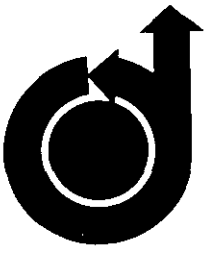

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PARTICLE SIZE MEASUREMENTS USING DIFFUSION BROADENING SPECTROSCOPY

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Abstract

A new technique for making in situ measurements of aerosol particles in the submicron size range has been investigated. Making use of the broadening of a monochromatic laser line due to random particle motion, the technique has been shown to be suitable for measurements of particle size in high temperature environments.

Particle diameters were measured in an acetylene/oxygen flame and attempts are being made to apply the technique for use in aluminum-oxygen flame. Particle size was determined as a function of mixture ratio and height above a flat-flame burner which was operated as a premixed acetylene/oxygen/nitrogen flame. Sizes were found to vary from 40 to 250 nm as height above the burner varied from 0.5 to 3.0 cm. Little variation was found as a result of mixture ratio changes. The flame was found to have large gradients in particle size on a scale comparable with the measurement volume (1 mm^3). Sizes measured from electron microscope photographs of soot particles collected from the flame showed reasonable agreement with those calculated from scattering measurements.

The results of this study have demonstrated the utility of the technique for determination of mean submicron particle sizes and have pointed the way toward methods for improvements to yield particle size distributions, as well.

Introduction

The formation of particulates in solid rocket motors is important from two standpoints: in the combustion zone particulates can alter propellant burning rates and radiative heat transfer which have a direct effect on combustor design; in the exhaust plume particulates are a primary cause of nozzle radiative heating, two-phase flow energy losses, and plume visibility. In order to develop improved smokeless propellants, fundamental research has been initiated to determine the physical mechanisms that occur in condensation processes. The occurrence of alumina (Al_2O_3) condensation in rocket motors, in particular, cannot yet be adequately predicted. To experimentally study the Al_2O_3 condensation processes, there is a direct need to develop and apply diagnostic techniques for measurement of particulates in the early stages of formation, i.e. sub-micron sizes.

Historically, sampling probes have been used to collect particles of interest which are viewed using electron microscopes. Results can be ambiguous because the collection process promotes particle agglomeration due to the electrostatic charges on the particles. In order to study the nucleation and agglomeration processes, in situ sizing techniques are required. In this research program, a new optical diagnostic technique, Diffusion Broadening Spectrocopy, is used to perform in situ size measurements of submicron particulates.

Research Objectives

The goal of this research program has been to make in situ measurements of mean particle diameters in the 1.0-100 nm size range in flowing, high temperature gases. The diagnostic technique selected for this program was Diffusion Broadening Spectroscopy. The DBS technique is independent of particulate properties and provides local submillimeter spatial resolution. Hinds and Reist[1] have demonstrated the feasibility of using DBS for submicron spherical particle size measurements. Penner, Bernard and Jerskey[2] first applied the DBS technique to flowing gases for the case of an ethylene-oxygen flame.

A secondary goal of this program was to create solid particulate aerosols with specific properties to be used in the validation of the experimental measurement technique. The aerosol had to be as monodisperse as possible, with particle mean diameter in the .001 to 0.1 μm range. The aerosol should be uniformly distributed in a steady, high temperature (500 °K - 2500 °K) gas flow. The above conditions are difficult to achieve and have been most closely realized by using specially designed laboratory flames[3]. An acetylene-oxygen flat flame burner provided carbon particles in the desired size range. An aluminum-oxygen flame was later used to provide alumina particles.

Validity of the DBS results was to be investigated by performing the following: (a) Scattering angle was to be varied and results compared to DBS theory. (b) Measurement location in the flame was to be varied to see if particle size increased with height above the burner. (c) Electron microscope photographs of sampled particulates were to be used to determine if DBS results were reasonable, and (d) the feasibility of measuring the geometric standard deviation of the particle size distribution was investigated.

Diffusion Broadening Spectroscopy-Theory

The use of the DBS technique for particle size measurements is now described. Hinds and Reist[1] first demonstrated the feasibility of DBS for use in stationary aerosols. Using concepts first proposed by Benedek[4], Hinds and Reist developed a theory for monodisperse aerosols and described effects of aerosol polydispersity. Good agreement between DBS experimental results, theory and electron microscope measurements were found for controlled monodisperse aerosols of latex spheres in the range 500 to 1,100 nm. Penner, Bernard and Jerskey[2] later included theoretical effects of gas flow velocity and demonstrated the feasibility of DBS application to an ethylene-oxygen flame.

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When laser light is scattered by submicron aerosol particles, Brownian motion gives rise to frequency fluctuations of the scattered light. The broadening of the scattered line profile can be measured, from which the particle diffusion coefficient can be inferred. Mean particle diameter is determined from the Stokes-Einstein diffusion relation, modified for large Knudson number effects. Small particles undergoing rapid Brownian motion cause greater broadening than large particles, thus the measured power spectrum of light fluctuations can be related to a mean particle diameter.

Consider two particles that are travelling through a focused submillimeter laser beam with equal average directed velocities U, but with opposite instantaneous components of random velocity. In general, radiation scattered from moving particles will be Doppler shifted by an amount Δf given by:

$$\frac{\Delta f}{f} = \frac{\bar{V}}{c} \cdot (\bar{e}_s - \bar{e}_i) \qquad (1)$$

where unit vectors $\bar{e}_s$ and $\bar{e}_i$ are in the scattered and incident radiation directions, respectively, vector $\bar{V}$ is the particle velocity, c is the velocity of light, and f is the laser frequency (on the order of 10^{14} Hz). The homodyne power spectrum resulting from many scattering centers simultaneously passing through the focal volume has been shown to have a Lorentzian profile[1]. The halfwidth (HW) of the power spectrum for the case of a stationary, monodisperse aerosol whose size is much greater than the molecular mean free path is given by:

$$HW = \frac{16\pi D}{\lambda^2} \sin^2(\theta/2) \qquad (2)$$

where θ is the scattering angle, λ the wavelength and D the particle diffusion coefficient, describing the mean squared length travelled by a particle per unit time. For the case of Reynolds number based on particle diameter approaching zero, the Stokes-Einstein diffusion coefficient is given by

$$D = kT\,(1 + 1.648\,\ell/d)/3\pi\mu d \qquad (3)$$

which is valid for either the molecular mean free path ℓ less than particle size d or, as is more typically the case, greater than d. Thus, the homodyne power spectrum halfwidth is given by:

$$HW = \frac{4\pi}{\lambda} \sin\frac{\theta}{2}^2 \frac{KT}{3\pi^2\mu d}\left(1 + 1.648\,\frac{\ell}{d}\right) \qquad (4)$$

The measurement of the homodyne spectral halfwidth, combined with knowledge of local gas temperature T and viscosity μ, yields a unique value of particle size in a stationary, monodisperse aerosol.

Turbulence that occurs on a scale less than the focal volume dimension can also broaden the homodyne spectrum. Larger scale turbulence causes a time varying Doppler shift of the optical spectrum, but has no effect on the measured homodyne spectrum. The homodyne spectrum is affected only by velocity variations simultaneously detected within the focal volume. The particle sizing technique is thus insensitive to turbulence and mean flow gradients providing that the focal volume is significantly smaller than the scale of local velocity variations.

In addition to the homodyne spectrum, a heterodyne spectrum centered in the Megahertz range can be produced by optical mixing of two coherent laser beams at the focal point. The heterodyne spectrum arises from the doppler shift due to the mean flow velocity and is employed in laser doppler velocimetry techniques. Thus the average flow velocity, average Brownian motion velocity and mean particle size can be measured by simultaneously recording the homodyne and heterodyne spectra.

Apparatus and Data Reduction

A photograph of the actylene-oxygen flame is shown in Fig. 1. A flat flame burner provided a relatively uniform and stable premixed flat flame. The burner surface consisted of bundled copper rods between which the premixed acetylene (C_2H_2), nitrogen and oxygen flowed. The 1-1/8 in. diameter burner surface was surrounded by an annular flow of nitrogen to stabilize the flame. The entire apparatus was water cooled. Gas flow rates were regulated and measured.

The light source, shown schematically in Fig. 2, was 100 milliwatt He Ne laser beam which was split into two beams and focused to intersect at the focal volume, allowing scattering to be observed at 25° and 60° from the incident beam. A collecting lens of 15.2 cm focal length was used to focus the enlarged (3X) image of the focal volume on the surface of an RCA 4832 photo-multiplier tube. An interference filter centered at 532.8 nm with a measured halfwidth of 1.65 nm was used to block flame emission. Photomultiplier current was passed to ground through a 0.1 MΩ resistor, providing a frequency response of 50 KHz. The amplified signal was observed on a Tektronix 465 oscilloscope and 315 Spectrum Analyzer, and was recorded as FM on analog tape at 50 in. per sec (ips).

Recorded data were analyzed using a digital spectrum analyzer (Spectral Dynamics 360-35), which displayed the real time power spectrum, allowing time variations in the spectrum to be observed. Data were replayed at 15 ips, high pass filtered at 1 KHz (real time) and sampled at a 16 KHz sample rate. Each computed power spectrum was determined from 2.5×10^5 data points. Bandwidth of the entire data acquisition system was 25 KHz. Prior to data reduction for each run, system accuracy was checked using a calibration square wave, whose power spectrum consists of peaks at odd multiples of the square wave frequency, with an f^{-2} rolloff.

Results and Discussion

Carbon aerosol measurements were attempted first in this study because soot formation in such flames is well documented[5]. Production of a relatively steady and monodisperse submicron aerosol is a difficult task and cannot be fully achieved with an acetylene flame. However, the DBS technique could be tested by: (a) varying the scattering angle and comparing results with theory, (b) varying measurement location in the flame and (c) comparing results with electron microscope photographs of carbon sampled from the flame.

In this flame, flame emission was so intense that proper alignment of the optical system was crucial to obtaining sufficient scattering signal-to-noise. The 28 milliwatt laser power used in this study provided a typical signal to flame emission ratio of 25 and signal to shot noise ratio of 40. Within 0.5 cm of the burner surface, however,

the scattered signal barely exceeded flame emission, making measurement of the smallest particles difficult.

Proper focussing was found to be critical for optimal scattering signal to flame emission signal. A 0.5 mm pinhole was drilled in the back side of the phototube mount, allowing a direct visual line of sight down the optical collection axis when the phototube is removed. A second laser beam was used to provide scattering at a different angle (60^o) than the first (25^o); it was aligned to intersect the first beam at the measurement location. A liquid aerosol was then sprayed through the measurement location and each beam was focused and realigned separately. When the beam was out of focus, a one millimeter diameter column of scattered light appeared when viewing through the pinhole. Proper focus caused the collection lens to appear completely red, i.e. the laser beam filled the entire collection solid angle. Poor signal to noise results from deviations from best focus because the laser beam transmission solid angle fills only a fraction of the total collection solid angle, the remainder being filled with flame emission. Final focus was obtained by viewing the scattered light for the desired acetylene-oxygen flame conditions. Through the pinhole, the flame background was barely visible with the laser off. With the laser on, the collecting lens appears filled with laser scattered light, and the phototube aperature is closed to focus on only the central portion of the beam.

Steady flame conditions were found to be highly desirable. The acetylene-oxygen flame appeared visually to be steady. The measured flame emission was relatively steady, with $\pm$ 10% intensity variations at frequencies of 5-15 Hz. However, the intensity of scattered laser light was not as steady. Regions containing gradients in flame emission oscillated in space over a distance of 1 mm. This oscillation was sufficient to observe 10-100 Hz changes in scattered light emission, which at times dropped to zero when few particulates passed through the focal volume. The intermittent nature of the aerosol occurrence made data reduction more difficult and introduced scatter in the results. Flame oscillations were observed to be due to room air currents, which could not be eliminated. At stoichiometric conditions with no particle formation, stable flame conditions occurred. It was concluded that to operate a rich acetylene-oxygen flame and to limit oscillations of carbon producing regions to less than 1 mm, an enclosed flame apparatus is necessary. A porous plug burner is also necessary to eliminate gradients that occur with our multiple-hole burner. However, flame oscillations that do occur do not in any way affect the measurement technique itself, since all signal fluctuations of frequency less than 1 KHz are filtered out during data reduction.

A typical power spectra of the phototube signal are shown in Fig. 3. Each power spectrum is obtained by Fourier Transforming 2.56×10^5 digital data points. The recorded analog phototube signal was sampled at 16 KHz; data was high pass filtered at 1 KHz. Shot noise is observed to be negligible since the power spectrum asymptotes to zero at high frequencies. Use of an analog spectrum analyzer directly attached to the phototube did not prove feasible since it did not afford the averaging capability of digital processing. Assuming a Lorentz line shape the power spectrum halfwidth (HW) was determined from the relation:

$$HW^2 = MHW^2 - 2f^2 \qquad (5)$$

where MHW is the measured halfwidth (i.e. the frequency at which the power spectrum has decreased to one half the maximum measured value), f is the filter frequency (1 KHz), and HW is the actual halfwidth of an unfiltered Lorentzian curve centered at zero frequency.

Mean particle diameters, shown in Fig. 4, were determined from the measured HW of the power spectra, using Eq. (4). Flame temperature was calculated using the AFRPL ISP computer program, which determines flame temperature and equilibrium concentration of 26 flame species using updated JANNAF thermochemical constants. Calculated flame temperatures had a strong dependence on the nitrogen flow rate.

The data of Fig. 4 indicates a definite trend of increasing particle size as height above the burner is increased. A theoretical increase of particle size with fuel-oxygen equivalence ratio has been postulated[6], but no definite trend was observed in this study. A typical power spectrum obtained for a location of 0.5 cm above the burner is shown in Fig. 6. While initial particle formation and visible radiation occurs at a height of 0.1 cm, sufficient signal to noise was not achieved below a height of 0.5 cm. Scattered light was also not visible through the 1.6 nm bandpass interference filter. Particles at these locations are believed to be too small to detect with the DBS apparatus at temperatures of 2200 ^oK. It is postulated by this author that the technique has a minimum detectable particle size due to particle radiation. As particle size decreases the particle radiation emitted decreases as d^2 while the Rayleigh scattered light decreases as d^6. This limitation will not exist at sufficiently low aerosol temperatures.

An increase in measured spectral halfwidth was observed as scattering angle θ increased from 25^o to 60^o. Two incident beams were focused within the focal volume of the detection system which was fixed. When the 25^o angle beam was used, the 60^o angle beam was blocked, and vice versa. Theory predicts a $\sin^2 \theta/2$ dependence of spectral halfwidth, for a monodisperse aerosol. Measurements at the two angles were made to compare with theory, which predicts a spectral halfwidth increase of 5.26. For the various flame conditions selected, spectral halfwidth increased by factors between 3.3 and 4.2 as θ increased from 25^o to 60^o. These large measured changes are felt sufficient to confirm that the spectrum observed was broadened due to particulate Brownian motion. The difference between theoretical and measured angle variation effects is believed due to deviations from monodispersity. In fact, the differences between dual angle measurements and theory are proposed as a possible technique to determine the particle size distribution[10].

Electron microscope photographs were taken of carbon particulates sampled on a Nichrome wire at 3 cm above the burner. A typical example is shown in Fig. 5. Particulates were observed to be in the 200 nm range, agreeing roughly with LDS results. The scanning electron microscope used was not capable of resolving particles smaller than 50 nm in this sample.

Other factors can contribute to the broadening of the homodyne power spectrum and thereby limit the applicability of the DBS technique. Time of flight broadening has been extensively reviewed in the literature since it gives rise to apparent turbulence in laminar flow systems. Time of flight broadening arises due to the finite duration of the scattered signal from each particle as it traverses the laser beam. The Fourier transform of a finite sine wave is not a delta function but has a Guassian profile. Superposition of many simultaneous particle signals, each of finite duration and of random phase, results in a homodyne spectral halfwidth of:

$$HW_{TOF} = \frac{U}{2a} = \frac{U}{2\,\frac{4\lambda}{\pi}\,\frac{F}{D}/\cos\frac{\theta}{2}} \qquad (6)$$

where U is the flow velocity and a is the local beam diameter resulting from focussing laser beam of diameter D with a lens of focal length F. To measure particle size in high velocity flow fields, time-of-flight broadening is minimized by increasing the laser beam diameter, and thus sacrificing spatial resolution.

For the case of rocket exhaust plumes the maximum velocity aerosol measurable with DBS is calculated by insuring that collisional broadening, given by Eq. (4) exceeds TOF broadening, Eq. (6) by at least a factor of four yielding:

$$U_{max}\ (M/S) = 0.00486\,\frac{a}{d} \qquad (7)$$

For a typical rocket exhaust velocity of 1000 M/S, a laser beam diameter of 2 cm is required to measure particles in the 1.0-100 nm range. This calculation assumes 180° backscatter using an argon laser and 2000° plume temperature.

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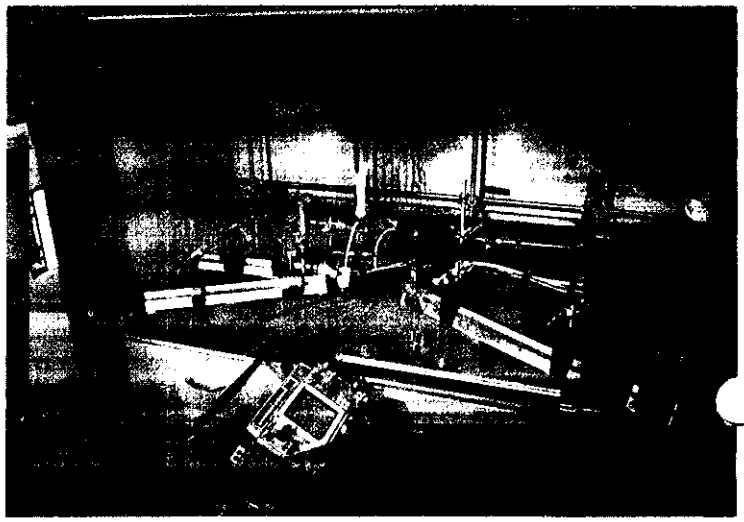

Figure 1. Photograph of Optical System

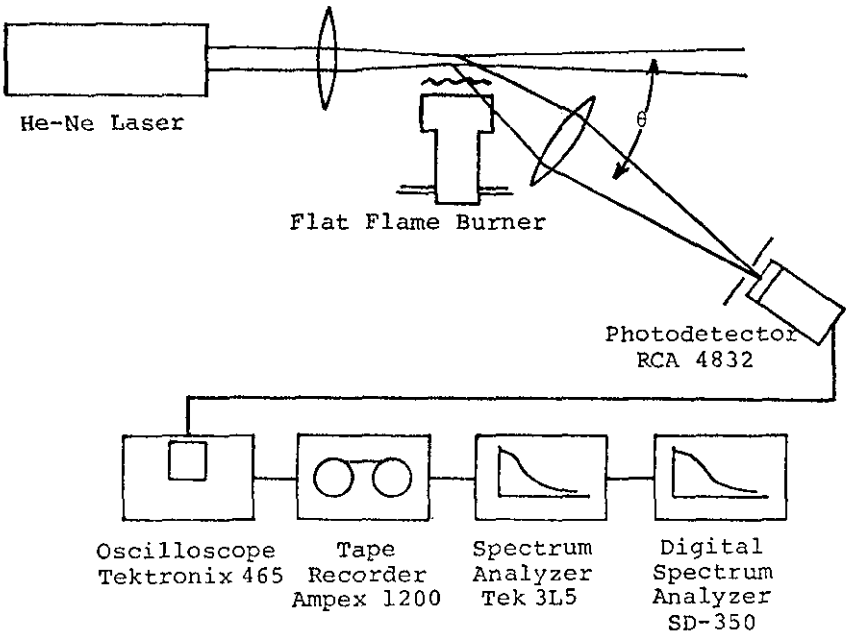

Figure 2. Schematic of Optical System

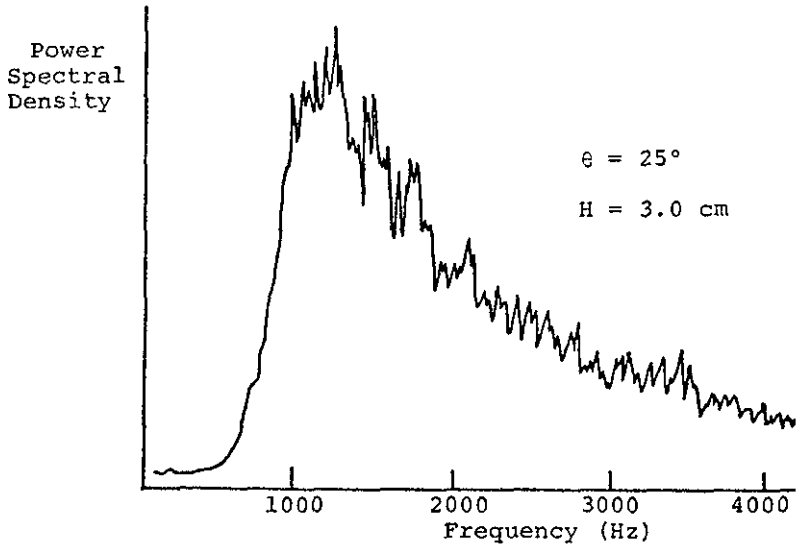

Figure 3. Typical Homodyne Power Spectrum

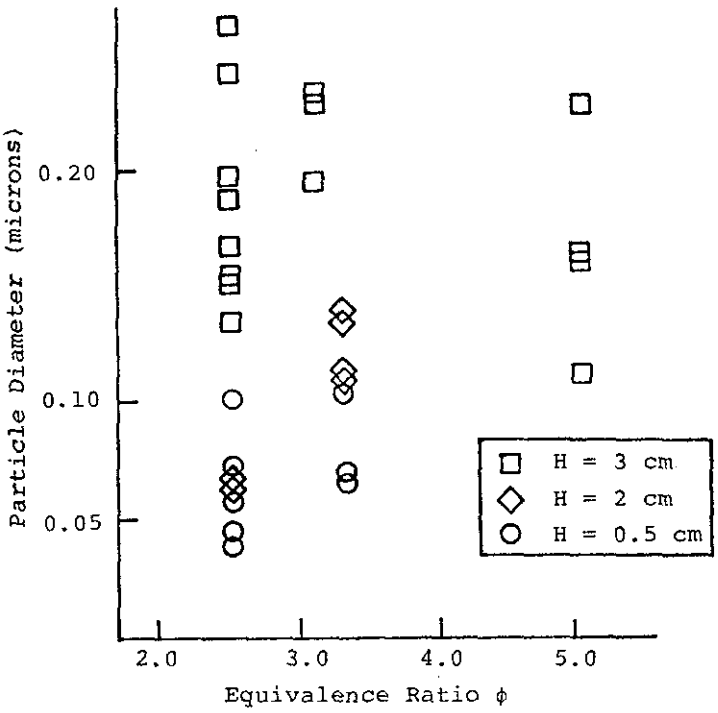

Figure 4. Measured Particle Diameter

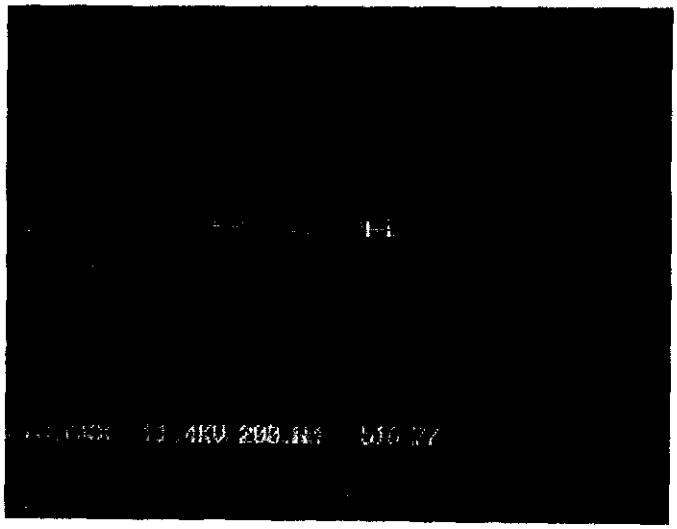

Figure 5. Electron Micrograph of Particulates
(Indicator Width = 200 nm)