Standard Activated Carbon Test Methods Solve Problems

Part 2

By George Nowicki, Henry Nowicki,
Wayne Schuliger and Barbara Sherman

Introduction

In the first article in this series, we covered some advanced activated carbon (AC) test methods.[1] The highlight of that article (and the take home lesson) was the advanced test method called Gravimetric Rapid Pore-Size Distribution (GRPD), invented by Dr. Mick Greenbank. GRPD delivers information about commercial activated carbons and other new research sorbent products and composites that no other testing method provides. The GRPD test method is important to the future of the activated carbon industry and it is worthwhile to understand the benefits.

This article is designed to focus on standard testing methods for solving AC problems for the activated carbon industry. Although the GRPD method can provide information not attainable from standard methods, the industry often relies on them to conduct business. Standard methods presented in this and later articles are presented in a manner that will show how standard methods can be applied by AC users to better manage purchasing and to troubleshoot working activated carbon adsorption systems. AC adsorbers range from less than a gram in cigarette filters to tons at municipal drinking water plants. Standard testing methods are relevant to all sizes of activated carbon adsorption units.

Standard test methods

ASTM International Activated Carbon Standards Committee volunteers are responsible for the greatest contributions to activated carbon industry development. The International test methods for activated carbon were developed under the jurisdiction of ASTM Committee D-28. Committee members have created the most widely used test methods for buyers and sellers of these materials. Test methods are updated from time to time and new test methods are slowly added to the standards. See Table 1 for the latest version of ASTM test method numbers and titles for activated carbon.

ASTM provides testing methods for many different types of materials to facilitate buyer-seller specifications for a wide variety of commercial materials. Standard test methods for AC are used by manufacturers, users and academia in characterizing and buying activated carbon. ASTM methods cover the proper way to perform the test, the required equipment, repeatability and test precision and how to interpret the data.

Activated carbon misunderstandings

Misunderstandings are a part of life. A consensus on word usage is a way to help decrease misunderstandings.[2] Usage of the terms *virgin* and *spent* or *exhausted* as related to activated carbon status can be misleading. *Unused* and *used* are the terms recommended by ASTM International.

Some authors state that chlorine taste and odor removal by activated carbon is a physical adsorption phenomenon, when it is actually a chemical reaction between chlorine and activated carbon. This can easily be demonstrated by treating a few particles of AC with five milliliters of hypochlorous acid, such as bleach. Particles will disintegrate and degrade to a dark brown solution. Pure chlorine gas will physically adsorb and desorb on activated carbon when there is absolutely no water present. When traces of water are present on carbon, chlorine chemically reacts with the carbon and is converted to chloride. Chlorine is an oxidizing agent and carbon is a reducing agent, similar to copper metal. At low concentrations, chloride adds no taste to drinking water. Standard test methods are available to provide AC capacity for chlorine taste and odor reduction in both used and unused activated carbons.

The phenol number test method has been removed from the list of accepted test methods because it gives erratic results, although it is still quoted by some scientists as a useful test method. Test results have unacceptable variances due to the amount of oxygen in the test solution; most of the oxygen comes from the test carbon samples. AC micro-pores concentrate atmospheric oxygen two to three times above the ambient atmospheric pressure. Phenol is oxidatively polymerized on the carbon surface in the presence of oxygen, producing a chemical reaction in addition to physical adsorption to explain removal of phenol from the solution. The original phenol number test method was based on a five-point isotherm and assumed physical adsorption. It was later learned the chemical reaction was dominant. This test should not be used in purchasing decisions. A good rule is to avoid the use of an unstable chemical as the basis of a test method, if it can be avoided.

Long-term storage of ACs can dramatically change their performance. Atmospheric oxygen and contaminants can negatively impact carbon performance; organic air contaminants can fill adsorption spaces in the carbon and oxygen can slowly oxidize (add oxygen functional groups) AC. Some examples are organic acids, peroxy acids, ketones, aldehydes, epoxides, anhydrides, lactones, esters, hydroxyl groups and other oxygen-containing groups. Treating activated carbons with ozone and other strong oxidizing agents provide surface modifications. Surface-modifier chemicals accelerate formation of oxygen functional groups in the starting activated carbon. Oxygen-containing organic functional groups are added to the periphery of the graphitic platelets, increasing the ion exchange and aqueous ionic metal attractions and possibly degrading selected physical organic adsorptions.

Another misunderstanding is that lower apparent densities (grams per cubic centimeter of material) are better than higher apparent densities (AD) because they adsorb more iodine or butane in standard ASTM activity test methods. Lower AD are produced when manufacturers increase activation furnace residence time and pluck off more carbon atoms to create larger adsorption spaces. Manufacturers produce a family of activated carbons with densities between 0.4 to 0.8 grams per cubic centimeter by controlling the time spent in an activation furnace. These lower density products have larger adsorption spaces, due to slower transit through the furnace; on average, lower densities mean more weakly adsorbate binding adsorption sites, loss of some high-energy binding sites and decreased mechanical strength. Activity numbers and mechanical strength are inversely related for a given type of activated carbon. Higher iodine and butane activity can be attained at the cost of lower high-energy binding site pore volume, and decreased mechanical strength and bulk AD. In today's regulatory market, higher density is often preferred for applications that involve adsorption of small molecules that are difficult to remove, such as diclorometh-ane and trihalomethanes, because they need high-energy adsorption sites to attract and hold them to the carbon surface. GRPD is used to determine the number of high- and low- energy sites. Iodine and butane activity numbers provide total binding sites and do not provide the distribution of binding sites. Theoretically, these higher apparent density carbons should cost less because they go through the activation furnace faster—all other manufacturing costs are independent of apparent density.

Apparent bulk density test method

Bulk received and dry apparent densities are simple and very useful ASTM tests that require low-cost equipment with low maintenance. Laboratories should conduct these tests on all incoming samples; users should request these tests on their projects. As the name received AD implies, it defines the material received at the testing laboratory. Labs need to assure that all parts of the received sample have an equal opportunity to be in the test sample, which is a 100-milliliter volume. Test results are obtained by a controlled free fall of particles into a 100-milliliter graduated cylinder, as defined in the ASTM test method. If the particles in the process application get reduced in size or gain weight by adsorbing organics, AD goes up. Dry apparent density is the result of heating the sample for three hours at 150°C and performing an AD. Both received and dry apparent density tests are reported in grams per milliliter (mL). Grams per cubic centimeter can easily be converted to pounds per cubic foot by multiplying the AD by 62.43.

Some sources of AD measurement error and solutions are provided. Labs do riffling and the sampler gets multiple samples of the incoming load for AD. In laboratory testing, slow free fall of irregularly shaped AC particles and not shaking the 100 mL graduated cylinder are critical. Sources of error, from improper filling techniques or shaking the graduated cylinder while filling, can greatly affect AD results. New analysts should observe that inverting the graduated cylinder after completing an AD test results in a five to 15 percent volume increase.

Moisture test methods

There are two approved ASTM test methods to determine AC moisture. The oven-drying moisture determination test method uses received and dry apparent densities to determine the percent of moisture on AC. Oven-drying should only be used when water is the only volatile matter present and when the carbon is not heat sensitive. Some carbonaceous materials change size and shape upon heating in air. The Dean-Stark moisture determination test, which uses the xylene-extraction method, is appropriate when the sample is suspected to contain nonwater-miscible volatile organic compounds in addition to water or if it is suspected that the activated carbon sample may be heat sensitive. The Dean Stark test apparatus is shown schematically in Figure 1.

Opening a home point-of-use (POU) device and passing water contents through a coffee filter will show carbon particles agglomerated together. After a few hours of air drying, the particles become free flowing. However, the particles are still filled 18 to 25 percent on a weight-weight basis with water. The intra-particle water can be removed by oven drying and organic solvent extraction. A typical specification between buyer and seller is one to two percent moisture.

Table 1. ASTM test method numbers and titles for activated carbon

D 2652-94 (1999)	Terminology Relating to Activated Carbon
D 2854-96	Test Method for Apparent Density of Activated Carbon
D 2862-97	Test Method for Particle Size Distribution of Granular Activated Carbon
D 2866-94 (1999)	Test Method for Total Ash Content of Activated Carbon
D 2867-99	Test Methods for Moisture in Activated Carbon
D 3466-76 (1998)	Test Method for Ignition Termperature of Granular Activated Carbon
D 3467-99	Test Method for Carbon Tetrachloride Activity of Activated Carbon
D 3802-79 (1999)	Test Method for Ball-Pan Hardness of Activated Carbon
D 3803091 (1998)	Test Method for Nuclear-Grade Activated Carbon
D 3838-80 (1999)	Test Method for pH of Activated Carbon
D 3860-98	Practice for Determination of Adsorptive Capacity of Activated Carbon by Aqueous Phase Isotherm Technique
D 4069-95 (1998)	Specification for Impregnated Activated Carbon Used to Remove Gaswous Radio-Iodines from Gas Streams
D 4607-94 (1999)	Test Method for Determination of Iodine Number of Activated Carbon
D 5029-98	Test Method for Water Solubles in Activated Carbon
D 5158-98	Test Method for Determination of the Particle size of Powdered Activated Carbon by Air Jet Sieving
D 5159-91 (1997)	Test Method for Dusting Attrition of Granular Activated Carbon
D 5160-95 (1998)	Guide for Gas-Phase Adsorpion Testing of Activated Carbon
D 5228-92 (1996)	Test Method for Determination of the Butane Working Capacity of Activated Carbon
D 5742-95	Test Method for Determination of the Butane Activity of Activated Carbon
D 5832-98	Test Method for Volatile Matter Content of Activated Carbon Samples
D 5919-96	Practice for Determination of Adsorptive Capacity of Activated Carbon by a Micro-Isotherm Technique for Adsorbates at ppb Concentrations
D 6385-99	Test Method for Determining Acid Extractable Content in Activated Carbon by Ashing

Iodine activity test method

All activated carbons are not the same, although this ASTM test method often indicates that vastly different carbons are the same. This is due to ASTM iodine numbers and butane activity numbers—both measure the total pore volume in samples. The iodine number indicates the amount of iodine adsorbed (in milligrams per one gram of dry powdered activated carbon) under controlled testing conditions.

AC users often apply the iodine test to help make decisions about when to replace used carbon. Carbon does not last forever and needs to be replaced with unused AC periodically to maintain specified process control. For example, the installed iodine number is 1,000. Users should periodically take samples out of working AC beds for iodine number tests. When iodine numbers hit 400, unused AC is added and the replacement cycle begins again.

GRPD is the most practical and cost effective test to determine cumulative and differential pore volumes as a function of adsorbate(s) binding strength (in units of calories per cubic centimeter) for the specific carbon that will be used in an application. In previous tests and reports on ten samples of activated carbon for ASTM iodine number and BET surface areas, all samples had similar iodine numbers and BET surface areas. When the same ten samples were tested using GRPD tests, some of the samples were quite different in high-energy binding sites. ASTM iodine, butane and carbon tetrachloride tests only measure total pore volume; they do not provide information that GRPD reveals about relative proportions of micro-, meso- and macro-pores. This is required information to measure carbon's ability to adsorb compounds that are in the application(s). Macro-pore sizes are best characterized by mercury intrusion; mercury does not spread on the carbon surface because its cohesive forces are stronger than its AC adsorptive forces.

Butane activity test method

ASTM butane activity numbers and predecessor carbon tetrachloride (CTC) tests are ratios (in percent) of butane or CTC weight adsorbed by an activated carbon to the weight of the AC sample. Iodine number, butane activity and carbon tetrachloride testing are used to determine the relative activation level and general total adsorption capacities of activated carbons by measuring initial total pore volume for unused AC or remaining total pore volume for used AC. These tests are a relative indicator of the porosity and surface area of an AC sample but these test results should not be generalized. Making a purchasing decision based solely on an iodine or butane number from different vendors is often not good judgement. However, it is common for purchasing agents who do not understand the fundamentals of AC to use this approach. Singly comparing iodine or butane numbers from different vendors and cost-per-unit volume or pound is still done today. Popular ASTM activity tests do not differentiate total pore volume into its incremental adsorption binding energies and corresponding partial pore volumes with different binding energies like the GRPD provides.

Figure 2. Particle sizing software output

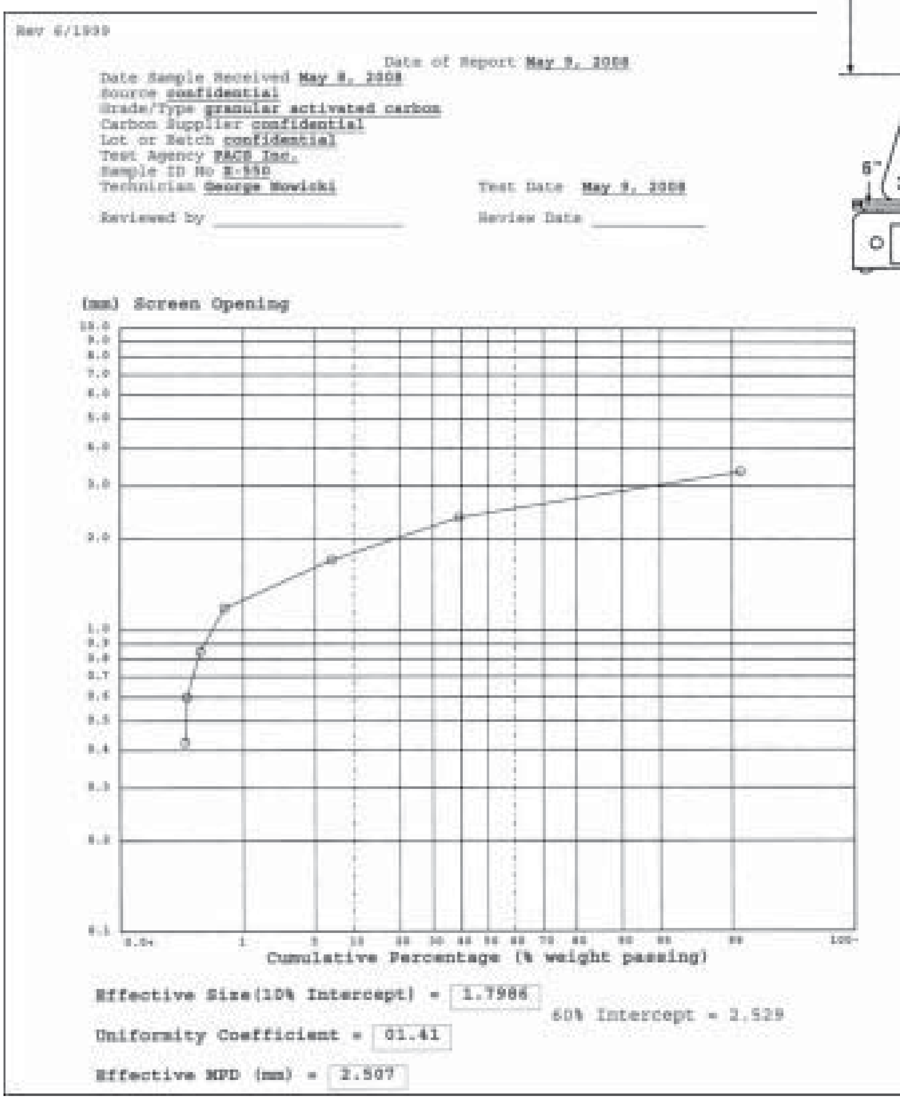
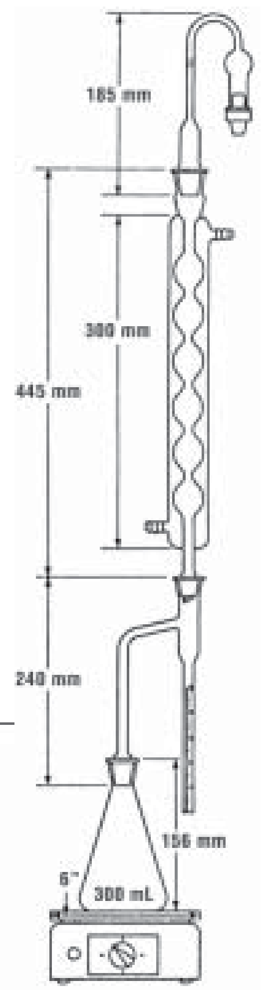


Figure 1. Moisture determination apparatus



The GRPD test should be used to compliment the ASTM butane and iodine activity tests. Large numbers of samples are run for iodine and butane. For example AC manufacturers and reactivators take samples off their furnaces and do AD, iodine number and butane activity tests to control their processes; AC users also make replacement decisions based on these activity lab numbers.

Quality assurance measures

It is good laboratory practice (GLP) to have available standard, known-value activated carbon materials for the test methods being provided. Standards are used on a regular schedule to assure test performance. Standards include materials for the iodine number, butane activity, butane working capacity, carbon tetrachloride activity number, received and dry apparent densities and both high and low molasses number decolorization standard activated carbons. Without representative test samples, the value of test results is diminished.

Attaining a representative sample is the most important part of performing laboratory testing, yet laboratory technicians performing the testing are typically not directly involved in sample collec-

Figure 2. Particle sizing software output (cont'd.)

Rev 6/1999

Date of Report **May 9, 2008**
Date Sample Received **May 8, 2008**
Source **confidential**
Grade/Type **granular activated carbon**
Carbon Supplier **confidential**
Lot or Batch **confidential**
Test Agency **FACS Inc.**
Sample ID No **X-550**
Technician **George Nowicki** Test Date **May 9, 2008**

Reviewed by ____________________ Review Date ____________

Effective MPD Calculation

U.S.S. Sieve No.	Weight Retained	Percent Retained	Mean Opening (mm)	Weighted Average
4 x 6	0.80	0.80	4.06	3.25
6 x 8	60.10	60.09	2.87	172.46
8 x 12	32.30	32.30	2.03	65.57
12 x 16	6.20	6.20	1.44	8.93
16 x 20	0.30	0.30	1.02	0.31
20 x 30	0.10	0.10	0.72	0.07
30 x 40	0.01	0.01	0.51	0.01
Pan	0.20	0.20	0.36	0.07
Total	100.01	100.00		250.67

Effective MPD (mm) = 2.507

Effective Size and Uniformity Coefficient

U.S.S. Sieve No.	Ell Tab 1 Opening (mm)	Pecent Retained On Sieve	Cumulative Percent Passing through Sieve
6	3.350	0.80	99.20
8	2.360	60.09	39.11
12	1.700	32.30	6.81
16	1.180	6.20	0.61
20	0.850	0.30	0.31
30	0.600	0.10	0.21
40	0.425	0.01	0.20
- 40	0.000	0.20	0.000

Uniformity Coefficient = 1.41

Effective Size = 1.7988

tion. Sample collectors should collect samples from the top, middle and bottom of adsorbers or supersacks. When AC samples arrive for testing, it is necessary to riffle them down to the required test size sample for the specific test to be performed. Riffling samples gives all the particles an equal chance of being part of the test sample. Grinding particles to a powder is another way to get representative samples for testing. Grinding is most important when the test uses a small amount of material and results depend on attaining equilibrium between solid and liquid phases.

When laboratory management uses commercial known standards or other sources of known materials, it is easy to assure the laboratory is in statistical control. This means there is evidence that known materials are tested on a defined schedule and results for each parameter fall within an acceptable range around the true value for that test parameter. Every test method has an acceptable precision.

Known standards are run as blind and double-blinds. In blind-standard testing, the analyst knows an unknown standard is being tested. With a double-blind standard, the analyst believes another regular sample is being tested but it is a known standard. For example, iodine numbers are reported in milligrams of iodine adsorbed per gram of dry powdered activated carbon. Butane and carbon tetrachloride are reported as grams adsorbed per 100 grams of received sample activated carbon. Butane working capacity is reported as the difference between butane activity and the amount blown off with a defined air stream through the butane-saturated carbon, in grams per 100 grams carbon. The molasses number has no units; it is a ratio of molasses decolorization optical density of the standard, divided by sample optical density, after standard contact with the same standard molasses solution, times 100.

Acquiring testing methods

Individual test methods or a book containing all of the AC tests are available from ASTM and a table listing the latest ASTM test methods titles and numbers is provided here (see Table 1). Individuals who order laboratory tests typically use the D- method numbers that show the latest revision. Test methods for AC begin with the letter D and are followed by the test method number, a hyphen, the year the test method was originally developed and the year that the test was last updated.

References

1. Henry Nowicki *et. al.*, Advanced Activated Carbon Test Methods. *Water Conditioning and Purification*, March 2008, p. 80-86.

2. George Nowicki *et. al.*, Activated Carbon Glossary. *Water Conditioning and Purification*, February 2008, p. 88-94.

About PACS

Professional Analytical and Consulting Services, Inc. (PACS) is in its third decade of providing activated carbon services and other services to engineers and scientists: laboratory testing, R&D, consulting, training and conferences. PACS hosts the International Activated Carbon Conference and Courses programs in Pittsburgh, Pa. every October. Information about the firm's services are available on its website www.pacslabs.com or by phone at (724)-457-6576.

About the authors

H. George Nowicki III, B.S., B.A. is a laboratory technician and new business developer for PACS. He can be reached at email: Georgepacs@aol.com or by calling (724) 457-6576. Henry Nowicki, Ph.D. and M.B.A. provides the introductory course for the Activated Carbon School titled "Activated Carbon Adsorption: Principles, Practices, Applications and Opportunities". Dr. Nowicki directs the day-to-day Testing and Consulting services for PACS. He can be reached at (724) 457-6576 or email: Henry@pacslabs.com and website: www.pacslabs.com. Wayne Schuliger, P.E. provides the PACS short course titled "Design, Operation and Trouble Shooting Activated Carbon Adsorption Systems". He utilizes his 40 years of activated carbon adsorption engineering experiences to provide consulting services and directs the technical activities at PACS engineering services. He can be reached at email: Waynepacs@aol.com. Barbara Sherman, B.A. and M.B.A. directs the day-to-day operations of 60 different PACS short courses and the bi-annual International Activated Carbon Conference and Courses program. In 2009 the IACC conferences are in Johannesburg, South Africa in May and Pittsburgh, Pa. in October in 2008 and 2009. She can be reached at Barb@pacslabs.com.