ISO9001
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NANOPIX mini

Small angle X-ray scattering analyzer system

Benchtop SAXS for nanostructure analysis

Rigaku

Leading With Innovation

Nanoparticle analysis by SAXS method

Nanomaterials are part of a variety of emerging nano-scale technologies that can be used in a broad array of technologies and products. Nanomaterials, materials where 50% or more by number of the constituent particles have one or more external dimensions in the size range 1–100 nm (2011/696/EU), can exhibit vastly different chemical or physical properties, or biological effects compared to their larger-scale counterparts. These effects may derive from altered chemical, biological, or magnetic properties, altered electrical or optical activity, increased structural integrity, or other unique characteristics of materials in the nanoscale range (including acute toxicity) not normally observed or expected in larger-scale materials with the same chemical composition. Materials or end products may also exhibit similar properties or phenomena attributable to a dimension or dimensions outside the nanoscale range.

Exposure routes for nanoparticles

Bulk use of nanoparticles

Beginning in the late 20th century, applications of nanotechnology have emerged in commercial products, although most have been limited to the bulk use of nanomaterials like SiO_2 ,TiO_2, Ag and ZnO nanoparticles in a variety of consumer products and packaging. It has been estimated that there are now thousands of commercial products incorporating such nanomaterials of uncharacterized toxicity.

Engineered nanoparticles

Since 2000, a new unique class of materials has come to the forefront of R&D worldwide: engineered nanomaterials (ENM). ENM are materials created by the manipulation of matter at the nanoscale to produce new materials, structures, and devices. Many ENM are actually nanoscale particles where two or three dimensions are in the 1–100 nm range. Unbound engineered nanoparticles (UNP) are of particular interest as they may be toxic to humans and animals subject to certain exposure routes.

Regulation of nanoparticles

Nanomaterials offer technical and commercial opportunities, but may pose risks to the environment and raise health and safety concerns for humans and animals. As such, countries around the world have enacted increasingly stringent laws concerning the manufacture and distribution of nanomaterials.

European Union

Although there are no explicit requirements for nanomaterials under REACH or CLP, they meet the regulations' substance definition and, therefore, the provisions apply. Final SCENIHR opinion for a definition of nanomaterial was adopted in 2010. In 2011, the EC released specific recommendations on the definition of a nanomaterial, which impacted a variety of different European regulations, including REACH and CLP. Beginning in 2012, registration of nanomaterials was being guided by ECHA. A major REACH deadline for data dossiers on chemicals produced in volumes of 1–100 t/yr is 2018.

United States

Two principal laws have governed the regulation of chemicals in the United States: The Toxic Substances Control Act (TSCA) and the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA). Until recently, the myriad of US laws and regulations regarding nanomaterials were considered to be "soft" and lacking in enforcement. This changed in 2016 with the passage of the Frank R. Lautenberg Chemical Safety for the 21st Century Act. The new US law designates that the EPA is principally responsible for enforcement, and mandates safety reviews for all chemicals in active commerce. In addition, a safety finding is required before new chemicals are allowed into the market.

Area	Chemical Law	Application to nanomaterials
US	Lautenberg Act (2016)	Mandates safety reviews for all chemicals in active commerce
		Requires a safety finding before new chemicals are allowed on the market
	TSCA (1976); FIFRA (1996); Clean Air Act; the Clean Water Act; Comprehensive Environmental Response, Compensation and Liability Act; and the Resource Conservation and Recovery Act (RCRA) FDA: Final Guidance for Industry (2014-5) Executive Order 13563	Safety standard is health-based standard
		Explicitly requires protection of vulnerable populations
		Enhanced EPA authority to require testing of both new and existing chemicals
		Limits on confidential information (CBI)
		Prioritizes chemicals that are persistent and bio-accumulative, and that are known human carcinogens and have high toxicity
		Preserves a significant role for states in assuring chemical safety
		All CNTs are required to be registered individually as new substances
	Significant New UseRules (SNURs)	Pre-manufacturing notice (PMN) to besubmitted before manufacture of certain substances
EU	REACH (2006) CLP (2009) BPR & PIC (2012) Second Regulatory Review on Nanomaterials (2012)	REACH implementation projects on nanomaterials (RIP-oNs) providesguidance on REACHcompliance: • RIP-oN 1: substance identification • RIP-oN 2: information requirements • RIP-oN 3: chemical safety assessment
	Regulation (EC) N° 1223/2009	Cosmetic products safety regulations include use of nanomaterials
	Decree 2012-232 (France only) on the annual declaration ofnanoparticle substances	Manufacturers, importers and distributors must report nanomaterials if they exceed 10 grams per year

What is small angle X-ray scattering?

SAXS is a valuable non-destructive method for assessing the distribution of nanoparticles or nanopores by size. SAXS is used to measure the size-distribution of particles in both liquid suspensions and dry ultrafine powders. SAXS measures the particles according to mathematical treatment of scattered X-ray data. SAXS is applicable for the measurement of aggregate size-distributions after appropriate dispersion in a liquid. In addition, SAXS can also be used to derive information on particle shape, particle porosity, primary particle sizes, particle size distributions and more.

How does SAXS work?

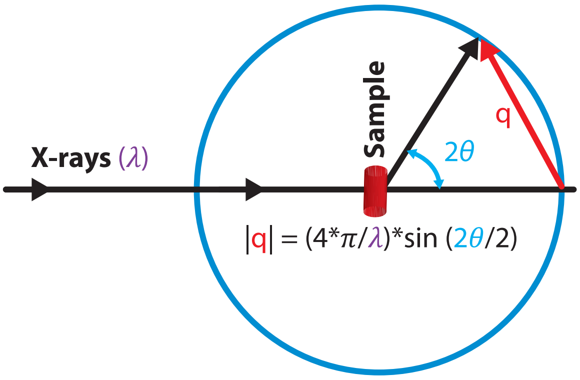
In the SAXS experiment, focused monochromatic X-rays interact with the electrons of the particles in a sample and are elastically scattered with different intensities as a function of (a narrow range of) scanned 2θ angles. For the simplest case, the scattered intensity $I(q)$ for a polydisperse system of non-interacting particles or pores with the same shape and electron density, but different sizes, can be expressed by:

$$I(q) = C \cdot \int_0^\infty D_v(r) \cdot r^3 \cdot I_o(q,r) \cdot dr$$

where C is a constant. $D_v(r)$ denotes the volume-weighted size distribution of the scatterer with size r. $I_o(q,r)$ is the scattering intensity of the radially symmetric scatterer of size r, with its forward scattering normalized to unity. The scattered intensity is collected as a function of the scattering angle 2θ according to $q = (4\pi/\lambda) sin\theta$, where λ is the wavelength of the incident monochromatic X-ray beam and q is the scattering vector. $I_o(q,r)$ is also often referred to as scatterer form factor $P(q)$. A variety of computational methods are used to compute the size distribution $D_v(r)$ versus r of scatterers from the above equation, where the mean particle size is given by:

$$\bar{r} = \sum r_i D_{vi}$$

Rigaku NANOPIX mini SAXS system



Simplified sketch of a SAXS measurement

NANOPIX mini — nanoparticle size distribution for b

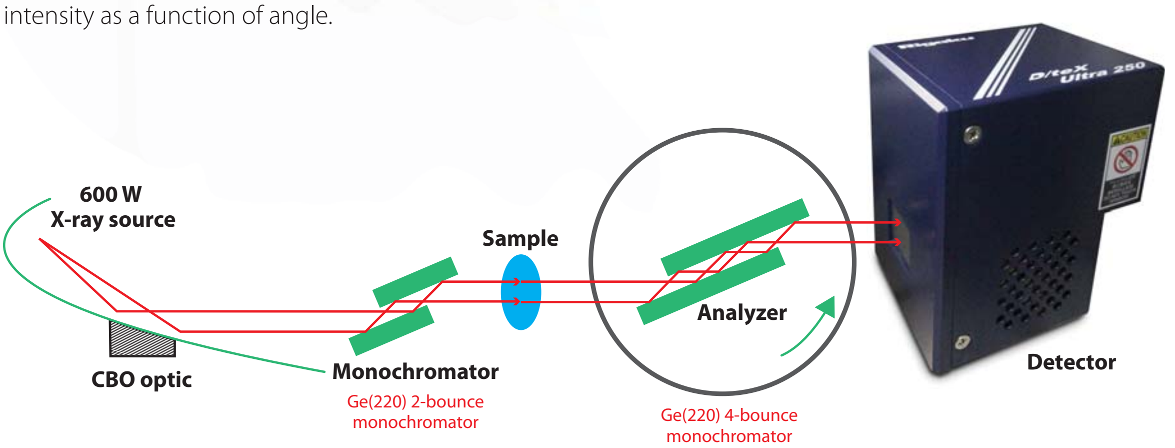
Rigaku NANOPIX mini is the first benchtop small angle X-ray scattering system dedicated to the characterization of nanoparticles in both research and production environments. With a revolutionarily small footprint and performance superior to traditional "big iron" systems, this compact instrument offers enhanced angular resolution through its line-focus X-ray source and superior combination of high figure of merit optics.

Features and benefits

- SAXS measurement in ultra-small angle X-ray scattering (USAXS) range
- Engineered for both quality control and research & development applications
- Non-technical operation for routine particle size distribution determinations
- Delivers nanoparticle characterization needed for regulatory compliance
- Perfect for opaque suspensions not easily addressable with other techniques
- Suitable for use with solids – like plastics, rubbers and polymers
- Compact benchtop design with a small countertop footprint
- Innovative design using proven components for low cost of ownership
- Automatic sample changer for higher throughput
- New easy-to-use SmartLab Studio II SAXS software
- Touch screen graphical user interface operation
- Compact Bonse-Hart USAXS camera design
  - CBO mirror and crystal monochromator integrated into the incident side
  - High-precision goniometer and crystal monochromator for analyzer side
  - D/teX Ultra 250 detector for high count rates and fluorescence suppression
  - No need to switch attenuator

Bonse-Hart ultra SAXS camera design

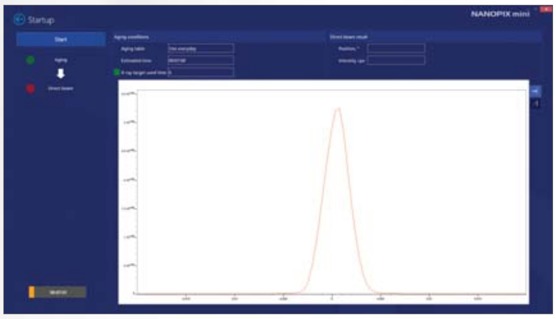
Rigaku NANOPIX mini consists of a sealed tube X-ray generator, incident beam conditioning optics, an automatic sample changer, scanning receiving optics and a silicon strip detector. The sealed X-ray tube emits Cu-Kα-radiation (λ = 0.154 nm), and can be operated at a maximum power of 600 W. Divergent X-rays from the source are transformed into a parallel beam, by Rigaku Cross Beam Optics (CBO), before passing through a high resolution PB-Ge(220)x2 monochromator and illuminating the sample. Scattered X- rays from the sample are captured by analyzing optics consisting of an ultra high-resolution Ge(220)x4 monochromator attached to an superior precision goniometer. Only angles that precisely satisfy the Bragg equation, for a given 2θ angle, are allowed to pass. As the goniometer scans through 2θ angles, pixels on the fi xed position 1D detector record the scattered intensity as a function of angle.



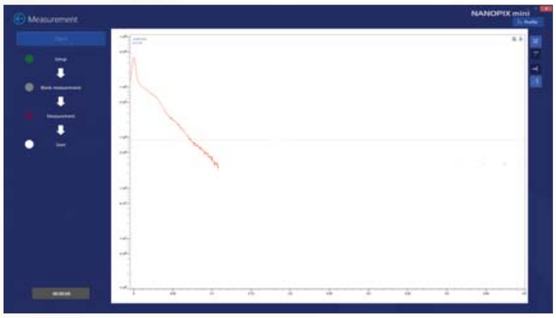
oth QC and R&D

SmartLab Studio II software

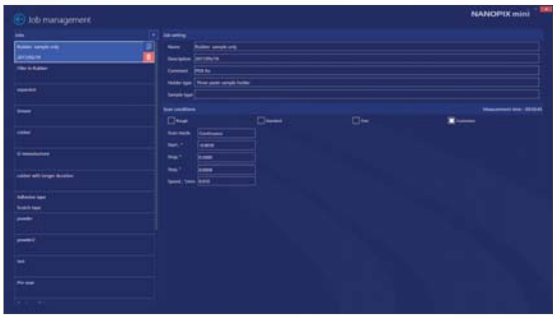
Rigaku NANOPIX mini employs the new SmartLab Studio II software suite for measurement and analysis of SAXS data. Offering comprehensive data analysis, automation options and reporting, the user interface was specifically designed for routine particle size and distribution by non-expert operators. For expert operators in an R&D environment, complex data reduction, such as Guinier and Porod analysis, is provided. SmartLab Studio II is a 64-bit application and offers all the benefits of the touch screen based Windows® 10 architecture.



Startup GUI



Measurement GUI



Job GUI

Applications

Since the 1960s, researchers have made great progress in synthesizing monodisperse nanoparticles with diverse shapes. Characterization is a key driver, where it is critical to understand the structure of the particle products – with both high accuracy and precision – to further advance synthetic methodology and probe structure–function relationships.

The table at right details some well documented industrial and medical nanomaterials applications that may be characterized using the SAXS method. Medical applications of nanoparticles range from metal oxides and metal polymers to fullerenes and emulsions. Industrial applications are more even exotic, reaching from organics like CNT to nanoparticle organic memory field-effect transistors and quantum dots.

Particle size and size distribution

The size distribution function is the key piece of information obtained from SAXS. When the shape of a particle is known or can be assumed, it become very easy to fit the data to determine the size distribution. Samples may range from solutions, suspensions or slurries to solid plastics, rubbers or polymers.

Particle shape

Information about the particle shape is included in the form factor that describes scattering from a particle and in the particle volume. Thus the shape of the scattering function is directly related to the 3D shape of the particle under certain conditions (like dilute solutions). Advances in a variety of mathematical treatments now allow researchers the ability to fit or model data to determine the approximate three dimensional form.

Pore size and porosity

Sophisticated treatment of SAXS data can allow researchers to determine the porosity, pore size distribution and internal specific surface area in particles.

Advanced characterization for R&D

For uniform sized particles, SAXS can allow a researcher to perform more advanced structural characterization, capable of determining core–shell morphologies or the edge length of polyhedral particles. Also, the specific surface area from nanoparticles can then be determined from an integral over the size distribution function. In addition, by using absolute intensity analysis, it is possible to obtain the particle volume fraction, or nanoparticle concentration.

Nanoparticle Assembly

There has been considerable interest in recent years in the assembly and/or self-assembly of nanomaterials. Indeed, a core challenge in nanotechnology is the rational design and assembly of nanoparticle subassemblies. SAXS has been used to understand nanoparticle synthesis. Another aspect of synthesis that may be studies with SAXS is the tendency of particles to aggregate.

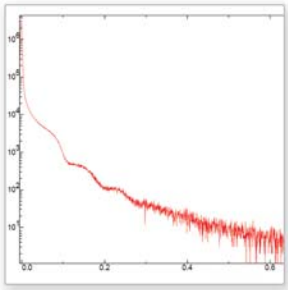
Industrial and medical nanoparticle applications

Nanomaterial	Applications
Silver nanoparticle ink	Printed electronics circuits
Calcium, Magnesium, Copper, Platinum, Palladium, Iridium, Titanium, Zinc	Food supplements
Carbon nanotubes (CNT)	Electronics, optics and materials science
Ceramic silicon carbide	Materials science
Cerium oxide	Medicine, antioxidant
Copper	Lead-free solder
Copper tungsten oxide	Photocatalytic environmental remediation
Encapsulated nanoparticles	Enhance bioavailability
Fullerenes	MRI contrast agents, X-Ray imaging contrast agents, photodynamic therapy and drug and gene delivery
Gold in a porous manganese oxide	Catalytic air pollution remediation
Gold with organics (NOMFET)	Nanoparticle organic memory field-effect transistors
Iron	Breakdown of chlorinated hydrocarbons in water
Iron oxide	Arsenic remediation in groundwater
Liposomes	Nanoparticles capable of carrying bothwater-soluble and oil- or fat-solublecompounds within a single particle
Lycopene	Nutraceutical
Micellar organic nanocapsules	Delivery system for hydrophobic substances
Nanoclays (layered mineral silicates)	Transparent barrier for packaging to block oxygen, carbon dioxide and moisture
Nanocomposites of nylon	Packaging materials used to increase shelf life
Nanodiamonds	Drug delivery, medicine
Nanoemulsions	Enhance bioavailability; extend shelf life; increase viscosity
Nanotetrapods studded with nanoparticles	Electrode material
Nickel with polymer	Medicine, prosthetic research
Oil-in-water emulsions	Modifies bioavailability
Palladium	Hydrogen sensor
Platinum-cobalt	Catalysts for fuel cells
Polyamidoamine (PAMAM) dendrimers	Potential carriers for drug and gene delivery
Polymer coated iron oxide	Medicine
Polymeric micelles	Drug delivery
Polystyrene (PS) and poly(methyl methacrylate) (PMMA) microspheres	Scientific research, diagnostics, electronics, pharmaceuticals
Protein filled NP	Medicine
Rubber, polymers	Materials science
Quantum dots	Optics, electronics, medicine, research
Semiconductor	Printed solar cells
Silica and silicates	Used to increase flow ability of powdered ingredients; Packaging materials used to increase shelf life
Silicon	Battery anode coatings
Silver	Antimicrobial and antifungal surfaces
Silver or gold	Food supplements
Titanium dioxide	Packaging materials used to increase shelf life
Zeolite	Catalyst support
Zinc oxide	UV protective coatings

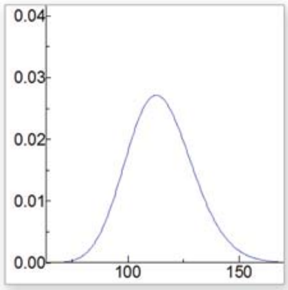
Examples

Particle size and distribution example

SAXS is a powerful method to determine both average particle size and size distributions. The plots show experimental data from silica nanoparticles as measured by the NANOPIX mini. The plot (at right) shows the 1D SAXS pattern of measured intensity as a function of 2θ angle. NANOPIX mini software evaluates the 1D SAXS pattern and calculates the volume-weighted particle size distribution (far right). The average diameter is estimated to be 111 nm, which agrees with TEM image analysis.



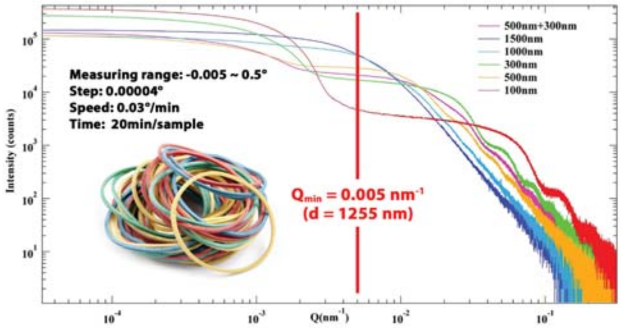
1D SAXS pattern of silica nanoparticles



Particle size distribution (nm)

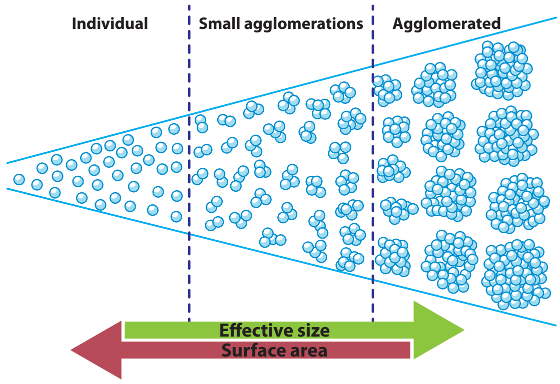
Filler particles in resins, rubbers and plastics

Use of particulate fillers to modify the mechanical properties of resins and rubbers is well documented. The filler modifies not only the mechanical properties of resins but also the physical and chemical properties such as melting temperature and electric resistance and so on. Some fillers, particularly those of very small particle size, reinforce polymers. Strength enhancement depends principally on the particle size of the filler, increasing with decreasing particle size. NANOPIX mini is the ideal instrument for quantifying filler particle size and size distribution in optically opaque samples like rubber where other methods are cumbersome. Shown at right is data from rubber samples with different monodisperse filler particle sizes showing clearly distinct scattering patterns.



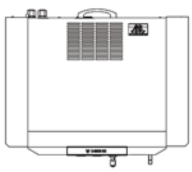
Particle aggregation

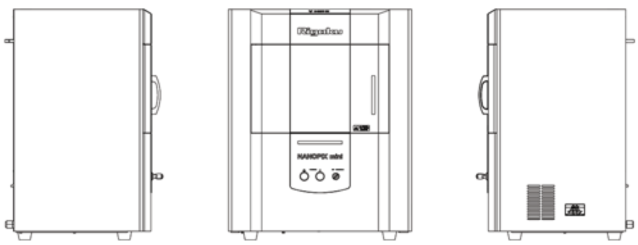
The tendency of nanoparticles to aggregate, often as a result of the drying stage during the synthesis process, is of particular importance to the manufacturing process of nanoparticles. Aggregation is the process whereby small molecules or particles can come together to form a secondary larger particle or cluster that is held together by one or more molecular interactions, such as Van der Waals forces or hydrogen bonds. This has considerable implications for the determination of the size and surface area of the nanoparticles, as well as for their reactivity or toxicity. NANOPIX mini is the ideal instrument, for both R&D and production, to develop and control production methods that lead to safe and effective products.



Specifications

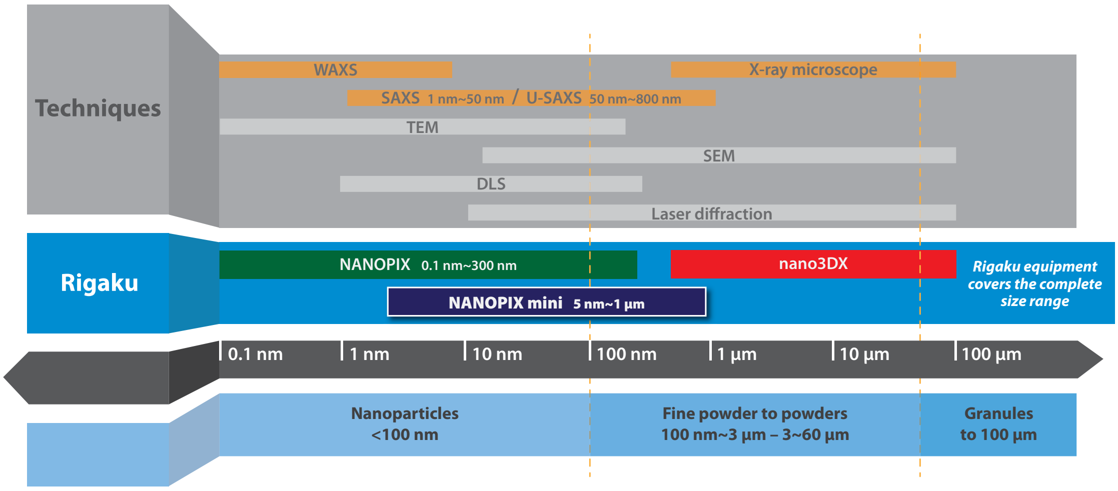
NANOPIX mini	
Particle sizing range	5 nm to 1000 nm
Two theta coverage	-0.5° < 2θ < +1.75°
Angular resolution	5.6 x 10^{-4}° (0.2 arc sec)
X-ray source	Cu-target X-ray tube (40 KV, 15 mA, 600 W)
Incident optics	Curved multilayer mirror CBO™ Ge(220) 2 bounce symmetric reflection
Sample holder	Capillary holder / multi sample holder
Analyzing optics	Ge(220) 4 bounce symmetric reflection
Detector	D/teX Ultra250
Software	NANOPIX mini Guidance SmartLab Studio II – MRSAXS plug-in
Cooling water	1 kW cooling water external circulator
OS / Computer	Windows® / PC, Monitor
Power	100 – 240 VAC ±10%, 1-phase, 50/60 Hz
Dimensions	580 W × 730 H × 500 D (mm)
Weight	Approx. 90 kg





Backed by Rigaku

Since its inception in 1951, Rigaku has been at the forefront of analytical and industrial instrumentation technology. Today, with hundreds of major innovations to our credit, the Rigaku Group of Companies are world leaders in the field of analytical X-ray instrumentation. Rigaku employs over 1,400 people worldwide in operations based in Japan, the U.S., Europe, South America and China.



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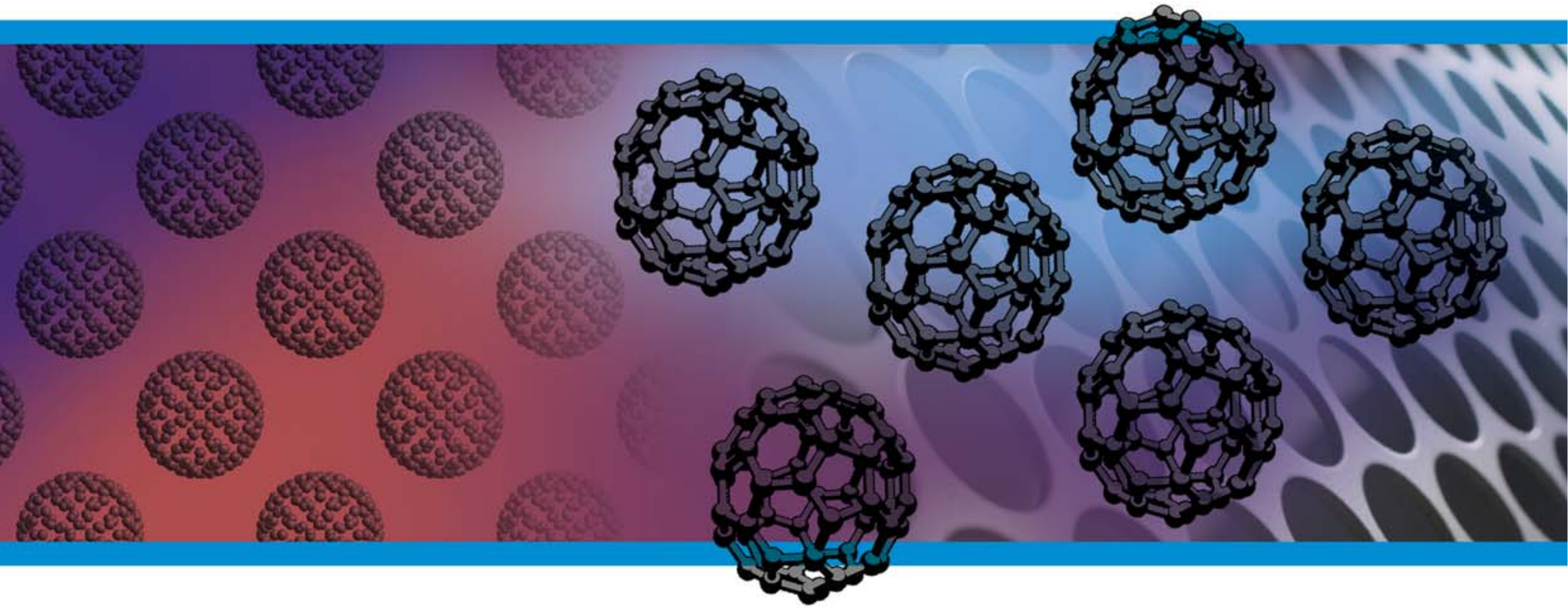

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