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Modern Methods of Particle Characterization

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FINE PARTICLE TECHNOLOGY

Since prehistory man has been aware of the importance of particle size in producing resources and wares with desired properties. Archeological evidence indicates that paints used for cave wall paintings are mixtures of finely pulverized pigmenting materials, predominantly carbon, ochre and hematite. Man came to realize that adding pulverized materials to clay not only improved its workability, but improved the drying process, reduced shrinkage and changed the characteristics of the resulting vessels. There also is evidence of using particles of certain sizes to control porosity. For many centuries, finely divided, calcined lime powder or gypsum mixed with sand was used in plasters and binders. Then, about 2000 years ago, the Romans improved upon the formula by adding volcanic (pozzolanic) ash, which produced a superior hydraulic cement that was used in building many structures that still stand.

Today, finely divided particulate materials and objects that incorporate or are produced from these fine particles are everywhere about us. Frequently encountered powders include cement, lime, fertilizer, cosmetic powders, table salt and sugar, detergents, bath and dental powders, coffee creamer, baking soda, and many other household items. Products in which the incorporation of powders is not so obvious include paint, toothpaste, lipstick, mascara, chewing gum, magnetic recording media, many medicinal products, slick magazine covers, floor coverings, and automobile tires. Such everyday items as fused ceramic bathroom fixtures and many small metal objects produced by powder metallurgy completely obscure their origins as powders. The gold trim of dinnerware, for example, started as a carefully controlled fine powder. Even microwave cooking utilizes particle technology. The desire to brown some foods cooked by microwave was solved by a wrapping of metalized polyethylene terephthalate (PET) film, a material containing fine grained metallic material that absorbs microwaves and produces localized elevated temperatures.

The applications of fine particle technology by no means are limited to commercial products, nor is the need to determine the properties of finely divided materials restricted to one area of technology. It begins in mining with discovering how fine an ore must be ground to release the sought-after mineral. Detailed physical studies of archeological items indicate that these processes were known in ancient times. Fine ceramic artifacts indicate a knowledge of processing naturally occurring rocks and minerals to control purity as well as particle size distribution in the clays, glazes, and pigments. Plasters used in decorating the pyramids and mortars used by Roman masons indicate similar attention to particle size.

Today the porosity of limestone and sandstone is characterized by quarry source and related to its expected rate of deterioration in urban environments before it is used in restoration of historic monuments. The mortars and plasters used in ancient and modern times owes its characteristics almost wholly to the selection of the proper sizes of the lime and filler particles.

Earth scientists use particle technology to solve various mysteries of nature. Geologists study the textural characteristics of clastic rocks to extract clues to the methods of transportation, sorting, and deposition of the fine materials incorporated in these rocks. This provides valuable information about the history of natural events and processes such as water flow, winds, glacier movement, and marine currents that occurred at the depositional site prior to lithification.

Petroleum geologists study the physical characteristics of strata deep within the earth in order to determine the capacity of the field and to assess the effort required to remove the petroleum. Oceanographers measure characteristics of marine sediment for clues to its origin as well as to determine its mechanical properties for mooring. Soil scientists examine characteristics of near-surface soils to assess qualities associated with agricultural production. Many of the physical characteristics of interest to these scientists are dependent upon characteristics of the fine particles from which the materials are composed.

Climatologists are concerned with airborne particles that affect weather, and historical climatologists study particle depositions in ice cores as evidence of weather patterns over thousands of years. Climatologists, paleontologists and other natural scientists have found evidence linking mass extinction to an excessive number of fine particles in the upper atmosphere that shielded solar energy from the earth's surface, initiating a chain of events that devastated flora and fauna world-wide. Civil engineers study the grain size of subsurface soils to assess load bearing capabilities.

Environmentalists must know the capacity of adsorbents such as carbon granules in order to prevent escape of harmful vapors into the atmosphere. They also must characterize soil to determine the percolation rate, diffusion, and retention characteristics of hazardous substance spills. These bulk characteristics, too, are dependent upon the characteristics of the individual particles that compose the bulk.

There is an optimum particle size, or at least a smallest and largest acceptable size, for most items involving particles. The taste of both peanut butter and chocolate is affected by the size of their respective ingredients. Extremely fine amorphous silica is added to tomato ketchup to control its flow. Pharmaceutical tablets dissolve in our systems at rates determined in part by particle size and exposed surface area. Pigment size controls the saturation and brilliance of paints. The setting time of concrete, dental fillings, and broken-bone casts proceeds in accordance with particle size and surface area exposure. Some materials, gums in particular, do not dissolve in water but absorb water to form viscous colloidal sols. The particle size of the powder determines the type of dispersion. Larger particles form a discontinuous mucilage and fine powders yield homogeneous dispersions. The former is an effective ingredient in laxatives while the latter finds use in adhesives.

Controlling the surface-to-volume (surface-to-mass) ratio is one reason for manipulating particle size. Another is to control interparticle pore size and pore volume for specialized applications. For example, at the turn of the nineteenth century, filters having sub-micron pore sizes were constructed from diatomaceous earth and used to retain bacterium. However, it was demonstrated that infectious particles far smaller than bacteria could pass through these filters, leading to confirmation of the existence of unfilterable infectious elements called 'viruses'.

Surface area and porosity as a function of particle size or surface area and porosity independent of particle size are other physical characteristics that play an important role in particle technology. The effectiveness of odor removers depends on the active surface area of the adsorbent in them. The tightness of the weave of a cloth raincoat, and therefore its porosity, is adjusted to retard water penetration but permit air and vapor passage for comfort. Adsorbent towels and tissues, on the other hand, are made to have pores that readily wick up liquids. The tips of felt-tip pens have a still different requirement: their pore structure must hold a viscous ink but release it when compressed. The pore structure of prosthetic devices influences whether or not tissue will attach. There is even a connection between the Sphinx of Egypt's Giza plateau and porosity. The Sphinx may be coerced into revealing its true age thanks to the porosity of the stone from which it is made. A model of the weathering process based on the porosity of the stone has been suggested that may yield a timeline back to the date of its creation.

Many behavioral aspects of fine particle systems come about simply because of the relatively large amount of surface exposed to its surroundings. As matter is subdivided, the free energy of the system increases proportional to the amount of new surface created. The work required to achieve the new surface is equal to or greater than the increase in free energy. However, the laws of thermodynamics dictate that a system spontaneously will seek the lowest free energy state that is possible under the circumstances. The study of the behavior of the system in seeking this state, and how it can be manipulated and utilized is the domain of fine particle technology.

A thought experiment that exemplifies these principals is as follows. Consider a container of oil and water, the oil floating above the water, the two liquid phases being separated by a surface of minimum area and minimum free energy. Adding work to the system by vigorously shaking the container results in oil droplets being dispersed in the water and the total surface of the oil-water interface being greatly increased. However, when allowed to again stand at rest, the droplets join to form larger and larger drops of oil, each having less surface than the sum of the surfaces of the individual droplets that formed it, thereby reducing surface free energy. This behavior continues until the minimum interface is achieved, that is, one mass of oil floating above the mass of water. The system could be manipulated by adding a surfactant that would be attracted to the surface of the oil droplets, thus lowering the free energy of these surfaces and suppressing or prohibiting their coalescence when the input of agitation energy is ceased.

The mechanism employed to achieve minimum energy in the example above is through the mutual attraction of matter. This non-specific attractive force is commonly referred to as van der Waals force. It gives rise to the phenomenon termed physical adsorption (or physisorption) and is also responsible for surface tension and condensation in liquids. At high temperatures surface energy is likely to be reduced by electron sharing and valence bonding with gas atoms creating the phenomenon known as chemical adsorption (or chemisorption). As has been exemplified, some of the attraction can be reduced by the addition of surfactants, which give rise to what is called double-layer phenomena.. These terms appear again in sections and chapters to follow.

Obviously, all the special attributes relating to particle size, surface properties, and pore structure could not have been achieved without precise measuring means. Particle size probably was measured crudely first in ancient Egypt. Surviving wall paintings show ground foodstuff being sieved—possibly through a rough cloth of woven reeds—to remove the large bits for further grinding. While undoubtedly it was recognized long ago that grinding to smaller and smaller sizes exposed progressively more surface area and promoted dissolution, truly assessing the extent of the exposed area and the consequences thereof got its start only in the eighteenth century. This is when it was discovered that charcoal heated and then cooled without exposure to air would take up several times its own volume of air upon subsequent exposure. That pores in the charcoal accounted for much of the gas uptake by its condensation in them and that all solids exhibited adsorption phenomena to different degrees was learned by the mid-nineteenth century. From that came the realization that gas adsorption measurements could yield much information about the physical surface and pore structure of solids. Continuing experimentation early in the twentieth century with gases being first adsorbed and then removed by heating revealed that more was involved in some instances than just physical adsorption. Oxygen gas, for example, removed from carbon was found not to be pure oxygen but to contain oxides of carbon. This suggested that two processes were involved in gas uptake on solids: one of purely physical character which, as used above, was given the designation physical adsorption, and one involving a chemical reaction which is termed chemisorption. Adjacent chemisorbed atoms become susceptible to reaction with one another to form new chemical species when the proper surface structures and conditions are present. This we now know is the action of catalysts. Today, chemists and chemical engineers tailor the pore size and surface properties of catalysts to produce everything from shortening to gasoline.

Providing quantitative measures of the several parameters defining particle size, surface area, pore size and volume, surface activity, object density, and a few other more specialized subjects is the purpose of the instruments and services Micromeritics offers. Following are details of just what is being determined when each measurement is made with Micromeritics' instruments.

PARTICLE SIZE

If all fine particles were spheres, their size would be defined explicitly by their diameter or radius. If cubical, the length along one edge would be characteristic; if of some other regular shape, another equally appropriate dimension could be chosen. Unfortunately the great majority of particles are quite irregular and an arbitrary definition of "size" is the only resort, short of detailed examination of each particle. Moreover, every collection of particles contains particles of many different sizes, commonly referred to as the particle size distribution. Hence a practical definition of particle size must permit a great number of particles to be examined in a relatively short time.

What is termed an equivalent spherical diameter best meets the requirement for a non-specific measure. Equivalence of size means that the "diameter" assigned to an irregularly shaped particle is the same diameter as that of a sphere which behaves identically when both are exposed to that same process.

There are numerous manual and automated techniques by which to determine the mass vs. equivalent size distribution of a collection of particles. Selecting the most appropriate technique is critical in attaining reliable data. No single technique is superior in all applications.

X-ray sedimentation

Micromeritics' SediGraph particle size analyzer measures the distribution of equilibrium velocities of particles settling through a liquid under the influence of gravity. Stokes' law relates these velocities to particle diameters for spherical particles. The instrument determines the settling velocity of the particles and applies Stokes' law to determine diameters. It thus measures non-spherical particles in terms of the diameter of a sphere of the same material that settles at the same velocity, i.e., it determines equivalent spherical diameters.

Most powders used in manufacturing processes are at some point mixed into or compounded with a liquid. Predicting the behavior of such a mixture is more likely to be successful if particle diameters are known. Since the sizing of particles by the sedimentation technique also involves dispersing powders in a liquid, the analysis essentially is performed *in situ*. This benefit also extends to studies of marine silts and sediments, the deposition of the solids being dependent upon their sedimentation velocity in a liquid, a fundamental measurement when sizing by the sedimentation technique.

The sedimentation velocity of suspended particles can be obtained by measuring the quantity of sediment produced as a function of time or by measuring the concentration of particles remaining in suspension with time. The latter approach is preferable mathematically and is employed by Micromeritics. The instrument design in which this approach is implemented utilizes a beam of low-energy X-rays to measure mass concentration in terms of the transmittance of the suspension relative to the suspending liquid. The transmittance to X-ray wavelengths is a function only of the mass concentration of the suspended particles. The X-ray beam is extremely narrow in the vertical dimension, and because it does not disturb the suspension it constitutes an ideal measuring probe.

Small particles settle quite slowly under gravity. To avoid the long settling times that would be required to measure both the larger, faster-settling particles and the smaller, slower-settling ones, the cell containing the particles is moved downward with time relative to the X-ray beam. The entire cell is thus scanned in a matter of minutes and particle size resolution is achieved as rapidly as could have been obtained by centrifuging the cell but without the mechanical complications of a rotating element.

Most of the analysis processes are automated to reduce or eliminate operator error, thus assuring repeatability and reproducibility of results. As examples, the movement of the cell is computer controlled as is the introduction of sample and the flushing away of it when the test is done. An accessory unit permits multiple samples to be selected and then analyzed automatically in any order desired.

Powdered materials having diameters from 0.1 to 300 µm (micrometers) can be measured with a precision of 1 mass percent over the entire size range provided three criteria are met: the particles must be more dense than the liquid in which they are suspended; the particles must disperse, or break free of one another, in the liquid; and the particles must absorb more X-rays than the liquid so that adequate contrast with the liquid is created. The last criterion generally means that the materials must contain elements having atomic numbers greater than 11 (sodium).

Powders, particularly fine ones, often are difficult to disperse, i.e., separate into individual entities with each particle free and not attached to one or more other particles. Unless the dispersed state is achieved, particle size measurement by sedimentation, or any other method for that matter, can be greatly misleading. Micromeritics has developed a series of liquids which greatly facilitates the dispersion of difficult-to-disperse powders. These liquids are available in both aqueous and organic formulations.

Static light scattering

The size of particles also can be determined from the manner in which they scatter light. The most common application of this technique is low angle light scattering (LALS) in which an assemblage of particles is illuminated by a source of monochromatic, coherent light. This is the technique employed by Micromeritics' DigiSizer.

In this instrument design, a lens is positioned in such a way that light scattered at a specific angle from any particle in the illuminated zone will intersect the focal plane at a specific distance relative to the focal point. The intensity of scattered light is measured at a number of predetermined positions corresponding to a set of scattering angles. Using these intensity vs. forward angle measurements, Mie or Fraunhofer theory (a special case of Mie theory) can be applied to extract particle size information. Mie theory predicts the intensity of scattered light over a 180-degree range of scattering angles. Using intensities measured only at low angles (<90 degrees), the sizes of particles over a range of about 0.1 to 1000 µm can be determined. Mie theory, in the strictest sense, applies only to spherical, isotropic particles with specific and known optical properties. However, Mie theory most often is applied to particle systems that do not exactly conform to the theoretical model. As with the sedimentation technique, particle size is reported as equivalent sizes. In the case of light scattering, the reported quantity vs. size distribution is that of spherical particles that most closely reproduce the same scattering pattern as that of the particle assemblage being analyzed.

All information about particle size and quantity resides in the intensity versus angle characteristics of the scattering pattern; therefore, precise measurement of the light scattering characteristics are fundamental to obtaining good particle size data. A unique design feature of Micromeritics' DigiSizer is the use of a high-resolution detector array (a charge coupled device or CCD) to measure scattered light. The spatial density of detector elements is so great that several million measurements are collected between 0 and 36 degrees of scattering angle and an angular resolution of a few thousandths of a degree is achieved. Due to the symmetry of the scattering pattern in the area of measurement, many of the intensity measurements are for the same scattering angle and these redundant measurements provide real-time signal averaging.

Another benefit gained by use of a CCD is a means of accommodating a wide range of light intensity. This is because the CCD is inherently an integrating device rather than a current-generating device such as a photodiode. The charge accumulated by a CCD element is proportional to the product of the intensity of incident light and the exposure time. Very low light intensities are measured by allowing long exposure times, and very high light intensities are measured using microsecond exposures. This capability is important in measuring a scattering pattern in which light intensities can vary over a range of ten orders of magnitude.

The high-resolution angular detection allowed by the area array permits the position of the optical axis (the position of the central, unscattered light beam) to be determined within a fraction of one pixel element, that is, a few thousandths of a degree. This point represents the origin of the polar axis about which the scattering pattern is centered. Relative to this point, a scattering angle can be assigned by software to all other detector element. If any mechanical or optical deviations cause the optical axis to move from the zero point, it is promptly determined by software and the detector array is dynamically remapped, thus, mechanical alignment is unnecessary.

Once the scattering pattern has been characterized by a set of angle vs. intensity data, the final step is to determine the sizes and quantities of particles that will most closely reproduce the measured scattering pattern. This is accomplished by an iterative process of fitting theoretical models to the data using a non-negative least square method.

The same caveat about liquid-solid dispersions that applies to the sedimentation technique and the SediGraph applies also to particle sizing by static light scattering. Unless the particles are separated, a true mass vs. size distribution cannot be achieved. However, in some applications, the objective may be to study dispersion or floculation characteristics. In this case, a sample recirculating system such as the DigiSizer's Liquid Sample Handling System provides a means by which the size distribution characteristics of the same sample can be measured repeatedly as the process under study evolves.

Electrical sensing zone

The electrical sensing zone (ESZ) technique, also known as the Coulter principle, analyzes the sample particle by particle rather than examining an assemblage of particles as done in the two techniques discussed previously. Micromeritics' Elzone analyzer utilizes this technique to count and size particles.

To analyze a sample by the ESZ technique, a homogeneously dispersed suspension of sample material is prepared in an electrolytic solution. A tube with a small aperture of short path length is submerged in the suspension, an electrode being positioned on both sides of the aperture. A pump establishes a flow of electrolyte through the aperture, providing a conductive path between the two electrodes and a small electrical current is established between them. Both electrolyte and particles pass through the aperture. The particles, being non-conductive, impede the electrical current flow as they enter the orifice. This creates an electrical signal proportional to the volume of the particle in the aperture. Each individual particle is counted and classified according to volume, thus producing a volume frequency distribution. If the particles are considered to be spherical, then particle diameter can be determined from volume.

The concentration of particles in the electrolyte is very dilute since two or more particles entering the orifice in close succession will cause an erroneous signal. However, statistical probability dictates that a coincidence of particles will occur in the orifice now and then, so a coincidence correction routine is built into the software to correct for such events.

The ESZ technique is applicable to a wide range of sample materials including plant and animal cells. It is particularly useful when the number distribution of particles by size needs to be determined. ESZ also is a very high-resolution method of particle sizing.

SURFACE AREA

There is an inverse relationship between particle size and surface area. A cube one centimeter on an edge has a surface area of 6 cm^2 . If the cube were fragmented into smaller cubes having edges of 0.1 cm there would be 1000 of the smaller cubes and the total surface area would have become 60 cm^2 . This ideal relationship is unlikely ever to be encountered because irregular particles break into smaller particles with a range of sizes and shapes. Actual particles of whatever size, if examined on a molecular scale, display planar regions, but they also are likely to include lattice distortions, dislocations, and cracks. This means that the actual exposed surface of particles is greater—sometimes very much greater—than would be calculated assuming any one geometric shape.

Micromeritics' provides several types of surface area instruments that permit determination of surface areas at the molecular level by measurement of a low temperature isotherm. At the upper end of the range are multipurpose, sophisticated units capable of providing timely results for both quality control and research and development needs. Midrange instruments include those for high throughput, round-the-clock, reliable service for quality and production control purposes. At the lower end are inexpensive, semi-automatic and manual instruments for occasional usage. Properties other than surface area can be determined from the data provided by these instruments—chemical activity and pore structure are examples; only the surface area function is described in this section.

All such instruments first free the sample of moisture and atmospheric vapors by application of heat and either evacuation or purging with a non-adsorbing gas, usually helium or nitrogen (nitrogen may adsorb at room temperatures on some materials). Then the sample temperature is reduced to that of liquid nitrogen, liquid argon, or another coolant appropriate for the gas or vapor to be adsorbed. The adsorbing gas is admitted in incremental doses in one instrument design (static volumetric technique), continuously as the sample itself permits in another design (adaptive rate technique), and as a component in a flowing mixture with nonadsorbing helium in still another design (dynamic, or continuous flow technique). The accumulated gas quantity adsorbed *vs.* gas pressure data at one temperature are then graphed to generate what is called an adsorption isotherm.

The data are then treated in accordance with gas adsorption theories to arrive at a specific surface area value for the sample.

Classical adsorption theory that has been in use since the 1930's and is still in use assumes that gas molecules admitted under increasing pressure to a clean, cold surface form a layer one molecule deep on the surface before beginning a second layer. The data treatment technique finds the quantity of gas forming this first layer, and then the area covered is calculated from the number of molecules of the gas and gas molecule dimensions. Actually, adsorbed gas molecules do not attach to a solid surface and thereafter remain attached while other molecules build upon them. In the first place, there are regions on all surfaces that are more attractive to gas molecules and regions that are less so. What we call adsorption is really the manifestation of a continual exchange between gas molecules temporarily residing on a solid surface and those nearby in the gas phase. The number of molecules attached to a solid at any instant increases as gas pressure increases until a point is reached where statistically it is reasonable to consider a monolayer to have formed. Only in the sense of an average condition does an adsorbed monolayer ever really exist, however.

Many modifications to the classical model have been offered over the years, some based on empirical or semi-empirical foundations and others derived from either thermodynamics or kinetic theory. All of these data reduction methods have the common attribute of applying only to a certain segment of the isotherm rather than over the full range. A more modern approach is to begin with basic principles of statistical thermodynamics, combine these building blocks with newly available computational techniques, and seek a single or unified theoretical model applicable over the total range of the isotherm. This approach utilizes density functional theory, and an efficient implementation of this theory by Micromeritics enables rapid calculations of this once computationally intractable data reduction task.

Density functional theory is a means by which the exact population density of a system of molecules at a specific temperature and pressure can be expressed mathematically. When the expression is solved for the state of minimum energy, the population density profile at equilibrium is described. Since the energy of the system must take into regard surface energies of a solid substrate exposed to the system of molecules, the population density profile reveals how various layers of molecules have formed on and near the solid surface. This method allows the acquisition of a family of profiles that describes gas adsorption over a range of pressures from near zero to the saturation pressure.

The less sophisticated Micromeritics instruments start with classical theory, but others, through their software computational capability, can report results obtained by classical theories as well as by recent, popular adsorption theories with applicability limited to specific conditions and ranges. Density functional theory can be utilized with all adsorption isotherms. However, it is best used with the more sophisticated instruments that are capable of collecting high resolution low-pressure data, thus, providing the highest quality results.

Accessory equipment is provided for minimizing operator involvement and speeding sample preparation. This includes units for degassing samples by the flowing-gas method or by applying heat and vacuum. A liquid cryogen storage and transfer system also is provided for making more convenient the supplying of sample coolant for all instruments.

PORE SIZE AND VOLUME

Solid particles from crushing or grinding operations and weathering or leaching processes often will be found to have cracks, cavities, and holes (collectively called pores) within their structure. Solid particles produced by condensation or crystallization processes may contain, or acquire after a period of time, cracks along grain boundaries and at positions where impurities are occluded. Fine particles also tend to stick together, or adhere to form aggregates or larger secondary particles, giving rise to another level of pore sizes. Adhesion is accelerated at elevated temperatures and with the mechanical application of pressure. Industrial processes that make use of this property are called firing in the case of pottery manufacture and sintering in powder metalurgy. Many of the pores in industrial products thus are comparable in dimensions to the primary particles themselves. In these cases the walls of the pores are the exposed surfaces of the particles, and, not surprisingly, these pores are likely to exhibit interconnectivity and great tortuosity. A few natural materials such as kaolin clay and mica occur as more or less orderly stacks of thin plates; graphite also can be produced with a similar structure. The pore dimensions are very small in one direction and relatively large at right angles to that direction.

Pore size is expressed either in terms of the diameter (or radius) of the opening, assuming it cylindrical, or simply as the width in a more general sense. Pores of widths less than 2 nanometers (nm), or 20 Angstrom units (Å), are referred to as micropores. Pores having widths from 2 nm to 50 nm (500 Å) are called mesopores, and pores of larger widths are referred to as macropores. The volume of all cracks, fissures, holes, channels, etc., within the body of particles or of larger objects is the total pore volume.

Micromeritics products acquire detailed pore information in two ways: 1) gas adsorption, and 2) mercury intrusion. The first technique for pore volume assessment condenses a gas in the pores and derives pore volumes from the quantities of gas (converted to condensed liquid volume) required. In the presentation above on surface area evaluation, it was described that an inert gas admitted to clean, cold surfaces first adsorbs to a monomolecular layer according to the classical viewpoint. Admitting more gas causes the layer to thicken to a depth of several molecules and, ultimately, to a layer of infinite thickness, i.e., condensation to bulk liquid when the saturation vapor pressure is reached. If, however, the solid is porous so that it has internal surface area, condensation of the gas will begin in the smallest pore spaces and progressively fill larger and larger pores prior to bulk condensation.

Equipment for measuring pore sizes and volumes is identical to that for determining surface area in most instances. What is required of the instruments is that gas admission to the cooled sample be continued beyond the first adsorbed gas layer to the point at which bulk condensation begins. Computation of results now also must account for the added complexity that gas continues to be adsorbed on exterior surfaces while condensation is occurring in the central core of pores which already had adsorbed gases on their walls before condensation started. This basically means that the computation must proceed in reverse, as it were, after all pores have been filled. This is so because the assumption that all pores are filled can be made only for the last increment of added gas before bulk condensation occurs. These calculations incorporate the Kelvin capillary condensation equation which holds for pores down to about 2 nm (20 Å) diameter, i.e., down to the micropore region.

There are numerous modifications to classical theory and additional theories which encompass microporous material analysis. Precise measurements down to quite low pressures are required. The Micromeritics volumetric physical adsorption instruments are equipped to carry out pore diameter and volume analyses and to report results by most of these techniques. Those units with high vacuum manifolds are most applicable for thorough analysis of micropore structure and for reporting density functional theory calculations.

The second way Micromeritics products determine pore size information is by mercury intrusion-- forcing liquid mercury into the pores and keeping inventory of the quantity penetrating them. Mercury has an exceptionally high interfacial tension and wets only a few materials, the resistance to wetting being quantified by a parameter known as the contact angle. When the contact angle is greater than 90°—mercury against most solids usually registers between 130° and 150°—increasing external pressures must be applied to cause mercury to penetrate progressively decreasing size pores. Quite high pressures are necessary to fill very small pores. Micromeritics manufactures two instruments, one capable of pressures to 207 MPa (30,000 psia), causing pore diameters to be filled down to 6 nm (60 Å) and the other with the capability of attaining pressures to 414 MPa (60,000 psia), filling pore diameters down to 3 nm (30 Å). Also offered is a device for measuring contact angles.

Sample material first is evacuated and then inundated with mercury in a mostly glass device termed a penetrometer. Pressure is applied hydraulically to both the mercury in the penetrometer and also about the sample. Subsequent penetration into pores is tracked by a change in electrical capacitance, which registers the volume of mercury penetrating pores; pressure transducers measure the corresponding pressure. Pore diameters and respective volumes are calculated from this information and from the value of contact angle. Each porosimeter instrument presents results as total pore volume, pore area, median and average pore diameters, percent porosity, incremental and cumulative pore volumes as a function of pore diameter, and more in tabular form. Various forms of graphical data also are presented.

DENSITY

Density is a prosaic property of all matter. It is simply the mass of a quantity of matter divided by the volume of that same quantity. Accurately determined, density reveals much about the composition of an alloy, provides information with which to keep a process under control, reveals the richness of a mineral body, and much more. There are three densities associated with powders. The absolute density (also termed the true or skeletal density) excludes the volumes of pores and of the interparticle spaces; the envelope density (sometimes called the apparent density) includes the pore volume but excludes interparticle spaces; and the bulk density includes both pore volume and interparticle spaces. For a powder, the latter changes with vibration and applied forces and is not an intrinsic property of the material.

The absolute and envelope densities of a nonporous object are identical. If the object is a relatively large cube, sphere, or other regular geometric shape, its volume is not difficult to determine nor is its absolute (and envelope) density difficult to calculate. Difficulty in measurement becomes apparent when the material in question is of irregular shapes and especially when it is also in small bits or granules. The difficulty increases if, in addition, the material also has pores, cracks, crevices, or deep concave regions. The absolute and envelope densities differ in this case, and require separate techniques to assess. Absolute density by definition excludes all pore volumes that have access to the outside. Envelope density includes pore spaces up to the plane of the surface.

Micromeritics provides multiple instruments, manual and automatic, specifically for determining absolute density. They accept a wide range of sample sizes and operate at a range of gas pressures. All use helium gas as the standard working medium but other gases can be employed. In both, a sample of the material in question first is placed in a sealed chamber of known volume and then exposed to a series of elevated and then released gas pressures to flush away atmospheric gases and vapors. Next, instead of venting the gas at elevated pressure to atmosphere, it is released into another chamber of known volume. The pressures in both chambers are determined both before and after the expansion of the gas. This permits calculating the volume of the sample, and division of this volume into the sample weight gives the density. The result is an absolute density value because the helium fills all open spaces including that of the pores. By cutting materials that have closed pores into smaller pieces and thus exposing more of the pores, an absolute density pycnometer also can be employed to evaluate the proportion of open and closed pores.

Micromeritics also produces an instrument for determining envelope density. It operates on the principle of immersing the object, or objects, to be evaluated in a fluid medium of known volume and measuring the displaced volume. The medium, instead of being a liquid as Archimedes used, consists of free-flowing, fine spherical particles. To ensure that beads conform to the external contour of the object being measured, the object is tumbled freely in a cylinder containing both it and the beads. Gradually the space is reduced by an intruding plunger until a prescribed force is achieved. Where the plunger stops when the beads are compacted about the object is a measure of the volume of the object and the pores not intruded by the beads. Dividing this volume into the object weight yields the envelope density of the object.

The envelope density of an object in and of itself is sometimes of great utility, for instance in controlling a sintering operation. Other useful information can be calculated from the envelope and absolute density values for the same object, viz., the porosity and specific pore volume of the object. These latter parameters indicate many things from the suitability of a catalyst substrate or the yield potential of an oil-bearing formation.

Bulk density is the parameter defining how granular, fibrous and powdery materials pack or consolidate under a variety of conditions. Knowing its value is useful in packaging, handling, and shipping all manner of products from breakfast cereal to cement. The Micromeritics instrument for measuring envelope density determines bulk densities as well. The weighed, granular test sample alone is tumbled in the cylinder and the volume it occupies is measured at any pre-selected force applied by the advancing plunger. Dividing sample weight by the volume now yields bulk density. Thus the compacting behavior of a material—measured in terms of its bulk density—is established.

ACTIVE SURFACE CHARACTERIZATION

Physical adsorption was described previously under 'Surface Area'. It is a relatively weak attraction between the gas and the surface molecules. Chemisorption, in contrast, involves stronger solid-gas attractions.

Chemisorption is the basis from which has been developed an array of man-made materials called heterogeneous catalysts. Without catalysts the modern world would be in short supply of fertilizers, pharmaceuticals, synthetic fibers, solvents, surfactants, gasoline, and other fuels, for deep within the tiny galleries, pores and cavities of catalysts occur the chemical reactions that support our industrial society. As a specific example, the metal rhodium exposed on the surface of a ceramic honeycomb structure is the heart of the exhaust system of automobiles. How it transforms the deadly exhaust gases of nitric oxide (NO) and carbon monoxide (CO) into harmless nitrogen (N_2) and carbon dioxide (CO_2) is typical of the action of a catalyst. At the high temperature of an automobile exhaust, carbon monoxide binds to the rhodium surface. When nitric oxide does the same, it dissociates into oxygen and nitrogen, and the bound oxygen reacts with the carbon monoxide to form carbon dioxide. Then when other molecules of nitric oxide and carbon monoxide land close to the remaining bound nitrogen a second carbon dioxide and a nitrogen molecule are formed.

Practical catalysts are characterized by having a high specific surface area, i.e., area per unit mass. They may consist of finely divided metal dispersed on the surface of a nonreactive, high surface area, refractory oxide such as alumina or silica. Other metal catalysts have an open, skeleton-like structure as a result of leaching away one metal of a bimetallic alloy. The newest and most exciting catalysts are termed zeolites. They consist primarily of aluminum, silicon, and oxygen but host an assortment of other elements. They are highly porous crystals veined with submicroscopic channels. The assorted other elements can be moved about or replaced and the channels can be altered in size to make zeolites very useful indeed.

The surface area and pore structure of catalysts obviously are critical to their behavior. Both parameters can be measured by the instruments described previously. These tests are conducted basically as described before and their description will not be repeated. However, because catalyst surfaces are highly reactive and can be altered by exposure to the atmosphere as when transferred from one instrument to another, Micromeritics chemisorption instruments incorporate provisions for making these measurements *in situ*. Critical parameters for chemisorption measurement are: the area of the active element; metal dispersion, i.e., what proportion of the active element is actually exposed; surface acidity; and the strength of acid sites.

The simplest chemisorption instruments utilize the titration (dynamic, or continuous flow) technique in which small, reproducible volumes of a reactive gas such as hydrogen, oxygen, carbon monoxide, sulfur dioxide, or ammonia are injected into a flowing carrier gas such as helium that passes over the sample catalyst. Gas composition downstream is detected by matched thermal conductivity detectors. Repeated injections of identical reactive gas quantities are made from which all, most, some, and then none of each pulse is chemisorbed. The cumulative chemisorbed quantity is derived by summing the proportions of all pulses consumed. Metal surface area, dispersion, acidity, and other important parameters are derived from the chemisorbed quantity, taking into account stoichiometric factors and the nature of both the gas and metal involved. Single-injection calibration or testing can be accomplished using either a syringe or a built-in injection loop. The instrument's two-port design permits high throughput. While sample preparation is being conducted on one port, an analysis can be performed on the other.

By adding to this instrument an accessory package which contains among other things a programmable furnace, temperature-programmed desorption (TPD), temperature-programmed reduction (TPR), and temperature-programmed oxidation (TPO) tests can be accomplished. Temperature-programmed desorption evaluates the gas being desorbed from a catalyst as its temperature is increased. First, the catalyst is outgassed, reduced, or otherwise prepared. Then reactive gas is chemisorbed onto the surface active sites of the sample surface. Ever increasing temperature is applied to the sample. At a certain temperature, the heat energy will exceed the bonding energy and the chemisorbed species will be released. If different active metals are present or if the active sites have more than a single activation energy, the chemisorbed species will desorb at different temperatures. The desorbed molecules enter the inert carrier gas stream and are swept to the detector which measures gas concentration. The volume of gas desorbed combined with stoichiometric factors and the desorbing temperature yield the number and strength of the active sites. Temperatures exceeding 1100 °C can be attained.

Temperature-programmed reduction determines the number of reducible species and the temperature at which reduction occurs. This analysis begins by flowing hydrogen, usually at 10% concentration in an inert gas stream, over the sample; the system is usually at ambient temperature. The amount of hydrogen consumed in reduction of oxide species with increasing temperature is monitored. Temperature-programmed oxidation examines the extent to which a catalyst can be reoxidized. First, metal oxides in the sample are reduced to the basic metal with hydrogen. Then the reactive gas, typically 2% oxygen, is applied to the sample as a steady stream while the sample temperature is increased. Again, the amount of oxygen consumed is monitored by the thermal conductivity detectors and quantified; these tests determine the extent of the reduction and the nature of the reoxidized species.

Temperature-programmed chemisorption reactions can be studied in greater detail by use of another Micromeritics instrument type. As in the instruments just described, reactive gas in an inert carrier stream flows over the catalyst sample after it has been outgassed, reduced, or otherwise prepared. Temperature- programmed desorption, reduction and oxidation studies are conducted as described before. This instrument design, however, permits testing from subambient to over 1000 °C.

The significant difference between this instrument design and the one described previously is that operation of this latter instrument type is automated. The valves, detector, and other critical internal components of the analysis system are designed and engineered for minimum dead volume, maximum response, and high resolution. Furthermore, by incorporating programmable heaters into the valves and internal gas lines, liquid vapors such as pyridine and quinoline can be used as chemisorbate probe molecules without loss due to condensation. This design feature also facilitates attaching a mass spectrometer or other external detector, thus permitting the identity of the reaction species to be determined. The latest model of this design is computer controlled from start to finish and results are reported as graphs and data tabulations.

The Micromeritics static volumetric chemisorption system is a version of the static volumetric physisorption unit noted in conjunction with surface area measurement. When employed as a chemisorption analyzer, an accessory permits the sample to be prepared on the analysis port. This eliminates the necessity of moving the sample holder between preparation and analysis ports, which would expose the sample to atmospheric contaminants. Not only can this unit be used for surface area and pore size and volume distribution determinations, but it also determines automatically active metal surface area and percent metal dispersion for catalyst materials.

Preparation and analysis of samples are directed through a graphical user interface to the computer system. Sample preparation uses the flowing gas techniques with hydrogen gas, either pure or in an inert carrier, to reduce completely the oxides on the catalyst. Complete removal of residual hydrogen after preparation is accomplished by applying heat and a high vacuum. Analysis is made by the static volumetric technique to obtain precise dosing of the reacting gas and rigorous equilibration following the dose. The first analysis measures both strong and weak interactions in combination. A repeat analysis after evacuation measures only the weak, or reversible, uptake of reactant. Automatic data reduction provides complete information about active metal surface area and percent metal dispersion. An analysis log reports pressures, temperatures, and volumes chemisorbed plus an elapsed-time record for each data point. Plots containing both the initial and repeat analysis curves are generated. A difference plot shows the strong component of chemisorption. It is fitted to a single straight line for computations of a single uptake number and subsequent computation of the percent metal dispersion.

NANOMATERIALS

Nanotechnology is anticipated to lead to a wide array of technical innovations in the near future. The prefix "nano" indicates a scale factor of 10^{-9}(one billionth). A particle of nano size has at least one linear dimension in the nanometer range. Since it requires about 3 to10 atoms (depending on the element) to span one nanometer, a few hundred atoms is about the limit of the dimension of a nanoparticle.

Nanoscience seeks to gain knowledge and understanding of nanoscale phenomena, while nanotechnology employs this knowledge in the development of new products. These products can be improved catalysts or materials with enhanced strength, wear-resistance, corrosionresistance or high temperature endurance but, in general, they are materials with enhanced performance. On the whole, nanostructured materials are providing novel opportunities in wide range of scientific fields.

But, being of nanosize is not what attracts such great interest in nanomaterials, it is their properties. The properties of nanomaterials are different from those of the same material at the macro scale. When materials are reduced to sufficiently small sizes, typically less than 50 nanometers (a few molecules), novel physical, chemical, and biological properties arise that provide opportunities for new applications. Furthermore, these surface properties can be optimized for particular applications through molecular modification. The fundamental reasons for the changes or enhancements of characteristics are the increased surface-to-volume ratio and the increase dominance of quantum effects that determine the material's optical, magnetic, and/or electronic properties. Working with nanoscale systems requires special tools for manipulating, measuring and controlling size and properties. A different knowledge set also is required since nanoscale phenomena involve quantum mechanics rather than classical mechanics as is the case with materials of larger scale.

Micromeritics instruments have been used in the investigation of nanomaterials for over a decade. As previously discussed, pores are classified according to diameter where micropores have diameters less than about 2 nm, mesopore sizes range from about 2 nm to about 50 nm and macropores have diameters greater than about 50 nm.

In addition to pore volume distribution, total surface area also can be determined from gas adsorption. Not only does increasing surface-to-volume ratio enhance reactivity, as previously noted, it also enhances the efficiency of the material in trapping or storing adsorbed gases and vapors.

Being a nondestructive test, gas adsorption is the preferred method of determining pore characteristics and surface area of nanomaterials. However, mercury porosimetry also is capable of measuring pores of nano dimensions. At 30 kpsi pressure, mercury intrudes into pores of 5nm diameter and at 60 kpsi, pores of 2 nm can be probed.

Sample density also is a valuable determination in the characterization of nanomaterials. A surprising amount of information can be gleaned from this seemingly simple measurement. For example, if the specific surface area of a mono-sized dispersion has been determined, the particle size of the material can be calculated provided that each particle is of the same regular geometry (typically spherical)l and without any porosity. The degree of crystallization of a material also may be inferred by comparing the measured density to the theoretical crystalline density of the material.

Particle sizing perhaps poses the greatest challenge in characterizing nanomaterials. Recall that the sought after properties of nanoparticles are size-dependent and usually do not prevail until size has been reduced to less than 50 nm. While most of the novel properties are size-dependent, many of the common methods used for generation of nanopowders result in different size distributions. Not only is there need for tighter control of size in the production process, there also is need for a fast, high resolution method of measuring distributions in the lower end of the nanoscale in order to control production.

CONCLUSION

Fine particles play essential roles in determining the characteristics of both natural and man-made materials and have considerable influence on processes such as dissolution, adsorption and reaction rate. In the majority of cases, these effects are a function of either the size, shape, surface area or porosity of the individual particles or of an agglomeration of particles. These particle-related characteristics must be controlled in order to optimize the desired effects, and efficient control requires measurement. These same particle characteristics are either the causes of, the results of, or a determining factor in natural phenomena. In this category, understanding or exploitation rather than control is more likely the objective and, again, measurements provide fundamental information used in achieving the objective.

As this article has illustrated, there likely are multiple techniques for determining the same particle dimension and each has its advantages and disadvantages. Selecting a technique that is inappropriate for the application can have a profound impact on the quality of the measurement you obtain..