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# Quartz Crystal Microbalances for Microscale Thermogravimetric Analysis

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**A new method for analyzing the chemical purity and consistency of microscale samples with a quartz crystal microbalance (QCM) sensor platform is described. The QCM is used to monitor submicrogram changes in the mass of a deposited thin film as a function of temperature, in a manner similar to that of a conventional thermogravimetric analyzer (TGA). Results correlated well with TGA measurements for a wide range of representative materials, including organic compounds, ionic detergents, oxidizing and inert powders, carbon nanotubes, and various mixtures of these samples. In each case, the sample mass was on the order of a few micrograms, compared to the need for several milligrams for conventional TGA analysis. This work illustrates the effectiveness of this approach for analysis of nanoparticles, thin films, and highly purified specimens on the microgram scale.**

Thermogravimetric analysis (TGA) is a widely used analytical method for determining changes in the mass of a material as a function of temperature. It provides a measure of the reaction kinetics associated with structural decomposition, oxidation, corrosion, moisture adsorption/desorption, and gas evolution. Recently, TGA has been employed to assess such reactions for a wide range of nontraditional materials, including sustainable forest products,[1] biofuel sources,[2] environmental contaminants,[3] pharmaceuticals,[4] nanocomposites,[5] and nanoparticles.[6] In many of these instances, analysis requires isolating multiple reactions during heating that result from material heterogeneity. Advances in TGA instrumentation have enabled better isolation of such reactions by dynamically controlling the heating rate during analysis.[2] However, the basic TGA method still provides only an average representation for a given sample (which is typically on the order of 1 mg or greater), making it difficult to measure small, laboratory-scale powder samples, thin films, and samples with minor modifications in surface or bulk chemistry.

Here, we describe a new method for detecting reaction kinetics in microgram samples at elevated temperatures by use of a quartz crystal microbalance (QCM) sensor platform. QCMs are highly sensitive acoustic devices capable of monitoring subpicogram mass changes in rigid coatings and thin films.[7−9] Devices are typically composed of a thin piezoelectric AT-cut quartz crystal[10−12] sandwiched between two metal excitation electrodes. When an AC voltage is applied to the electrodes, the quartz crystal oscillates at a characteristic frequency based on the crystal geometry, referred to as the resonant frequency. Any perturbation of the crystal surface (e.g., adsorbed mass) alters this characteristic frequency in a predictable way allowing one to readily determine mass changes at the near-molecular level.

Because of their sensitivity and stability, QCMs can be used to monitor film thickness during deposition,[13] to detect toxic and hazardous gas species,[14] and to assess moisture, humidity, and dew point levels.[15] These devices are also being explored for emerging applications in the areas of life sciences,[16] polymer processing,[17] and nanotechnology.[13] However, in each of these applications, the sensors are operated at or near ambient conditions. Here, we extend the application of QCMs to elevated temperatures in order to characterize decomposition kinetics in a manner similar to that of TGA. To demonstrate the method, representative materials have been analyzed with QCM and compared to analogous TGA measurements. Selected materials include those that exhibit characteristic loss of mass at high and low temperatures, mixtures of these materials, and complex mass loss materials, such as a heterogeneous sample of carbon nanotubes, which is composed of several forms of carbon coupled with residual metal catalyst particles.

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## EXPERIMENTAL SECTION

**Dispersion and Mixture Preparation.**[18] Carbon black, aluminum oxide, and Pluracol TP 440 surfactant (abbreviated here as Pluracol) were obtained from commercial sources. Purified carbon nanotubes were obtained from commercial sources following synthesis by a high-pressure carbon conversion process (HiPCO). Mixtures of carbon black and $Al_2O_3$ with Pluracol TP 440 were prepared by use of concentrated surfactant and stirring in the samples powders until no aggregates of material were visible. These mixtures were then diluted to a 1.0% volume solution in water for deposition onto the QCM surface. Mixtures of carbon black and aluminum oxide were made by combining the two powders and stirring until the combined material appeared homogeneous and uniformly gray. To disperse the carbon black or aluminum oxide powder, the mixture was added to ultrapure water and sonicated until visibly homogeneous. All other single-component dispersions were made by sonicating the materials with a dispersant until a homogeneous mixture was obtained.

**Thermogravimetric Analysis.** A commercial TGA instrument with infrared heating was used to perform all thermogravimetric analysis measurements. All TGA experiments were performed in 100 $\mu$L ceramic pans. The pans were equilibrated to 40 °C in the instrument, and then heated at a rate of 10 °C/min to a maximum temperature of 800 °C. After reaching the peak temperature, cooling to ambient temperature was rapidly accomplished due to the relatively small volume of the TGA furnace; mass loss data were not acquired during the cooling process. During each analysis, air was introduced to the samples at a rate of 25 mL/min, to maintain an oxidizing environment around the sample. For liquid materials such as Pluracol TP 440, thick films were prepared for analysis using the following procedure. Silicon wafers were cut to fit into the TGA pans, coated with the test material and allowed to dry to create a surfactant film (typically 20 mg to 30 mg). These films were analyzed in the same manner as the powder materials (10 °C/min to 800 °C, 25 mL/min air flow).

**Quartz Crystal Microbalance (QCM) Analysis.** Ten MHz AT-cut quartz crystals (1.37 cm diameter) with chromium/gold electrodes (0.51 cm in diameter) (International Crystal Manufacturing, Oklahoma City, OK) were mounted in spring-loaded fixtures to minimize edge clamping and then analyzed with a Hewlett-Packard (HP) 4194A impedance analyzer equipped with a HP 16047 test fixture. To apply a coating for testing, dispersions were drop cast (2 $\mu$L per drop) onto the crystal surface by use of a pipet. Each drop was allowed to dry for 20 min on a hot plate at 75 °C to remove added water. The resonant frequency of each QCM was determined before and after coating as well as after each heating step. Film thickness was determined using an Ambios Technology profilometer or atomic force microscopy. Carbon black material was deposited by spray coating prepared mixture in chloroform onto the crystal face with an air gun. The chloroform evaporated rapidly at ambient conditions following deposition. It should be noted that solvents for the deposited materials must be carefully chosen in order to ensure that the material can be evenly distributed within the droplet area upon drying. Deposition and drying conditions should be evaluated for each new material deposited on the crystal face to ensure film uniformity and validity of the Sauerbrey equation.

To heat the materials to the appropriate test temperatures, the QCMs were removed from their spring-loaded fixtures and placed on an aluminum oxide tray. A muffle furnace with an integrated temperature controller was employed for all heating experiments. Each microbalance was heated at a rate of 10 °C/min to the desired temperature, held isothermally for one minute, and then cooled at a rate of 10 °C/min. Once the materials reached ambient temperature, the resonant frequency of each QCM was remeasured with the impedance analyzer.

For all experiments, control QCM oscillators (i.e., without coatings applied) were heated alongside the test materials to compensate for stresses induced by thermal cycling. The average change in resonant frequency of the control crystals for each thermal profile was used as the correction factor.

**Calculation of Mass.** Frequency measurements were related to mass changes by use of the Sauerbrey equation,[19,20] as follows:

$$\Delta f = \left[ \frac{-2f_o^2}{A\sqrt{\rho_q \mu_q}} \right] \Delta m \tag{1}$$

where $A$ is the active area (here, $A = 0.2043$ cm$^2$), $\rho_q$ is the density of quartz ($\rho_q = 2.48$ g/cm$^3$), $\mu$ is the shear modulus of quartz ($\mu = 2.947 \times 10^{11}$ g/cm$^3$s$^2$), $f_o$ (MHz) is the resonant frequency of the QCM, and $\Delta f$ (Hz) is the frequency shift correlating to the change in mass $\Delta m$. The resonant frequency of each QCM was measured initially ($f_o$), after application of coating, and after each successive heating. Minor changes in the resonant frequency were observed for control QCMs due to stresses induced by successive heating. Stresses due to thermal heating have been well documented to have an effect on the frequency of quartz crystal microbalances.[21] In many cases, to account for temperature effects, dual QCM geometries have been used, in which one electrode functions as a reference.[22,23] To account for thermal stresses here, a correction factor was applied based on the average change in baseline frequency for a control QCM due to a particular heating profile (see Supporting Information (SI) 1 and 2). This approach is similar to other reference crystal methods discussed in the literature successfully used for correcting for thermal stresses.[23] This heating correction became significant at temperatures above 425 °C, where thermal stresses increase as the Curie temperature of quartz (573 °C) was approached (SI 2). In addition to correction for thermal stresses, adsorbed water was accounted for in those instances in which substantial loss of mass was observed at 100 °C. When this mass loss exceeded 5 wt %, the coating mass was corrected for the adsorbed water, and the weight percent loss for the QCM

(18) Certain commercial equipment, instruments, or materials are identified in this document. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products identified are necessarily the best available for the purpose.

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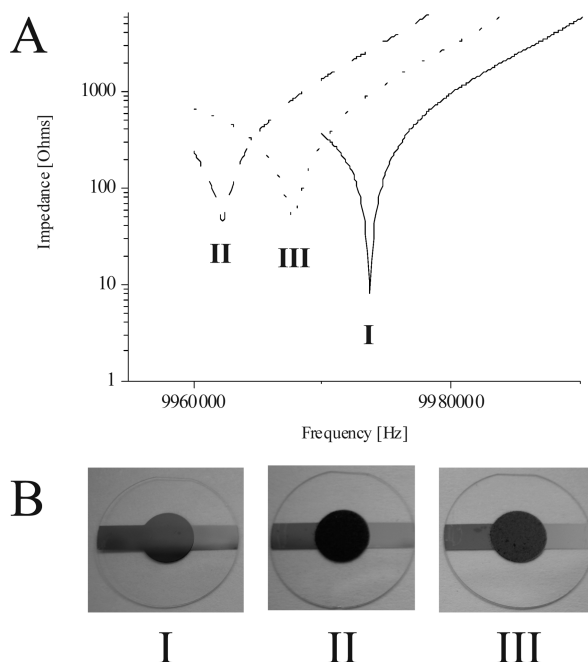
**Figure 1.** QCM method for determining mass loss as a function of temperature. (A) Examples of the shift in frequency seen in a crystal. The first frequency recorded is on a bare crystal (I), which was then coated (II). The shift to lower frequency can be correlated to the mass deposited on the surface. With a heating of the material (heated to 460 °C), mass is lost resulting in a shift toward the initial frequency (III). (B) Example crystals of a bare QCM (I), one that had been coated with carbon black material (II) and after heating (III) to 460 °C.

measurements was recalculated based on the water-corrected frequency shift. An example of a detailed calculation can be found in the SI.

## RESULTS AND DISCUSSION

Figure 1A illustrates the progression of measurements used to acquire TGA-like data by the QCM method. The frequency of minimum impedance was first determined and recorded as the initial resonant frequency of the bare crystal (I). A thin, rigid coating was then applied to the QCM surface, and the addition of this mass resulted in a shift to a lower resonant frequency (II). A broader peak is noticeable due to partial damping of the crystal oscillation (II). For the coating methods employed in these investigations, masses between 0.1 $\mu$g and 15 $\mu$g were deposited, with frequency shifts on the order of 200 Hz to 20 kHz. The QCM was then heated to a temperature near the oxidation temperature of the material as previously determined by TGA. After the initial heating (III), the resonant frequency increased, indicating a loss of mass due to oxidation and removal of the carbonaceous material. With each additional thermal excursion, the resonant frequency continued to shift back toward the initial frequency, as mass was gradually removed from the crystal surface. Figure 1B shows images of the QCMs with a decomposing sample as the crystal progressed through the heating process with a bare (uncoated) QCM shown on the left (I). A test material was then deposited on the active area (i.e., the center circular area, Figure 1B, II). After each heating step, the material was removed from the surface resulting in a lighter film (Figure 1B, III). After heating to the maximum temperature, the coating was no longer visible.

The Sauerbrey equation is used to describe the relationship between mass and the change in resonant frequency (eq 1) for uniform, rigid thin films on the quartz surface. In the case where a film acts as an ideal mass layer, and thus fits the Sauerbrey equation, the acoustic phase shift $\varphi$ across the film is less than $\pi/2$.[24] The phase shift is described by the equation:

$$\phi = \omega h \sqrt{\frac{\rho}{G}} \qquad (2)$$

where $\omega$ is the angular frequency, $h$ is the height of the film, $\rho$ is the film density, and $G$ is the shear modulus. For the films in this paper, the phase shift was calculated using eq 2, and for aluminum oxide films we take $\rho = 3.97 \times 10^3$ kg m$^{-3}$,[8] and $G = 124$ GPa, to calculate $\varphi = 3.4 \times 10^{-4}$. For single-walled carbon nanotube films we take $\rho = 9000$ kg m$^{-3}$,[25] and $G = 8$ GPa,[25] to calculate $\varphi = 6.7 \times 10^{-2}$. Based on these approximations for the phase shift through the film is much less than $\pi/2$ and according to Ballantine et al., the Sauerbrey equation is a valid approximation of the mass deposited on the surface when in the nanometer thickness regime. In the case where more viscoelastic or thicker films (over 1 $\mu$m) would be deposited on the QCM, a more rigorous determination of the mass on the surface would be needed.

A change in admittance is to be expected in all systems in which a sample is interacting with a resonator and can have an impact on mass determination for the system.[26] For the materials used here, this change can be seen as spreading and increase in the impedance in Figure 1A. Estimation of mass change is calculated from the difference in the resonate frequency ($f$–$f_o$). Here, we use the assumptions made in the Sauerbrey equation which does not account for damping; however, changes in resonate frequency due to small changes in damping will change the resonate frequency by a small amount as well.[26] The films have been found to be thin and rigid, it is anticipated that the impact of this damping is to be consistent throughout the heating cycles and play little role in the mass determination.

Good agreement in curve shape was generally observed when the TGA and QCM methods were compared for single-component materials. For example, Pluracol TP 440 was chosen as a representative material with a well-known thermal profile that decomposes at a relatively low temperature (300 °C).[27] Figure 2A shows a TGA plot of weight percent remaining versus temperature. The Pluracol began decomposing at 145 °C, and mass loss continued until there was less than 1% remaining at 350 °C. QCMs were coated with Pluracol films and then heated to temperatures around the temperature of maximum weight loss, which is termed the oxidation temperature, or $T_o$, of the material. For Pluracol, this temperature is 282.4 °C. QCM evaluation temperatures were specified to be at 25 °C intervals from 200 to 300 °C with a final evaluation at 600 °C to ensure the removal

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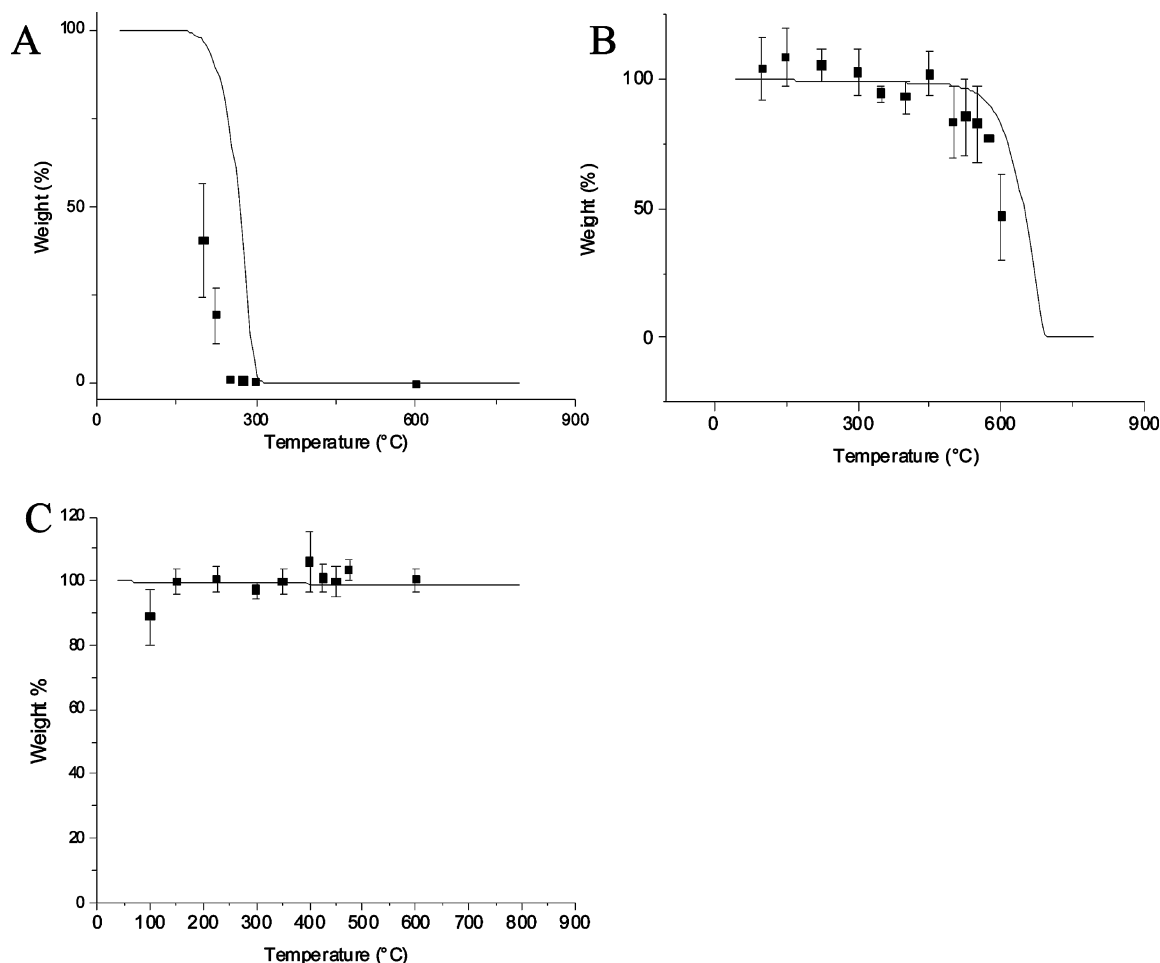
**Figure 2.** TGA and QCM plots for materials with simple thermal profiles. Weight vs temperature curve for TGA (line) and QCM (points) for (A) Pluracol, (B) carbon black, and (C) aluminum oxide.

of all carbon-based constituents. The QCM data were plotted as weight percent remaining versus temperature (°C) along with the TGA curve in Figure 2A. At 300 °C, decomposition was virtually complete (1.63% weight percent remaining by TGA, −0.06% weight percent remaining by QCM), and there was little change in mass (−0.35% by TGA, −0.56% by QCM) between 300 and 600 °C.

The QCM data followed the shape of the TGA curve closely, but reflected mass loss at slightly lower temperatures. These variations in reaction temperatures were anticipated due to differences in the thermal environment and heating profile between the two techniques. In the case of the TGA instrument, flowing gas was employed during analysis, allowing for immediate removal of reaction byproducts. Moreover, the TGA furnace had a small volume, allowing rapid equilibration of the sample at each specific temperature and rapid cooling following data acquisition. In comparison, the muffle furnace used to heat the QCMs consisted of a relatively large volume of stagnant air, which led to differences in byproduct removal. The control thermocouple is located at the midpoint of the furnace volume and accurately reports temperature of the furnace. The furnace size and placement of the crystals within this volume, however, impacts the actual temperature of the QCM surface. We estimate this could be as much as 25 °C. It was observed that the crystals can be heated to 600 °C with a dwell time of 20 min before the alpha to beta phase transition occurred; this transition should occur at the

Curie point of 573 °C in quartz. However, despite differences in temperature, the time for decomposition reactions to proceed was greater for the QCM method due to exposure of the films to multiple thermal cycles and a considerably longer cooling period. Taken together, these differences resulted in observed shifts toward a lower temperature of reaction for all QCM measurements reported herein.

To further illustrate the validity of the QCM method, a second material with a different mass loss profile was analyzed. Carbon black is a graphitic carbon that oxidizes at a higher temperature than that of unstructured amorphous carbons.[28] A carbon black sample was heated at a rate of 10 °C/min to 800 °C in the TGA to yield a single weight loss event (Figure 2B), beginning at approximately 450 °C and ending around 700 °C. Quartz crystal microbalance oscillators were coated with carbon black by spraying chloroform dispersions into the center of the active area of the quartz crystal to create a uniform coating. Each QCM was then heated to 525 °C, 550 °C, 575 °C, and 600 °C and cooled to room temperature in between each temperature. The oxidation temperature for carbon black was found to be 662 °C by TGA, but the QCM samples were not heated over 600 °C, because the Curie point of AT-cut quartz is 573 °C,[21] at which a phase change

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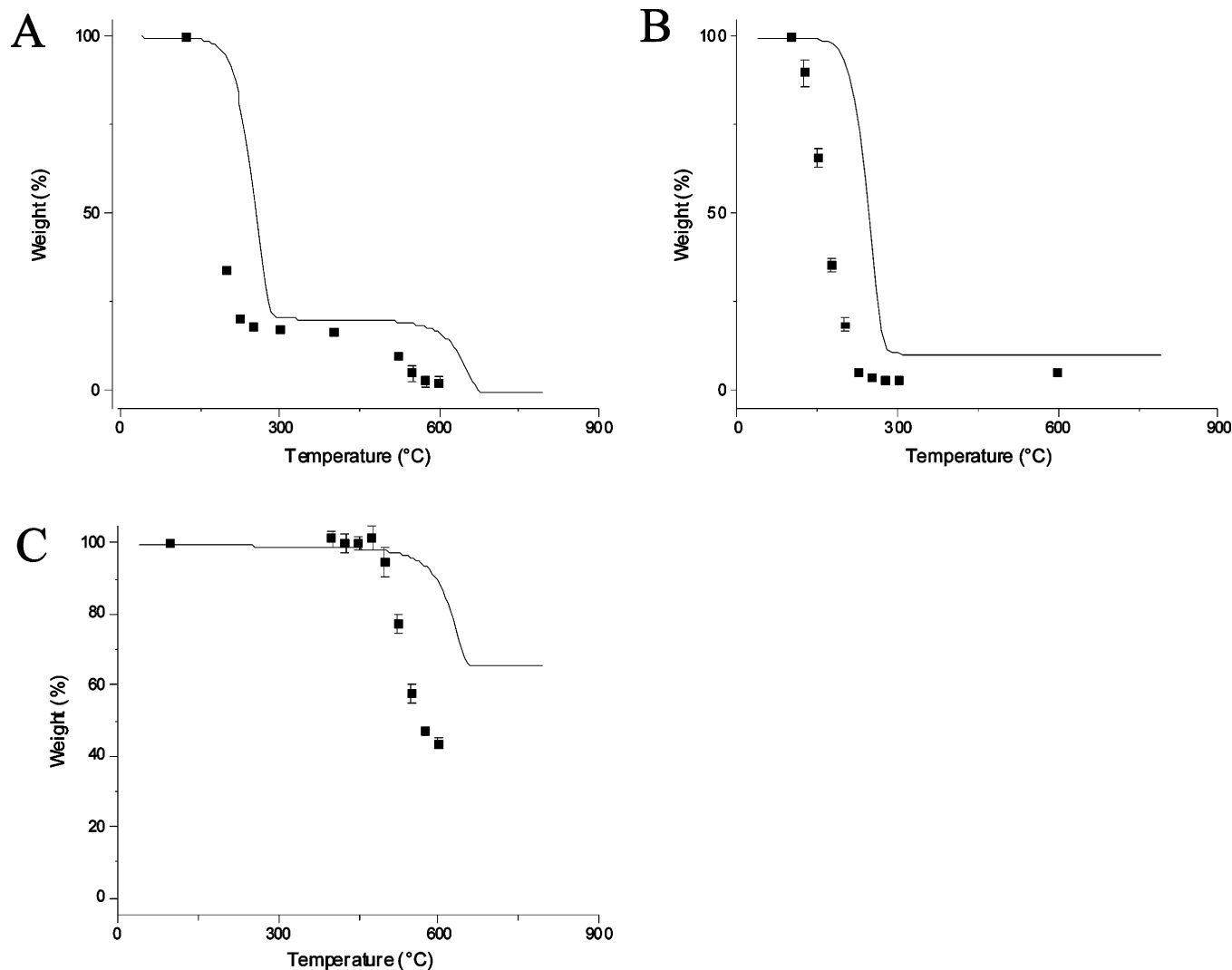
**Figure 3.** Mixtures of materials with simple thermal profiles. Weight vs temperature curve for TGA (line) and QCM (points) for (A) carbon black and Pluracol, (B) Pluracol and aluminum oxide, and (C) carbon black and aluminum oxide. Error bars are present on all data points for QCM measurements, although they may not be visible on the plot.

occurs in the quartz that alters its piezoelectric properties. As seen with the Pluracol sample, the QCM data showed a change in mass at lower temperatures as compared to the TGA (Figure 2B), with an average deviation of approximately 9%. These results are commensurate with the variations observed in the Pluracol experiments.

Aluminum oxide was chosen as an example material that is inert over the temperature range analyzed. Figure 2C compares the QCM and TGA data. Both the TGA and the QCM data fall closely along 100% (average deviation of ±1.3 wt %, with the largest deviation of ±3.6 wt %) over the entire temperature range, indicating that this material is unaffected by the thermal environment.

In addition to single-component materials, Figure 3 illustrates the utility of the QCM method for analyzing materials of greater complexity. Figure 3A is a mixture of carbon black and Pluracol, for which the oxidation of the two individual materials occurs at substantially different temperatures. Per TGA, the mixture is reduced to 18.6% weight at 350 °C due to the decomposition of Pluracol, and then loses an additional 15.1% of the original sample mass at 600 °C as the carbon black oxidizes. The temperatures for the QCM analyses were chosen to (1) reflect the initial weight

loss event, in which the Pluracol is removed, (2) provide a baseline value between 350 and 500 °C, during which no mass change is anticipated, and then (3) reflect mass loss due to the decomposition of carbon black. As seen in Figure 3A, both oxidation reactions are clearly reflected in the QCM data for the mixture, with the onset temperatures of reaction closely approximating those obtained for each single component material.

Figure 3B demonstrates a mixture of an inert material, aluminum oxide, with one that decomposes at a low temperature, Pluracol. It should be noted that for these experiments the average oxidation temperature of Pluracol by TGA was observed to be (253.1 ± 1.9) °C, which is less than that observed for the single component material (Figure 2A, 282.4 °C). One explanation for this difference can be attributed to incorporation of water during the mixing process. The residual mass observed in the TGA and QCM data after heating to the maximum temperature corresponds to the mass fraction of aluminum oxide present in the mixture. The original mixture was prepared to obtain a mass percent of 14.8% aluminum oxide when mixed. Thermogravimetric measurements reflect a weight percentage of 10.4% aluminum oxide, and QCM shows a weight percentage of 4.9% aluminum oxide. Settling
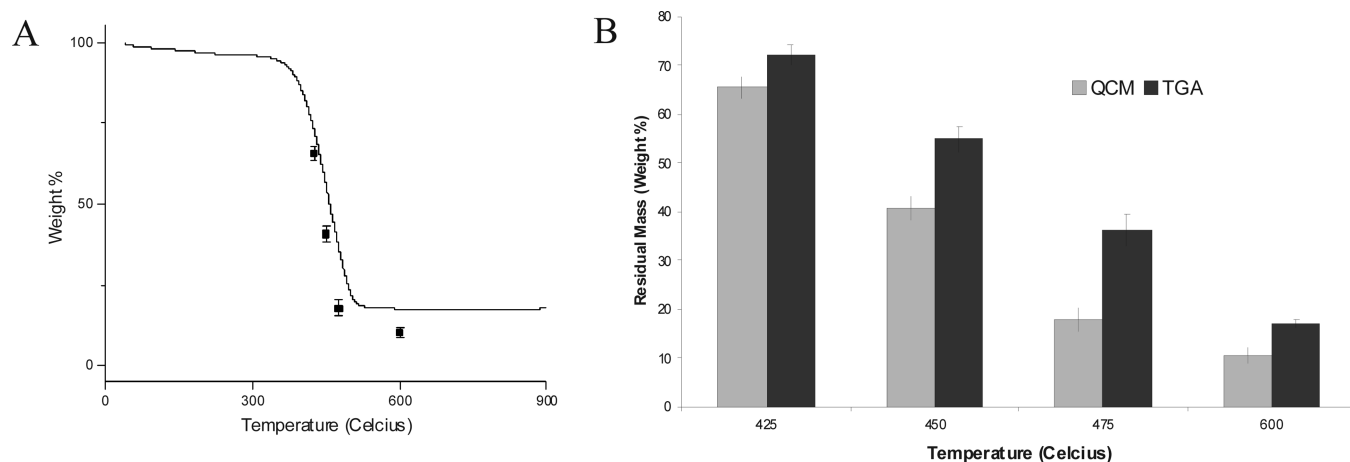
**Figure 4.** TGA and QCM plots of carbon nanotubes. (A) Thermal profile for a carbon nanotube material with TGA (line) and QCM (points) plotted together. (B) Residual mass for carbon nanotube samples as determined by TGA and QCM. Each bar represents 24 sample runs, with error bars representing one standard deviation.

of the aluminum oxide within the dilute Pluracol solutions was observed, and TGA measurements reflect an averaging of this effect with increasing sample volume. Similar results were obtained for mixtures of carbon black and Pluracol (not shown). Aluminum oxide was also mixed with a 0.25% solution of sodium deoxycholate (DOC) to demonstrate a surfactant with a more complicated decomposition. Figure 3C illustrates a mixture of two powders, carbon black, and aluminum oxide. Here, the temperature limit of the QCM method prevents complete decomposition of the carbon black, and the residual mass must be corrected for incomplete removal of the carbon black in order to obtain the fraction of aluminum oxide present. For both mixtures (Figure 3A−C) and individual materials (Figure 2A−C), differences were observed in the actual temperature of reaction between TGA and QCM. As previously stated, heating conditions varied between the methods due to chamber volume, gas flow, actual sample temperature, and heating and cooling rates. Our results demonstrate the validity and utility of the new QCM-based test method. Future research will attempt to more precisely control the thermal profile in order to more closely match that of the TGA instrument.

One proposed application of the QCM method is to determine the chemistry of engineered nanoparticles such as carbon nanotubes. TGA has been shown to be an effective method for verifying the quality of these materials (e.g., carbon vs metal content). However, it requires relatively large samples on the order of 5−10 mg for each analysis, and three or more repeated measurements are recommended to confirm consistency.[29] In contrast, the QCM method requires much smaller samples (1−10 $\mu$g) that are easier to obtain from laboratory-scale, batch processes or expensive purification procedures, such as those used to remove metal catalysts from carbon nanotubes after production. With the QCM approach, both chemistry and homogeneity can be analyzed with as little as 3 $\mu$g of material, leading to a 1000-fold reduction in sample volume and thus cost. The QCM method could further be applied as an inexpensive technique for determining the effects of process modifications on chemical purity and for screening material quality batch-to-batch. To illustrate the use of QCM for

analyzing nanoparticles, Figure 4A compares TGA and QCM results for a HiPCO-produced carbon nanotube sample. This sample is clean burning, with an average oxidation temperature of 455 °C. The QCM measurements again closely match the TGA results, with a small shift in temperature of reaction, as previously discussed. Reproducibility is an important factor in applying this technique for materials analysis. Figure 4B provides the residual mass for 24 samples was determined by TGA and QCM at 425 °C, 450 °C, 475 °C, and 600 °C, illustrating that the QCM technique exhibits reproducibility similar to that of the TGA method. Sampling of other carbon nanotube materials shows this method can be used to evaluate consistency within a material and evaluate purity material-to-material.

## CONCLUSION

The QCM method has been shown to be an effective approach for analyzing the chemistry and homogeneity of material samples ranging from single component organic compounds to complex engineered nanoparticles. The primary advantage of this method is its ability to analyze small samples, including thin films, providing a 3-fold increase in resolution, compared with state-of-the-art analysis by TGA. This is particularly significant for nanoparticles, such as carbon nanotubes, for which purification yields are quite low, often resulting in only a few micrograms available for analysis.

Correlation of results with TGA was observed for all materials tested. General use of the QCM technique for process and quality control applications should not require additional modification or a more elaborate heating configuration, as one or more independent temperatures can be used to track changes resulting from process variables or purification procedures.

## SUPPORTING INFORMATION AVAILABLE

Additional information including one figure and four tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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