Thermogravimetry-Mass Spectrometry for Carbon Nanotube Detection in Complex Mixtures

The MIT Faculty has made this article openly available. Please share how this access benefits you. Your story matters.

<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>As Published</td>
<td><a href="http://dx.doi.org/10.1021/es203198x">http://dx.doi.org/10.1021/es203198x</a></td>
</tr>
<tr>
<td>Publisher</td>
<td>American Chemical Society</td>
</tr>
<tr>
<td>Version</td>
<td>Author's final manuscript</td>
</tr>
<tr>
<td>Accessed</td>
<td>Fri Nov 23 02:26:19 EST 2018</td>
</tr>
<tr>
<td>Citable Link</td>
<td><a href="http://hdl.handle.net/1721.1/78935">http://hdl.handle.net/1721.1/78935</a></td>
</tr>
<tr>
<td>Terms of Use</td>
<td>Creative Commons Attribution-Noncommercial-Share Alike 3.0</td>
</tr>
<tr>
<td>Detailed Terms</td>
<td><a href="http://creativecommons.org/licenses/by-nc-sa/3.0/">http://creativecommons.org/licenses/by-nc-sa/3.0/</a></td>
</tr>
</tbody>
</table>
Thermogravimetry - mass spectrometry for carbon nanotube detection in complex mixtures

Desirée L. Plata*,1,2,3, Christopher M. Reddy1, and Philip M. Gschwend2

1Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02543
2Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
3Civil and Environmental Engineering, Duke University, Durham, North Carolina, 27708

*Corresponding author: desiree.plata@duke.edu

ABSTRACT

In spite of the growth of the carbon nanotube (CNT) industry, there are no established analytical methods with which to detect or quantify CNTs in environmental matrices. Given that CNTs have relatively high thermal stabilities, we investigated the use of thermal techniques to isolate and quantify single wall carbon nanotubes (SWCNTs). Test materials included ten types of commercial SWCNTs, representative biological macromolecules (bovine serum albumin and methylcellulose), soot, natural coastal sediments, and SWCNT-amended sediments. Different SWCNTs exhibited widely diverse degradation temperatures, and thermal analytical methods may require SWCNT-type specific parameters. To improve quantification capabilities, evolved gases were monitored by mass spectrometry. SWCNTs produced diagnostic ion ratios, reflective of their high carbon and low hydrogen and oxygen contents. Current detection limits are roughly 4 µg_{SWCNT} per sample (e.g., 100 µg_{SWCNT} g^{-1}_{sediment} and 40 mg sample), controlled by interfering ions associated with the instrument’s non-airtight design. While future
modifications could improve this limitation, the current method is sufficient for
quantifying SWCNTs in laboratories and industrial sites where SWCNTs are handled.
Furthermore, the method shows promise to distinguish between incidental (e.g., soot) and
engineered (e.g., SWCNTs) nanoparticles, which is not possible with current state-of-the-
art techniques.

INTRODUCTION

Carbon nanotubes (CNTs) have generated an impressive list of potential and
demonstrated applications\(^1\)\(^-\)\(^3\), and the CNT industry is growing at a remarkable rate,
doubling nearly every two years\(^4\). Historically, no industrially important chemical has
been synthesized, used, and disposed of without some release to the environment. Thus,
environmental levels of CNTs will likely increase with growth of the industry. Present
CNT analytical techniques are limited to electron microscopy (EM) and spectroscopic
analyses of small (mg), relatively pure samples. Some attempts have been made to
measure CNTs in complex matrices\(^5\), but further work remains before recoveries
accurately reflect environmental concentrations. As a result, there is no way to monitor
the release of industrially synthesized CNTs or to gauge their transport and ultimate
biological exposure levels.

Successful isolation and detection of CNTs from environmental matrices (e.g., air,
water, and sediment) will rely on unique chemical or physical properties of the CNTs that
are distinct from other ubiquitous carbon forms. CNTs are cylinders of \(sp^2\)-hybridized
carbon atoms arranged in repeating, aromatic rings. While variations in synthetic
approaches and post-fabrication handling result in a diverse class of materials\(^6\), the
majority of CNTs will exist as agglomerated, hydrophobic particles\(^7\). A physically and
chemically similar particle that is ubiquitous in the environment is black carbon (BC),
which can be produced from forest fires or as a by-product from incomplete combustion
of fossil fuels (i.e., natural or incidental nanoparticles, respectively)\(^8\)\(^-\)\(^11\).

Methods to measure BC in environmental samples have been under development
for approximately 30 years\(^8\), and a recent laboratory inter-comparison\(^12\) revealed that
thermal oxidation techniques (e.g., chemo\(\text{thermo}\)l oxidation at 375\(^\circ\)C\(^13\)) successfully
isolate BC soot from other BC materials\textsuperscript{14}, such as wood char. Thermal methods (e.g., thermogravimetric analysis or TGA) are also used to determine the purity of commercial carbon nanotubes, which typically contain several forms of carbon (e.g., single-walled CNTs (SWCNTs), multi-walled CNTs (MWCNTs), “multi-shell” carbon\textsuperscript{15}, fullerenes, and amorphous carbon), as well as residual metal catalysts, and there is promise that similar techniques may be used to isolate CNTs in environmental samples.

To establish the feasibility and limitations of such analyses for the quantification of CNTs in the environment, we determined the thermal stability of several commercially available SWCNT powders, two representative biological macromolecular materials (i.e., bovine serum albumin (BSA) and methylcellulose), and representative environmental mixtures (e.g., urban dust, diesel particulate matter, marine sediments, and SWCNT-amended sediments). To improve detection, online mass spectrometry (MS) was employed to monitor gases evolved during temperature-programmed oxidations (TPOs) and hydrogen-assisted thermal degradations (HATDs). Using unique mass loss temperatures and evolved gases, we evaluated the promise of TGA-MS as a tool to separate and quantify incidental and engineered organic matter.

**EXPERIMENTAL METHODS**

**Samples.** SWCNT powders were purchased from multiple manufacturers and characterized by Plata et al.\textsuperscript{6} (Table 1). Non-SWCNT test materials included potentially interfering materials: fullerenes (C\textsubscript{60}, Materials and Electrochemical Research Corporation), MWCNTs (Nanocyl), and bovine serum albumin, as well a non-interfering compound (methylcellulose). Un-amended environmental matrices and mixtures included a sediment sample collected from Dorchester Bay, Massachusetts\textsuperscript{16}, urban dust (National Institute of Standards and Technology Standard Reference Material (NIST SRM) 1649a), diesel particulate matter (NIST SRM 1650), and chestnut wood char\textsuperscript{12}. SWCNT-amended sediments were prepared by thoroughly mixing SouthWest Nanotechnologies Purified (SWP) SWCNTs to pre-sieved, ground, and homogenized
Dorchester Bay sediment (DBS). Less-concentrated sediment samples were prepared by serial dilutions with un-amended DBS. Several materials that were pre-combusted and expected to be free of organic carbon were also analyzed. These included ground (to a fine powder) Ottawa quartz sand, quartz fiber filters (QFFs), and platinum sample pans.

**Thermogravimetric analysis-mass spectrometry.** TPOs and HATDs were performed using a TA Instruments Q50 TGA interfaced to a Pfeiffer ThermoStar quadrupole mass spectrometer (MS) via a heated capillary transfer line (200°C, 2 mL min⁻¹ sampling rate). Sample sizes were 3-3.3 mg for relatively pure samples (i.e., non-sedimentary material) and 40-44 mg for environmental matrices (e.g., sediments and soils). Masses were known to 0.001 mg.

TPOs were conducted in dry air (100 mL min⁻¹) with a thermal program (80 °C, 10 min hold, 5°C min⁻¹ to 900°C, 60 min hold). HATDs were conducted in ultra high purity hydrogen (10 mL min⁻¹) with a thermal program (80°C, 60 min hold, 5°C min⁻¹ to 900°C, 60 min hold). Ion currents m/z 2, 4, 12, 14, 16, 18, and 20-79 were scanned in 60-s sequence. Between runs, platinum sample pans were washed with 25 % (v/v) HNO₃, rinsed with copious 18 MΩ water, and combusted at 900°C in air for 1 hr.

The proposed method bears similarity to thermal-optical methods (i.e., thermal optical transmittance/reflectance (TOT/R)) for distinguishing elemental carbon and organic carbon (EC/OC), especially with regard to the use of sequential reactive atmospheres (e.g., helium followed by a helium/oxygen mixture). In EC/OC, the formation of higher thermal stability material from lower thermal stability material during the analysis (i.e., “charring”) is acknowledged, accounted for optically, and subsequently used to correct the data. In our method, we explicitly seek to avoid charring altogether, as CNTs confound the optical correction technique¹⁷, and it will result in interferences that introduce significant error.

**Correction for TPOs:** To account for instrumental drift between sample analyses, ion ratios (X_{sample} /Y_{sample}, e.g., 18_{sample}/44_{sample}) were normalized to a standard run using the ratio of the average ion current m/z 28 in the sample (28_{sample}) to the average ion
current m/z 28 in the standard (28_{\text{standard}}) (Eqn 1). The ion m/z 28 was selected as an indicator of N\textsubscript{2}, which is the principle component of the dry air carrier gas that was delivered at a constant rate.

\[
\frac{18_{\text{sample}}}{44_{\text{sample}}}_{\text{corrected}} = \left( \frac{18_{\text{sample}}}{44_{\text{sample}}} \right) \times \left( \frac{28_{\text{sample}}}{28_{\text{standard}}} \right) \tag{1}
\]

**Correction for HATDs:** Our particular TGA-MS was not designed to be airtight, and small air leaks in the system resulted in interfering background signals due to N\textsubscript{2}, O\textsubscript{2}, and Ar (m/z 28, 32, 40, respectively). The N\textsubscript{2} and O\textsubscript{2} interferences were not improved by placing the TGA-MS in a sealed Ar-filled chamber. Ethene (m/z 28) is an important mass formed by carbon nanotube (CNT) reaction with H\textsubscript{2}, and to lower interference from N\textsubscript{2}, the ion current m/z 28 for each sample was background subtracted. The correction was performed by subtracting the average ion current m/z 28 during a background segment (no sample degradation) of each analysis (28_{\text{background}}), normalized for signal drift using ion current for Ar (m/z 40), from the ion current m/z 28 during the rest of the thermal program (28_{\text{sample}}) (see Eqn 2).

\[
28_{\text{sample,subtracted}} = 28_{\text{sample}} - 28_{\text{background}} \left( \frac{40_{\text{sample}}}{40_{\text{background}}} \right) \tag{2}
\]

Ion ratios were then normalized as described by Eqn 1.

As with any mathematical treatment, error could be introduced by the manipulations detailed in equations 1 and 2. For equation 1, if the 28_{\text{sample}} and 28_{\text{standard}} signals have relative errors smaller than or equal to the relative errors on 18_{\text{sample}} and 44_{\text{sample}} (which they typically do), then the increased error is small (e.g., 7% to 7.2% error following correction). For equation 2, if 28_{\text{sample}} is large relative to 28_{\text{background}} and
40_{\text{sample}} and 40_{\text{background}} have similar error magnitudes, then the error introduced by the subtraction step is incrementally small compared to the uncorrected error (e.g., a typical sample might go from 5% to 6% error following the correction step).

RESULTS AND DISCUSSION

When subjected to increasing temperatures in a reactive atmosphere, carbonaceous materials degrade at characteristic temperatures that are reflective of their structures and potentially other factors, such as the presence of residual catalytic metals mixed with the material. Each mass loss event (i.e., a peak in a differentiated mass loss plot or thermogram) may then, presumably, be attributed to a distinct phase in the sample.

**TPO of SWCNTs.** SWCNTs exhibited a diverse range of oxidative temperatures from 375 to 540°C (Figure 1). All mass losses were due to the oxidation of carbonaceous material (as confirmed by MS and discussed later), except in the case of the volatilization of molybdenum oxides (around 690°C) from the SWP sample.

The majority of SWCNT powders produced two oxidation peaks: (1) a lower thermal stability signal that is conventionally presumed to be due to the oxidation of amorphous carbon and (2) a higher thermal stability signal that is conventionally presumed to be due to the oxidation of SWCNTs. In some cases (e.g., SES), contaminant phases were not amorphous carbon, but instead, are higher thermal stability material such as MWCNTs (see Supporting Information (SI) for representative MWCNT stability, which has a peak oxidation around 600°C) or multi-shell carbon (i.e., soot). In other cases (e.g., Nano Am., MER, CNI, and ManX), only one phase was readily apparent in the thermogram, and this could be the result of either very pure SWCNTs or the co-oxidation of multiple phases. For example, a tested C_{60} fullerene sample oxidized around 525°C (see SI), and, in theory, would have been thermally indiscernible from all of the Fe, Co, and Mo containing tubes (i.e., SWP, NanoAm, SES), as well as the Fe-containing ManX sample.
Several factors can influence the apparent thermal stability of a material, including the heating rate, oxygen supply, and oxygen’s access to the carbon surfaces (e.g., surface area and material packing). The temperature program, sample size, and bulk oxygen supply were well controlled in these experiments. Thus, the observed differences in SWCNT oxidation temperatures must be due to some intrinsic property (or properties) of the SWCNTs. Other researchers have noted that the SWCNT oxidation temperature is inversely related to the total metal content, suggesting that metals may catalyze the oxidation. Some have suggested that this catalysis results from the formation of metal oxides that generate concentrated microenvironments of oxygen in close proximity to the SWCNT lattice. However, it is also possible that different catalytic metals may produce SWCNTs with distinct properties (e.g., strain due to chirality or the average surface area of SWCNTs) that influence the oxidation temperatures of the nanotube products. While our data showed no significant correlation between the metal content and the oxidation temperature, clearly, the type of metal mixture was important to the oxidation temperature of the SWCNTs (Figure 2; $n=10$, see SI for metal-specific data). For example, all Ni/Y catalyzed SWCNTs had maximum thermal oxidation temperatures around 420°C (413 – 428°C, excluding the CSI sample, which has a complex thermogram), whereas Fe/Co/Mo catalyzed samples exhibited much higher thermal stabilities (between 510 and 540°C). Furthermore, in spite of a large spread in Ni content (range of 10 wt %) of Ni/Y catalyzed samples, the oxidation temperatures were fairly consistent between samples. To our knowledge, there has been no systematic study of metal catalyzed oxidation of recalcitrant carbon forms. However, NiO is known to be an efficient oxidation catalyst, and others have shown that different transition metals have distinct effects on the degradation of some materials.

Unfortunately, the crystalloid forms of the metals in these CNT samples were unknown and are not typically determined by manufacturers. The metal content is likely too low to obtain informative x-ray diffraction data. X-ray photoelectron spectroscopy would yield information on the metals present in the top several nm of the sample, yet carbonaceous coatings obscure many of the metals in SWCNT powders. As an exercise,
we assumed the metals were present as typical metal oxides\(^6\) and calculated the total possible metal oxide content to determine if there was a correlation between oxide content and oxidation temperature; there was no such correlation (SI).

The wide distribution in SWCNT thermal stability across catalyst types demonstrates that no single thermal oxidation technique will quantify all SWCNTs.

Knowing the type of SWCNT likely to be present in a field or lab sample (e.g., Ni- vs. Co- catalyzed), one could tailor the analytical method to isolate and quantify the desired variety of SWCNTs.

Here, we will focus on developing techniques to quantify the SWP nanotubes, which have been selected as a standard material for SWCNTs by NIST.

**TPO of natural organic materials.** Thermal isolation approaches require minimal overlap in the thermal stability of SWCNTs and other natural materials. Several representative “natural” materials were chosen, including samples that contain no BC or SWCNT (i.e., a carbohydrate, methylcellulose, and a protein, BSA) and samples that contain different types of BC (i.e., wood char and diesel particulate matter) (Figure 3a).

Methylcellulose had a low thermal stability and narrow thermal response window, perhaps consistent with its relatively oxidized chemical character, and did not interfere with SWP analysis. In contrast, the heteropolymer BSA had a broad oxidation range with some mass loss that interfered with SWP. Molecules with high nitrogen contents, such as proteins, have a tendency to char, forming higher stability materials during the thermal treatment. Visible charring was evident following BSA oxidation, and environmental matrices with high protein contents (e.g., cells or tissue) will likely suffer from significant interference\(^17\). These may be overcome with tandem analyses (e.g., TGA-MS) that enable the distinction between evolved gases due to char-derived BC and native BC in the sample (e.g., water evolved from char but not soot).

Natural BC in a sample matrix may exist in several forms, including wood char or BC soot. Wood char had a lower thermal stability than SWP (Figure 3a), perhaps due to greater oxygen access resulting from the porous structure of char. In spite of the lower thermal stability of wood char, there was still a slight interference with the oxidation.
onset of the SWCNTs. BC soot, on the other hand, was thermally distinct from SWP largely decomposing at temperatures >600°C (Figure 3a). The higher stability of the former is likely due to the multi-layer structure of aromatic sheets present in BC soot spheres, which limits oxygen access to the dense interior of the particles and increases the ultimate oxidation temperature. In contrast, SWCNTs are made up of hollow cylinders that have higher surface-area-to-carbon ratios. This structural difference between BC and SWCNTs may provide an opportunity to distinguish the two materials using thermal techniques.

While it makes intuitive sense, experiments should be undertaken to prove that differences in oxygen access to carbon influence relative thermal stabilities of materials. For example, comparative experiments with variable carbon geometries (i.e., all sp²-hybridized, aromatic sheets, but differing surface area to total carbon ratios; e.g., graphene, fullerenes, SWCNT, MWCNT, soot) but constant moles of carbon would indicate relative oxidation kinetics (e.g., by monitoring evolution of reaction products). (Nanomaterials would have to be metal-free to avoid confounding effects that result from metal contamination). Reaction rates could be related to the oxygen-access parameters (e.g., surface area as measured by nitrogen absorption) to confirm the existence of a causative relationship. Alternatively, a single material could be exposed in different geometries (e.g., constant mass, variable surface access or crucible shapes) or thicknesses (e.g., variable mass, same area). Such investigations would contribute to many fields that invoke thermal analysis, especially for carbonaceous materials.

**TPO of complex environmental matrices.** In more complex environmental matrices, full resolution of the diverse carbon phases may not be possible using thermal methods alone. Aerosol concentrates of urban dust had significant mass loss throughout the thermogram to 600°C, co-oxidizing with most SWCNTs (Figure 3b). These interferences likely arose from the presence of recalcitrant sooty or fly ash materials derived from incomplete combustion processes in urban environments, such as diesel exhaust or industrial emissions. Sediment collected from Dorchester Bay, MA had a thermal distribution consistent with the presence of fewer combustion-derived, high-
thermal stability materials (Figure 3c). As a result, there was less interference with SWP SWCNTs. Nevertheless, the co-oxidizing phases were not negligible, and an additional dimension of information was sought to improve detection limits of SWCNTs in environmental mixtures.

**TPO-MS: Unique ion ratios from SWCNTs.** Mass spectral analysis of the gases evolved during the thermal program revealed important masses associated with each compound class (see SI for spectra). When dry air was used as a reactive gas, all oxidized test materials yielded an expected combustion product, CO$_2$ (m/z 44). Carbon monoxide (CO, m/z 28) is another common combustion product, but its evolution was obscured by an interfering signal from N$_2$ (also m/z 28), the principle component of dry air. (Using a mixture of helium and oxygen (80% He, 20% O$_2$) as a reactive gas later alleviated this interference). In addition to the typical carbon-derived combustion products, the oxidation of methylcellulose and BSA formed H$_2$O (m/z 18) and either NO and/or CH$_2$O (m/z 30). This is consistent with the appreciable H, O, and N contents of these materials. In contrast, oxidation of BC soot and SWCNTs produced no measurable H$_2$O, NO, or CH$_2$O. Historically, geochemists have taken advantage of these differences in chemical structure to identify distinct materials in complex mixtures. For example, BC soot, with very few functional groups, has O/C and H/C ratios below 0.3, whereas most chars have O/C ratios from 0.3-0.5 and H/C ratios from 0.3-0.75$^{25}$. Thus, the two closely related materials can be distinguished with elemental analysis, and it is possible that SWCNT and BC may be identified by analogous means.

The variability in H-to-C and O-to-C ratios can be represented in a van Krevelen diagram (H/C vs. O/C ratios). These were originally employed for the study of coals, where low H/C and O/C materials were considered BC or soot-like. Using a similar concept, we monitored depletions in H, O, and N relative to C (i.e., m/z 18 (due to H$_2$O) and 30 (due to CH$_2$O or NO)) relative to m/z 44 (due to CO$_2$)) and sought to use those as an indicator of SWCNT abundance. As distinct materials oxidized at different temperatures, ion ratios varied throughout the course of the thermal treatment. Thus, ion ratios were calculated at the expected temperature of maximum SWCNT oxidation (here,
525°C). Natural sediments were amended with variable amounts of SWP SWCNTs. SWCNT powders have very low H, O, and N, contents, and as a result, they had low 18/44 (i.e., H$_2$O/CO$_2$) and 30/44 (i.e., CH$_2$O or NO/CO$_2$) ion ratios relative to unamended sediments (Figure 4). Increased SWCNT contents in amended sediments corresponded to reduced 18/44 and 30/44 ion ratios, and these were detectable at concentrations as low as 30 µg$_{SWCNT}$ g$_{sediment}^{-1}$. While these detection limits are sufficient for many laboratory-based experiments and indoor air concentrates where SWCNTs are being handled or produced (50 µg m$^{-3}$)$^{27}$, they may not be sensitive enough to measure SWCNTs in environmental samples (0-1200 ng g$_{dry sediment}^{-1}$)$^{28,29}$. The current lower bound on the detection of SWCNTs is limited by baseline CO$_2$ (i.e., high m/z 44) derived from co-oxidizing natural sedimentary organic matter and CO$_2$ leaks.

As CO$_2$ is a generic product of organic carbon oxidation, it will likely present a barrier to the detection of a trace contaminant in any sample matrix. Therefore, we investigated the use of an alternate reactive gas, H$_2$, to potentially produce SWCNT-specific masses.

**HATD of SWCNTs, natural organic materials, and complex environmental matrices.** Heating SWCNTs in pure hydrogen, rather than an oxygen-containing atmosphere, increased the maximum degradation temperature of all SWCNTs (Figure 5). In some cases, the thermal program did not fully degrade the SWCNTs or associated contaminants (ManX, CLex, SES), in spite of a prolonged exposure (60 min) to H$_2$ at 900°C. In addition to shifts in the thermal stability, there was increased resolution of previously co-oxidizing phases in some samples (e.g., MER and NanoAm.). Phases that were not observed in TPOs became apparent in HATDs, and this suggests potential value in a type of multi-dimensional analysis (e.g., HATD and subsequent TPO). Additionally, the increased resolution afforded by HATD demonstrates that the use of TPO alone is not sufficient to determine SWCNT purity. TPO is often used exclusively to determine the quantity of carbonaceous impurities in SWCNTs$^{21,22,30}$, where low thermal stability peaks are considered amorphous carbon and the mass remaining at the end of the TPO is
considered to be metal oxide. While the approach appears to be valid in some cases (e.g., for the CNI sample), TPO does not necessarily separate all carbon-based SWCNT co-products.

In addition to increased phase resolution in SWCNT powders, HATD reduced interferences from natural materials (Figure 6). Methylcellulose and BSA’s principle mass losses occurred below 350 and 450°C, respectively, well below SWCNT degradation temperatures. However, BSA charred into a high thermal stability material (as it did in TPO), and 20% of the initial mass remained after the HATD treatment. Diesel particulate matter survived prolonged HATD treatment at 900°C (Figure 6a). The small mass loss peak below 300°C in the diesel soot sample was attributed to labile organic compounds associated with the BC particles and accounted for 19% of the total mass of the sample (NIST SRM 1650b Certificate of Analysis reports 20.2 ± 0.4 % total extractable materials). SWP SWCNTs degraded at lower temperatures than BC soot, between 750 and 900°C. Thus, SWCNTs and BC soot might be separable via thermal methods. While the effective range of this method (i.e., fraction of SWCNT vs. BC) remains to be determined, the approach could provide a route to differentiate engineered nanoparticles from natural or incidental nanoparticles, which has been challenging to date.

This is promising for specific applications (e.g., laboratory air), but thermal interferences in complex environmental mixtures persisted. In the case of urban dust, mass losses overlapped with those of SWP SWCNTs to a greater extent than under TPO. Coastal sediments had almost identical co-degradation with SWP SWCNTs during both TPO and HATD. To overcome this limitation, diagnostic masses from SWCNT degradation were sought to identify the materials in natural environments.

**HATD-MS: Unique ion ratios from SWCNTs.** The mass spectra of evolved gases during HATD showed that all test materials produced ethene (m/z 28) (SI). Methylcellulose and BSA also produced H₂O (m/z 18), reflecting the enriched oxygen content of these materials relative to SWCNTs, which produced no detectable H₂O. Test materials produced few other diagnostic ions. However, SWCNTs degraded at rates that
were sufficient to draw down the signal of the reactant gas, H$_2$ (m/z 2). This
consumption of H$_2$ and depletion of H$_2$O was detectable in SWCNT-amended sediments
down to (at least) 100 ug$_{\text{SWCNT}}$ g$^{-1}$ sediment (Figure 7; i.e., both ratios 2/28 and 18/28 are
depleted in the SWCNT-amended sediment relative to pure sediment). This is at least ten
times too high to access the expected sedimentary concentrations of 0-1200ng g$^{-1}$ sediment

Readily accessible improvements. The detection limit in the HATDs was set by
either (1) co-degradation of sedimentary phases or (2) interference with the mass 28
signal due to an air leak in the TGA-MS, which was not designed to be airtight (see SI for
supporting data). In addition to designing a leak-free instrument, these limitations could
be overcome in at least three accessible ways.

First, enhanced mass spectral resolution would allow one to distinguish between
N$_2$ and ethene using their mass defects. Ethene’s exact mass is 28.05 amu, whereas N$_2$’s
exact mass is 28.01 amu. Many mass spectrometers readily distinguish these two ions,
but the mass spectrometers that are typically sold for TGA applications (i.e., residual gas
analyzers (RGA)) have mass resolutions of only about 1 amu! Clearly, the resolving
power of this RGA MS is insufficient to distinguish N$_2$ and C$_2$H$_4$. In addition, the RGA
has detection limits on the order of micrograms, whereas other mass spectrometers have
sensitivities in the picogram range (especially for non-fragmenting molecules).

Second, evolved gases could be cryogenically collected or otherwise captured and
then chromatographically separated and quantified via traditional gas chromatographic
methods, including flame ionization detection or improved mass spectral analysis.
Detection limits in the “offline” systems orders-of-magnitude improvements over RGA
and could offer additional discerning information (e.g., isotope ratios). Also, it is
important to note that RGAs have limited sampling rates (2 mL min$^{-1}$). With typical
TGA reactive gas flows between 10 and 100 mL min$^{-1}$, one is only sampling 2-20% of
the gases evolved during the TGA furnace; the rest of the signal is simply flushed away.
With cryogenic focusing, all or most of the signal due to SWCNTs could be quantified,
rather than being flushed away as it is in online RGA MS.
Lastly, existing software for deconvoluting mass loss and or mass spectral information (e.g., such as those used in Rock-Eval\textsuperscript{14}) could potentially enable computational peak separation where thermal separation is not possible, especially where the evolved gases are unique.

Were the issues completely resolved, given the current pan geometry (40 mg\textsubscript{sediment}) and a better mass spectrometer (with 0.1 to 1 ng sensitivity), one could measure 2.5-25 ng\textsubscript{SWCNT g\textsubscript{sediment}^{-1}} easily, well within the range of expected environmental concentrations\textsuperscript{28,29}.

**Current applications of TGA-MS to detect SWCNTs in the environment.**

Without additional modification, this method might successfully distinguish between natural and engineered nanoparticles (i.e., BC soot and SWCNTs). Until now, this has been a significant challenge, and it presents an impasse to quantification of engineered nanoparticle release from industrial manufacturing sites. For example, several groups\textsuperscript{27,31,32} have relied on light-scattering techniques to measure the release of nanoparticles during CNT production or post-fabrication handling. In all cases, 30-50 nm particles were detected, but it was unclear whether these were BC soot or CNTs or both. Occasionally, EM is used to distinguish the two materials, but this method is neither quantitative nor comprehensive. In addition, recent standard methods for measuring carbon nanotubes by the National Institute of Standards and Health (NIOSH) recommend the use of breathing zone air samplers (ca. 15 L min\textsuperscript{-1}) to collect particles on a filter, followed by elemental analysis\textsuperscript{33}. Blanks collected in low exposure areas are meant to provide a background measure of incidental or natural nanoparticles. However, processes used to produce CNTs can co-produce BC soot\textsuperscript{54}. Thus, carbon abundance near CNT-handling and production sources will reflect both engineered nanoparticles and incidental particles and the NIOSH method will not give a true representation of production-derived engineering nanoparticles. In the case of CNTs and BC soot, their mechanisms of toxicity are quite different, and distinguishing the two will be important.

To surmount this limitation, particles could be collected and subjected to HATD, where SWCNTs would be degraded and quantified, while BC soot would be preserved.
for subsequent quantification by TPO. Thus, thermal analysis under suitable gas mixtures provides a low-cost, high-throughput method for the isolation and quantification of carbon phases that are otherwise difficult to distinguish.

ACKNOWLEDGMENTS

We thank the Martin and Chesonis Families for support via MIT and the MIT Institute for Soldier Nanotechnologies.

SUPPORTING INFORMATION AVAILABLE Metal reduction potentials, metal vs. oxidation regression, mass spectra from TPO and HATD, m/z 28 source identification.

REFERENCES


Table 1. Single-walled carbon nanotubes used in this study

<table>
<thead>
<tr>
<th>SWCNT supplier name</th>
<th>Symbol</th>
<th>Metal content (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SES Research</td>
<td>SES</td>
<td>0.47 Fe, 2.8 Co, 0.69 Mo</td>
</tr>
<tr>
<td>Carbon Solutions Inc.</td>
<td>CSI</td>
<td>22.4 Ni, 6.0 Y</td>
</tr>
<tr>
<td>CarboLex, Inc.</td>
<td>CLex</td>
<td>24.3 Ni, 5.0 Y</td>
</tr>
<tr>
<td>Materials &amp; Electrochemical Research Corp.</td>
<td>MER</td>
<td>3.53 Ni, 10.5 Co</td>
</tr>
<tr>
<td>Helix Material Solutions</td>
<td>Helix</td>
<td>15.3 Ni, 5.3 Y</td>
</tr>
<tr>
<td>Manufacturer X&lt;sup&gt;d&lt;/sup&gt;</td>
<td>ManX</td>
<td>1.21 Fe, 0.08 Mo</td>
</tr>
<tr>
<td>Nanocs Inc.</td>
<td>Nanocs</td>
<td>20.3 Ni, 4.2 Y</td>
</tr>
<tr>
<td>Nanostructured &amp; Amorphous Materials</td>
<td>NanoAm</td>
<td>0.24 Fe, 2.87 Co, 1.00 Mo</td>
</tr>
<tr>
<td>SouthWest NanoTechnologies Inc. (SWeNT, Inc.)</td>
<td>SWP</td>
<td>0.07 Fe, 4.1 Co, 6.9 Mo</td>
</tr>
<tr>
<td>Carbon Nanotechnologies Inc.</td>
<td>CNI</td>
<td>22 Fe</td>
</tr>
</tbody>
</table>

<sup>a</sup>Companies that manufactured single-walled carbon nanotubes (SWCNTs) for commercial sale in the United States during September 2005 and March 2006 are listed. <sup>b</sup>Symbols used in the tables, figures, and text of this paper do not represent notations employed by the manufacturers. <sup>c</sup>As determined in Plata et al.<sup>6</sup> <sup>d</sup>Manufacturer closed on April 26, 2006 and requested that we protect the identity of the business name.
Figure 1. Differentiated oxidation thermograms of SWCNT powders. Each SWCNT sample is catalyzed with either (a) Ni and Y, (b) Fe, Co, and Mo, or (c) Fe and Mo (Man X), Fe (CNI), or Ni and Co (MER). Multiple mass loss peaks are due to the oxidation of different phases, which are all carbonaceous (except for the highest thermal stability peak in the SWP sample, which is due to the loss of molybdenum oxides). For thermograms with two major peaks, the lower stability peak was attributed to amorphous carbon and the higher thermal stability peak was attributed to SWCNTs, except in the case of SES.
Figure 2. Temperature of maximum SWCNT mass loss rate as a function of total metal and type of metal. The metal content of each SWCNT powder is detailed in Table 1.
Figure 3. Differentiated oxidation thermograms of representative materials that are likely to be found in the environment. (a) Relatively pure test materials exhibited a wide range of oxidation temperatures, some of which overlapped with SWCNTs. (b, c) Environmental matrices, such as urban aerosol concentrates and sediments, had broad mass loss peaks that would obscure some, but not all, SWCNT oxidation temperature ranges. Note that mass losses at low temperatures are partially due to water loss from associated minerals. Thermograms for C_{60} and MWCNTs are available in the Supporting Information.
Figure 4. Diagnostic ion ratios observed in thermal oxidations of SWCNT-amended coastal sediments. Increasing amounts (weight percent indicated in figure legend) of SWCNTs were added to sediment collected from Dorchester Bay, MA. (a) When oxidized, pure SWCNTs yielded very little mass fragment 18 (due to H$_2$O) and mass fragment 30 (due to NO or CH$_2$O), and depletions in the 18/44 and 30/44 ion ratios were observed with increasing SWCNT content of the sediments. (b) The lower bound on SWCNT detection was set by co-oxidizing carbonaceous material, which generated CO$_2$ and increased the baseline signal of ion current m/z 44.
Figure 5. Differentiated thermograms of SWCNT powders subjected to hydrogen-assisted thermal degradation. Each SWCNT sample is catalyzed with either (a) Ni and Y, (b) Fe, Co, and Mo, or (c) Fe and Mo (Man X), Fe (CNI), or Ni and Co (MER). Multiple mass loss peaks are due to the degradation of different phases, which are all carbonaceous. Some phases that were not observed in the TPOs are apparent during HATDs (e.g., MER, NanoAm). After 60 min of thermal decomposition in H₂ at 900°C, some material in the SWCNT powders was not fully degraded.
Figure 6. Differentiated hydrogen-assisted thermograms of representative materials that are likely to be found in the environment. (a) Relatively pure test materials exhibited a wide range of degradation temperatures. Natural materials did not overlap with the mass loss of SWCNTs. (b, c) Environmental matrices, such as urban aerosol concentrates and sediments, had broad mass loss peaks. Note that some mass losses are partially due to mineral dehydration at low temperature. The sediment sample exhibited reduced interference with SWCNT degradation ranges in HATD. Thermogram for MWCNTs are available in the Supporting Information.
Figure 7. Diagnostic ion ratios observed in hydrogen-assisted thermal degradation of SWCNT-amended coastal sediments. Increasing amounts (weight percent indicated in figure legend) of SWCNTs were added to sediment collected from Dorchester Bay, MA. (a) When subjected to hydrogen-assisted thermal degradation, pure SWCNTs yielded very little mass fragment 18 (due to H$_2$O) and consumed mass fragment 2 (due to H$_2$), and depletions in the 18/28 and 30/28 ion ratios were observed with increasing SWCNT content of the sediments. (b) The lower bound on the detection of SWCNTs was set by co-degrading organic material in the sediments, which generated ethene and increased the baseline signal of ion current m/z 28. Note, that the system was not designed to be air tight, and air leak corrections were made using equation 2 to account for m/z 28 signal due to leaked N$_2$. 