

**Diagnostics of Carbon Nanotube Formation in a Laser Produced Plume:
Spectroscopic *in situ* nanotube detection using spectral absorption and surface
temperature measurements by black body emission.**

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ABSTRACT

Carbon nanotubes hold great promise for material advancements in the areas of composites and electronics. The advancement of research in these areas is dependent upon the availability of carbon nanotubes to a broad spectrum of academic and industrial researchers. Although there has been much progress made in reducing the costs of carbon nanotubes and increasing the quality and purity of the products, an increase in demand for still less expensive and specific nanotubes types has also grown.

This summer's work has involved two experiments that have been designed to further the understanding of the dynamics and chemical mechanisms of carbon nanotube formation. It is expected that a better understanding of the process of formation of nanotubes will aid current production designs and stimulate ideas for future production designs increasing the quantity, quality, and production control of carbon nanotubes.

The first experiment involved the measurement of surface temperature of the target as a function of time with respect to the ablation lasers. A peak surface temperature of 5000 K was determined from spectral analysis of black body emission from the target surface. The surface temperature as a function of various changes in operating parameters was also obtained. This data is expected to aid the modeling of ablation and plume dynamics.

The second experiment involved a time and spatial measurement of the spectrally resolved absorbance of the laser produced plume. This experiment explored the possibility of developing absorbance and fluorescence to detect carbon nanotubes during production. To attain control over the production of nanotubes with specific properties and reduce costs, a real time *in situ* diagnostics method would be very beneficial. Results from this summer's work indicate that detection of nanotubes during production may possibly be used for production feed back control.

INTRODUCTION

What is so important about carbon nanotubes?

Nanotechnology, the use of materials with dimensions of nanometers, represents engineering at the molecular scale, at a dimension beyond those typically used by chemists and much below those of the bulk dimensions used by engineers. It is within this interfacial domain of measure that materials of great promise for material and electronic advancement have been observed and proposed. Many of these promises have focused on the use of nanometer scaled tubes discovered in 1991 by Iijima.¹ These tubes, with dimension of nanometers in diameter and microns in length, can be described as the elongation of fullerenes into tubes. Fullerenes are spherical or elliptical in shape, the most well known being that composed of sixty carbon atoms and having the shape of a soccer ball, as proposed by Smalley in 1985.² Examples of a fullerene and two nanotubes can be seen in Figure 1. Carbon nanotubes are the building materials for many proposed nanostructures; therefore, an understanding of their properties and techniques for their utilization are essential to progress toward nanotube-based nanostructures.

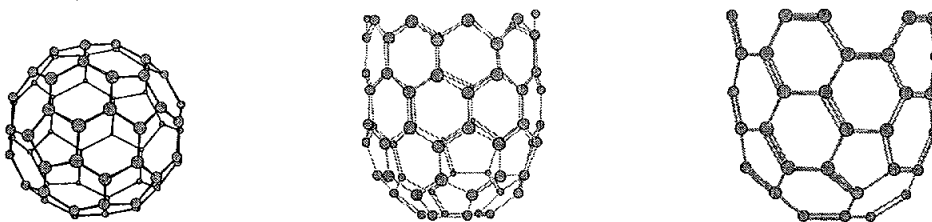


Figure 1: C_{60} , (9,0) metallic zigzag tube, and (5,4) semi-conducting armchair tube.

What are the problems?

Although much progress has been made in many areas of carbon nanotube production, characterization and applications, current production methods are still financially prohibitive for most commercial application and many academic research groups. Current production methods also result in tubes of various purity, diameter, length, and chirality. A more thorough understanding of the chemical mechanisms and better production feedback controls are essential to improve the production of carbon nanotubes and meet the demand for affordable quantities of nanotubes of selective properties.

What has been done to elucidate the chemical mechanisms?

Initial work on the elucidation of the chemical mechanisms has been done on the postproduction evaluation of the targets and products as a function of various production parameters.³⁻⁶ Recent *in situ* work has followed various species during nanotube formation. Nickel atom, cobalt atom, C_2 , and nonspecific larger carbonaceous materials

have been followed during nanotube formation in a laser-produced plume.⁷⁻¹² *In situ* work has been much more productive in explaining the chemistry involved in tube formation than the post analysis work. Scott *et al.* presents a summary of current thought with respect to the carbon nanotube formation mechanisms based on both the initial post production analysis and the recent *in situ* reports.¹³ Questions remain about the role of the catalyst in its atomic and condensed particle form as well as the time and spatial variables involved in carbon nanotube formation.

What are the current methods of production feedback controls?

Currently, there is no production feedback control employed in the laser production methods at JSC. Production parameters such as gas flow, oven temperature, and laser output are monitored by the operators during production. The quality and quantity of tube production must be done post production.

The HiPco process of carbon nanotube production, at Rice University, does employ feedback through the monitoring of CO₂ produced during the disproportionation of CO on iron to form C₂ and CO₂.¹⁴ Increased production of CO₂ is correlated to increased production of reduced carbon which will eventually lead to the formation of carbon nanotubes. By tuning parameters so that CO₂ output is optimized, the production of nanotubes is also optimized.

CO is not the feedstock in the laser method, and there is no CO₂ produced. The laser method would need a different species to provide feedback.

What else do we need to know?

Although there are many variables involved in carbon nanotube formation that can be explored, a method of detecting the presence of nanotubes *in situ* in real time during nanotube production would be very valuable in elucidating the chemical mechanisms and providing real time production feedback control.

EXPERIMENTAL

How can we do experiments that will give us the information we need?

At NASA-JSC any approach to studying surface temperature and the detection of nanotubes *in situ* during nanotube formation would have to be designed with respect to the current production configuration. The nanotube production configuration at JSC follows that developed at Rice University¹⁵ and has been described previously by Arepalli, *et al.*^{7,8} Briefly, the setup includes a carbon target (19 mm diameter) which is doped with 1% nickel and 1% cobalt and is supported on a rod in an oven which is heated

to 1473 K during normal production. The target and rod are centered within a 50.8 mm quartz tube. A smaller 25.4 mm quartz tube is centered within the 50.8 mm tube and extends to within 6 mm of the target. Argon flows through the tubes toward the target at a pressure of 67 kPa and a flow rate of 100 sccm. Two Nd:YAG ablation lasers follow a path through the inner tube to strike the flat end of the target at normal incidence. The green (532 nm) Nd:YAG laser fires 50 ns prior to the IR (1064 nm) Nd:YAG laser.

The JSC nanotube production approach and facilities are very conducive to spectroscopic probing of intermediate species and products. We made use of spectroscopic techniques to measure the surface temperature of the target upon ablation and to measure the absorption of the laser produced plume during production. The former to provide empirical values for modeling projects and the latter to explore the possibility of developing production feedback controls.

Experiment 1: Target Surface Temperature Measurements

The surface temperature of the target was measured using existing fiber optics and optical dispersion techniques. A new optical collection configuration was introduced to collect blackbody emission directly from the target surface. The experimental setup is illustrated in Figure 2. This differs slightly from the nominal production configuration in that there is only a 25.4 mm tube rather than the 25.4 mm tube within the 50.8 mm tube as described above. Also there is a Y in the tube, at an angle of 45°, with the shorter leg being 19.0 mm in diameter. Due to the smaller diameter tube, a smaller diameter target was used, 12.0 mm rather than 19.0 mm.

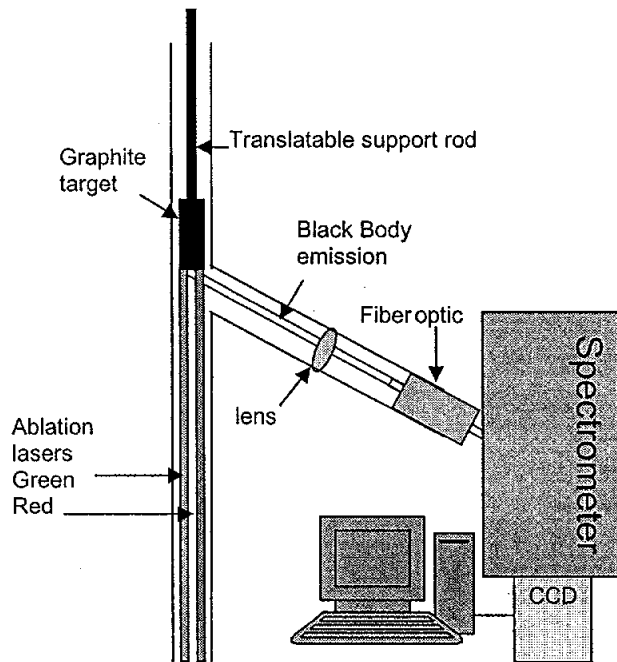


Figure 2: Surface temperature experimental setup

Studies involving the green laser also included a notch filter at 532 nm to avoid saturating the detector with scattered laser radiation. A temporal gate of 12 ns was used for collecting emission using various slit widths on the spectrometer depending on the amount of radiation emitted upon ablation.

Experiment 2. Absorbance measurements of the laser produced plume.

One of the attractive properties of the carbon nanotube is that its conductivity has been calculated to be a function of tube chirality and diameter.¹⁶ An example of two different chiralities can be seen in Figure 1, the extremes of zigzag and armchair. It has been only recently that spectroscopic measurements of the band gaps associated with carbon nanotubes have been measured.¹⁷⁻²⁰ Absorption and fluorescence measurements have been well studied for nanotubes suspended in solution. Fluorescence of nanotubes requires very good solvation as it is thought that if any of the individual tubes within the ropes is a metallic conductor, fluorescence from excited electronic states will not be observable due to quenching by the metallic tubes which allow for a path of non-radiative electronic relaxation. Since there is a distribution of chirality and diameter in the production of nanotubes, the presence of metallic tubes in a rope is quite probable. Not until dispersion techniques had improved, was it possible to measure band gaps of isolated tubes by detection of fluorescence.

In the JSC nanotube production facility we hope to detect nanotubes *in situ* during carbon nanotube formation using recently reported absorption bands. Absorption was chosen rather than fluorescence because the JSC facility is equipped to measure light in the visible wavelength range of nanotube absorption but not in the infrared region of nanotube fluorescence. It was expected that tubes initially form individually in the gas phase before they flocculate into bundles later in time. Flocculation or the condensing of tubes into bundles would broaden the absorption bands and would likely quench fluorescence.

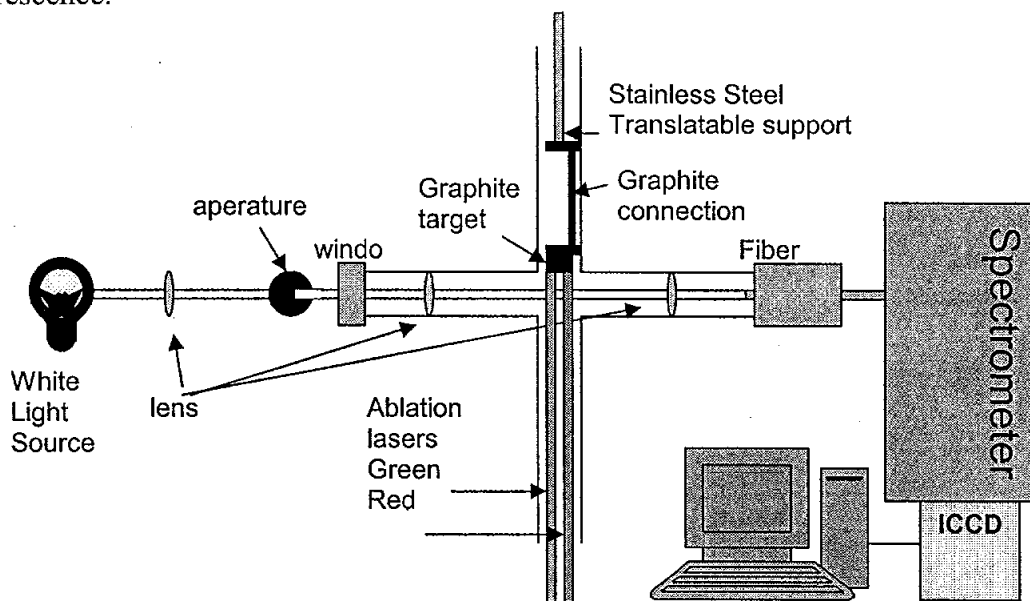


Figure 3: Experimental set up for absorbance measurements.

The experimental setup for absorption measurements differs from production in the following ways. An x-tube is used in place of the standard production tubes. The x-tube is 25.4 mm in diameter along the optical path of the ablation lasers and a 19 mm in diameter along the path perpendicular to path of the ablation lasers, rather than the 25.4 mm tube within the 50.8 mm tube as described above. The light transmitted through the optical path of the white light is collected by an optical fiber and dispersed with a spectrometer onto a CCD so that a wavelength resolved transmission spectrum is obtained. The CCD is gatable with respect to time of ablation and the graphite target is mounted on a translatable stage so that it is possible to probe for nanotubes in both temporal and spatial dimensions. A simplified experimental set up is illustrated in Figure 3.

RESULTS and ANALYSIS

Experiment 1. Surface Temperature

Emission from the target surface was collected using the y-tube design. The y-tube performed as designed, allowing for a consistent signal of much greater intensity than did previous diagnostic setups which collected emission transmitted through the standard quartz production tube. Although the y-tube design appears to be fairly robust, it was found that operating under lower pressures than 500 Torr at 1200 degrees Celsius caused the y-tube to begin a collapse that would slowly continue when operating at 1200 degrees Celsius even at the normal operating pressures of 500 Torr.

Emission from the surface of the target was collected under many different experimental parameters. In all the experiments the emission was resolved by wavelength. In experiments involving the ablation lasers, the emission was also resolved with respect to the time of ablation. This was done by collecting wavelength resolved emission at a variety of time delays from 200 nanoseconds prior to the laser pulse to 3 microseconds after the laser pulse with a time gate of 40 nanoseconds. Although greater time resolution is possible, 12 nanoseconds being the shortest time interval, shorter times result in poor statistics and poor signal quality. Experimental conditions included lasers operating in standard production parameters, operating singly, operating in reverse order, and operating with time delays of 0, 50, and 500 nanoseconds. Argon flow rates were also varied. Helium was used a substitute buffer gas for Argon. Oven temperature was operated at the standard 1200 and also 1000 degrees Celsius. Emission was collected from the center of the target to the edge of the target at 1 mm increments.

It would be difficult to report all the results of these experiments within the limits of a report of this nature, so only a few remarks will be made here in hopes of writing a more comprehensive report at a later date. Methodology of the analysis and then some of the general results are described below.

Although the y-tube is designed to collect emission from the target surface, emission from the laser-produced plume is also unavoidably present. Analysis requires a discernment to be made between the plume emission and the surface black body emission. Two methods were developed that would allow for this discernment, the first will be referred to as the ratio method and the second as the baseline curve fit method.

Method 1: The ratio method.

This method assumes an emission entirely from black body at a wavelength that was as far from the plume emission as possible while still being in a responsive region of the detector. This emission was then compared to the black body emission of the target under conditions in which no lasers were being used, assuming a black body temperature equal to the ambient temperature of the oven. The ratio of the emission intensity at a given wavelength to the intensity of emission under ambient oven conditions at the same wavelength can be used to determine the blackbody temperature of the emission of the former. Since the emission produced by laser ablation may include contributions from the plume in addition to emission from the surface the temperature obtained from the emission intensity ratios will give an upper limit temperature.

Method 2: The curve fit method.

The curve fit method involves correcting the raw data for the instrument response and then fitting the data to calculated black body curves. This method involves many data across the spectral range and therefore emission from C_2 and other sources is unavoidable. Therefore a subjectively determined baseline underneath any structured spectrum is interpreted as the blackbody emission. Spectra taken under ambient oven conditions and corrected for response fit very well to a black body curve of the ambient temperature, 1473 K.

Our results from method one and two indicate a peak surface temperature of 3000 K and 5000 K respectively. The ratio method was used in Figure 4 to calculate temperature at a number of different time delays with respect to the time of laser ablation. From this, it is noted that there is a steep temperature gradient across the target and that the target returns to near ambient temperatures within a few milliseconds. Figure 4 represents a temporal temperature profile at different positions on the target surface. The 'zero' position is taken to be the center of the target where the 4.8 mm diameter laser beam is also centered. As the target is moved one millimeter in, the 45° angle of collection is such that emission is collected from a spot on the surface one millimeter outward from the zero position. Only three of these steps will move the emission spot from the laser spot. It should also be expected that the laser's energy profile across the spot is not flat and drops off from the center toward the edge. From Figure 4 it is clear that there is little change in temperature after moving 2 millimeters away from the center position.

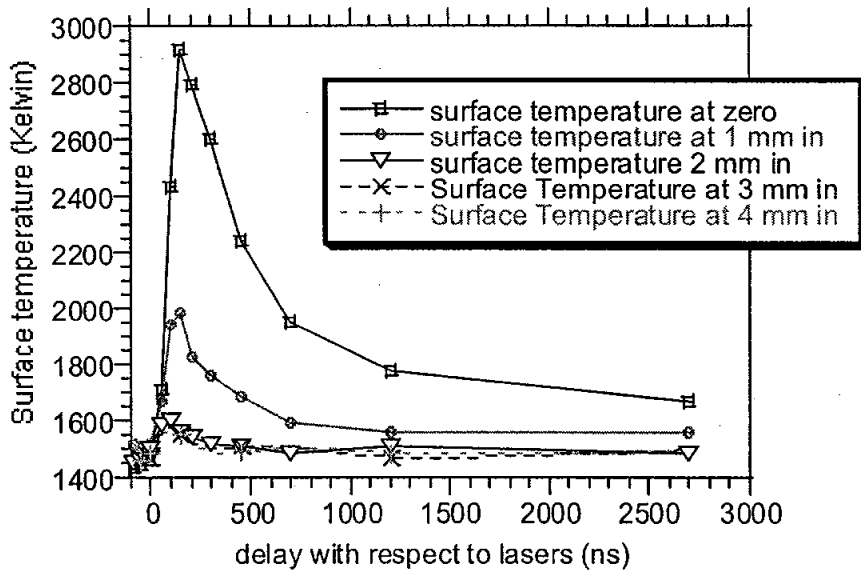


Figure 4: Surface temperature as a function of time for the standard laser combination. The different curves represent temporal profiles of temperature at different positions on the target surface.

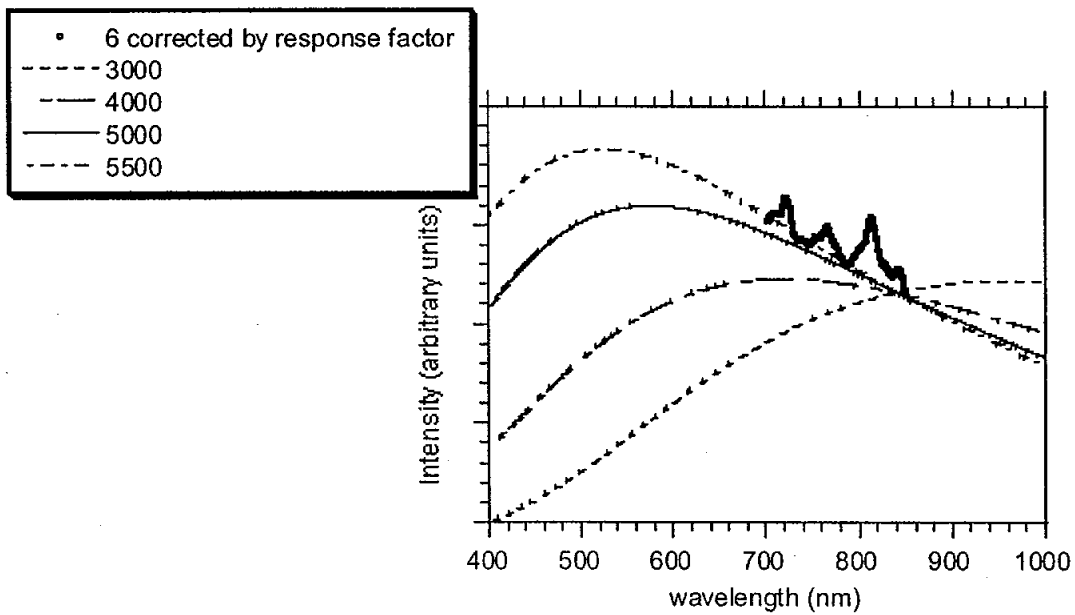


Figure 5: An illustration of the surface temperature obtained using a corrected spectrum fit to a calculated black body emission. The surface temperature obtained using this method, method two, appears to be between 5000 K and 5500 K rather than 3000 K as determined using the ratio method, method one.

Using the temporal temperature profile for the zero position, the spectrum collected at a time corresponding to the peak temperature was fit using the second method of analysis. An illustration of this method can be seen in Figure 5. Fitting to a background emission subjectively determined to fall in the valleys of what appears to be a C₂ emission spectrum, a black body curve fit of between 5000 and 5500 Kelvin seems reasonable.

Clearly, additional analysis needs to be done using both methods to determine there consistencies and inconsistencies in various parts of the temporal temperature profile. Such analysis will provide excellent opportunities for my undergraduate students to engage in this research. Results of this additional analysis will be reported to the nanotube team through student presentations and written reports.

Experiment 2. Absorption measurements.

Results of our absorption studies indicate a strong flat absorbance with a fairly linear bias toward shorter wavelengths. Although this absorption does not appear to be highly structured information on the absorbing material may be found by thorough analysis. However, even without a thorough analysis of the data a few preliminary results may be given.

It is clear that material begins to absorb within a few microseconds of ablation. The amount of absorption decreases after its initial peak to reach a fairly constant level after approximately one hundred microseconds. This level of absorption remains constant until the next laser pulse perturbs the system. All of our data was taken under sixty Hertz operation conditions. Figure 6 shows the relation of transmission with time of ablation.

There appears to be a great deal more absorbance in front of the target than behind the target. This may be because the ablated materials remain longer near their turning point. They are ablated from the target with the particles decreasing in velocity as they are slowed by the incoming buffer gas coming. The particles eventual stop and begin accelerating in the other direction to blow by the target. By time they have traveled past the target they will have gained a good deal of velocity, aggregated into clusters, or deposited out onto the walls of the quartz tubing. No absorption is observed at distances of 3 cm or more in front of the target surface and saw a much lesser amount of absorption behind the target.

A target without metal catalyst was also used under the same conditions as the standard production target. This 'blank' target also produced a fairly steady level of absorbance with a flat short wavelength biased spectrum. However, at early time delays, there is some difference in the spectrum obtained using the standard and the 'blank' target as can be seen in Figure 7.

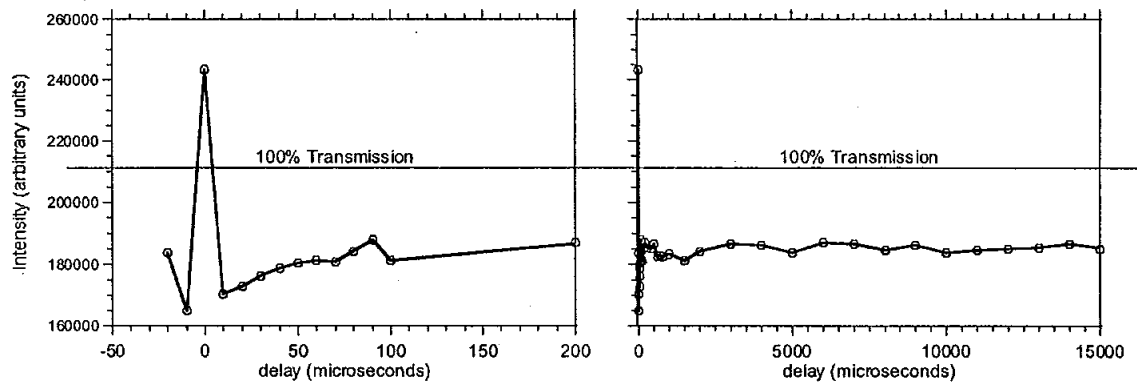


Figure 6: Temporal profile of transmission with respect to laser pulse. The profile shows a fairly constant transmission from some hundred microseconds after the laser pulse to 15 milliseconds after the laser pulse at a position 2 cm in front of the target. There are 16.7 milliseconds between laser pulses when operating at 60 Hertz.

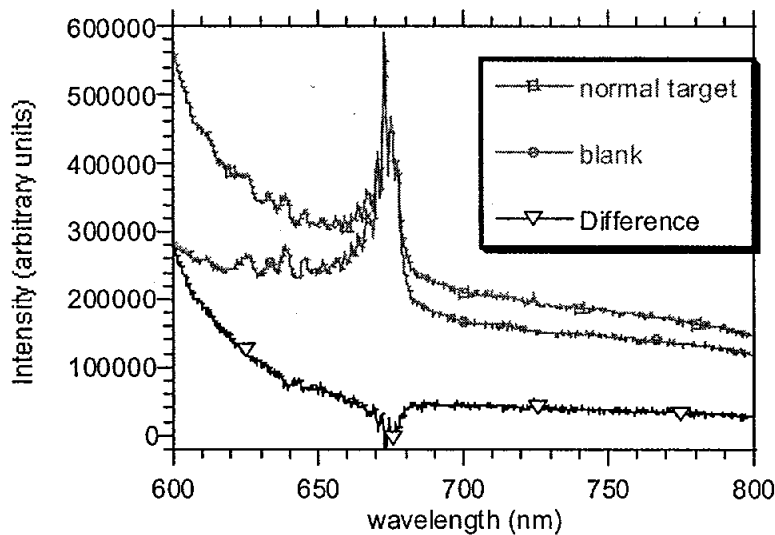


Figure7: Difference in emission during time immediately following ablation of target. The standard target exhibits additional emission at the shorter wavelengths.

The standard target appears to exhibit additional emissions at shorter wavelengths than does the 'blank' target. If the "blank" emission is assumed to be resulting from C_2 emissions, the emissions observed when using the standard target must be due to other species than C_2 . It may be that the ablations lasers are acting as probes. It is known that nanotubes absorb the shorter 532 nm wavelengths of the 'green' Nd:YAG laser, although

one may expect that emission associated with that absorption should occur on a much faster time scale. The use of a 532 nm Nd:YAG laser as a possible probe laser in future experiments should be considered.

CONCLUSIONS

This summer's work has focused on a determination of target surface temperature as a function of ablation parameters and on the development of a method to measure absorption of species ablated from the target in spatial and temporal dimensions.

Emission from the target surfaces was measured and an initial analysis of that data appears to show a surface temperature in the range of 3000-5500 K under standard production conditions. Temporal temperature profiles under many different parametric conditions were taken. The data needs further analysis and once confidence in the results is obtained, they may be incorporated into other theoretical models of ablation and plume dynamics.

Absorption measurements were taken during carbon nanotube production that indicates a great deal of material is present at all times within the standard 16 msec window (Lasers run at 60 Hz). This absorption does not have any clear absorption features, but may have some wavelength dependence that may be useful when further analyzed. Also, there are indications that suggest other methods for probing carbon nanotubes during production.

There are some common difficulties with both of these experiments which should also be considered when planning for future studies. One of these difficulties is the changing of the target surface due to the 'pitting' of the target as material from the center of the target is ablated away while material outside the area of the laser spot remains. Spectra taken in the beginning of a run and hours later after significant pitting has occurred can be very different. A method to avoid pitting needs to be developed before reproducibility of spectra can be obtained over longer periods of time.

A second difficulty involves the coating of optical components with carbonaceous deposits. Deposits on the lenses decrease the transmission of the light source. This is a problem similarly encountered when using the production tube for diagnostics, but to a lesser degree. The optics of the y-tube are much less affected by these deposits than are the optics of the x-tube, probably because they are upstream and farther from the target. A method for introducing the buffer gas through the side arms of the x-tube or the design of longer arms on the x-tube which can incorporate longer lens may also be beneficial. A smaller hole than the current half inch hole in the 1 inch tube at the joint with the sidearm may also help prevent material from depositing on the lenses and would also help maintain a flow within the larger one inch tube.

Although progress has been made in developing methods of probing nanotubes during production, there are still other factors that also have remained elusive to the scientist's probing. Metals are thought to play a role as atoms in a 'scooter' mechanism but also as larger nanoparticles or clusters in a 'root' mechanism. Knowledge of the presence of the metal atoms and the metal clusters would help determine the plausibility of the two mechanisms. Although work has been done to follow the metal atoms, none has been done to detect *in situ* the metal nanoparticles. It would also be interesting to follow the progress of fullerenes with and without the presence of the metal catalysts during the formation of carbon nanotubes.

Work in carbon nanotubes has made great progress in the last few years. It is exciting to see that ideas that were only exploratory a few years ago have matured into rigorous scientific and engineering projects. Those working in the field today have a much firmer grasp of the issues, properties, challenges, and promise than they did just a few years ago. As the field of carbon nanotubes gathers momentum, it will continue to deliver new materials and applications beyond current imagination. NASA is well situated to take full advantage of these material advances. It has been great adventure for this author to be a small part of this project.

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