Thermal Analysis of Nanoparticles: Methods, Kinetics, and Recent Advances

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ABSTRACT

This chapter provides an overview of the thermal techniques available to study nanoparticles, with particular attention to thermogravimetric analysis, calorimetry and differential scanning calorimetry. The advantages of thermal analysis for nanoparticle characterization include minimal sample preparation and rapid analysis of a number of properties. Relevant measurements include: purity and composition, phase changes, coating/functionalization composition and properties, and kinetics of reactive processes. Because of their low cost and high speed, thermal analysis tests are suitable for quality control, environmental monitoring, and research, particularly for verification of the nanoparticle's morphology and composition. New thermal analysis techniques are being developed that require much less sample. As these techniques become robust, they will broaden the scope and applications for thermal analysis of nanoparticles.

KEYWORDS: nanoparticles, thermal analysis, characterization

INTRODUCTION

Nanoparticles continue to remain an important and diverse class of materials with applications in all major areas of the economy, including manufacturing, medicine and energy, with new products finding their

way to market. The Project on Emerging Nanotechnologies reported over 1600 nano-containing consumer products on the market as of October 2013, as compared to 54 products in 2005 when the first edition of this book was published('Project on Emerging Nanotechnologies' 2013). Many of today's nanoparticle containing product databases are now retired or obsolete, although the Dutch Nanodatabase (www.nanodb.dk) seems to be the most up-to-date reporting over 5,000 nanomaterial-containing products available in Europe (Hansen, Hansen, and Nielsen 2020). The main classes of nanoparticles utilized in products include carbon-based (nanotubes and fullerenes), metallic (including gold, silver, iron and copper), metal oxide (iron oxide, ZnO, TiO_2, CeO_2, SiO_2 among others), and quantum dots.(Hornyak et al. 2009) A quick review of the literature shows there are endless possibilities of nanoparticle coatings that can be applied to the surfaces of these particles in order to improve solubility, improve biocompatibility, target interactions with other molecules, or prevent interactions with the nanoparticle's environment(Richman and Hutchison 2009). In fact, most nanoparticles used in commercial products have employed surface modifications such as an oxide layer or organic functional groups. More complex nanoparticles, specifically those targeted for drug delivery, continue to grow more advanced in their composition and ability to perform a given task (Mitchell et al. 2021). Analytical characterization of the materials, including the core, coatings and any other factors that may impact nanoparticle use, are essential to understanding their potential in a commercial product, evaluating the effects of their release into the environment, or developing them for biological or medical applications.

Nanoparticle characterization is not a trivial task and becomes more difficult as we advance our technology further.(Richman and Hutchison 2009) The methods available for bulk-scale analysis of materials are not necessarily applicable to nanoparticles. Because of these and sample preparation challenges, complementary analytical techniques are often used to confirm the values of specific measurements(Decker et al. 2009). Some of the most common methods for analysis include microscopy (scanning electron microscopy, transmission electron microscopy, fluorescence), spectroscopy (Raman,

UV/visible, FTIR, fluorescence), elemental characterization (neutron activation analysis, inductively coupled plasmon techniques) and particle sizing methods (dynamic light scattering, field flow fractionation). (Hornyak et al. 2009)

Technique	Properties
Scanning electron microscopy	Particle sizes, morphology, degree of agglomeration/aggregation/networking.
Transmission electron microscopy	Particle internal structure, especially crystallinity
Raman spectroscopy	Sizes for very small particles, order/disorder
UV/Visible spectroscopy	Electronic structure
Fourier transform infrared spectroscopy	Surface chemistry, especially chemical groups
Magnetic coercivity	Magnetic properties, presence of magnetic domains
Light scattering	Particle sizes/shapes, esp/ for larger particles (> 100 nm)

In general, microscopy methods provide a means for visualizing the sample's size, shape and morphology. Spectroscopy and elemental characterization are often used to identify the nanoparticles' elemental and structural characteristics, and particle sizing methods yield information about size and shape. Many standard protocols have been adapted, when necessary, to address the unique challenges of small particle size and limited sample volumes that come with nanoparticle analysis. The above table is not a complete

list of techniques or their measurable results but is an introduction to the analytical data most commonly reported.

Thermal analysis methods, which measure the properties of the sample as a result of change in temperature or heat flow, are often used to provide quick information on nanoparticles in the manufacturing or laboratory setting. A thermal investigation can provide information about particle and coating composition, crystallinity, and formation kinetics. Thermogravimetric analysis, calorimetry and differential scanning calorimetry are the most common thermal analysis methods utilized for nanoparticle work and are discussed here in more detail. The application of these methods can be direct in some cases using the same procedures developed for bulk-scale materials. However, with small quantities of material, it may be necessary to concentrate and dry a sample to ensure the minimum sample volume for the analytical technique is met (typically ~ 10 mg). Future applications of thermal analysis methods for nanoparticle samples are discussed at the end of the chapter.

THERMAL ANALYSIS METHODS

Thermogravimetric analysis (TGA). Thermogravimetric analysis (TGA) describes the process in which the sample mass is monitored as it is heated at a controlled rate in a controlled atmosphere. The sample is introduced onto a balance within a furnace and heated using a specific temperature program. The atmosphere can be reactive (*e.g.*, oxygen, air), inert (*e.g.*, argon, nitrogen) or vacuum. The major data outputs are thermograms, either the % weight loss with time or temperature. First and second derivatives of the % weight loss vs temperature thermogram are heavily utilized for data analysis.

As a result of the heating, the sample mass will either increase or decrease as a result of changes in the material. Some of the most commonly observed transitions include desorption of an adsorbed species such as water, oxidation of metal species, decomposition via pyrolysis, and even combustion in the case

of carbonaceous materials. Further information can be obtained by coupling the TGA to an evolved-gas analysis technique, such as Fourier-transform infrared spectroscopy (FTIR), mass spectrometry (MS), or gas chromatography mass spectrometry (GC-MS). A key TGA measurement is the residual mass (Mres) of the sample at a given temperature, usually given as a percentage of the original sample mass:

$$Mres\ (\%) = \frac{M_{\mathrm{r,T}}}{M_s}\ 100\%$$

where Mres (%) is the residual mass expressed as a percentage, $M_{r,T}$ is the mass remaining at a specific temperature (T), and M_s is the initial mass of the sample. At the end of an oxidizing sample run, the residual mass is often referred to as the ash content. Other important TGA metrics are the temperatures in which events occur. Temperatures of importance can be determined by differentiating the thermogram with respect to temperature or time and identifying the peaks. This can show features that may not be easily discerned or quantified in the thermogram (*e.g.*, shoulders). The onset temperature at which major transitions occur may also be quantified. Step-by-step methods for using TGA to quantitate the amount of surface coating on a nanoparticle have been published.(Dongargaonkar and Clogston 2018)

Differential scanning calorimetry (DSC)

Calorimetry is the measurement of the evolution or absorption of heat during chemical reactions, phase transitions, and other physical changes. Thermodynamic properties such as changes in enthalpy or entropy can be obtained. In the case where a chemical reaction occurs kinetic data such as reaction rate and activation energy can be determined. Many types of calorimetry can be applied to nanoparticle samples, but Differential Scanning Calorimetry (DSC) is perhaps the most widely used. In DSC, the difference in heat flow between two cells, one containing the sample and the other, a reference material, is determined. The sample and reference cells are heated independently such that the temperature difference is monitored and maintained at zero; that is $\Delta T = T_S - T_R = 0$. As a material undergoes a phase

transition, the amount of heat needed to maintain a constant sample temperature will vary,, depending on whether the transition is endothermic or exothermic. The difference in energy needed to match the sample temperature to the reference is the amount of excess heat released or absorbed as a result of sample transitions. In the most basic form, the information from DSC can be described by

$$\frac{dH}{dt} = mC_p \frac{dT}{dt}$$

where dH/dt is the DSC heat flow signal, m is the sample mass, C_p is the sample heat capacity, and dT/dt is the heating rate.(O'Neill 1966) Physical changes in the material, such as melting, crystallization, and glass transitions, can all be observed using DSC. As differential thermal analysis (DTA) and TGA both involves direct temperature measurement, they can be combined in the same instrument and their data can thus be recorded simultaneously (see Figure 1).

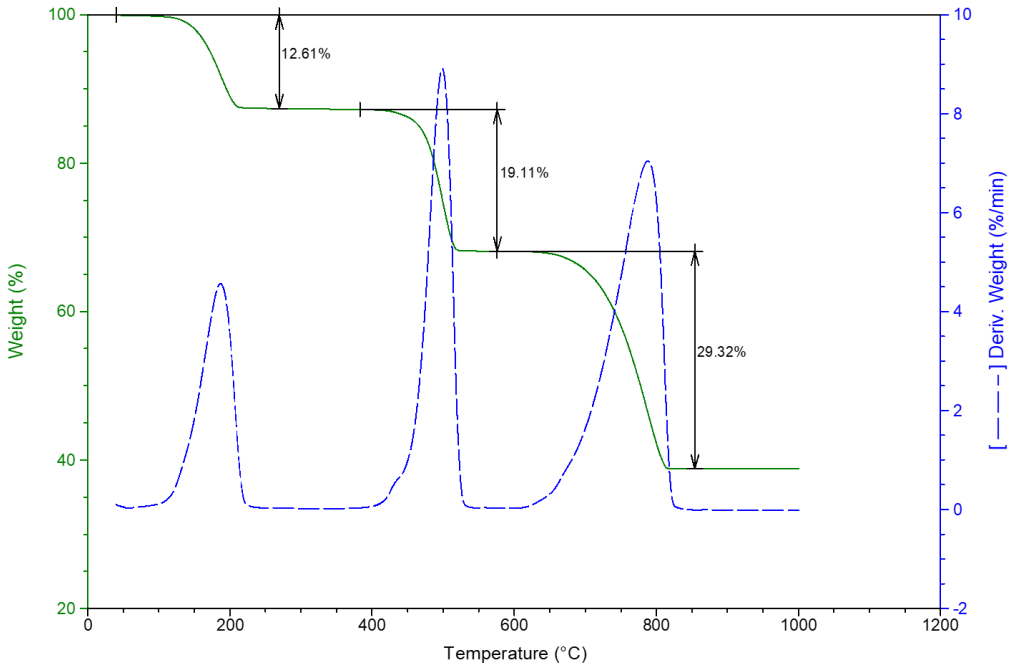

Figure 1 – Simultaneously recorded TGA and DTA scans of a sample of calcium oxalate.

Other calorimetry methods can determine other thermodynamic parameters of nanoparticle systems. Isothermal titration calorimetry (ITC) can be used to measure enthalpy changes and interactions between nanoparticles and materials binding to the surface, including binding affinities and stoichiometry. ITC is well suited for measurements in biological and/or nanoparticle solutions for drug delivery because it allows for solution-based measurements.(Bouchemal 2008)

THERMAL ANALYSIS OF NANOPARTICLE PURITY AND COMPOSITION

As with any material, nanoparticle purity and composition are vital to know from both an applications perspective and as key output variables for any process control-based quality plan. The wide variety of production methods hint at the challenges involved. For example, some nanoparticles are made through solution-based processes in which nanoparticles form as the precipitates of a chemical reaction. Here, by-products can be trapped inside or adsorbed onto the particles. For drug-delivery applications, a common method involves sol-gel chemistry where some of the suspension solution can become trapped within the nanoparticles.(Sarmento et al. 2006) TGA can be used to determine how much of a certain component is present in the final mixture as a mass percentage. One challenge is that often, prior to analysis, nanoparticles must be isolated from the encapsulating solution through centrifugation or other means of separation. The chemical composition is determined by heating the nanoparticle sample and comparing the oxidation temperature transitions to those of the pure components.(Dong and Feng 2005) The mass loss at each temperature is used to quantitatively determine chemical constituents.

TGA and DSC have also been used to validate protein encapsulation in nanoparticles by measuring the composition and heat flow results from the sample containing encapsulated proteins versus the pure nanoparticle samples. The difference in the thermograms provides evidence of protein encapsulation and can give an estimate of the mass of protein per nanoparticle.(Ma et al. 2004) TGA and DSC are bulk-scale techniques, with even their relatively small sample sizes of a few milligrams still containing very

large numbers of nanoparticles. Therefore, in order to relate the total mass loss determined by their techniques to the mass loss experienced by the individual nanoparticles, information about the size and morphology of the nanoparticles is required. Such data includes the average size of the nanoparticle as measured with light scattering or electron microscopy. Similarly, the mass of nanoparticles loaded into other systems, such as liposomal membranes, can be evaluated using similar TGA methods.(Amstad et al. 2011)

DSC can be used to evaluate crystallization behaviors and interactions of drugs with the nanoparticle-based delivery systems.(Siekmann and Westesen 1994) DSC has been used, for example, to evaluate interactions between indomethacin, a lipophilic drug, and solid lipid nanoparticles prepared for pharmaceutical drug delivery. Kinetic studies in the DSC were used to evaluate whether the indomethacin was associated with the lipid system and if so, how it was migrating through the bulk of the nanoparticle.(Castelli et al. 2005) Microemulsion synthetic methods also benefit from calorimetric determination of the nanoparticles and synthesis matrix to garner information about how changes in the synthetic process may impact nanoparticle composition.(Fini et al. 2003) From measurements such as these, the synthesis of the nanomaterials could be tuned to obtain particles of desired sizes.

By comparison to standards, the purity of synthesized nanomaterials can be measured by DSC and TGA. Thermogravimetric analysis can provide composition information for non-metal-based nanoparticles. One example of this is the application of TGA for the analysis of carbon nanotubes (CNTs).(Hornyak et al. 2009; Bannov, Popov, and Kurmashov 2020) Besides the nanotubes themselves, the soot samples typically consist of amorphous carbons, adsorbed hydrocarbons that are by-products of the synthesis conditions, other types of structured carbon, and metal catalyst particles. By heating the CNT powder in an oxidizing environment, CNTs will decompose at a given temperature characteristic of the nanomaterial, with individual transitions observable for each component. The observed oxidation

temperatures are around 200 °C for amorphous carbons, ~ 400 °C for single-wall carbon nanotubes, ~ 600 °C for multi-wall carbon nanotubes, and anything over 650 °C is attributed to metal catalyst and its oxidation products. (Mansfield, Kar, and Hooker 2010) Desorption of associated hydrocarbons typically occurs at temperatures below 200 °C. The use of TGA in the case of CNTs, can provide a measure of purity for CNT material, as measured by the percentage of the sample that degrades in the temperature range of interest. Furthermore, TGA is one of the fastest methods to measure relative percentages of single-walled versus multi-walled carbon nanotubes in a sample, but there are many challenges in obtaining accurate ratios, as many of the components tend to have overlapping temperatures(Mansfield, Kar, and Hooker 2010). There is significant work towards understanding peak fitting to truly understand composition (Banash 2021) and this remains an area of development for carbon nanomaterials.

Organic materials such as polymer-based particles or lipid nanoparticles can be measured with thermal methods. For example, TGA can determine purity, and DSC can measure component interactions. (Sarmento et al. 2006) Nanoparticles made from polyelectrolytes with opposite charges form more complex mixtures than just the physical mixture of the two components, which yields a distinct broad exothermic peak in the DSC. (Sarmento et al. 2006) When the two components are mixed but do not interact significantly, two distinct exothermic peaks (one for alginate (negatively charged), one for chitosan(positively charged)) are observable. These typically occur at the same temperatures as those for the pure components. Mixtures that interact with each other usually have a different thermal signature, often with one broad peak that defines the mixture. By utilizing TGA to evaluate the composition, one can distinguish if particles are a mixture of the two components, or a more complex, thermally stable system. This technique is also commonly used to demonstrate miscible and immiscible polymer blends by the same technique.

Chemical composition is also important for determining what is attached to the core of a nanoparticle. Simultaneous thermal analysis (STA) can be used to validate the attached coating, as can TGA and DSC individually. In some systems, composition is theoretically known but needs to be validated after a synthesis. In a $[Ni(en)_3](NO_3)_2$ nanoparticle population(Farhadi and Roostaei-Zaniyani 2011) two major transitions were observed in the thermogram which validated the theoretical calculated weights of each ligand (en, or ethylenediamine, and NO_3) from the complex, indicating the nanoparticle population was the expected composition. The DTA curve showed that these mass losses consisted of an endothermic event (release of ethylenediamine) followed by exothermic decomposition of the complex, giving additional information about the kinetics of the reactions to form the nanoparticles.(Farhadi and Roostaei-Zaniyani 2011)

Other nanoparticle coatings, such as adsorbed non-covalent polymer or protein coatings, are particularly important to study, as these can be naturally occurring and lead to dramatic changes in how the nanoparticle interacts with the environment. Adsorbed coatings are often added to protect nanoparticles from the environment or improve solubility in the given environment. Adventitious coatings may develop as a nanoparticle travels through a natural environment. Measuring these adsorbed coatings is complex, as many factors associated with the nanoparticle (surface properties such as size, charge) and properties of the adsorbed moiety (charge, hydrophobicity) govern these interactions. Some examples include protein coronas, which form as a result of exposure to protein systems, and adsorbed natural organic matter in water samples. Quantitating the number of associated proteins (either different types or quantities of a single protein) on the nanoparticle surface under biological conditions is of importance as more and more nanomaterials get introduced into biological systems for therapeutic or inadvertent means.(Sebby and Mansfield 2010) Isothermal titration calorimetry has been used to measure stoichiometric affinity, and enthalpy of protein-nanoparticle interactions.(Cedervall et al. 2007)

Mass loss due to decomposition of nanoparticles at specific temperatures can be used to determine a) dehydration of the nanoparticle or associated protein, b) decomposition of the surface ligands/associated proteins and c) decomposition of the nanoparticle. The nanoparticle concentration, protein concentration and surface area are used to calculate the number of proteins per nanoparticle. In some cases, it may be necessary to correct the mass measurements for the loss of water to obtain the mass loss due only to surface coatings.(Wang et al. 2012) The corrected mass measurements can then be used to estimate functional group density and coverage on the nanoparticle surface. Surface coverage can be estimated through simple surface packing models.(Cedervall et al. 2007) Nanoparticle coating thermal analysis can further be complicated by changes in the nanoparticles prompted by the removal of the coating. Secondary analysis, such as mass spectrometry or FTIR, can be used to distinguish between physi- and chemisorbed materials and the oxidation or reduction of the inner material and this has been successful demonstrated for fatty acid coated magnetite nanoparticles (Rudolph, Erler, and Peuker 2012).

EVALUATION OF NANOPARTICLE-CONTAINING COMPOSITES

Nanocomposites include materials in which nanoparticles are added to a matrix material to tailor the optical, mechanical, magnetic, electrical or thermal properties. Thermal analysis methods are often used to examine the differences between the matrix versus the matrix with incorporated nanoparticles. Changes in the thermal performance of composites with the addition of nanoparticles can be monitored using DSC and TGA. Shifts to higher decomposition temperatures, as measured by TGA, indicate increased thermal stability of the composite material.(Hasan et al. 2006) The measurement of glass transition temperatures and melting points with DSC can be used to measure differences in degree of crystallinity and heat of fusion.(Hasan et al. 2006; Rittigstein and Torkelson 2006; Shah et al. 2005) Mass loss profiles via TGA can also be used, in conjunction with mass spectrometry, to determine what is being released

from the composite at a given time (water, decomposition products), which can provide further information of the composite composition.(Kanniah et al. 2012) Using the information obtained from TGA and DSC, any enhancements or negative changes from the original composite structure can be evaluated. Not only does thermal analysis give information about the bulk properties that may affect the processability of the composites, but it also can give information about how the particles are integrated into the composite network.

MONITORING KINETICS OF THERMAL TRANSITIONS

Thermal analytic techniques can be used to monitor kinetic behavior of nanoparticle systems. One example is using DSC to determine the cure kinetics of nanocomposites, as the cure can be affected by nanoparticle composition and density within the composite. DSC can also measure glass transition temperatures, which can be used to predict nanoparticle mobility within the matrix.(Shah et al. 2005) The cure kinetics can be measured by monitoring the evolution of heat and measuring the activation energy. Curing is typically exothermic, so the degree of cure is defined as the heat released during a cure, divided by the total heat of reaction, with the cure itself identified as a maximum in the measured total heat. The rate of cure is calculated as:

$$\frac{d\alpha}{dt} = \frac{1}{H_g}\frac{dH}{dt}$$

Where the $d\alpha/dt$ is the reaction rate, H_g is the total heat of the reaction, and dH/dt is the change in the heat evolved during the cure at a certain time.(Rosso and Ye 2007)

Calorimetry provides a means for the measurement of many types of nanoparticle kinetics. Direct measurement via a micromechanical calorimeter of particle energies opened up the field for nanoparticle

energetic measurements via thermal analysis.(Bachels, Schäfer, and Güntherodt 2000) When combined with size classification, it is possible to obtain the size dependent enthalpies of formation, an invaluable metric as it is a direct probe of how surface-to-volume ratio affects cohesive energy density (Xie, Wang, and Qi 2004). The technique can be further extended to allow for nanoparticle energetics in catalyst sintering applications to be measured, which is extremely useful as many of these nanoparticles are used to make other nanomaterials such as carbon nanotubes.(Campbell, Parker, and Starr 2002) A related measurement , the enthalpy of adsorption, can also be used to predict energetics of nanoparticle oxide formation.(Navrotsky 2003) Oxide formation is perhaps the most important mechanism in terms of catalyst deactivation, so knowledge of the thermodynamics is important in developing methods of mitigation and prevention. A complete study of oxidation of nickel nanoparticles was completed in 2008 (Song et al. 2008) in which multiple theories were examined to represent the oxidation kinetics. In the end, it was found that nanoparticle oxidization occurred in a diffusion dominated way for this particular nickel nanoparticle system and the work is a great reference for others interested in oxidation kinetics in metallic nanoparticle systems.

Nanoparticle energetic state and the growth process as a result of reactant concentrations are measurable through calorimetric means. Experimental enthalpies are obtained by integrating the dynamic calorimeter signal over time. Many different microemulsion synthesized nanoparticle systems have been studied using this method. Rate equations can also be determined from the work if the time constants used are greater than that of the calorimeter.(Aliotta et al. 1995) Rates of reactions for kinetic processes, such as thermal dehydration of nanoparticle populations have been measured by constructing Arrhenius plots from DSC thermograms.(Al-Kady et al. 2011) The Arrhenius plots can be used to determine the energy of activation for the hydration process. In one case, the higher activation energy indicated a chemical reaction rather than diffusion-controlled reaction (hematite nanoparticles (Al-Kady et al. 2011))

and there was a highly ordered transition state in the dehydration process. Other aspects, such as reactivity of nanoparticles have been studied using non-isothermal TGA measurements.(Park et al. 2005)

INNOVATIONS IN THERMAL ANALYSIS FOR NANOPARTICLES

There is room for improvement for today's thermoanalytical techniques to become more appropriate for nanoparticle systems. Smaller sample sizes, ability to increase sensitivity, and monitoring nanomaterial-matrix interactions are of importance. Recent developments in thermoanalytical methods have made nanoparticle analysis on small scales possible.

Nanocalorimetry is a microchip-based system capable of measuring samples on the order of nL in volume or micrograms to nanograms in mass(Yi and La Van 2012) and has a resolution below 5 nW when measuring heats of reactions.(Lee et al. 2009) The small sample volumes allow for the measurement of as-produced samples and their interactions with the environment, as well as interactions between nanomaterials and cells, which is of importance in the area of nanomedicine.(Yi and La Van 2012) As with any thermoanalytical technique, accurate temperature, power, and mass measurements are needed. The measurements of these small-scale interactions are difficult as the compensation for the heat loss in these systems is not as controlled as in large scale instrumentation. Overall, the application of nanocalorimetry has led to advances in understanding binding reactions between biological systems and nanoparticles, crystallization and melting behaviors of particles, and size-dependent thermodynamics and kinetics (Li and LaVan 2019). Further development to push towards femtowatt measurements,(Burke and LaVan 2013) improved uncertainty analysis and the push for aqueous environmental analysis will yield the next phase of nanocalorimeters.(Yi and La Van 2012)

Thermogravimetric analysis has also been advanced significantly to provide decomposition information on nanotechnology-relevant scales. In the late 1970's, the use of more sensitive balances for TGA,

specifically utilizing quartz crystal microbalances, was suggested as a potential improvement. Work at the National Institute of Standards and Technology led to the development of a microscale-TGA instrument which requires 1000-fold less sample than traditional instrumentation (Mansfield et al. 2010) and overcomes previous challenges associated with use of quartz crystal microbalances. Thermogravimetric analysis has been limited by sensitivity of the microbalance, with commercial instruments requiring at least 1 mg of sample. As nanoparticle applications require tighter controls on nanoparticle compositions, often the yield from synthesis is far below the 1 mg size limit for traditional instruments. The microscale-TGA method replaces the microbalances in traditional instruments with piezoelectric quartz crystal microbalances to allow for analysis on sample masses of 1 – 10 μg and sensitivities of mass detection on the order of ng.(Johnson and Mansfield 2012) After a correction for thermal changes in quartz at elevated temperatures (which previously limited use of quartz crystal microbalances), decomposition data has been obtained for a number of materials.(Mansfield et al. 2010) Carbon nanotube decomposition can be monitored using microscale-TGA, as well as quantitative measurement of coatings on gold and silica nanoparticles,(Mansfield et al. 2014; Mansfield et al. 2010; Sebby and Mansfield 2010) all of which could be compared to conventional TGA or other analytical results. This new TGA instrumentation will enable measurements of limited nanoparticle populations, such as those that may be obtained from environmental or biological samples without complex sample preparation or tedious sample analysis. Further development of the microscale-TGA measurements for nanomaterial analysis would include the linking of microscale-TGA to secondary detection instrumentation (Raman, mass spectrometry) to yield more information about the decomposition products, improving sensitivity and commercialization of the instrumentation.(Mansfield and Quinn 2011)

CONCLUSIONS

Thermoanalytical methods are now widely used for the study of nanomaterials and products containing nanoparticles. Thermal analysis has many advantages that complement other nanoparticle analysis techniques. In most cases, preparation of the nanoparticle sample is minimal (*i.e.*, concentration of the sample) and no additional modifications (*i.e.*, fluorescent labeling, etc.) are needed to complete the analysis. A wide range of techniques can be used including thermogravimetric analysis, differential scanning calorimetry and other calorimetric systems. Commercial instrumentation is available and interpretation of results is often easy enough that thermal analysis can be applied in the manufacturing setting to compare batch-to-batch reproducibility. Nanoparticle purity and composition can be assessed quickly on the laboratory scale with minimal sample preparation and results can be compared to other analytical methods to provide further certainty of the composition. Interactions that may influence nanoparticle coatings can also be determined using thermal methods, including those in which the nanoparticle may be exposed to environmental systems such as water or biological media. Kinetics of nanoparticle systems is increasingly important as more complex synthetic methods are used. Nanoparticle systems, such as nanocomposites, can be characterized for composition and kinetics of reactions as related to nanoparticle content.

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