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Environmental Consequences of Nanotechnologies

Method Selection Framework for the Quantitation of Nanocarbon

Scientific Operating Procedure Series (SOP-C-3): Selection of Methods for Release Testing and Quantitation of Solids, Suspensions, and Air Samples for Carbon-Based Nanomaterials

Rebecca A. Crouch, David P. Martin, Victoria K. Hicks,
Jonathon A. Brame, Aimee R. Poda, Mark L. Ballentine,
Alan J. Kennedy, and Anthony J. Bednar

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Abstract

There is significant concern regarding the health and safety risk of nanocarbon (for example, nanotubes, graphene, fullerene), and the current capability gap for accurately determining exposure levels encumbers risk assessment, regulatory decisions, and commercialization. Given the various analytical challenges associated with the detection and quantitation of nanocarbon, it is unlikely that a single method or technique will prove effective for all forms of nanocarbon, all exposure scenarios, or all possible environmental systems. The optimal approach, or series of techniques, will likely depend on the nature of the material being measured, its concentration, and the matrix in which it is contained. In this work, a preliminary decision framework is presented that assists the user in determining which analytical methods are best suited for a given sample.

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Preface

This study was conducted for the US Army Environmental Quality and Installations Research Program under Project Number O6O272OA/835, “Advanced and Additive Materials: Environmental Sustainability in Army Acquisitions.” The technical monitor was Dr. Elizabeth A. Ferguson.

The work was performed by the Environmental Chemistry Branch of the Environmental Processes and Engineering Division, US Army Engineer Research and Development Center, Environmental Laboratory (EL). At the time of publication, Amber L. Russell was Branch Chief, Dr. Brandon J. Lafferty was Acting Division Chief, and Dr. Elizabeth A. Ferguson was the Technical Director for Military Environmental Engineering and Sciences. The Deputy Director of EL was Dr. Jack E. Davis and the Director was Dr. Edmond J. Russo Jr.

COL Teresa A. Schlosser was the Commander of ERDC, and Dr. David W. Pittman was the Director.

1 Introduction

1.1 Background

The high level of uncertainty regarding the potential environmental health and safety (EHS) impacts of nano-enabled technologies may lead decision makers to employ an overly cautious approach to risk management. There is a need for intelligent prioritization of limited laboratory resources when generating data for risk-based models. In 2015, we proposed a tier-based framework (figure 1) that focused on relevant and useful testing for enabling risk decisions. At the same time, this framework limited unnecessary testing by determining when nano-specific scrutiny of a technology was not warranted because enough information had been collected (Collier et al. 2015). Martin et al. (2016) evaluated this framework using a conductive nanosilver ink case study, and Diamond et al. (2017) evaluated it using a photocatalytic cement containing TiO₂ nanoparticles. Nano Guidance for Risk Informed Deployment (NanoGRID), a tool for guiding data collection during EHS testing (<https://nano.el.erdcdren.mil/tools.html>) more commonly known as NanoGRID, will also incorporate this framework. Implementing this framework across the user community will minimize the resources devoted to analysis while still obtaining quantitation with a relevant limit of detection and desired level of certainty about EHS potential impacts.

Figure 1. Overview of Collier et al.'s (2015) tiered guidance framework designed to collect the most relevant data for assessing the EHS impacts of nano-enabled technologies.

Instrument manufacturers provide guidance for instrument optimization (that is, inductively coupled plasma mass spectrometry (ICP-MS) tuning for metals analysis), and US Environmental Protection Agency (EPA) methods establish standards for analyte determinations in environmental samples (for example, EPA Method 6010D (SW-846): Inductively Couple Plasma –Atomic Emission Spectrometry (Rev. 4, 2014) and EPA Method 6020B (SW-846): Inductively Coupled Plasma- Mass Spectrometry (Rev. 2, 2014)). Published methods for detection of various forms of nanocarbon provide additional information for analysis of nanomaterials in various en-

vironmental matrices and in the presence of other possible analytes of interest. Several SOPs already detail specific methods to identify and characterize a range of nanomaterial samples, with examples listed in table 1.

Table 1. Previously published scientific operating procedures (SOPs) for identification and characterization of nanomaterial samples.

Report/SOP	Report title	Techniques	Reference
ERDC/EL SR-15-1	Determination of Nanomechanical Properties by Atomic Force Microscopy	AFM	Cuddy et al. 2015
ERDC/EL SR-15-2	Environmental Consequences of Nanotechnologies: Nanoparticle Dispersion in Aqueous Media	Dispersion/ Dissolution	Coleman et al. 2015
ERDC/EL SR-15-3	Characterization of Nanomaterials Using Field Flow Fractionation and Single Particle Inductively Coupled Plasma Mass Spectrometry	FFF; SP-ICP-MS	Bednar et al. 2015
SOP-P-1	Purification and Concentration of Nanoparticles Using Diafiltration	Diafiltration	Miller et al. 2015
ERDC/EL SR-16-1	Nanomaterial Dispersion/Dissolution Characterization	Dispersion/ Dissolution	Miller et al. 2016
ERDC/EL SR-16-3	Surface Area Analysis Using the Brunauer-Emmett-Teller (BET) Method	BET	Brame et al. 2016
ERDC/EL SR-17-1	Quantifying Nanoparticle Release from Nanotechnology	Isolation/ Purification; Particle detection; Size determination	Martin et al. 2017

The specific system under investigation will dictate which nanocarbon-containing materials may be present and which detection instrumentation will be needed. Specific case studies in the references provide each individual analysis technique. For various microscopic techniques, such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), and atomic force microscopy (AFM), see Safarova et al. 2007; Koshino et al. 2013; Oshida et al. 2013; Li et al. 2008; and, Tu 2018. For total organic carbon (TOC), see Kuila et al. 2014 and Benoit et al. 2012. For thermogravimetric analysis (TGA), see Li et al. 2008. And for ICP-MS, see Ge et al. 2008; Antes et al. 2012; and, Lim et al. 2017. The standardized methods

stated above, in addition to those produced and accepted by the US Geological Service, EPA, and others, exist for many recommended identification, isolation, and characterization techniques carried out in environmental-sample matrices. These methods are cited where relevant throughout this text.

1.2 Objective

This scientific operating procedure (SOP) describes the framework developed under Task 2 of the US Army Environmental Quality and Installations Research Program 6.2 focus area Advanced and Additive Materials: Environmental Sustainability in Army Acquisitions (Project 0602720A/835). The purpose was to guide selection of the most appropriate methods to quantify nanocarbon in environmental matrices and other application-specific matrices. The primary objective of Task 2 was to develop a framework to provide guidance for characterizing material post release from a nanotechnology in suspension/solution, solid, or air matrices. This is a critical need, because current approaches fail to provide a high degree of confidence that there is no detectable carbon nanotube (CNT) release. Without sufficient technical confidence that nanotubes are not detectable above a certain concentration in a matrix in a material-release scenario, the potential for exposure cannot be understood, and the regulator precautionary principal may lead to overly conservative Environment, Safety, and Occupational Health assumptions. With a robust, orthogonal framework in place, greater confidence can be given to analytical results in the case that they do not clearly identify the presence of carbon nanomaterials.

1.3 Approach

Specifically, this SOP provides guidance for determining whether nanocarbon is released from a nanotechnology during testing as well as recommended methods for isolation and/or enrichment and characterization of release materials. Challenges associated with nanocarbon detection in release scenarios include functionalization diversity and the need for element-specific detection, the tendency toward aggregation, interference from natural organic matter or organic matrix components, and the need for very low limits of detection. This SOP combines best laboratory practices available from the literature with research experiences of ERDC scientists and collaborators.

1.4 Scope

Release testing is a critical, albeit often overlooked, step in the risk assessment of nanotechnologies (Brame et al. 2015). The hazard of a nanoparticle itself may have little relevance if it is never released from the bulk technology, and material released from the technology during use is not necessarily identical to the parent material. Previously, we developed guidance for evaluating samples for the presence and characterization of nanomaterial post release from a nanotechnology, whether in suspension /solution, solid, or air samples (figure 2) (Martin et al. 2017).

Figure 2. Overview of Martin et al.'s (2017) procedure for characterizing material generated during release testing of nano-enabled technologies and determining whether this material can still be considered a nanomaterial.

The following framework supplements this procedure with additional guidance regarding which specific methods are the most appropriate for quantifying and characterizing nanocarbon during release testing. Complete characterization is critical to understanding the fate, effects, and transport of nanomaterials in the environment. Finally, this framework incorporates a number of factors, including the composition of the nanomaterial, desired detection limits, and potential interferences, using existing data in the literature (Petersen et al. 2016; Kovochich et al. 2017).

2 Procedure

The following procedural framework is divided into four sections: procedures for suspensions and solutions, procedures for solid samples, procedures for air samples, and a summary. In many cases, multiple lines of evidence will be needed to adequately characterize nanocarbon in various matrices.

2.1 Procedures for suspensions/solutions

Each matrix suspected of containing nanocarbon requires a unique characterization framework. Figure 3 shows the process required for evaluation of nanocarbon in suspensions and solutions.

Figure 3. Overview of the screening and characterization framework for nanocarbon in suspensions/solutions.

To avoid unnecessary testing, first screen liquid samples (suspensions and solutions) for nanocarbon material using a variety of common techniques, as listed in table 2. The techniques include metals, gravimetric, TOC, Raman, near IR fluorescence (NIRF), photoacoustic, and photothermal analysis, each with associated advantages and disadvantages.

Table 2. Screening techniques for nanocarbon in suspensions/solutions.

Screening Technique	Detection Limit	Availability	Advantages	Disadvantages
Metals Analysis	+++	+++	Rapid, few interferents	Indirect, must have residual metals
Gravimetric Analysis	---	+++	Simple	Need clean sample
TOC Analysis	-	+++	Straightforward, well established	Interference
Raman Analysis	+	+	Positive identification	Needs calibration
NIRF Analysis	+++	+	Positive identification	Limited applicability
Photoacoustic Analysis	-	---	Broadly applicable	Specialized, high variability
Photothermal Analysis	+	---	Broadly applicable	Specialized, thin samples only

+: fair detection limits or availability;

+ + +: very good detection limits or widespread availability;

-: poor detection limits or limited availability;

---: very poor detection limits or very limited availability.

Using the flowchart shown in figure 4, first screen samples suspected to contain nanocarbon (although this is not always necessary depending on the amount of information that is known about the sample prior to screening). For example, the first test would verify the presence or absence of unique residual metals using inductively-coupled plasma (ICP) atomic or optical emission techniques, ICP-mass spectrometry (MS), atomic absorption spectrometry, graphite furnace atomic absorption, or a combination thereof. Reduce false positive and false negative rates by carrying out confirmatory/orthogonal analyses.

Figure 4. Flowchart of screening framework for nanocarbon in suspensions/solutions.

To varying degrees, unfunctionalized nanocarbon and nanocarbon functionalized with positively or negatively charged moieties may interact with or adsorb metal ions from the surrounding environment. If residual metals are detected, digest samples and use ICP-MS operated in standard or single-particle detection mode to undergo comprehensive metals analysis (Bednar et al. 2015). Samples will continue on to further isolation/enrichment and characterization only if metals are observed; otherwise, no further investigation is necessary. However, if the results of metals analysis are inconclusive or unavailable, next determine the presence of other species, which can be done using various specialized methods, such as EPA Methods 6010D (EPA 2014) and 6020B (EPA 2014) for metals, to check for particular materials.

Continue with Raman spectroscopy only if other nonmetal species (for example, organic environmental contaminants, small molecules, or biomolecules) are present. Move on to the isolation/enrichment and characterization steps if nanocarbon is observed. Alternatively, continue with gravimetric analysis, such as TGA, if other species are absent, and then continue on to the isolation/enrichment and characterization steps if nanomaterial is observed. If gravimetric analysis does not yield any observable nanomaterial, attempt the Raman pathway, and if Raman spectroscopy reveals no nanocarbon, use NIRF. A positive result for

nanocarbon from NIRF means the sample can undergo further isolation/enrichment and characterization. Otherwise, and especially if the presence of nanocarbon is highly suspected or the EHS risk is already known to be particularly high, attempt specialized methods such as photoacoustic or photothermal methods (among others). These specialized methods may require specialized training for accuracy and precision. After successful nanocarbon detection with methods specific to the particular sample, further characterize the samples. If no nanocarbon is subsequently detected, then no further isolation/enrichment or characterization is necessary.

There are several available techniques for enriching the sample or isolating the nanocarbon to assist in detection of nanomaterial (table 3) after initial screening tests but prior to characterization. These tests can be divided into two major categories: analytical separation and bulk enrichment/separation.

Analytical separation techniques also have their unique advantages and disadvantages. For example, FFF provides a robust size separation with easy eluent analysis, but it is a technique that requires advanced training to master. Capillary electrophoresis is another excellent technique for particle size-based separations, but it is an emerging technology with limited availability and few trained specialists. Two other options are ultracentrifugation and size-exclusion chromatography, with their associated advantages of being well established. Ultracentrifugation's main disadvantage is that it requires a significant amount of sample information to be effective, which may be unavailable in some instances. Size-exclusion chromatography's main disadvantage is that it can be limiting for samples with large particles or agglomerates.

Bulk enrichment/separation techniques include evaporation, centrifugation, and filtration, which all serve to concentrate the sample; however, while centrifugation and filtration have the advantage of retaining only the portion of the sample that is of interest, evaporation serves simultaneously to concentrate any interferents that may be present. Meanwhile, centrifugation tends to be highly dependent upon the nature of the sample, and filtration leads to some degree of sample loss. Use detection-limit needs for each sample to select the appropriate technique.

Subsequent to any necessary isolation/enrichment treatments, the methods listed in the last section of table 3 can typically be used to chemically and/or physically characterize nanocarbon materials in further detail. The techniques for test material analysis should be chosen based on the specific nature of the sample. For example, certain techniques, such as FFF, are effective for certain forms of nanocarbon but not all. Nanotubes, due to their cylindrical morphology, are not best suited to FFF, for example. The most common methods for characterizing nanocarbon in liquid matrices are SP-ICP-MS (if metals are present), optical absorbance spectroscopy, NIRF, electrospray-differential mobility analysis, and multi-angle light scattering. The major advantage of SP-ICP-MS is that it is rapid and suffers from few interferences; however, it is an indirect method and requires the co-occurrence of detectable levels of residual metals. Optical absorbance spectroscopic techniques are very commonly used for characterization, but they can be limiting in the case of nanocarbon, since they provide only limited data. For example, if used to analyze CNTs, the only information this technique would yield is the diameters of the CNTs; in addition, interferences with this technique cannot be avoided. Alternatively, NIRF can be used for increased sensitivity and specificity; however, this technique still only provides particle or nanomaterial diameter. Two less common techniques (electrospray-differential mobility analysis and multi-angle light scattering) can provide additional characteristic information. Electrospray-differential mobility analysis can yield rapid, comprehensive characteristic data, while multiangle light scattering is able to measure both length and diameter of CNTs, for example. However, electrospray-differential mobility analysis requires training that is more specialized, and multiangle light scattering requires specific sample conditions or complex data modeling. Finally, electron microscopy (for example, scanning or transmission) can be used on an isolated sample with the ultimate detection limit (that is, a single nanocarbon particle), yet this can be the equivalent of finding a needle in a haystack. In contrast, the general methods described above have bulk detection capability.

Martin et al. (2016) provides an excellent example of the effectiveness and applicability of this framework. The study used a previous version to evaluate the potential nano-specific release, exposure, and hazard associated with typical use of both a nanosilver ink and electronic circuits printed using the ink. The framework guided determination of the potential for nanomaterial release from both forms of the technology in simulated-use scenarios, including spilling of the ink, aqueous release (washing) from the

circuits, and UV light exposure. A number of analysis techniques, including ultracentrifugation and SP-ICP-MS, characterized the material released from the printed circuits upon aqueous exposure. The results of the tests suggested that the majority of the material was ionic in nature, allowing researchers to conclude that nano-specific regulatory scrutiny may be less relevant.

Table 3. Characterization techniques for nanocarbon in suspensions/solutions.

Technique	Advantages	Disadvantages
Bulk Enrichment/Separation Techniques		
Evaporation	Simplicity, cost	Also concentrates interferents
Centrifugation	Rapid separation based on size	Protocol is highly dependent on material
Filtration	Simplicity, cost, ideal for microscopy	Possible sample loss
Analytical Separations Techniques		
Field Flow Fractionation	Robust size separation, easy eluent analysis	Finicky technique
Capillary Electrophoresis	Good size resolution	Emerging technique
Analytical Ultracentrifugation	Wide range of size resolution	Need significant information on material
Size Exclusion Chromatography	Well established, simple method	Cannot handle large particles/aggregates
Other Characterization Techniques		
SP-ICP-MS	Rapid, few interferents	Indirect, must have residual metal
Optical Absorbance Spectroscopy	Common instrumentation	CNT diameter only, interferents
Near-IR Fluorescence	Sensitivity, specificity	CNT diameter only, limited applicability
Electrospray-Differential Mobility Analysis	Rapid, comprehensive data	Specialized technique, no aggregations
Multi Angle Light Scattering	Length and diameter can be measured	Specialized technique, complex modeling

2.2 Procedures for solid samples

Figure 5 gives an overview of the recommended pathway to characterization of nanocarbon in solid samples. Similar to liquid samples, first screen solid samples for possible nanocarbon material using a variety of common techniques, the most common of which are listed in table 4. The techniques include metals, gravimetric, TOC, Raman, NIRF, and microscopic analysis, with associated advantages and disadvantages.

Use the flowchart shown in figure 5 to screen samples suspected to contain possible nanocarbon, and then continue on to the flowchart in Figure 6 for a more detailed guidance. If a sample is already known to contain nanocarbon and/or forms of nanocarbon, the screening stage can be skipped. Using the flowchart in figure 6 as shown, first perform microscopy such as TEM/SEM, AFM, or a combination of these with spectroscopic techniques, such as x-ray diffraction or x-ray fluorescence, which can detect characteristic morphologies or carbon atoms, respectively, to search for the presence of organics.

Figure 5. Overview of the screening and characterization framework for nanocarbon in solid samples.

While the microscopies recommended here (table 4) are relatively available and reliable, these techniques can be highly subjective, and an experienced technician should perform them, with confirmatory/orthogonal analysis to reduce the rate of false positives and negatives. Perform TOC analysis if microscopic methods do not detect organics, and perform further characterization using the techniques listed in table 5 if the TOC analysis subsequently detects carbon.

Table 4. Screening techniques for nanocarbon in solid samples.

Screening Technique	Detection Limit	Availability	Advantages	Disadvantages
Metals Analysis	+++	+++	Rapid, few interferents	Indirect, must have residual metals
TGA	---	+++	Simple	Need clean sample
TOC	-	+++	Straightforward, well established	Interferences
Raman Spectroscopy	+	+	Positive identification	Needs calibration
Near-IR Fluorescence	+++	+	Positive identification	Limited applicability
Microscopy	?	+++	Well established, direct observation	Sampling bias, no positive ID

+ : fair detection limits or availability; - : poor detection limits or limited availability;

+++ : very good detection limits or widespread availability;

--- : very poor detection limits or very limited availability.

Figure 6. Detailed chart of screening protocols for nanocarbon in solid samples.

However, apply a screen for metals if microscopy detects organics or if TOC analysis does not detect carbon. Digest samples and undergo comprehensive metals analysis, for example using ICP-MS, if unique residual metals are detected. Samples will continue on to further characterization if metals are observed but if neither initial screening nor digestion and complete metals analysis detects metals, then apply a gravimetric technique such as TGA.

Further characterize samples using techniques listed in table 5 if TGA detects nanocarbon. If TGA detects no nanocarbon, then use Raman or NIRF spectroscopy as a final means to search for its presence. Characterize samples further only if Raman or NIRF detects nanocarbon.

Use the methods listed in table 5, among others depending on the specific nature of the sample, to chemically and/or physically characterize in further detail nanocarbon materials in solid samples. The most common methods for characterizing nanocarbon in solid matrices are microscopy (for example, TEM, SEM, or AFM), Raman spectroscopy, IR (vibrational) spectroscopy, and X-ray photoelectron spectroscopy (XPS); some less common or emerging techniques are thermogravimetric analysis-mass spectrometry (TGA-MS), microwave methods, and hyperspectral imaging. Table 5 describes the general advantages and disadvantages of each technique.

Table 5. Characterization techniques for nanocarbon in solid samples.

Technique	Advantages	Disadvantages
Commonly Utilized Techniques		
Microscopy	Readily available, detailed morphology	Labor intensive, sampling bias
Raman Spectroscopy	Broad applicability, sensitivity	Less readily available
Infrared Spectroscopy	Readily available	Limited morphological information
X-ray Photoelectron Spectroscopy	Detailed chemical information	No morphological information
Less Common / Emerging Techniques		
TGA-MS	Can supply chemical information	Limited sensitivity
Microwave Method	Sensitive, may couple with thermal imaging	Highly specialized
Hyperspectral Imaging	Can work in complex matrices	Less readily available, complicated analysis

Specifically, of the more common methods to characterize nanocarbon in solid matrices, only Raman spectroscopy is less readily available. For the most part, the four more commonly utilized techniques provide broad applicability, with microscopy enabling detailed morphological analysis and Raman, IR, and XPS yielding chemical information such as the presence of certain functional groups, chemical bonds, and interactions. Microscopy and spectroscopy also yield nonredundant, complementary information.

The three less common techniques may be applied in cases where the more common methods are unsuccessful or inconclusive. TGA-MS provides a more specialized method to obtain chemical information, but its sensitivity is limited. Hyperspectral imaging can be used in cases with a more complex matrix, but analyzing the obtained images and data can be extremely complicated and subjective, and the technique is much less available.

As a specific example, microwave methods have been adapted as part of the current US Army Environmental Quality and Installations Research Program under Project Number 0602720A/835, “Advanced and Additive

Materials: Environmental Sustainability in Army Acquisitions” by collaborators at Texas A&M University in College Station, Texas (Sweeney et al. 2017), with installation, setup, and prove-out activities conducted by Ms. Victoria Hicks during her student internship at ERDC-EL in Vicksburg, Mississippi, May–July 2018. The first system installed was a microwave-induced heating apparatus in which solid samples are housed within a borosilicate glass tube, into which a k-type thermocouple is inserted without allowing the thermocouple tip to touch the glass. A power source is used to apply 30 W to the sample for 10 s, and temperature of the sample is recorded for the duration of the experiment. The procedure is repeated four to six times, moving the thermocouple to a different location within the sample column each time, followed by a series of four to six treatments of 50 W for 6 s. The second system installed was an RF calorimeter, consisting of an RF generator operating at ≤ 3 dB relative to a mW, or dBm, (approximately 2 mW) with parallel plates for performing nondirect contact experiments on solid samples using an infrared thermal imaging device and/or thermocouple. Both of these systems are specialized and require advanced training, but they are very sensitive, selective, and have the advantage of being able to couple to a thermal imaging device.

In another example of the utility and effectiveness of this framework, Diamond et al. (2017) investigated the release potential and environmental impacts of free n-TiO₂, or cement-TiO₂ complexes, from cement amended with photoactive nano-scale TiO₂ (n-TiO₂). This framework guided categorization, characterization, and testing decisions to determine potential for release, fate, and toxicity of cement-TiO₂ composite. Release scenarios included runoff during construction and abrasion of cured concrete. Tested material included as-delivered cement powder (with or without n-TiO₂ and particles released using standard abrasion test methods). The n-TiO₂ in cement was determined to be nearly 100% anatase, and material released during abrasion contained nano- to micron-sized particles of free and matrix-bound TiO₂. In combination with results of comparative toxicity testing, which indicated no increase in toxicity in the presence of simulated solar radiation versus laboratory lighting, the study provided evidence that environmental risk of cement-TiO₂ composite may not be significantly increased relative to standard cement and demonstrated the successful application of the framework for assessing impacts of released nanomaterials.

2.3 Procedures for air samples

Nanocarbon in air samples require a unique characterization framework for screening and characterization methods. If the nanomaterial is immediately observed, differential mobility sizer (DMS) / fast mobility sizer (FMS) analysis can be carried out followed by isolation and characterization. However, if it is not detected, the presence of larger particles will determine if further isolation and characterization is necessary. Figure 7 gives an overview of the recommended screening and characterization pathway for nanocarbon in air samples.

Figure 7. Screening and characterization framework for airborne nanocarbon.

Use the flowchart shown in figure 7 to carry out a potential screening analysis of samples suspected to contain possible nanocarbon. The specific technique will depend on the amount of information that is known about the sample prior to screening. Table 6 lists the screening and characterization techniques recommended for analysis of air samples. Screening for nanocarbon in air samples requires different techniques than for liquids or solids, which both follow approximately the same pathways for screening and characterization. There are exceptions to this recommendation (for

example, air samples are collected onto a filter and later extracted into a solvent). In this case, first screen for nanomaterials using a condensation particle counter (CPC) or surface area monitor (SAM), and use a DMS /FMS for further screening if nanomaterial is observed. If CPC/SAM does not detect nanomaterial, and larger particles are not of concern, then no further screening or characterization is required. However, if DMS/FMS detects larger nanomaterial particles of concern, then carry out further isolation and characterization using the techniques listed in table 6.

Table 6 lists three of the most common isolation techniques and three of the most common quantitation/characterization techniques for detecting nanocarbon in air samples: filtering, impinging, and impacting. Filters have the advantage of being readily available and are useful for simple applications, but re-suspending filtered particles can be difficult. Alternatively, impingers place air sample components directly into suspension / solution-form, but there is no particle-size resolution with this technique. Lastly, impactors are very effective at separating aerosols into particle-size bins but can require complex instrumentation and be limited in sample-size capacity. Overall, the appropriate isolation method(s) for optimal nanocarbon detection and characterization capability must be chosen on a per-sample basis.

The three most common quantitation/characterization methods for nanocarbon in air samples are the techniques used for initial screening of the samples, which include CPC, SAM, and DMS/FMS. CPC and SAM methods provide no particle-size information; however, CPC is rapid and readily available, and SAM provides data complementary to mass/number. Finally, DMS/FMS techniques provide particle-size information but suffer from low temporal resolution. Thus, a combination of these techniques, as recommended in figure 7 are likely to provide the necessary characterization information for an air sample suspected of containing nanocarbon, and using a combination of appropriate isolation and quantitation/characterization techniques should improve limits of detection.

Table 6. Techniques for analyzing airborne nanocarbon.

Technique	Advantages	Disadvantages
Quantification/Characterization Techniques		
Condensation Particle Counter	Rapid, readily available	No particle-size information
Differential / Fast Mobility Sizer	Gives particle-size information	Low temporal resolution
Surface Area Monitor	Complementary data to mass/number	No particle-size information
Isolation Techniques		
Filter	Readily available, ideal for microscopy	Potentially difficult to resuspend particles
Impinger	Take particles directly to suspension/solution	No particle-size resolution
Impactor	Can separate aerosol into particle-size bins	Complex equipment, limited sample size

2.4 Summary of procedures

This framework supplements previous guidance (Martin et al. 2017) with additional recommendations regarding which specific methods are the most appropriate to use for quantifying and characterizing nanocarbon during release testing. Complete characterization (including nanomaterial composition, desired detection limits, and potential interferences) is critical to understanding the fate, effects, and transport of nanomaterials in the environment. Figure 8 summarizes the method selection framework for the quantitation of nanocarbon in solutions/suspensions, and solid and air samples, which are described in detail in sections 2.1–2.3. Further framework details are summarized in figure 9 (for solutions/suspensions) and figure 10 (for solids).

Figure 8. Summary of the method selection framework for the quantitation of nanocarbon.

Figure 9. Summary of framework for suspensions and solutions.

Figure 10. Summary of framework for solids.

3 Reporting

3.1 Analysis of results

The analysis and reporting of results for quantitation of nanocarbon are highly method dependent and discussed in the references provided. Additionally, include details concerning the specific protocols used to simulate release scenarios when reporting the chemical and physical analysis results, since this will aid in the determination of ultimate EHS impact.

3.2 Key results provided

This SOP provides a framework for isolating/enriching and characterizing nanocarbon released from nanotechnology during testing in suspension/solution, solid, and air matrices. Users should refer to suggested analytical methods when possible or otherwise review the procedure for potential modification based on the specifics of the system to be investigated.

3.3 Quality Assurance / Quality Control considerations

A wide variety of experimental conditions affects the behavior of nanocarbon. These can be found in the referenced materials.

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Acronyms and Abbreviations

AFM – atomic force microscopy
BET – Brunauer-Emmett-Teller
CNT – carbon nanotubes
CPC – condensation particle counter
DMS – differential mobility sizer
EHS – environmental health and safety
EL – Environmental Laboratory
EPA – US Environmental Protection Agency
ERDC – Engineer Research and Development Center
FFF – field flow fractionation
FMS – fast mobility sizer
ICP-MS – inductively-coupled plasma-mass spectrometry
NIRF – near IR fluorescence
SAM – surface area monitor
SEM – scanning electron microscopy
SOP – scientific operating procedure
SP-ICP-MS – single particle ICP-MS
TEM – transmission electron microscopy
TGA – thermogravimetric analysis
TGA-MS – TGA-mass spectrometry
TOC – total organic carbon
XPS – X-ray photoelectron spectroscopy

Glossary

- Agglomerate, n — in nanotechnology, an assembly of particles held together by relatively weak forces (for example, Van der Waals or capillary), that may break apart into smaller particles upon processing; a collection of weakly or loosely bound particles or aggregates, or a mixture thereof, in which the resulting external specific surface area is similar to the sum of specific surface areas of the individual components
- Aggregate, n — strongly bonded or fused particles where the resulting external specific surface area might be significantly smaller than the sum of calculated specific surface areas of individual components
- Dispersion, n — a mixture of nanomaterials in a continuous phase of a different composition or state, for example, water or sediment
- Dissolution, n — disassociation of an originally solid solute into a solvent (usually aqueous herein)
- Matrix, n — the liquid, solid, or air environmental sample matrix which is suspected to contain nanomaterial
- Media, n — the liquid, solid, or air matrix into which nanomaterial is spiked in the laboratory
- Nanomaterial, n — a material with any external dimension measuring in the nanoscale or having internal structure or surface structure in the nanoscale
- Nanoparticle, n — see Nanomaterial (n)
- Nanoscale, n — the size ranges from approximately 1 nm to 100 nm
- Nanotechnology, n — a technology which applies scientific knowledge to manipulate and control matter in the nanoscale to make use of size- and structure-dependent properties and phenomena distinct from those associated with individual atoms, molecules, or bulk materials
- Primary particle, n — the non-aggregated size of individual as-produced manufactured nanoparticles
- Size, n — the physical dimensions of a particle determined by specified measurement conditions
- Solubility, n — the degree to which a material (the solute) can be dissolved in another material (the solvent) so that a single, homogeneous, temporally stable phase (a suspension down to the molecular level) results
- Solution, n — a homogeneous and temporally-stable single-phase suspension of a solute in a solvent

- Stability, n — the measure of a dispersion that quantifies the rate of change of physicochemical parameters (for example, concentration, agglomeration, dissolution, or other selected characteristic)
- Suspension, n — a dispersion of nanoparticles, aggregates, or agglomerates in liquid media
- Test material, n — nanomaterials, including formulation specific additives, including coating, dispersant, etc.

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