Activated Carbon: Advanced Test Method

By Henry Nowicki and Barbara Sherman

Introduction

Development and application of advanced test methods can reveal important new information about activated carbons and other sorbents. Table 1 contains a list of sorbent information opportunities with an advanced non-classical testing methodology. Standard and authoritative test methods provided by ASTM and AWWA have served the activated carbon industry customer well. In the early history of activated carbon usage, we were interested in removing milligrams per liter of target compounds. Today, many customer applications require the removal of micrograms per liter, thus necessitating new activated carbon test methods as described here. Classical standard activated carbon test methods information is extended with the determination of the sorbents adsorption energy distributions (AED). Most AED to date have been made with activated carbons, but other sorbents have been run at our laboratory.

The purpose of this article is to inform water and air sorbent treatment users and manufacturers about an advanced test method to evaluate the adsorption performance of activated carbons and other sorbents. To be truly scientific, theories must be predictive not only in the sense of explaining things we already know, but must somehow predict 'risky or uncertain' in the sense of suggesting physical phenomena not previously observed or likely to have been anticipated for activated carbons or other materials.

Dr. Mick Greenbank, the inventor and developer of this sorbent testing methodology, has provided the history and examples of case studies for this

To be truly scientific, theories must be predictive not only in the sense of explaining things we already know, but must somehow predict risky or uncertain outcomes in the sense of suggesting physical phenomena not previously observed or likely to have been anticipated for activated carbon material.

Table 1. Applications and advantages for adsorption energy distribution (AED) determinations

- Differentiates activated carbons with the same ASTM Iodine Number
- Provides Freundlich aqueous- and gas-phase isotherms with target compounds
- Monitors the degree of reactivation, regeneration and initial activation level
- Differentiate activated carbon supplies from a single production batch from a supply of combined batches of activated carbons lots
- Provide information about the location of chemical impregnants in activated carbon structure
- Determine the activity of the outside versus the inside of individual GAC granules
- Determine the GAC penalty of carbon blocks compared to free flowing GAC
- Enable the determination of the GAC raw material source: coal, wood, coconut shell or other based materials
- Inventors of new activated carbons need to compare their materials against the world of activated carbons, to quickly determine potential markets
- Facilitates a marketplace survey for opportunities a client's new activated carbon offers
- Characterization of a family (0.2-0.8 g/cc apparent densities) of activated carbons
- Reveals the adsorbtion energy distribution site(s) in low iodine number sorbents
- AED determinations help clients to select the best activated carbon for each application
- Demonstrates your knowledge and willingness to use the best test methodology
- Improved data quality and decisions: precision and accuracy improved which allows small sorbent mass for testing and small differences to be meaningful
- Thin GAC beds, of only 3-5 granules, can be evaluated with this advanced test method. Granules against the containing barrier have been compared with granules not against the barrier in the middle of the thin bed
- Forensic analysis cases; is it new or used GAC? What is the raw product source: wood, coconut shell, bituminous coal, etc.
- Data from this method has agreement with Greenbank's physical model for activated carbons which needs to replace old structural models for activated carbons
- Activity as a function of particle size is possible
- Difference in sorbent performance between thermally cleaned and not cleaned received GAC
- Provides a thermogravimetric analysis chromatogram from the sorbent cleaning step
- Provides a thermogravimetric analysis of the sorbent
- Provides a simultaneous BET surface area and pore size distribution determination in addition to characterization of the sorbent adsorption energy distribution
- Can obtain adsorption binding site(s) information in a wide variety of materials besides activated carbons
- This method can be automated and comply with GLP and GMP standards
- Determines the location of chemical impregants of concern: surface, specific areas, overall evenly or not evenly spread in GAC
- The instrument could provide mass spectral analysis of the initial off gases and desorbed gases

methodology,[1,2] which he refers to as Gravimetric Rapid Pore Distribution (GRPD). We are using the functional name adsorption energies distribution (AED) here, which avoids the word 'pore', perhaps the most often used misleading word in adsorption fields.

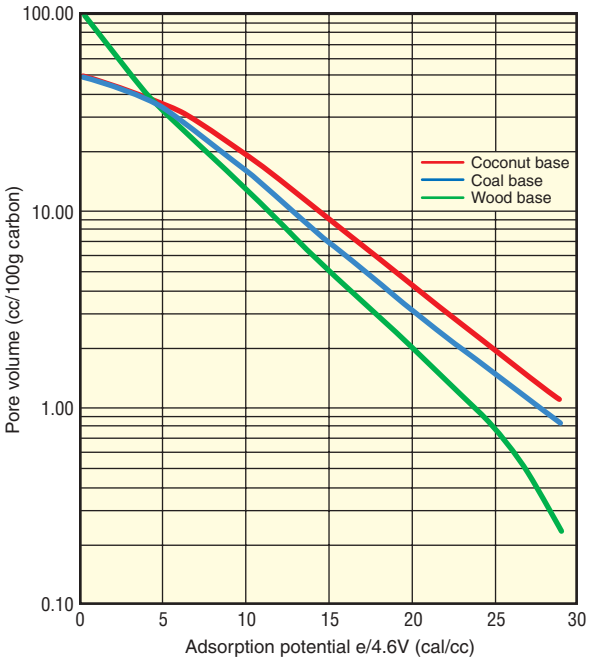
Test procedure outline and data reduction

It is now possible to determine the adsorption energies distribution (AED) in activated carbons and other sorbent materials. All activated carbons are not the same. Some adsorbates from water and/or air are more difficult for some activated carbons to remove. Activated carbons can have widely varying performance in specific client applications even though the carbons have the same iodine number. Determination of the AED has helped clients select the best carbon in these difficult applications.

Figure 1 shows an AED example output, pore volume on the Y-axis ordinate versus adsorption energy on the X-axis abscissa, for three types of activated carbons: wood, bituminous coal and coconut shell based materials. Our adsorption energy distribution determination is a vapor-phase gravimetric based method.

The AED method enables over a thousand adsorption and desorption data points, covering eight orders of challenge gas concentration in relative pressure (isothermal basis or relative ratio of sorbent mass to the available challenging adsorbate) and three orders of magnitude in activated carbon loading. The mass adsorbed was also divided by the mass of clean sorbent to generate a weight percent loading for easier comparisons.

Figure 1. Carbon characteristic curves (cumulative)



The cumulative raw data for three carbon types are plotted in Figure 1. Before analysis begins, the sample is cleaned thermally in a stream of inert nitrogen or argon gas; this provides loss of water and volatiles. After cleaning, the challenge adsorbent gas C134a [also known as 1,1,1,2-tetrafluoroethane (TFE)] is introduced and the loading increases as the temperature is decreased, with an automated temperature program. The sample temperature is decreased to a point near, but above, the TFE condensation temperature. High temperature has minimal carbon loading and low temperature has maximum activated carbon TFE loading. Then the temperature is increased back to the starting high experimental temperature automatically, to remove adsorbate.

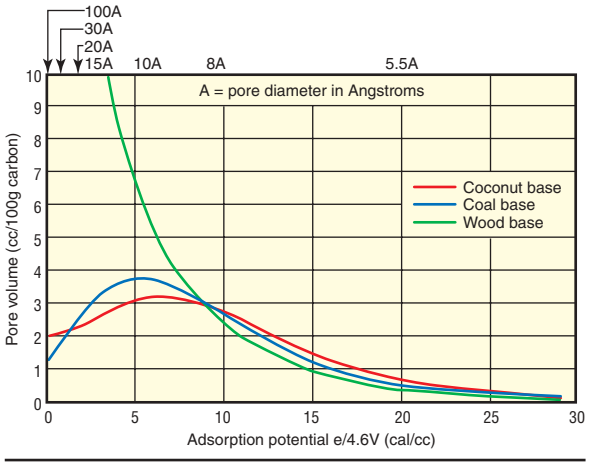
The condensed TFE adsorbate will fly out of the adsorption space when the energy delivered by increasing temperature rise is more than the adsorption energy, holding adsorbate to the sorbent surface. The adsorption and desorption curves cannot be distinguished in most activated carbon runs. Figure 1 contains both the adsorption and desorption curves for the three types of carbons. None of these commercial carbons reveal any hysteresis, typical of carbons. Hysteresis is the failure of a property that has been altered by an external agent (heat in our case) to return to its original value when the cause of the alteration is removed. Figure 1 shows that the loading and unloading of inert adsorbate is independent of the path. Figure 2 provides the differential adsorption energy in calories per cubic centimeter of adsorption space (cal/cc) distribution for these three carbons. The differential presentation of adsorption energies provides the absolute value at each energy on the x-axis.

Performance prediction models

From the three characteristic curves shown in Figure 1 (the relationships of loading and unloading sorbate, pore volume versus adsorption potential energy) adsorption performance predictions can be made. To do performance predictions, the characteristic curve data are fit to a polynomial equation, a mathematical expression of two or more terms. The polynomial equations are one of the main outputs of this advanced test method. These polynomials presented below fully describe all of the physical adsorption properties of these carbon samples. Every sorbent run in this method yields a diagnostic polynomial equation.

The characteristic curves are the only carbon related information required to predict physical adsorption performance using the Polanyi–Manes Adsorption Potential theory. In the early 1900s Polanyi initiated this adsorption model as his doctoral thesis. Upon your request we can send you a 70-page technical paper which descirbes the Polanyi-Manes model. Dr. Milton Manes and Dr. Henry Nowicki have given a 16-hour course (for the last 19 years) which fully covers the Polanyi model. It is agreed by most to be the best available model to handle heterogenous adsorbents, like activated carbons. These single and multicomponent, gas- and liquid-phase, computer models are used to predict carbon performance once the characteristic curves in Figures 1 and 2 are obtained. To do performance predictions, the data are fit to a polynomial equation. These individual polynomials fully describe all the physical adsorption properties of these individual carbon samples. The three polynomials derived from the tabular data used to construct Figure 1 are below. From these polynomials, Freundlich isotherms can be computer generated using the Polanyi-Manes model. These isotherms are not shown here (See Table 2).

Figure 2. Differential characteristic curves (continued)



In the polynomial equations in Table 2, 'y' is the common logarithm of pore volume in cc/100 g carbon and 'x' is the adsorption potential energy in cal/cc.

The graphical presentations in Figures 1 and 2 reveal the relative amount of high adsorption energy sites in the 25-30 calories per cubic centimeter range of adsorption space and the intermediate adsorption energy sites 25-10 down to the low adsorption energy sites 0-10 calories/cc.

Gas and aqueous adsorption isotherms

The characteristic curves are also mathematically converted into adsorption isotherms using the Polanyi programs. In a typical 17-21-page report using this advanced test method, we provide three aqueous isotherms for a range of adsorbate adsorbabilities. Methyl-tertiary-butyl ether (MTBE) is a weakly adsorbed compound; benzene is more strongly adsorbed and phenol at pH 7.0, the strongest adsorbed of the three, has the highest loading capacity. The typical report includes isotherms for these three compounds. The client can rapidly compare the expected adsorption perfor-

mance of their sorbent material against known commercial sorbents. MTBE is difficult to remove from water because it needs high energy binding sites in its sorbent. Phenol binds to a wide range of binding energy sites. To pick the best activated carbon for a MTBE application, the activated carbon user needs a carbon with the highest (25-30 cal/cc) number of adsorption sites.

Table 2. Polynomial equations

Carbon name	Characteristic curve polynomial – 3rd degree
Coconut-base	y = 5.6334E-05x3 – 3.0968E-03x2 – 1.3312E-02x + 1.6731E+00
Coal-base	y = 5.8955E-05x3 – 2.8880E-03x2 – 2.6182E-02x + 1.7029E+00
Wood-base	y = -6.3875E-05x3 + 2.5948E-03x2 – 1.1114E-01x + 2.0183E+00

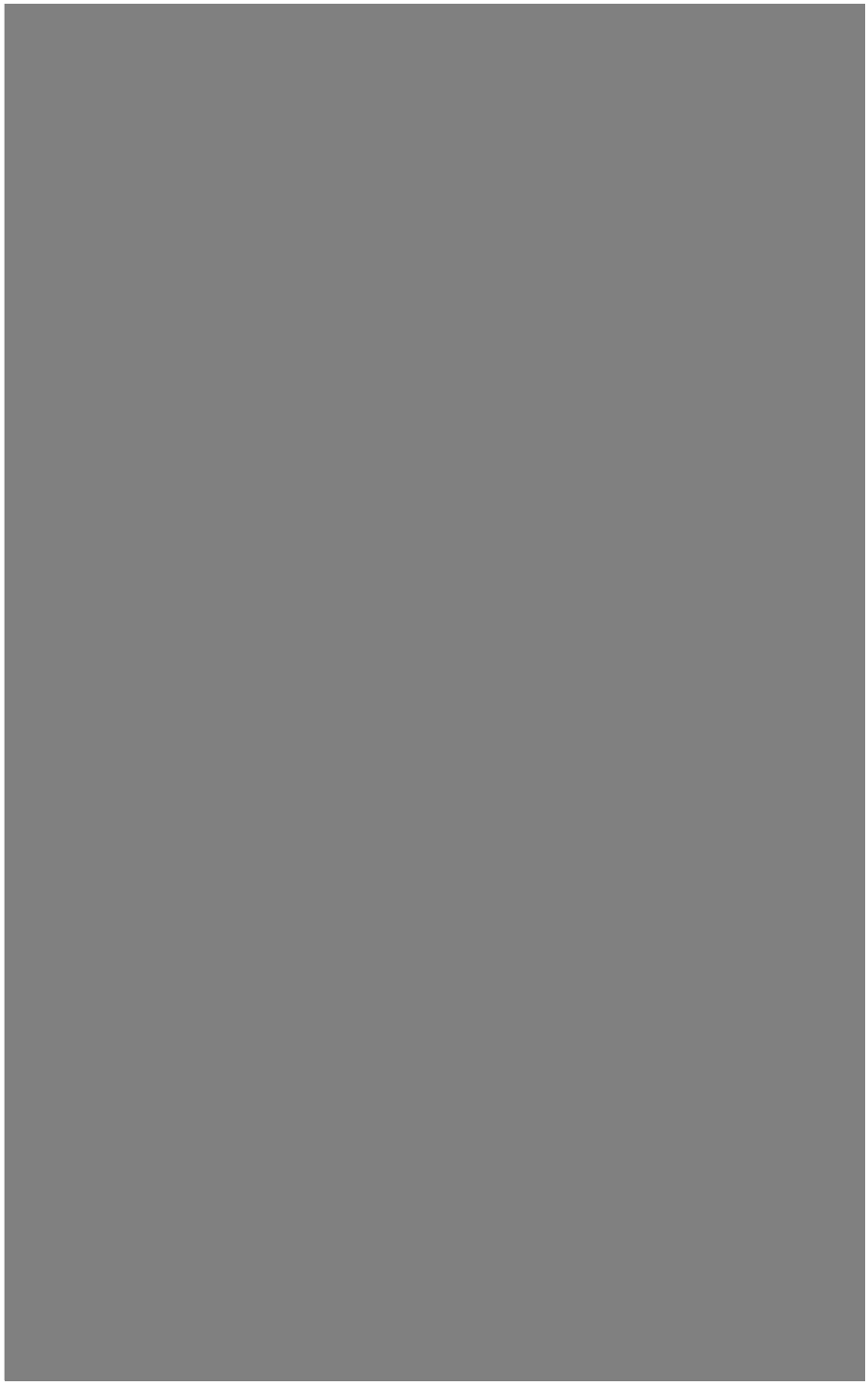
New capabilities for you

This method provides the best precision and accuracy, due to the inherent gas-phase basis of the method. The method is based on continuous mass measurement of the clean sorbent sample, gaining and losing mass, to four decimal places as the temperature is changed. The challenge gas concentration is effectively changed over eight orders of relative concentrations. This method uses an inert, stable gas-phase challenge which does not have the interferences that the water based reactive and unstable iodine number method exhibits. It provides the opportunity to test single granules, or parts of the granule, due to the method's low mass sensitivity. The method differentiates binding sites from high energy to low energy sites; other test methods only provide the summed final total capacity. The method uses a high purity, inert, safe, globally available and low cost challenge gas: 1,1,1,2-Tetra-fluoroethane (TFE). The method is highly automated, thus removing subjectivity of the operator. The method is based on a foundation of classical thermochemistry principles and other long-tested and used scientific advancements, which we will discuss in a later publications (or make available upon your request).

Recommendations

The authors and industry colleagues are not recommending abandonment of the classical ASTM and AWWA test methods in favor of this advanced test method. The authors *are* recommending that the activated carbon industry (users and manufacturers) become aware of this method and use it in critical and sensitive activated carbon applications. Many applications and problems need this advanced method, because many problems are not completely solvable by existing classical methods. Some examples where this new advanced test method is useful are listed in Table 1.

Running a few sorbent samples and understanding the data output in a typical 17- to 21-page report is a good and recommended start. It is almost always wise to get ahead or keep up with the latest scientific advancements, which are valuable to your core business. This method is an important part of the future for the activated carbon industry. In 2006 and beyond, the authors will facilitate presentations on the applications listed in Table 1 and help provide a commercial instrument to spread this test method globally.[3,4] Widespread use of this advanced method is expected to develop many more applications and improve the sorbent industry market size.



What is acceptable to what is achievable

In order to provide users with better sorbents, advanced testing methods are needed. Present test methods cannot uncover the best activated carbon for many specific activated carbon user applications. A few years ago we provided this method on 12 GAC samples from several vendors for a municipal drinking water facility. We discovered the best GAC for their application; all had essentially the same iodine number. Interestingly, the best GAC for the client was one of the lowest priced, not the highest priced vendor GAC. Other examples of the benefits of the new advanced test method will be provided.[3, 4]

This is what the modern concept of quality aims to eliminate; namely, the transition from what is acceptable to what is achievable. Historically, new testing methods have been major contributors to our scientific advancements. We expect this advanced activated carbon and other sorbent test method to improve the industry.

References

1. Greenbank, Mick, *History and Development: Gravimetric Rapid Pore Distribution (GRPD) Method*. International Activated Carbon Conference (IACC-16) Pittsburgh, Pa., Oct. 6-7, 2005.

2. Greenbank, Mick, *Case Studies and Applications for the GRPD Technology*, IACC-16, Pittsburgh Pa., Oct. 6-7, 2005.

3. Nowicki, Henry, *Determination of Adsorption Energy Distributions in Activated Carbons and other Sorbents*. Pittsburgh Conference, Orlando, Fla., 200-20P. March 12, 2006.

4. Nowicki, Henry, *Advanced Test Methods can Help the Activated Carbon Industry.* 18th International Activated Carbon Conference & Courses (IACC&C-18) Pittsburgh, Pa., Oct. 19-20, 2006.

About the authors

S *Henry Nowicki, Ph.D./MBA directs and provides testing and consulting for PACS: Testing, Consulting and Training. Dr. Nowicki is in his second decade of providing products and services for the activated carbon industry: routine and non-routine stationary and mobile laboratory testing, R&D for new sorbents and technologies, consulting, expert witness services and an introductory activated carbon two-day short course titled Activated Carbon Adsorption Principles, Practices and Opportunities.*

S *Barbara Sherman, MS directs over 50 short courses, conferences and expositions for PACS, which has an extensive offering of activated carbon continuing education short courses. For more information, call (724) 457-6576, e-mail: HNpacs@aol.com or visit www.pacslabs.com.*

Authors' note

During Dr. Mick Greenbank's three years with PACS, our Pittsburgh/Orlando based science firm, he lowered the cost to manufacture the testing instrument and most importantly found the ideal challenge gas 1,1,1,2-Tetraflourethane (TFE) for his methodology. Previously his test method was performed with methane, ethane and propane as a suite of challenge gases. This tri-fold suite covered six-orders of relative gas concentration, whereas TFE covers eight-orders of concentration. To detect and quantify the number of the highest energy binding sites in a sorbent, you need the lowest concentration of challenge gas and a difficult molecule to adsorb. TFE is the ideal challenge gas. We take our hats off to Mick. Presently, there are only a few working instruments to deliver these testing results. We appear to have the interest of select scientific instrument manufacturers to bring this instrument to the marketplace in the near future. Once the instrument is in the hands of more individuals and more individuals are trained on its use, we expect this methodology to impact the sorbent industry. This method could become the recognized best-available test method, a worthy goal. Much international and domestic cooperation is necessary to accomplish this goal. Cooperation is in the best interest of the activated carbon industry manufacturers and users.