

RAPID INSPECTION OF CARBON NANOTUBE QUALITY

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ABSTRACT

Carbon nanotubes have unique properties of interest for applications in aerospace, electronics, and biotechnology. However, the properties of different batches of carbon nanotubes can vary considerably depending on chemical purity and the nanotube types present (*e.g.*, diameter and chirality distribution). Distinguishing the constituents of each nanotube batch is challenging, with many different techniques used in concert. Thermogravimetric analysis (TGA) provides one measure of nanotube purity by assessing the material's thermal stability (*i.e.*, how it oxidizes with temperature). Unfortunately, however, TGA analysis requires a relatively large specimen for each measurement (several milligrams), making it inappropriate for rapid screening of incoming materials. Moreover, the measurement provides only an average purity for the analyzed sample, and variability can occur on a much finer level. As many applications will utilize only a small quantity of nanotubes, new approaches are needed to assess variability for a much smaller specimen size. This paper describes a new analysis method that uses a quartz crystal as a miniature microbalance for determining mass changes at elevated temperature. Thin nanotube coatings are spray deposited onto the crystals, and shifts in a crystal's resonance frequency are directly correlated with changes in coating mass during heating due to volatilization of different carbon species. By monitoring the response of the crystal at one or more temperatures, different nanotube specimens can be directly compared. This paper demonstrates concept feasibility by comparing quartz crystal results with conventional TGA analysis and discusses methods for applying the technique in process and quality control settings.

INTRODUCTION

Carbon nanotubes exhibit electrical, mechanical, and thermal properties that make them attractive for numerous applications, including multifunctional composites, biomedical devices, drug delivery, and next-generation electronics, among many others¹. However, their chemical and structural characteristics can have a strong influence on material behavior², making it important for product developers to be able to rapidly inspect new materials post-synthesis in

order to optimize product performance and ensure quality control. In addition, certain chemical impurities that result from the various material synthesis processes can affect dispersion stability, with even a small change in concentration leading to a significant effect on processability. Finally, purification to remove such impurities can introduce nano- and macro-scale defects which can alter the interface between the nanotubes and other materials (*e.g.*, a polymer matrix), again affecting the ability to uniformly apply the nanotubes in a given application. These issues are further complicated by the fact that most synthesis routes for carbon nanotube manufacture do not produce a homogeneous material, but instead generate a mixture of nanotube types (*i.e.*, different diameters, lengths, and chiral angles), along with potentially large quantities of carbonaceous and metallic impurities. As a result of this variability, nanotube characterization remains a key challenge for material manufacturers, application developers, and regulatory agencies investigating potential health and safety risks.

Thermogravimetric analysis (TGA) is commonly employed to help assess nanotube purity^{3,4,5}. This technique analyzes changes in the weight of a specimen in relation to changes in temperature under given atmospheric conditions. In the case of carbon nanotubes, an oxygen-containing atmosphere (*i.e.*, air) is typically used, allowing the different forms of carbon present to oxidize with increasing temperature. This oxidation results in a net weight loss over time. As weight loss curves only provide the onset temperature for oxidation, it is typical to examine the derivative of the weight loss versus temperature, with the maximum value corresponding to the average oxidation temperature. When this oxidation temperature is low, the material is generally considered to be less pure, allowing one to compare materials from batch to batch to obtain a relative measure of carbon purity⁶. The maximum temperature for the measurement is selected to be sufficiently high as to allow all of the carbonaceous material to oxidize, leaving behind only residual metal. This metal typically consists of catalytic particles from the synthesis reactions, as well as impurities introduced during purification or mixing.

TGA analysis does provide a qualitative measure of the carbonaceous species present, as well as the quantity of residual metal. However, it should be noted that conventional TGA instruments determine an average purity across a relatively large quantity of bulk nanotubes (*i.e.*, several milligrams). Because many applications will utilize these materials in much smaller quantities, a technique capable of quickly sampling and assessing homogeneity in a small specimen is needed. This paper describes just such a new measurement approach, based on a quartz crystal microbalance (QCM) platform. A QCM is a sensing device capable of measuring small mass changes in real-time by monitoring shifts in the resonance frequency of a thin quartz crystal (*i.e.*, the frequency of minimum impedance). When the crystal is oscillated, its resonance frequency will decrease proportionally as a mass is applied to the crystal surface. QCM sensitivity is extremely high, allowing one to measure changes as small as a few nanograms⁷. At present, QCMs are used to monitor film thickness, detect the presence of toxic gases, and measure the progression of molecular interactions such as moisture uptake in paints⁸.

In addition to these more conventional applications, advanced measurement systems based on QCM technology are under development. For example, a new QCM-based calorimeter has been reported which measures mass changes, heat flows, and viscoelastic damping in thin films⁹. The QCM is thermally coupled to a heat sink through a Peltier thermopile used as a heat flow sensor. The device is placed in an adiabatic thermal environment for stability, and the QCM is coated with a thin film of the desired test material. As the film undergoes exothermic reactions (*e.g.*, on exposure to humid air), heat flow is generated and detected as a voltage

change at the thermopile. At the same time, the change in mass associated with water adsorption is detected at the QCM. By combining data, complete reaction processes can be described.

Here, we utilize an alternative method for analyzing exothermic reactions in carbon nanotubes. A small quantity of bulk carbon nanotubes is placed directly in the center of a QCM, shifting the resonance frequency of the crystal in direct proportion to the applied coating mass. The crystal is then heated to one or more temperatures, resulting in a weight loss due to volatilization of the nanotubes. This weight loss is registered by a corresponding shift in the resonance frequency of the crystal, bringing it closer to the original value. By tracking frequency shifts with temperature, specific points on the TGA curve can be analyzed. The quantity of tubes sampled by this technique is considerably less than that needed for TGA measurement (*i.e.*, a few micrograms as compared to a few milligrams). As a result, this approach can bring to light variations within the material on a much finer scale than possible with conventional analytical instruments. In addition, because of its simplicity and the small quantity of material required for each analysis, this method is particularly well suited for rapid sampling and inspection of a new material in order to quantify its homogeneity.

To demonstrate the validity of this approach, results from elevated temperature QCM testing are compared with TGA measurements for a series of nanotube specimens. Three specific temperatures along the carbon volatilization curve were selected for QCM analysis, and the mass percentages after heating were compared to illustrate the degree of homogeneity in the material. Recommended standard practices for TGA characterization were followed¹⁰ to maximize repeatability of analytical results.

EXPERIMENTAL PROCEDURE

Several grams of single-walled carbon nanotubes were received from a commercial supplier, all of which were produced in a single manufacturing run¹¹. No purification processes were employed to remove amorphous carbon or metallic impurities, providing a real-world specimen with which to evaluate the sensitivity of the two techniques to non-nanotube constituents. Scanning electron microscopy (SEM) was used to characterize the material upon receipt, examining specifically the size and quantity of the metal particles present and the degree to which an amorphous carbon coating encased these particles.

A series of thermogravimetric analyses were performed on the material, including testing of over twenty five randomly sampled specimens (2-4 milligrams per measurement). To the maximum extent possible, different regions of the as-received bulk material were sampled to minimize any effects due to settling and differentiation of the different constituents over time. Weight loss profiles were obtained in an air atmosphere from near ambient temperature (30 °C) to a maximum temperature of 800 °C to ensure all of the carbon-containing constituents oxidized. The remaining weight percentage of the sample at 800 °C was recorded and referred to as the residual metal content (M_r). It should be noted that the final temperature was sufficiently high as to either partially or fully oxidize the residual metal catalyst remaining in the sample; therefore, this value is slightly higher than the actual metal content in the as-received material. A linear heating rate of 5 °C/minute was employed, as suggested by Arepalli, et al.⁶ The derivative of the TGA weight loss curve with temperature (dm/dT) was used to determine the oxidation temperature of each sample (*i.e.*, the maximum of the derivate, denoted T_o). In certain specimens, multiple peaks were observed in the derivative curve. These were individually determined and referred to as oxidation temperature 1, oxidation temperature 2, etc. (*e.g.*, T_{o1} ,

T_{o_2}). As previously mentioned, the oxidation temperature, as determined by TGA, is used by many researchers as a measure of the material's thermal stability, with higher oxidation temperatures typically associated with purer, less-defective carbon nanotubes¹². To assess the homogeneity of the overall bulk material, the standard deviations of both the oxidation temperature and the residual mass (σ_T and σ_M) were determined. Because the initial mass used for each TGA measurement varied slightly from sample to sample, a coefficient of variance (c_v) was calculated for each parameter, indicating the % of the mean represented by the standard deviation. The material was considered to be statistically invariable when c_v was less than 2 %.

For the elevated temperature QCM measurements, a stable dispersion was first prepared by mixing approximately 2 milligrams of the bulk carbon nanotubes with approximately fifty milliliters of trichloromethane (*i.e.*, chloroform). It should be that because of the “fluffy” nature of the carbon nanotube material, precise weighing at these quantities was not practical; as a result, the concentration reported is only approximate. The mixture was agitated ultrasonically for 45 minutes to break up the agglomerates, creating a relatively stable nanotube suspension in the chloroform. This suspension remained stable for several hours, allowing sufficient time to prepare coatings from the material. Coatings were deposited by spraying the dispersion onto masked QCMs with a small-volume spray gun.

The resonant frequency of each QCM was determined before and after the coating was applied using a standard laboratory impedance analyzer. The QCM devices used for this study were obtained commercially and possessed a resonance frequency of 10 MHz prior to coating. Upon applying the coating, the resonance frequency decreased proportionally with the applied mass, as estimated by the Sauerbrey equation⁷:

$$\Delta f = [-2 * f_0^2 * \Delta m] / [A * (\rho_q * \mu_q)^{1/2}] \quad (1)$$

where Δf = the shift in resonance frequency (*e.g.*, due to applied coating or on heating)

f_0 = the resonance frequency of the uncoated QCM

Δm = the change in mass resulting in the corresponding resonance frequency shift

A = the active area of the quartz resonator (*i.e.*, the electrode area)

ρ_q = the density of quartz, 2.648 g/cm³

μ_q = the shear modulus of quartz, 2.947 x 10¹¹ g/cm-s²

The coated crystals were then heated to temperatures of 375 °C, 400 °C, and 425 °C using a small muffle furnace, with a heating rate of 10 °C/minute, a dwell time at temperature of 10 minutes, and a programmed cooling rate of 10 °C/minute. Achieving this cooling rate with the muffle furnace was difficult as temperature decreased, and the actual cooling rate could not be easily determined. The temperatures examined were based on initial results from the TGA analyses, in which the first oxidation temperature was near 375 °C. The resonance frequency of each QCM was re-measured after the device had cooled to room temperature, and the resulting shifts in frequency were used to determine the changes in mass due to heating, as previously described. On heating, the coating mass decreased due to volatilization of a portion of the carbon-containing components, resulting in an increase in the resonance frequency of the QCM. Figure 1 shows typical coated QCM devices, illustrating the difference in mass change when crystals were heated to 375 °C, 400 °C, and 425 °C. Seventy two QCM crystals were characterized before and after coating and before and after heating (*i.e.*, 24 tests per temperature). The means, standard deviations, and coefficients of variance were calculated for

375 °C, 400 °C, and 425 °C, and the QCM means were compared with the average results (at each temperature) from the TGA data.



Figure 1. QCM devices coated with carbon nanotubes (*i.e.*, black coating covering the gold electrode in the center of each crystal). From left to right: the crystals have been heated to temperatures of 375 °C, 400 °C, and 425 °C, with significant mass loss occurring at 425 °C. In this latter case, the underlying gold electrode is clearly visible.

RESULTS

SEM analysis of the as-received carbon nanotube material indicated the presence of a significant quantity of impurity particles. These particles were determined by Energy Dispersive Spectroscopy (EDS) to be comprised of nickel and yttrium, likely residual catalyst materials from the synthesis process. Estimation of particle size using the image analysis capabilities of the SEM revealed that the particles had an average diameter of approximately 80 nanometers. Where carbon nanotubes were present, the materials were highly bundled, resulting in long “ropes” with no visible isolated nanotubes. Both the metallic particles and the nanotube bundles were encased in amorphous carbon, as shown in Figure 2. Because of the high surface area associated with the particulates and the extent to which the materials appear coated, it was anticipated that the amorphous carbon content of the material was relatively high. High contents of amorphous carbon significantly reduce the thermal stability of the overall material, resulting in oxidation at a much lower temperature. In addition, the presence of a large concentration of metallic particles (such as was evident for this material) can catalyze oxidation reactions, further reducing the material’s thermal stability.

These observations were confirmed through TGA analysis, which revealed a relatively low onset oxidation temperature (~325 °C), as well as two distinct oxidation peaks in the derivative curve, as shown in Figure 3. The two peaks in the derivative curve (368.87 °C and 406.04 °C) occurred at significantly lower temperatures than typically observed in purified specimens (*i.e.*, 500-600 °C¹²), confirming the relatively low content of single-walled carbon nanotubes in the bulk material. In addition, the weight percentage remaining post-analysis was over 40 %, indicating that the material contained a high metal content.

As previously discussed, twenty-five specimens, randomly sampled from the original bulk material, were analyzed by TGA, resulting in average properties of T_{o1} of 369.8 ± 2.4 °C,

T_{O_2} of 403.1 ± 7.2 °C, and M_r of 41.9 ± 1.2 %. Coefficients of variation were 1.39 %, 0.64 %, and 2.78 % respectively. These results indicate that the bulk material is relatively homogeneous, with only slight variability from specimen to specimen, as evidenced by the uniformity of the curves in Figure 4. The predominant source of this variability was the difference in residual metal content, which ranged from 40.52 % to 45.08 % over the course of the 25 experiments. These values represent oxidized metal, and the extent of oxidation can depend on particle size. As variations in particle diameter were observed via SEM, the recorded variability in metal content may be attributable in part to differences in oxidation.

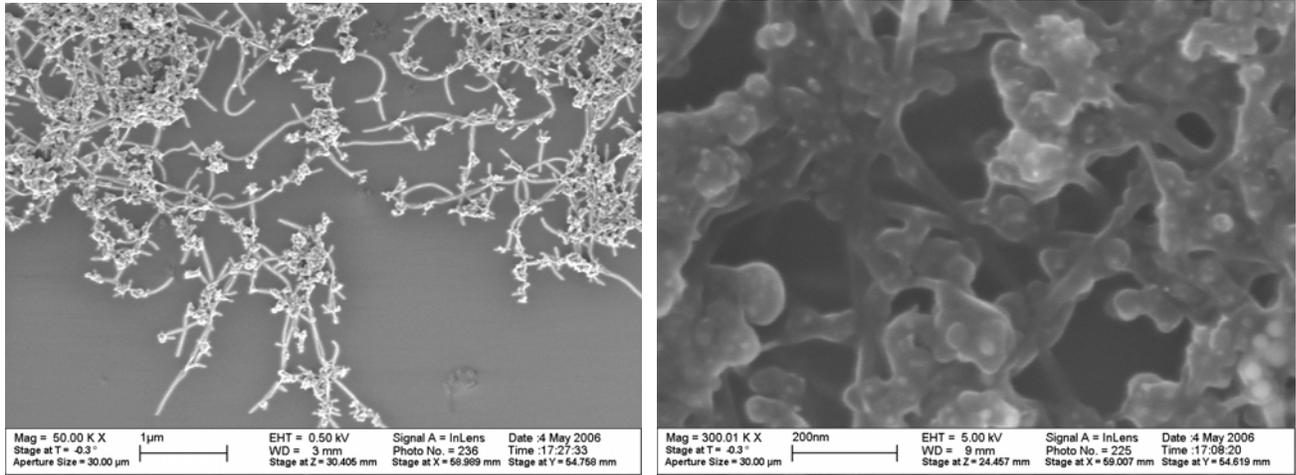


Figure 2. SEM micrographs of the as-received carbon nanotube material. The left image shows the presence of large nanotube bundles (possibly ropes), as well as a significant quantity of metallic particles. The right image shows that the particles and ropes are encased in amorphous carbon.

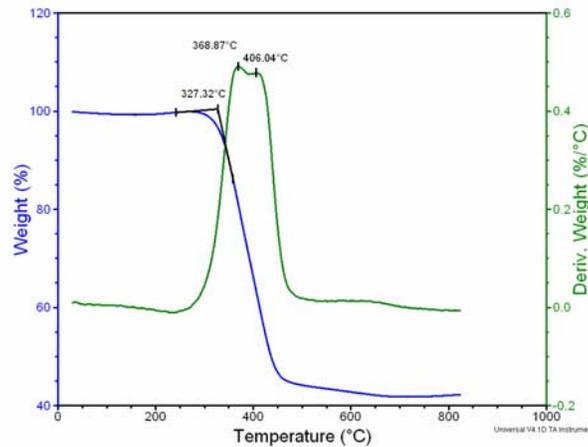


Figure 3. TGA data showing oxidation of the bulk carbon nanotube material with temperature. The deflection point in the weight loss curve (left; 327.32 °C) reflects the initial temperature at which the amorphous carbon begins to oxidize. Peaks in the derivative curve (right; 368.87 °C and 406.04 °C) represent oxidation of higher order carbons, likely carbon nanotubes.

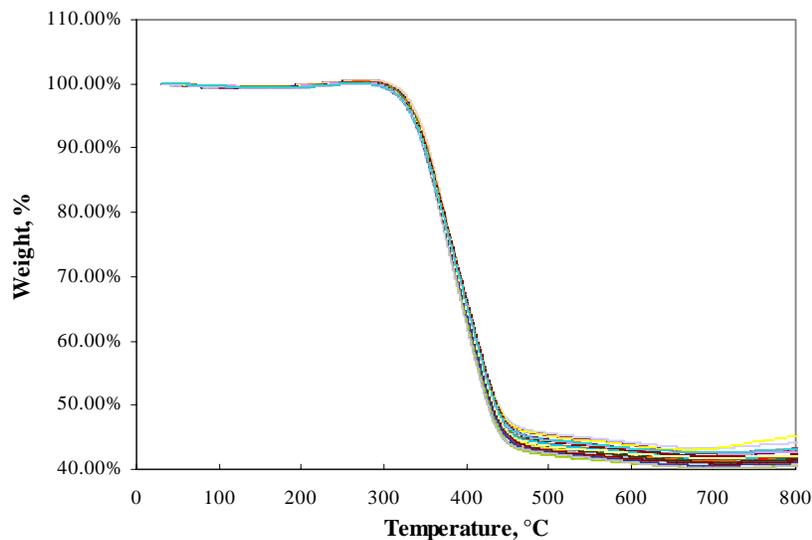


Figure 4. Comparison of 25 TGA measurements for the bulk carbon nanotube material.

As anticipated, mass changes in the carbon nanotube material were also observed on heating using the elevated temperature QCM technique. Characteristic changes in the resonance frequency of the quartz crystal were observed after application of the carbon nanotube coating and after heating of the material in air. The addition of mass due to the applied coating decreased the resonance frequency, while volatilization of material during heating increased the resonance frequency (*i.e.*, due to mass loss). Because only a fraction of the applied coating was affected by heating, a difference remained between the final resonance frequency and the initial resonance frequency (*i.e.*, for the uncoated QCM). This difference can be directly correlated to the mass remaining after heating to each specific temperature.

Figure 5 shows data for a typical crystal heated to 400 °C. The resonance frequency of the QCM was initially 9.9889 MHz. Application of the carbon nanotube coating decreased this frequency to 9.9756 MHz. From this data, the Sauerbrey equation indicates that the applied coating mass was 22.09 micrograms. Heating the crystal to 400 °C in air increased the resonance frequency to 9.9799 MHz. Here, a decrease in coating mass of 7.14 micrograms was calculated. These results indicate that 67.67 % of the initial carbon nanotube mass remained after heating this particular coating to 400 °C. This result is quite similar to the average value determined by TGA at this temperature (*i.e.*, 65.45 %).

However, despite the relative similarity of results for this particular coating to the results obtained by TGA, a comparison of elevated temperature QCM data for over 70 specimens of the bulk carbon nanotube material indicated a substantial degree of variability not observed in the TGA measurements. As shown in Table 1, while the average data for the two techniques are similar, the coefficients of variance differ substantially. For example, after heating to 375 °C the average mass remaining was 75.88 ± 16.26 % using the QCM method, with a coefficient of variance of 21.42 %. At the same temperature, TGA data indicated an average remaining mass of 77.90 ± 0.64 %, with a coefficient of variance of only 0.82 %. At all three temperatures analyzed, the average values were quite close between the two techniques; however, variability was several orders of magnitude greater for the QCM measurements. This difference can be observed visually in the histograms in Figures 6 and 7 for QCM and TGA data respectively.

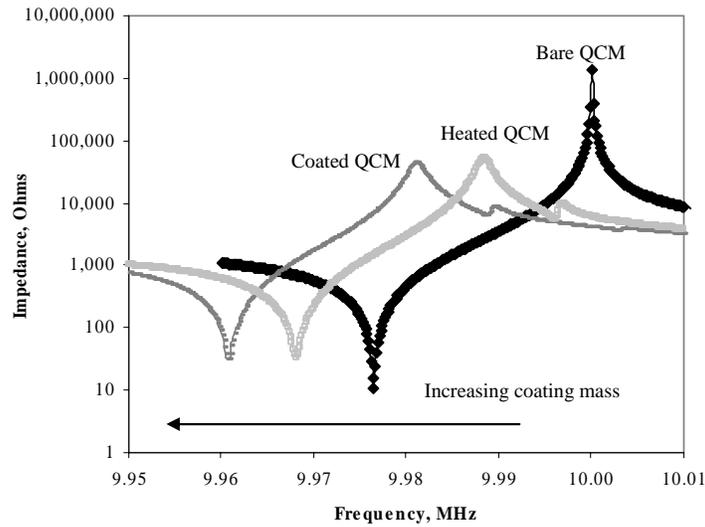


Figure 5. Impedance data for typical QCM coated and heated to 400 °C. The resonance frequency (f_0) is defined as the frequency of minimum impedance.

Table 1. Comparison of TGA and QCM results at the three examined temperatures.

	375 °C		400 °C		425 °C	
	TGA	QCM	TGA	QCM	TGA	QCM
Average	77.90 %	75.88 %	65.45 %	65.62 %	53.38 %	49.77 %
Std Dev.	0.64 %	16.26 %	0.96 %	14.02 %	1.12 %	14.55 %
Coeff. Var.	0.82 %	21.42 %	1.47 %	21.37 %	2.10 %	29.24 %

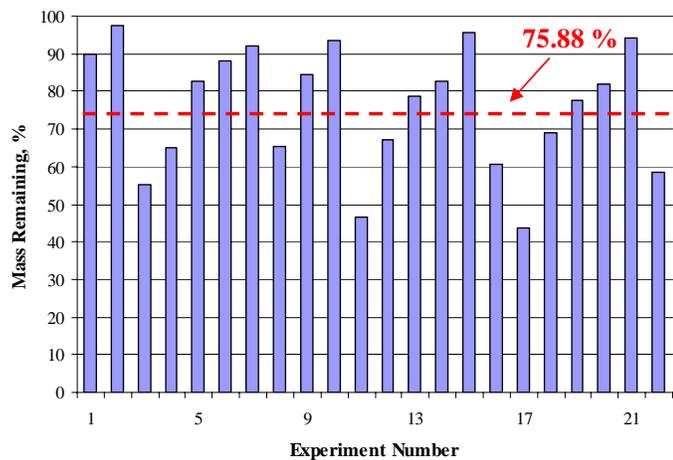


Figure 6. Histogram showing the degree of variability in thermal stability of 22 carbon nanotube coatings heated to 375 °C using the elevated temperature QCM method. The data for mass remaining ranged from 43.53 % to 97.37 %, with an average of 75.88 %.

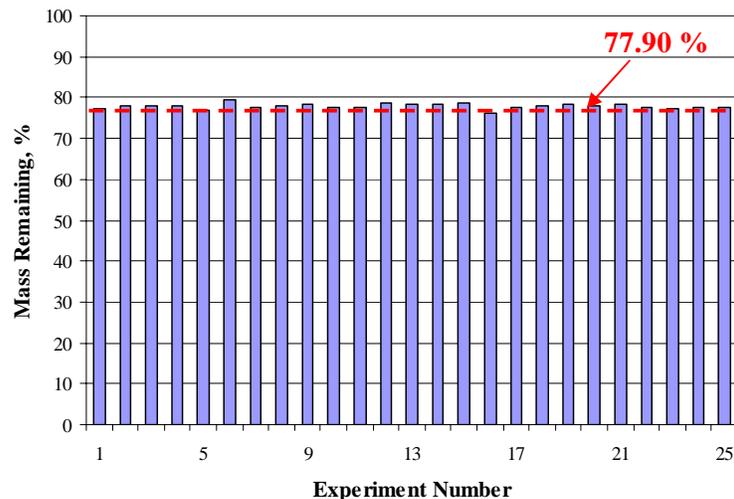


Figure 7. Histogram showing the degree of variability in thermal stability of 25 carbon nanotube specimens heated to 375 °C during TGA measurements. The data for mass remaining ranged from 76.25 % to 79.39 %, with an average of 77.90 %.

DISCUSSION

Several significant differences exist between the TGA and QCM approaches, the most notable of which is the amount of material investigated by the technique. Approximately 2-4 milligrams of bulk carbon nanotubes were analyzed per TGA run compared to 10-20 micrograms per QCM measurement. All QCM trials (~70) combined did not require as much material as one TGA measurement. As a result, the data obtained per TGA trial represents an average purity for a relatively large quantity of bulk carbon nanotubes. In contrast, each QCM trial represents the purity of only a small fraction of that same material. At the level probed with the QCM technique, variations in the size and quantity of residual metal particles, the extent of encapsulation of these particles with amorphous carbon, and the degree of macroscopic bundling of the carbon nanotubes into “ropes” can lead to substantial differences in thermal stability.

The aggregate effect of these differences can appear relatively minor, as evidenced by the apparent homogeneity observed in the repeated TGA analyses. However, when one considers how the material will be used in applications such as those in microelectronics, biotechnology, and gas detection, even small variations in material composition can have a profound effect on electrical and thermal behavior. For example, the role of metallic impurities becomes pronounced at these levels, due in part to the relatively large size of these particles (*i.e.*, average of 80 nanometers), their ability to catalyze (*i.e.*, accelerate) certain surface reactions, and their interference with electrical performance. Additionally, even subtle variations in metal content, bundling, or encapsulation can have a profound influence on the ease with which the material can be processed, either into dispersions, films, coatings, or composites. Even if sufficient properties can be achieved in the final product (*e.g.*, structural reinforcement of polymer composites), the inability to create a uniform distribution may lead to the use of higher load fractions of nanotubes, often at a significant cost penalty. These issues illuminate the need to not

only analyze the overall homogeneity of a given bulk specimen, but also to assess the distribution of its constituents at a level important for product manufacturability.

This paper describes one proposed approach for screening carbon nanotube materials. Statistical comparison of the average QCM data (against average data from TGA analyses) confirmed the validity of the method as an indicator of material quality (see Table 2). Although considerable variability was observed from coating to coating, the average thermal stability was statistically the same as that observed by TGA. SEM analysis (Figure 2) confirmed the variability determined by QCM. Metallic particles represented a large fraction of the bulk material and varied in both size and distribution. Amorphous carbon was evident throughout the sample, creating agglomerated, bundled ropes that likely contained a distribution of nanotube diameters and lengths. Finally, these ropes varied in both size and degree of isolation from the metal particles. These observations clearly support the data acquired through numerous QCM trials. Each coating likely possessed subtle differences in composition leading to not so subtle differences in thermal stability.

Table 2. One sample t-test comparing QCM data to a hypothetical mean (*i.e.*, TGA average).

	<u>375 °C</u>	<u>400 °C</u>	<u>425 °C</u>
Number of Trials	22	23	22
Mean	75.88	65.62	49.77
Standard Deviation	16.26	14.02	14.55
Standard Error of Mean	3.47	2.92	3.10
Coefficient of Variance (%)	21.42%	21.37%	29.24%
Variance	264.31	196.60	211.82
Hypothetical Mean (from TGA)	77.90	65.45	53.38
Calculated t	-0.58	0.06	-1.16
Critical t value (95% confidence)	2.08	2.07	2.08

However, additional investigation is warranted to develop best practices for using the QCM approach for carbon nanotube analysis. Although statistical analysis indicated no differences between the TGA and QCM measurements, minor differences did exist in the time and extent of thermal exposure of the carbon nanotube material. In the case of the TGA measurements, a heating rate of 5 °C/minute was used, with no holds at temperature. In the case of the QCM measurements, a heating rate of 10 °C/minute was used, with a 10 minute soak at the maximum temperature. Moreover, TGA data were acquired during heating, whereas QCM data were acquired after the crystal had cooled to ambient temperature. While such differences are not extensive, they may account for the slight variations in the average thermal stability recorded for each technique.

In addition to differences in thermal exposure, the study described herein relied on spray deposited films from non-optimized dispersions using chloroform as the solvent. While the nanotube suspensions appeared visibly stable, non-uniform deposition was observed for many films, as shown in Figure 8. In certain instances, droplets were noted, likely due to rapid solvent evaporation at the nozzle of the spray gun. In other cases, agglomerated metal particles were clearly visible, some in excess of 5 micrometers in diameter. At the temperatures used for this

study, oxidation of these particles is unlikely. As the particles contribute to the overall mass of the coating, their relative stability at these temperatures can bias the mass change data resulting in a decrease in mass loss at a specific temperature. Conversely, such particles can potentially dislodge from the coating during normal handling and testing of the QCM, resulting in an increase in mass loss not related to a thermal effect. While it is desirable for any characterization technique to be insensitive to dispersion conditions, SEM analysis of the applied coatings suggests that optimizing the dispersion for improved spraying will reduce the uncertainties associated with the measurement.

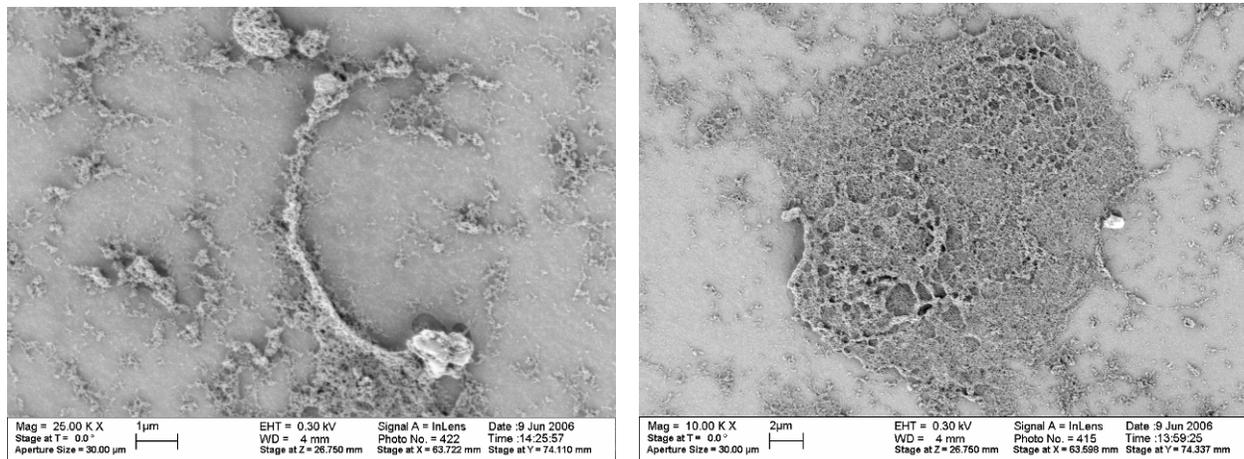


Figure 8. SEM micrographs of different regions of a carbon nanotube film. The image at left shows several large agglomerates resulting from incomplete dispersion. The image at right illustrates denser regions likely formed as droplets at the spray nozzle.

CONCLUSIONS

This paper describes a new measurement approach for determining the purity and homogeneity of small specimens of bulk carbon nanotubes. The method utilizes a quartz crystal microbalance for thermal analysis of a thin nanotube coating. Validation of this approach was achieved by comparing results with those obtained by conventional TGA analysis. All specimens were derived from a single batch of as-produced carbon nanotubes, without additional purification. TGA data indicated that the raw material contained large fractions of both amorphous carbon and residual metal catalyst. Despite the lack of purity (*i.e.*, with respect to single walled carbon nanotubes), repeated TGA measurements indicated that the material was relatively homogeneous, with only slight variability from specimen to specimen. The predominant source of this variability was the metal content. Comparison of average QCM data at 375 °C, 400 °C, and 425 °C with average TGA results at those temperatures indicated no statistical difference between the two techniques. However, QCM analysis of over 70 specimens illustrated a substantial degree of variability not observed by TGA. SEM analysis confirmed this variability. Metal particles varied in size and distribution; highly bundled nanotube ropes were present; and the entire specimen was encased in a thick amorphous carbon coating. These results illustrate that the elevated temperature QCM method can serve as an effective screening tool for assessing the quality of carbon nanotube materials, bringing to light variability at a level not previously possible with conventional analytical instrumentation.

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- ¹¹ Carbolex, Broomall, PA, see www.carbolex.com. *** Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.
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