ERDC/EL SR-16-3

US Army Corps
of Engineers®
Engineer Research and
Development Center

ERDC
INNOVATIVE SOLUTIONS
for a safer, better world

Environmental Quality and Technology Research Program

Surface Area Analysis Using the Brunauer-Emmett-Teller (BET) Method

Scientific Operating Procedure Series: SOP-C

Jonathon Brame and Chris Griggs

September 2016

Environmental Laboratory

The U.S. Army Engineer Research and Development Center (ERDC) solves the nation's toughest engineering and environmental challenges. ERDC develops innovative solutions in civil and military engineering, geospatial sciences, water resources, and environmental sciences for the Army, the Department of Defense, civilian agencies, and our nation's public good. Find out more at www.erdc.usace.army.mil.

To search for other technical reports published by ERDC, visit the ERDC online library at http://acwc.sdp.sirsi.net/client/default.

Environmental Quality and Technology
Research Program

ERDC/EL SR-16-3
September 2016

Surface Area Analysis Using the Brunauer-Emmett-Teller (BET) Method

Scientific Operating Procedure Series: SOP-C

Jonathon Brame and Chris Griggs

Environmental Laboratory
U.S. Army Engineer Research and Development Center
3909 Halls Ferry Road
Vicksburg, MS 39180-6199

Final report

Prepared for U.S. Army Corps of Engineers
Washington, DC 20314-1000

Under Project 405624, "Environmental Consequences of Nanotechnologies"

Abstract

Many of the unique, intrinsic properties associated with nanomaterials arise from the large surface-to-volume ratio of these exceptionally small materials. Surface area properties may also be relatable to environmental fate and hazard implications; therefore, accurately measuring surface area is extremely important for material characterization. The most commonly used method of measuring the surface area of nanomaterials is the Brunnauer-Emmett-Teller (BET) surface adsorption method. This protocol has been developed to describe the theory, application, limitations and sample preparation requirements to enable more accurate, precise and well informed use of the BET method. Two materials (nano aluminum oxide and nano graphene) were taken through a sample BET analysis to provide an example of the methodology and how to apply it for surface area analysis. Although the specific requirements for BET analysis will vary with different instrument models and manufacturers, the purpose of this protocol is to provide a foundational understanding of the steps involved, how to perform them in a repeatable and reliable manner, and to provide the theory behind the analysis.

Contents

Figures and Tables

Figures

Tables

Preface

This procedure was developed under the Engineer Research Development Center (ERDC) Environmental Quality and Technology (EQT) Research Program under Project 405624, titled "Environmental Consequences of Nanotechnologies." Procedures link to the ERDC NanoGRID (Guidance for Risk Informed Deployment) framework for testing the exposure and hazard of nanotechnology Environmental Health and Safety (EHS). The technical lead of the research program was Alan Kennedy.

The work was coordinated by the Environmental Chemistry Branch (EPC) of the Environmental Processes and Engineering Division (EPE) at the U.S. Army Engineer Research and Development Center – Environmental Laboratory (ERDC-EL). David Morrow was the Branch Chief, CEERD-EP-C, Warren Lorentz was the Division Chief, CEERD-EP-E; and Dr. Elizabeth Ferguson was the Technical Director for Military Environmental Engineering and Sciences. The Deputy Director of ERDC-EL was Dr. Jack Davis and the Director was Dr. Elizabeth Fleming.

COL Bryan S. Green was the Commander and Executive Director of ERDC, and Dr. Jeffery P. Holland was the Director.

Unit Conversion Factors

Multiply	By	To Obtain
angstroms	0.1	nanometers
cubic feet	0.02831685	cubic meters
cubic inches	1.6387064 E-05	cubic meters
cubic yards	0.7645549	cubic meters
degrees Fahrenheit	(F-32)/1.8	degrees Celsius
ounces (mass)	0.02834952	kilograms
ounces (US fluid)	2.957353 E-05	cubic meters
pints (US liquid)	4.73176 E-04	cubic meters
pounds (mass)	0.45359237	kilograms
quarts (US liquid)	9.463529 E-04	cubic meters
square feet	0.09290304	square meters
square inches	6.4516 E-04	square meters
square miles	2.589998 E+06	square meters
square yards	0.8361274	square meters

1 Introduction

This Standard Operating Procedure (SOP) described herein for assessing the properties of nanotechnologies was developed under Task 2: Optimized Scientific Methods of the ERDC/EL Environmental Consequences of Nanotechnologies research program. The primary goal of this Task was to develop robust SOPs for investigating the environmental health and safety (EHS) related properties of nanotechnologies including nanomaterials and products incorporating nanomaterials.

This SOP describes how to determine the surface area of powdered nanomaterials using the Brunauer-Emmett-Teller (BET) nitrogen gas adsorption method, including discussion of the strengths and weaknesses of this method and general guidance for its application. Two materials (nano aluminum oxide and nano graphene) were taken through the steps for BET analysis using a Nova 3200e BET surface area analyzer (Quantachrome Instruments) as a demonstration of the techniques and methods involved.

1.1 Background

1.1.1 History of BET analysis

As particles decrease in size, the ratio of the surface area to the overall volume of the particle increases. As opposed to bulk materials, where the majority of atoms making up the material reside inside the interior volume, many nanomaterials are made up predominantly of surface atoms. Reactions occurring at the surface of a material (e.g., dissolution, oxidation, photo-excitation, etc.) are consequently more pronounced in surface-dominated nanomaterials. Accurate determination of surface area may also provide the capability to predict environmental fate, transformation and dosimetry for hazard assessments (Hull et al. 2012; Kennedy et al. 2015). The hazard relevance of various dose metrics, including surface area, can be determined using the ERDC NanoExpert tool: https://nanoexpert.usace.army.mil/. Additionally, it has been suggested that volume specific surface area may be a more expedient indicator of nano-unique properties than particle size (Kreyling et al. 2010). It is therefore vital to accurately characterize the specific surface area of nano-

materials in order to fully understand the role they play in associated nanotechnologies.

The most commonly accepted means of characterizing surface area is the commonly referred "BET" surface area analysis, named for Stephen Brunauer, Paul Hugh Emmett and Edward Teller, the authors of the 1938 paper originating the theory behind the multi-molecular adsorption process used to determine surface area (Brunauer et al. 1938). Brunauer, Emmett and Teller's work extended the concept of Langmuir (1918) adsorption to multiple molecular layers, allowing measurements of adsorption phenomenon to be correlated to physically relevant properties of a material such as total surface area, pore-size distribution, micro-pore analysis and porosity.

1.2 BET assumptions

As with any theory, it is important to understand the assumptions underlying BET analysis to enable confident use of the data acquired by using this method.

Homogeneous surface. Similar to Langmuir adsorption, BET adsorption assumes that the surface of the material is homogeneous and that adsorption occurs equally across the entire surface with no preferential sorption sites. Each adsorption site is either unoccupied or occupied with a single adsorbate molecule (maximum one molecule per sorption site). The total adsorption can then be expressed as a fractional coverage of the surface.

Limited molecular interactions. Once adsorbed, a molecule can then act as a single sorption site for another gas molecule. No other inter-molecular interactions are considered, including lateral interactions between adsorbed molecules, interactions between gas-phase molecules, or non-sorption interactions between the gas and adsorbed phase molecules.

Local equilibrium. The uppermost layer (either surface-sorption sites or adsorbed molecules) is in equilibrium with the gas/vapor phase molecules. The rate of adsorption is equal to the rate of desorption, with no net change in the number of adsorbed molecules at a given vapor pressure (the system is saturated).

Kinetically limited process. The rate of reaction is limited by kinetic rather than diffusion constraints, and in order for the reaction to proceed,

energy must be provided in the form of heat. For the surface adsorption layer, the amount of energy required is equal to the heat of adsorption, while each subsequent layer is treated as a condensed liquid and the energy required is equal to the heat of condensation, or heat of liquefaction. These kinetic processes are homogeneous across the material (each molecular layer requires the same energy for adsorption).

Infinite adsorption at saturation. Once the saturation pressure (p_o) is reached, the number of adsorbed layers is large enough that the material is assumed to be completely surrounded by condensed liquid-phase adsorbent.

1.3 BET theory

Using these assumptions, the adsorption can be modeled for each adsorbed layer using the Arrhenius equation to determine kinetic rates of adsorption/desorption based on surface coverage fraction. The generalized BET equation for gas adsorption can then be described as follows (Brunauer et al. 1938):

$$v = \frac{v_m c p}{(p_0 - p)[1 + (c - 1)\left(\frac{p}{p_0}\right)]} \qquad (1)$$

Here v is the adsorbed volume of gas, v_m is the adsorbed monolayer volume, p is the equilibrium gas pressure, p_0 is the saturation pressure and c is the BET constant. This equation can then be rearranged as a linear function of p/p_0 as follows:

$$\frac{1}{v[\left(\frac{p}{p_0}\right) - 1]} = \frac{c - 1}{v_m c}\left(\frac{p}{p_0}\right) + \frac{1}{v_m c} \qquad (2)$$

The y-intercept and slope of this function can then be used to solve for the constants c (=slope/intercept +1) and v_m (=1/(slope+intercept). The specific surface area (S, surface area per unit mass) can then be found by the equation:

$$S = \frac{v_m N A}{22{,}400 \times m} \qquad (3)$$

The constant N is Avogadro's number (# of molecules per mole), A is the cross-sectional surface area of a single adsorbed gas molecule, m is the mass of nanomaterials used in the measurement and 22,400 represents the Standard Temperature and pressure (STP) volume of one mole of gas. This surface area is given in units of area/mass (e.g., m^2/g), which can be converted to a volume-specific surface area by multiplying by the material density.

1.4 Scope

This SOP is used to investigate the specific surface area of powdered nanomaterials used in nanotechnologies. It is applicable to a wide variety of nanomaterials classes including fullerenes, nanotubes/wires, metals, semiconductors, composites, organics and virtually any other nanomaterial that can be measured in a dried/powdered form. This document is not meant to replace the operational instructions of any individual BET analysis instrument, but is rather meant as a guidance document for uniform sample preparation and to identify the general procedures common across various instruments. Note that most standard BET methods require several milligrams of dried material, which precludes analysis of suspended particles or small samples (e.g., Nanocomposix wet preps). There are alternative surface area measurement techniques that can overcome some of these challenges, such as the methylene blue adsorption method described by He and Tebo (1998).

2 Terminology

2.1 Related documents

This document is intended to provide a general overview of BET theory, application and use. There are several publications available from the American Society for Testing Materials (ASTM) that provide more specific guidance on the BET analysis of various material types. A few key examples include:

- ASTM B922-10 Standard Test Method for Metal Powder Specific Surface Area by Physical Adsorption
- ASTM D6556-14 Standard Test Method for Carbon Black—Total and External Surface Area by Nitrogen Adsorption
- ASTM C1069-09(2014) Standard Test Method for Specific Surface Area of Alumina or Quartz by Nitrogen Adsorption
- ASTM D1993-03(2013) Standard Test Method for Precipitated Silica-Surface Area by Multipoint BET Nitrogen Adsorption
- ASTM C1274-12 Standard Test Method for Advanced Ceramic Specific Surface Area by Physical Adsorption

2.2 Definitions

- adsorption, v—the process by which atoms, ions or molecules are attracted to and retained at the surface of a solid or a liquid.
- adsorption isotherm, n—a plot of the quantity of adsorbed material versus the equilibrium material concentration (or partial pressure) at a constant temperature.
- monolayer, n—a single, closely-packed layer of atoms or molecules adsorbed to the surface of a material, such that every sorption site is filled with exactly one adsorbed molecule.

- pore space, n—the void or unfilled area within a material that is accessible for reaction and/or adsorption.

- saturation, n—the concentration (or partial pressure) at which no further adsorption occurs with increasing concentration.

2.3 Acronyms

- BET – Brunnauer, Emmitt and Teller
- SOP – Standard operating procedure

3 Materials and Apparatus

3.1 Materials

- Liquid nitrogen
- Helium gas (99.9% pure)
- Nitrogen gas (99.999% pure)
- BET surface area analysis instrument including:
    - Vacuum system (10^{-4} Torr)
    - Heating apparatus
    - Pressure gauge
- Sample holder (bulb) of known volume
- Precise laboratory balance (<0.1 mg precision preferable)

3.2 Apparatus

There are a variety of commercially available BET analysis instruments from many different manufacturers. Some of the more prominent include:

- Micromeritics
- Quantachrome
- Porous Materials, Inc.

4 Procedure

The specific procedure for a BET analysis instrument will vary, and it is recommended that the user follow the instructions provided by the manufacturer. The procedure outlined below is intended to have general applicability. Where instrument-specific instructions are given, note that the instrument used for this analysis is a Quantachrome Instruments Nova 3200e surface area analyzer. In general, BET analysis requires:

- Careful measurement of sample mass
- Degassing the sample using heat, vacuum
- Measuring adsorption
- Analyzing measurement for analysis

A more detailed explanation of these steps follows.

4.1 Specimen preparation

BET analysis requires a clean, pure, dry sample. Prior to analysis, samples can be left in a desiccator or oven at low temperature to ensure that they have as little remaining water vapor as possible.

Once samples are ready for analysis, the next step is to carefully record the mass of sample introduced to the measurement system. Most BET analyzers use glass tube sample holders with rod inserts (to reduce the total volume of the tube). Often the glass holders will have small bulbs at the end of the tube to hold the sample. When measuring out the sample, ensure that there is enough sample to measure an accurate mass, but not so much that it overfills the sample holder. It is often beneficial to record the mass of the clean, empty, dry glass sample tube as well. Record the mass of sample introduced into the tube for later analysis.

Once the sample has been measured into the sample tube and the mass has been recorded, the sample should be de-gassed. This can be done separately by attaching the tube to a vacuum pump and heating the tube to release water vapor (usually ~100–110 °C), or often can be done with the BET analysis instrument. Note that depending on the instrument, some BET analyzers have a separate degassing port and some allow degassing and analysis using the same port. Allow the sample to degas for a mini-

mum of 1–hour (often better to allow several hours, or overnight, especially if the sample was not entirely dry) before starting the analysis.

4.2 Analysis

The analysis is generally performed by the BET analysis instrument, according to specifications input by the user. For specifics, consult the user manual for the individual instrument. For the Quantachrome instrument used in the example analysis, the samples are immersed in a liquid nitrogen bath while the instrument performs the nitrogen adsorption tests. As mentioned in Section 2.2, the adsorption process is kinetically limited, and the cold temperature of the liquid nitrogen facilitates rapid kinetic equilibrium. The instrument must be calibrated using the same sample test tubes that are used for analysis. During the actual test, the instrument will introduce known quantities of ultra-pure nitrogen gas into the tube while recording the pressure (P/P_o), this enables the plotting of equation 2 and determining the parameters therein.

5 Reporting

5.1 Analysis of results

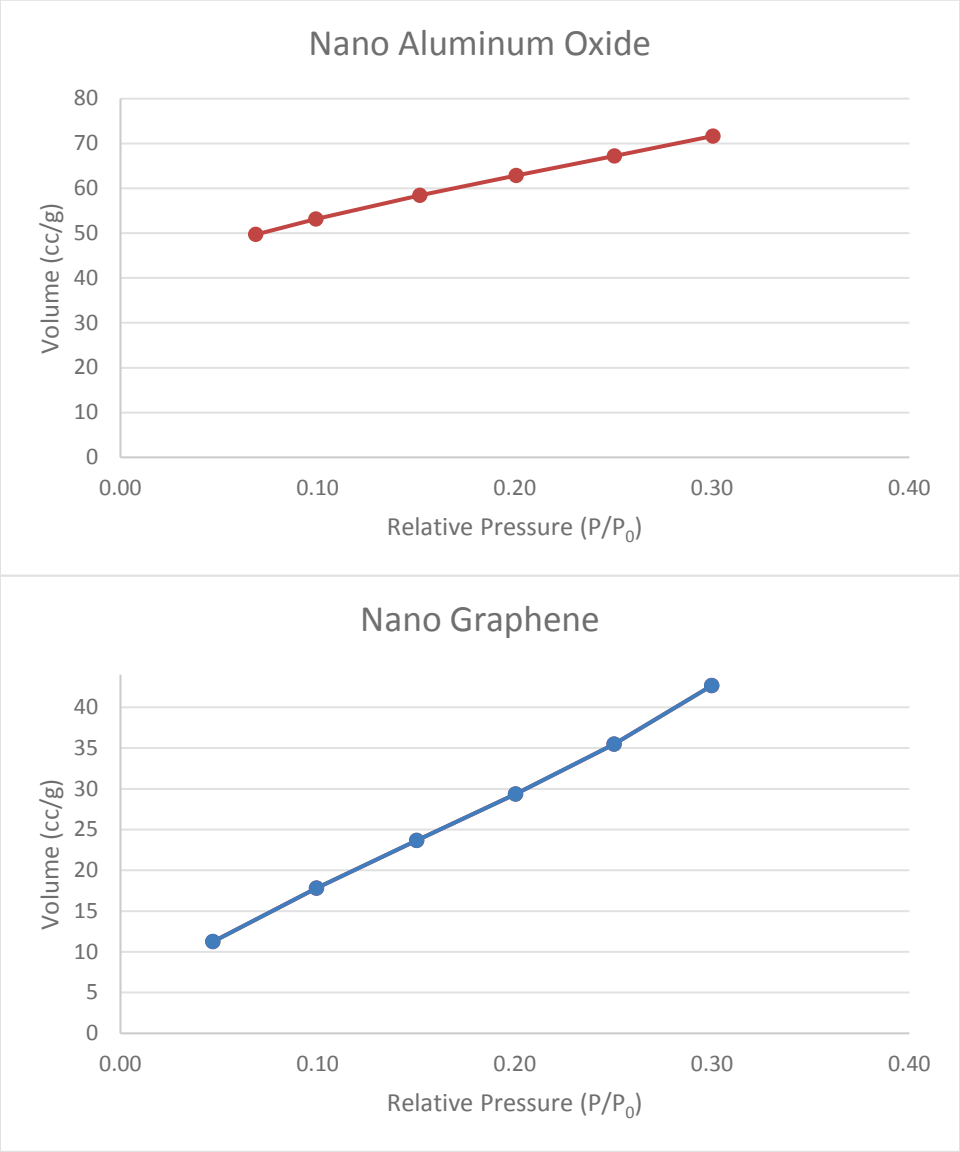
The raw data provided by the BET analyzer instrument is in the form of a table indicating the volume of gas (nitrogen) introduced per mass of sample (cc/g), along with the relative pressure (P/P_0) during analysis. Table 1 shows example data for two samples: a high surface-area nano aluminum oxide and a nano-scale graphene powder.

Table 1. Pressure and volume data from BET analysis of nano aluminum oxide and nano graphene.

Nano Aluminum Oxide		Nano Graphene	
Relative Pressure (P/P0×10-2)	Volume (cc/g)	Relative Pressure (P/P0×10-2)	Volume (cc/g)
6.86	49.69	4.69	11.24
9.91	53.15	9.94	17.81
15.18	58.44	15.0	23.66
20.07	62.85	20.0	29.37
25.05	67.24	25.0	35.49
30.04	71.67	30.0	42.64

Figure 1 shows the plotted data from Table 1.

Figure 1. Volume of nitrogen plotted as a function of relative pressure as measured during BET surface analysis of nano aluminum oxide (top) and nano graphene (bottom), measured using a Quantachrome Nova 3200e surface area analyzer.



5.2 Key results provided

The data in Table 1 can be used to calculate the mass-specific surface area of the material measured according to equations 2 and 3. Most instruments include this calculation automatically as a part of the software. For the data shown in Table 1 and Figure 1, the instrument reported surface areas of 223.13 m^2/g for the aluminum oxide and 167.94 m^2/g for the nano graphene.

In addition, BET can be used in calculations of volume specific surface area, which provides a complementary definition of nanomaterials to the arbitrary size range of 1 to 100 nm. Kreyling et al (2010) provides methods and additional details on the merit of the calculations. They conclude that a volume specific surface area greater than or equal to 60 m^2/cm^3 is a practical definition of a nanomaterial.

References

Brunauer, S., P. H. Emmett, and E. Teller. 1938. Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society* 60(2): 309–319. doi: 10.1021/ja01269a023.

He, L. M., and B. M. Tebo. 1998. Surface charge properties of and Cu (II) adsorption by spores of the marine bacillus sp. strain SG-1. *Applied and Environmental Microbiology* 64(3): 1123–1129.

Hull, M., A. J. Kennedy, C. Detzel, P. Vikesland, and M. A. Chappel. 2012 Moving beyond mass: The unmet need to consider dose metrics in environmental nanotoxicology studies. *Environmental Science and Technology* 46(20): 10881–10882. doi 10.1021/es3035285.

Kennedy, A. J., M. S. Hull, S. Diamond, M Chappell, A. J. Bednar, J. G. Laird, N. L. Melby, and J. A. Steevens. 2015. Gaining a critical mass: A dose metric conversion case study using silver nanoparticles. *Environmental Science and Technology* 49(20): 12490–12499.

Kreyling, W. G., M. Semmler-Behnke, and Q. Chaudhry. 2010. A complementary definition of nanomaterial. *Nano Today* 5(3): 165–168. doi:10.1016/j.nantod.2010.03.004.

Langmuir, I. 1918. The adsorption of gases on plane surfaces of glass, mica, and platinum. *Journal of the American Chemical Society* 40(9): 1361–1403.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
September 2016	Final report	30 Sep 2015 - 30 Sep 2016

4. TITLE AND SUBTITLE

Surface Area Analysis Using the Brunauer-Emmett-Teller (BET) Method: *Standard Operating Procedure Series: Characterization (C)*

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

Jonathon Brame, Chris Griggs

5d. PROJECT NUMBER
405624

5e. TASK NUMBER
A1110

5f. WORK UNIT NUMBER
CD0776

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Environmental Laboratory
U.S. Army Engineer Research and Development Center
3909 Halls Ferry Road
Vicksburg, MS 39180-6199

8. PERFORMING ORGANIZATION REPORT NUMBER

ERDC/EL SR-16-3

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Headquarters, U.S. Army Corps of Engineers
Washington, DC 20314-1000

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES -

14. ABSTRACT

Many of the unique, intrinsic properties associated with nanomaterials arise from the large surface-to-volume ratio of these exceptionally small materials. Surface area properties may also be relatable to environmental fate and hazard implications; therefore, accurately measuring surface area is extremely important for material characterization. The most commonly used method of measuring the surface area of nanomaterials is the Brunnauer-Emmett-Teller (BET) surface adsorption method. This protocol has been developed to describe the theory, application, limitations and sample preparation requirements to enable more accurate, precise and well informed use of the BET method. Two materials (nano aluminum oxide and nano graphene) were taken through a sample BET analysis to provide an example of the methodology and how to apply it for surface area analysis. Although the specific requirements for BET analysis will vary with different instrument models and manufacturers, the purpose of this protocol is to provide a foundational understanding of the steps involved, how to perform them in a repeatable and reliable manner, and to provide the theory behind the analysis.

15. SUBJECT TERMS

Surface area, BET, adsorption, nanomaterial, Nanotechnology; Surfaces--Areas and volumes, Nitrogen--Absorption and adsorption, Aluminum oxide; Graphene, Nanostructured materials, Environmental risk assessment, Materials--Research

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Jonathon Brame
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER *(include area code)*
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	SAR	20	601-634-4204