_k for $k \neq j$ have a multinomial distribution with parameters n and $\phi_{1,j}$, $\phi_{2,j}$ and ϕ_k for $k \neq j$, where

$$\phi_{i,j} = v(j)p_{i,j} / \sum_{h=1}^5 v(h)p_h. \quad (A-6)$$

The MLEs of $\phi_{1,j}$, $\phi_{2,j}$ are, respectively, $\hat{\phi}_{1,j} = N_{1,j}/N$ and $\hat{\phi}_{2,j} = N_{2,j}/N$. The corresponding MLEs of $p_{1,j}$ and $p_{2,j}$ are $\hat{p}_{1,j} = w(j)\hat{\phi}_{1,j}/S$ and $\hat{p}_{2,j} = w(j)\hat{\phi}_{2,j}/S$ where

$$S = \sum_{j=1}^5 w(j)\hat{\phi}_j. \quad (A-7)$$

The resulting MLE of $F(x)$ is

$$\hat{F}(x) = \sum_{k=1}^{j-1} \hat{p}_k + \hat{p}_{1,j} = \left[\sum_{k=1}^{j-1} w(k)\hat{\phi}_k + w(j)\hat{\phi}_{1,j} \right] / S. \quad (A-8)$$

If we now define two other sums

$$S_1 = \sum_{k=1}^{j-1} w(k)\hat{\phi}_k + w(j)\hat{\phi}_{1,j}, \quad (A-9)$$

and

$$S_2 = w(j)\hat{\phi}_{2,j} + \sum_{k=j+1}^5 w(k)\hat{\phi}_k = S - S_1, \quad (A-10)$$

then the maximum likelihood estimate of $F(x)$ can be written as $\hat{F}(x) = S_1/S$. It follows from well known properties of MLEs that $\hat{F}(x)$ is an asymptotically unbiased estimate of $F(x)$. Furthermore, we can derive an asymptotic variance for $\hat{F}(x)$ which can be used to compute confidence limits for $F(x)$. Strictly speaking, the MLEs used here are conditional MLEs, but this is not a problem because they enjoy the same asymptotic properties as the unconditional MLEs. Rather than using the Fisher information matrix approach to finding the asymptotic variance, we will use the standard linearization with partial Taylor series yielding a formula for the asymptotic variance.

In general, if a statistic Y is a function of a finite collection of other statistics, $Z_1, Z_2, \dots, Z_m$, say $Y = g(Z_1, Z_2, \dots, Z_m)$, then the variance can be expressed approximately as a linear combination of covariances,

$$\text{Var}[Y] \cong \sum_i \sum_j c_i c_j \text{Cov}(Z_i, Z_j) \quad (\text{A-11})$$

where the coefficients are obtained by taking partial derivatives,

$$c_k = \frac{\partial g(z_1, z_2, \dots, z_m)}{\partial z_k} \quad (\text{A-12})$$

evaluated at each $z_i = E(Z_i)$; $i = 1, 2, \dots, m$.

In the present application we let, $Y = \hat{F}(y)$ and $m = 6$ where four of the Z -variables are of the form $\hat{\phi}_k = N_k/N$ for $k \neq j$, and the other two "split" variables are $\hat{\phi}_{1,j} = N_{1,j}/N$ and $\hat{\phi}_{2,j} = N_{2,j}/N$. For the first four such variables, the coefficients are of the form

$$c_k = \begin{cases} w(k)S_2/S^2 & ; k < j \\ -w(k)S_1/S^2 & ; k > j \end{cases} \quad (\text{A-13})$$

and the coefficients corresponding to the variables $\hat{\phi}_{1,j}$ and $\hat{\phi}_{2,j}$ are, respectively $c_{1,j} = w(j)S_2/S^2$ and $c_{2,j} = -w(j)S_1/S^2$. The covariances in the above expression are obtained by noting that conditional on $N = n$, the six variables consisting of the four counts $N_k = n\hat{\phi}_k$ for $k \neq j$ and the split counts, $N_{1,j} = n\hat{\phi}_{1,j}$ and $N_{2,j} = n\hat{\phi}_{2,j}$ have a multinomial distribution with parameters n and ϕ_k for $k \neq j$, $\phi_{1,j}$ and $\phi_{2,j}$. In general, for any two multinomial variables, U_i and U_j with parameters n , p_i and p_j we have

$$\text{Cov}(U_i, U_j) = \begin{cases} np_i(1-p_i) & ; i = j \\ -np_i p_j & ; i \neq j \end{cases} \quad (\text{A-14})$$

Thus, the asymptotic variance formula for $\hat{F}(y)$ has thirty-six terms:

four terms of the form $c_k^2 \phi_k (1-\phi_k)/n$; $k \neq j$,

twelve terms of the form $-c_k c_h \phi_k \phi_h /n$; $k \neq j, h \neq j, k \neq h$,

one term of the form $c_{1,j}^2 \phi_{1,j} (1-\phi_{1,j})/n$,

one term of the form $c_{2,j}^2 \phi_{2,j} (1-\phi_{2,j})/n$,

two terms of the form $-c_{1,j} c_{2,j} \phi_{1,j} \phi_{2,j} /n$,

eight terms of the form $-c_{1,j} c_k \phi_{1,j} \phi_k /n$; $k \neq j$,

and eight terms of the form $-c_{2,j} c_k \phi_{2,j} \phi_k /n$; $k \neq j$.

Appendix B: Photographs and Distribution Analysis of BCR Calibration Quartz
Particles

Photographs and Distribution Analysis of BCR Calibration Quartz Particles

The purpose of the work presented in this appendix is to benchmark the method used in the body of this report to analyze particulate collected from tokamak vacuum vessel surfaces. To accomplish this we have performed the procedure on quartz material with a known particle size distribution.

A number of calibration particle size distributions are commercially available; most are available from Duke Scientific Inc. Figure B-1 shows a photograph of polystyrene latex spheres viewed through at 1000X magnification with an optical microscope. To some extent this is a calibration photograph itself. This is because the scale mark of 10 μm placed on Figure B-1 has been placed there using the pixel to micron scaling factors described in Section 3 of this report. These scaling factors were determined from the micrometer measurements also described in Section 3. This type of "calibration" only applies to one aspect of the overall distribution construction process used in this study.

Figure B-1. 10.2 μm polystyrene latex spheres photographed at 1000 X with a Nikon optical microscope.

The following steps in the distribution construction process must be verified. First, as demonstrated in Figure B-1, the scale factors must be verified and determined to accurately measure the physical particle size viewed in a specific optical microscope objective. Second, the

overall distribution construction process must be verified by conducting the analysis process on a material with a known distribution. This material should have a size distribution similar to the material of interest. To accomplish this objective, five samples of quartz reference material were obtained from Duke Scientific Inc. The polystyrene latex spheres are not adequate calibration material for this sizing process because they are very uniform monodisperse distributions with very little spread from their calibrated particle sizes. In the case of the particles in Figure B-1, the reported particle size is 10.2 μm .

B.1 BCR Quartz Reference Material

Figures B-2 through B-4 show photographs of the various BCR samples at various magnifications. Generally, the magnifications used have resolutions corresponding to the particle sizes present in the reference material. Though not pictured BCR 68 and 70 show particles similar in shape and morphology as the particles in Figures B- 2 through B-4.

Figure B-2. BCR-66 quartz reference material viewed at 100 X magnification.

Figure B-3. BCR-67 quartz reference material viewed at 20 X magnification.

Figure B-4. BCR-69 quartz reference material viewed at 5 X magnification.

The calibration records provided by the manufacturer of the BCR quartz reference material are attached at the end of this appendix. These data are in the form of sedimentation or mass based particle sizes. We were unable to obtain reference material with calibrations in the form of count or number of particles per size class that would be directly comparable with the results of the particle counting technique used in this study. Therefore, it is necessary to determine the mass median