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Characterization of Engineered NMs in the Environment: Technology constraints and confounding factors

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Applications list

Industry Segment	Type of Nanomaterial	Application Area
Defense	Active Tunable Nanofibers/ Nanoparticles; Nanocomposites, Carbon Nanotubes	Camouflage fabric that can vary color based on surface charge and hence tunable control of the infrared signature for active camouflage. [1]
	Polymer/Nano-iron oxide Composites Polymer/Nano-aluminum Composites Bismuth /Carbon Nanoparticles	Propellants for firearms due to extreme exothermic reaction from the iron oxide particles that is equal to or superior to existing toxic and carcinogenic propellants. Rocket Primers and Rocket Fuels are being" greened" by substituting nanomaterials for lead. [2, 3]
	Magnesium Nanoparticles, Zinc Nanoparticles	Added to paints and coatings for corrosion resistance. Appear to have better wear life than traditional chrome plating and safer to use. [4]
	Carbon Nanotubes	Bullet-proof multilayer-epoxy composites manufactured with CN sheets, the size of a piece of plywood 4' x 8' foot, provide a shield that can stop a 9mm bullet and weighs no more than a pack of playing cards[5]
Energy	Carbon Nanotubes	Aim is to produce inexpensive solar cells containing carbon nanotubes that can be painted or printed on flexible plastic sheets. May enable homeowners to print their own solar panels via an inkjet printer. [6]
	Pd and V doped carbon nanotubes	Enhance hydrogen fuel cells by increasing storage capacities and showing faster hydrogen absorption kinetics. [7]
	Nanoparticles	Laboratory experiments have shown that certain nanoparticles can stimulate algae growth as a source of biofuels [8]
Aerospace	Carbon nanotube/epoxy composites	Graphite/epoxy composites are being replaced by CNT/epoxy composites. These are stronger and lighter in weight than traditional composites [9]
	Clay nanoparticles	Being incorporated with polymers to create fire retardant aircraft interiors. [10]
	Aluminum nanoparticles	Increase propulsion energy mixed with liquid hydrogen for jet and rocket fuels. [11]

Applications list

Electronics / IT	Carbon Nanotubes	Carbon nanotubes are central to the design of a nanoengineered battery. Need for lightweight, ultra thin and flexible batteries for consumer products and medical devices [12]
	Carbon Nanotubes	Experimental Nano-thin film loud speakers have been created. [13]
	Carbon Nanotubes	Printable water-based inks containing CNTs enable the production of transparent, electrically conductive thin films that may replace conductive thin films made with indium-tin oxide. Applications are cell phones, touch screens, and flexible displays. [14]
Automotive	Nanoparticles	Color fast automobile paints contain non-fading nanoparticles along with scratch, chemical, UV resistance and self cleaning properties [15]
	Nanomaterials	An oil base nanomaterial coated with a surfactant, to maintain the nanomaterials in solution, are used in thermal conductive motor oils. They're used in automatic transmissions and hydraulic steering applications [16]
	Magnetic nanoparticles	Used to create magnetic fluids that are used in shock absorbers [17]
	10 nm Cerium oxide nanoparticles	Forms part of the Environ™ diesel fuel catalyst which improves combustion due to the increased surface area of the cerium oxide nanoparticles[18]
Construction Materials	Nanomaterials	Nanomaterials in a sheer coating repel dust and water. This could lead to self-cleaning windows and self-cleaning solar panels. [19]
	Nanomaterials	Nanomaterials provide a barrier for concrete. The nano-additive slows down the penetration of chloride and sulfate ions from road salt. This may double the life of concrete. [20]
	Nanomaterials	Coatings for bricks, clay, plaster, and stone include anti-damp coatings that are water repellent and anti-fungal/algae [21]
Coatings	Nanomaterials	Nanoparticle based, organic corrosion inhibitors are replacing costly chromate based corrosion Inhibitors. Estimated costs of the DoD when dealing with end of life chrome plating are in the $20 Billion range. These new coatings will substantially save money [22].
Textiles / Apparel	Quantum Dots	Textile dyes obtain pure and bright hues. Nanocrystals as colorants are stable and, when mixed with dyes, can produce a spectrum of colors, which is not attainable by either dyes or pigments [23].

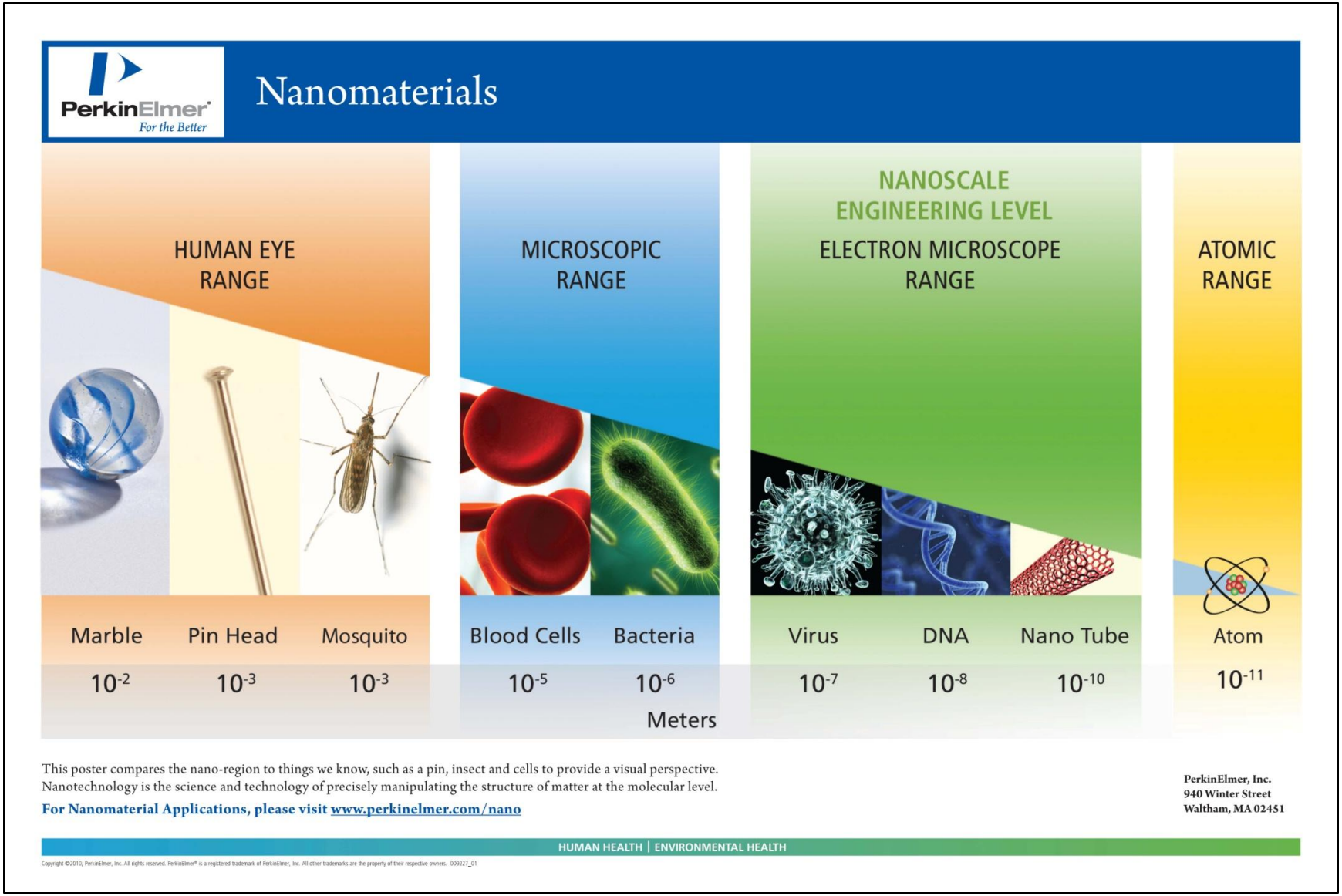
Applications list

	Wax Nanoparticles	A water repellent spray coating made up of super hydrophobic 1 nanometer wax particles creates a fabric that is resistant to water and dust. [24].
	Nanoparticles and Nanofibers	Laboratory experiments have shown that it is possible for excess body heat to be stored in a garment. The stored heat in the garment is released back to the skin when needed [25].
	Silver nanoparticles	Integrated with sports clothing to prevent microbial growth, and odor [26].
Cosmetics / Personal Care Products	Nano titanium dioxide & nano zinc oxide	Used in some cosmetics. The applications include: eye liners, moisturizers, lip sticks, make-up foundations, soaps, sunscreen, mascara, and nail polish. [27] [28]
Food & Beverage	Carbon Nanotubes, Nanoparticles	Nanomaterials are used in food packaging. The penetration of light, moisture, or gases can alter the sensory characteristics of food products, as well as foment spoilage. Nanomaterials enhance packaging barrier properties. An example is clay nanoparticles are used as an oxygen barrier in boil-in plastic bags [29]
	Polymeric and Liposome Nanoparticles	Nanomaterials are being used to deliver vitamins and nutrients in foods. The nanomaterials are coated with the vitamins and nutrients and carry them through the stomach to the blood stream [30]
	Polymeric and Liposome Nanoparticles	Interactive foods are being developed in the laboratories that allow you to choose the desired flavor and color of a food. A nanoparticle is coated with the flavoring or color and then trigger by some human trigger, possibly chewing [31] [32].
Medicine / Health	Bioactive Nanomaterial	Northwestern University's researchers have developed a material of nanoscopic fibers that stimulate stem cells present in bone marrow to produce cartilage containing type II collagen and repair the damaged joint. This minimally invasive therapy activates the bone marrow stem cells and produces natural cartilage [33].
	Ceramic Nanoparticles	Nanoparticle-ceramic composites are used on dental applications for crowns, bridges, and inlays that require high strength [34].
	Carbon Nanotubes	Various carbon nanomaterials are used to enhance imaging properties of a variety of MRI and CT-based contrast agents [35].

Applications list

Sensors	Nano-electronics	Current laboratory research focuses on nanoscale sensor array probes are used as electronic noses to detect gases and bio-metabolites [36]
	ZnO Nanowires	Georgia Tech Laboratory researchers have been able to produce a self-powered nanosensor. It's made of freestanding zinc-oxide nanowires that have the ability to generate electrical potential when placed under stress. [37]
	Unknown	Researchers have developed electronic motion detection by a nanoelectomechancial bridge and a single-electron transistor can detect movements as small one thousandth of a nanometer [38]
Recreation	Unknown	Skis and Snowboards--Cerax Nanowax, which moved from the laboratory to commercial usage in a relatively rapid 15 month time span, was introduced in Europe in September of 1999. Nanogate Coating Systems is now among the "top ten of ski wax suppliers," according to Dieter Moeller of Nanogate, product manager for Cerax. [39]
	Carbon Nanotubes, Nanoparticles	High end ($) golf club shafts are made with nano-composites to make the shaft stronger and more flexible. Racing bicycle components. [40]
	Clay Nanoparticles	According to a tennis ball manufacturer, clay nanoparticles mixed with plastics and synthetic rubber create an airtight surface. This sealant is used in double core tennis balls. The double core tennis balls have twice the bounce because the nanoparticles lock in air more effectively. [41]

Nanoscale Engineering



Engineered Nanomaterials

Carbon Nanotubes (CNTs)

Graphene

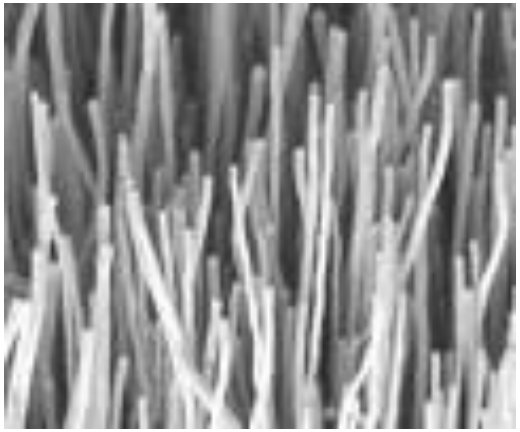
Nanoplates

Nanoparticles (NPs)

--Nanocomposix Corp

Fullerene
Or
Bucky Ball

--Andy Gion



Nanofibers
Nanowires

Key Nanomaterial Characteristics that need to be assessed

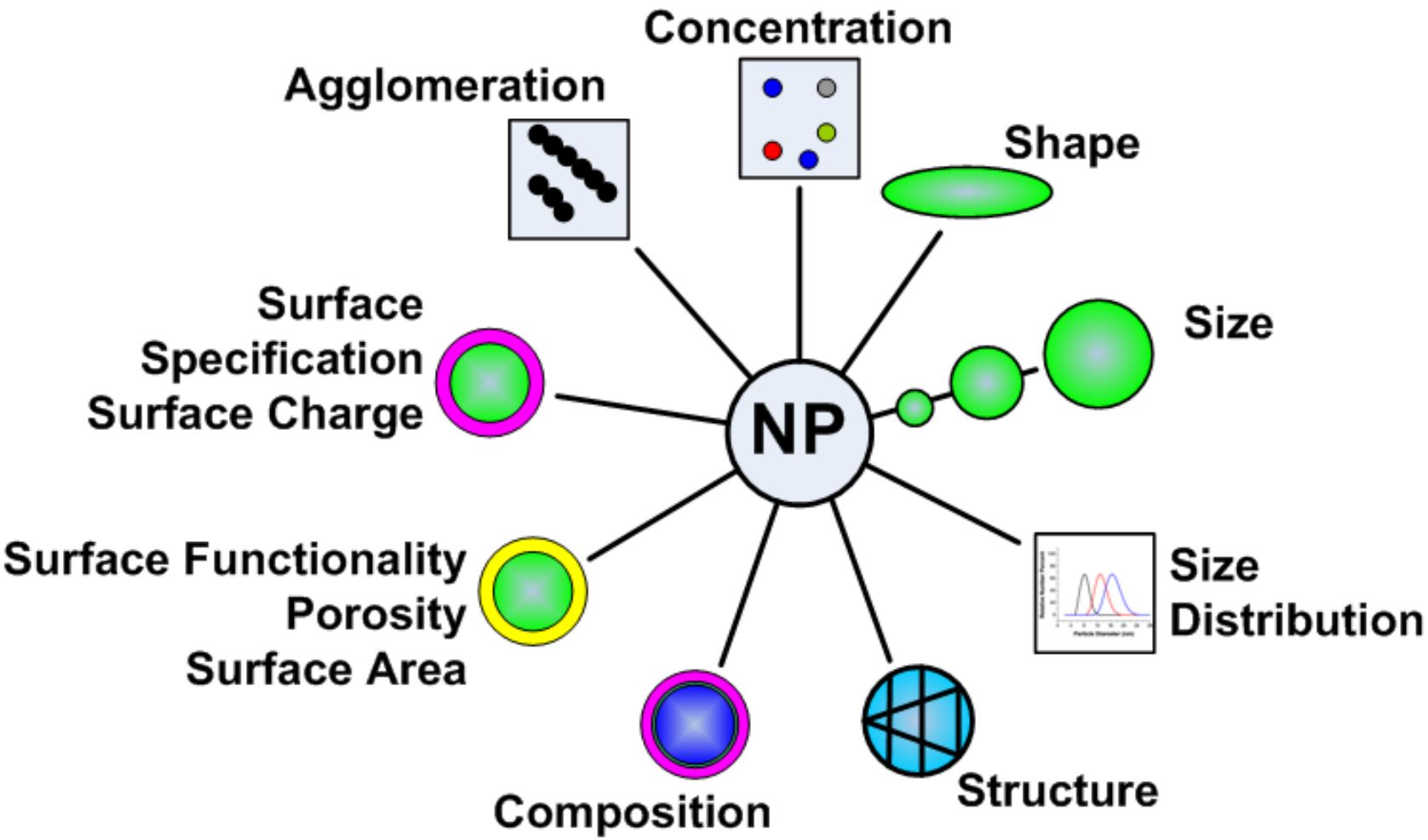


Figure adopted from Hassellöv, M., and Kaegi, R., *Analysis and characterisation of manufactured nanoparticles in aquatic environments*, Chapter 6 in *Environmental & Human Health Impacts of Nanotechnology*, Eds., Lead, J.R. & Smith, E., 2009 Blackwell Publishing Ltd.

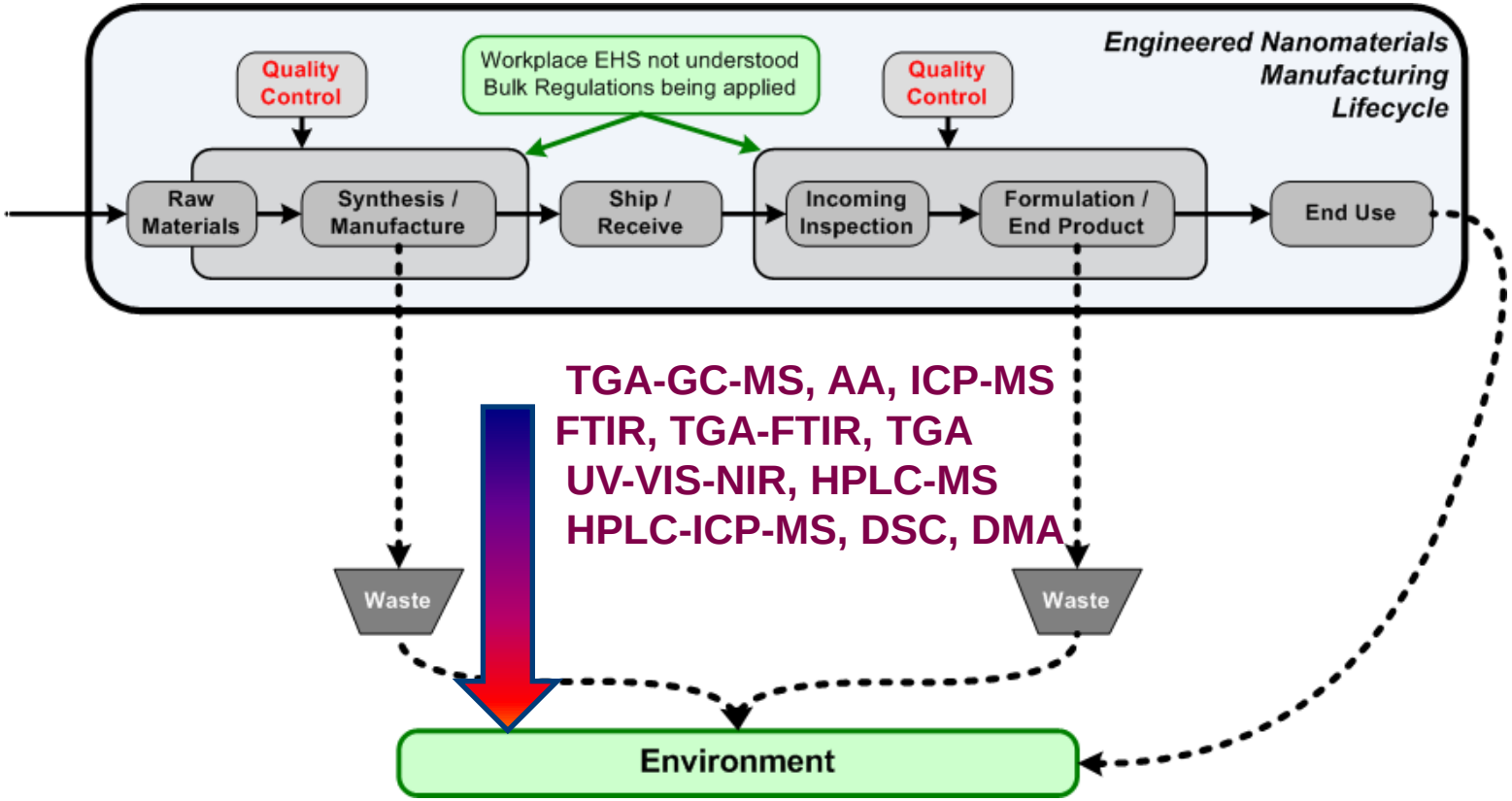
Nanomaterial Characteristics & Analytical Technologies

Table 4. **Nanomaterial characteristics and applicable analytical technologies.**

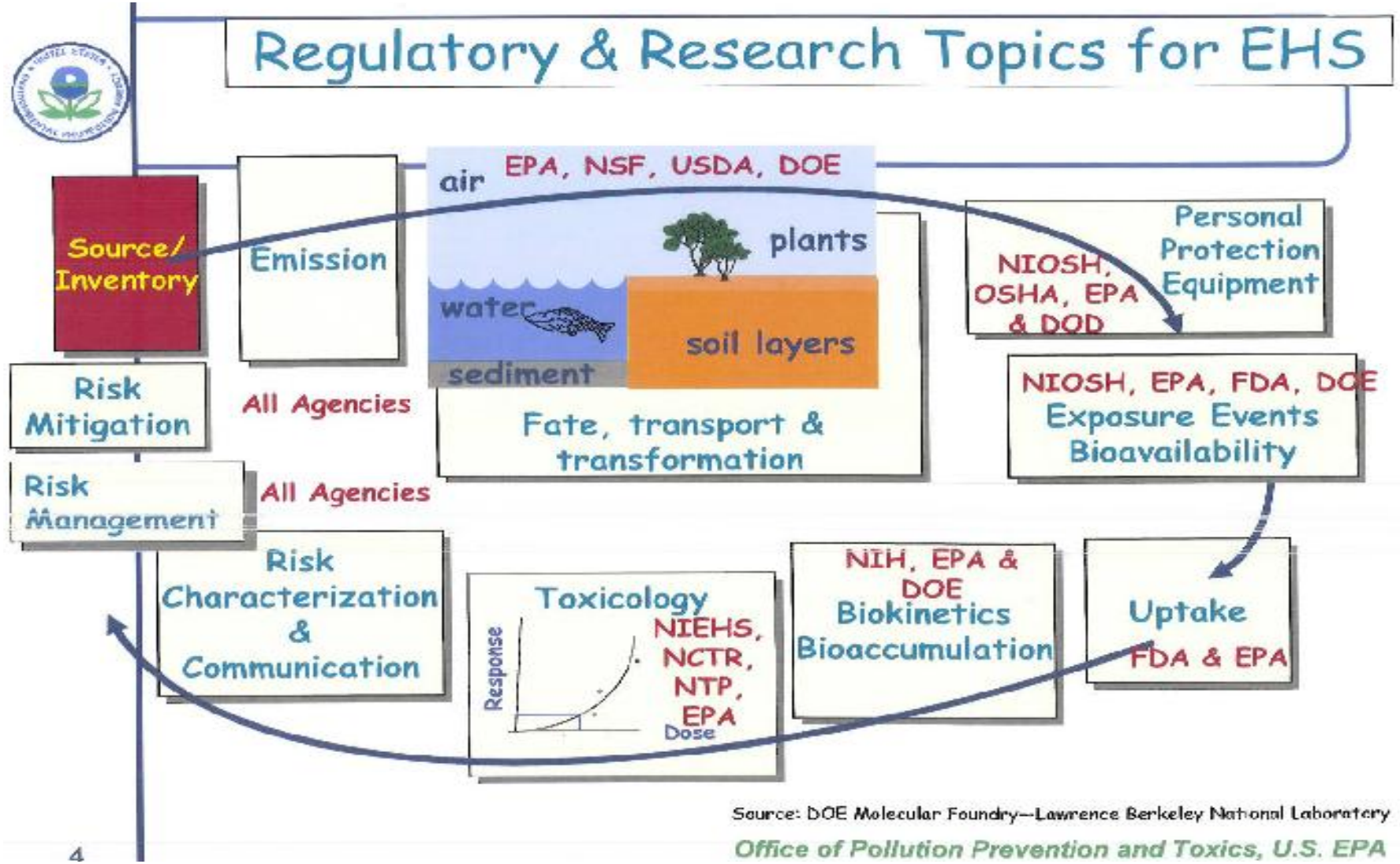
Analytical Technique		Nanomaterial Characteristics								
		Concentration	Particle Size	Particle Size Distribution	Surface Charge	Surface Area	Shape	Agglomeration	Structure	Composition
Inductively Coupled Plasma – Mass Spectrometry	ICP-MS	●								●
Field-flow Fractionation + ICP-MS	FFF-ICP-MS	●	●				●	●		●
Liquid Chromatography – Mass Spectrometry	LC-MS	●								●
Optical Spectroscopy – UV/Vis	UV/Vis	●	●							●
Fluorescence Spectroscopy	FL	●	●					●		●
Turbidity			●	●				●		
Scanning Electron Microscopy	SEM		●	●			●	●	●	
Transmission Electron Microscopy (+EDX)	TEM		●	●		●	●	●	●	●
Atomic Force Microscopy	AFM		●	●	●	●	●	●		
Confocal Microscopy			●	●			●	●	●	
Field Flow Fractionation	FFF		●	●			●	●		
Dynamic Light Scattering	DLS		●	●			●	●		
Static Light Scattering	SLS		●				●	●		
Molecular Gas Adsorption (BET)	BET				●	●				
Dialysis			●							
Electrophoresis and Capillary Electrophoresis			●	●						
Ultrafiltration			●	●	●					
Centrifugation			●	●				●		
Filtration			●	●						
Nanoparticle Tracking Analysis	NTA		●	●				●		
Size Exclusion Chromatography	SEC		●	●						
Selected Area Electron Diffraction	SAED		●	●					●	
Zeta Potential by DLS					●					
X-ray Diffraction	XRD								●	
Thermogravimetric Analysis	TGA		●							●
Quartz Microbalances			●							●
Differential Scanning Calorimetry	DSC									●
Dynamic Mechanical Analysis	DMA									●
Fourier Transform Infrared Spectroscopy	FT-IR									●
FT-IR Imaging									●	●
Raman Spectroscopy			●						●	●
TGA coupled with Gas Chromatography – Mass Spectrometry	TGA-GC/MS									●
Laser Induced Plasma Spectroscopy	LIPS		●							
Hydrodynamic Chromatography	HDC		●	●						
Laser Induced Breakdown Detection	LIBD		●	●				●		
X-ray Photoelectron Spectroscopy	XPS				●	●				●
Electron Energy Loss Spectroscopy	EELS (+EDX)									●

● Commonly used in the characterization of nanomaterials ● Microscopy techniques ● Not widely applicable ● Available from PerkinElmer

Engineered Nanomaterial Manufacturing Lifecycle



Environmental Cycle for Nanomaterials



Citation

- **Synthesis, characterization and behavior of Manufactured Nanoparticles in the Environment.**
  - **Speaker:** *Jamie Lead –U of Birmingham at the* **5th International Conference on the Environmental Effects of Nanomaterials and Nanoparticles – August 2010 , Clemson, SC,**

- **Excerpts from A. W. Salamon's notes:**
  - **"There are no techniques to characterize NPs in soils and in water." [field analysis]**
  - **"Use as many analytical techniques as possible to characterize NPs."**
  - **"When uncoated NPs enter the natural water environment, they are immediately coated with organic materials from the environment. This may change the toxicity and make the NPs more stable and non-toxic."**
  - **"Natural NPs look almost identical to Engineered NPs."**

Citation

- **Field and laboratory arsenic speciation methods and their application to natural-water analysis [HPLC-ICP-MS]**
  - **Authors:** *A.J.Bednar, J.R. Garbarino, M.R. Bukhardt – USGA; J.F. Ranville, and T.R. Wildeman -- Colorado School of Mines*

- **"Arsenic can exist in natural water in a variety of inorganic and organic forms. … Many of these species are the result of natural processes, such as mineral weathering or biological activity, yet the number of possible anthropogenic sources is increasing, primarily from mining and agriculture."**

Citation

- **Characterizing Manufactured Nanoparticles in the Environment: Multimethod Determination of Particle Sizes [FL, TEM, AFM, FFF, DLS]**
  - **Authors:** *R. F. Dominogos , M.A. Baalousha, et al. – U Montreal, U Birmingham, McMaster U, McGill U, Canadian National Water Research Inst.*

- **"The mobility, fate, and bioavailabity of manufactured nanoparticles in the environment depend on the their size, shape, charge, and other properties. Unfortunately the characterization and quantification of nanoparticles is a difficult analytical challenge since measurements are highly dependent upon:**
  1. **Particle size and nature,**
  2. **Sample concentration and solution physicochemistry, and**
  3. **Fundamental principals of the analytical technique"**

Citation

- **Influence of Stability of the Acute Toxicity of CdSe/ZnS Nanocrystals to *Daphnia Magna* [UV-VIS, DSL, FFF-ICP-AES, FFF-ICP-MS]**
  Authors: *H. E Page, E.K. Lesher, and J.F. Ranville – Colorado School of Mines*

- **"Most toxicology studies have suggested two pathways by which QD nanocrystals can cause impairment: dissolution and release of toxic metals, and toxic effects associated with nanoscale properties (nanoparticle size, surface chemistry, etc). *Derfus et al* reported that CdSe-core QDs produced cyto-toxic effects, which were correlated with the release of free Cd^{2+} due to surface oxidation. This toxic effect was exacerbated by exposure to air and ultraviolet (UV) light, which served to accelerate the oxidation process. … The principal objective of this study is to relate the toxicity of QD's to specific physical and/or chemical aspects of QD."**

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    - Elemental Analysis (EA2400) application
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    - TGA-FTIR application
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Nanomaterials Reference Library

Nanotechnology is the understanding and control of matter at dimensions between approximately 1 and 100 nanometers [size], where unique phenomena enable novel applications. — *National Nanomaterial Initiative.*

PerkinElmer's analytical Instruments enable engineers and scientists to measure and better understand nanomaterials and their diverse applications. On this page you will find some scientific papers about Nanomaterial applications (from synthesizing to end use) that illustrate PerkinElmer's contribution to this revolutionary science.

- Application Notes
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- Nano Resource & Education Education Centers

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Developing a method – step 1

- **Ask a series of questions**
  1. **What is the physical state of the material?**
     - A composite, a liquid, a powder?
  2. **What NP characteristics need to be analyzed?**
     - Rank them by importance.
  3. **What type of information is required?**
     - Quantitative, Qualitative, a mixture of both?
  4. **What analytical accuracy and precision are required?**
  5. **What do you know about the material?**
  6. **Is the sample complex or simple?**
  7. **What is the history of the sample?**
  8. **What is the material's future?**
  9. **How many samples must be run?**
  10. **What is the required analysis turnaround time?**
  11. **Are the safety hazards to be concerned about?**

Developing a method – step 2

- **Review the Characterization Matrix and Identify the instruments for your investigation.**

Developing a method – step 3

- Your sample may be similar to another sample type that already has a published method. ISO or ASTM may have methods, test reports, or guidance documents that may be modified to meet your needs.

- ISO examples:
  - Nanotechnologies — Determination of metal impurities in carbon nanotubes (CNTs) using inductively coupled plasma - mass spectrometry (ICP-MS)
  - [Revised Draft Dec. 02, 2010] Detection of surface bound molecules to gold nanoparticles using Fourier Transform Infrared (FT-IR) spectroscopy

Developing a method – step 4

- Ask the experts if you are not sure.
  - Data interpretation
  - They may recommend additional testing
  - They may recommend solutions to your problem
- Where to find the experts
  - Universities
  - Consultants
  - Instrument manufacturers

Recent Nano in the Environment investigations and developments

"[Single Particle] SP-ICPMS is the first analytical technique to characterize silver nanoparticle size distributions in surface water at concentrations relevant to release from consumer products."

—E. M. Heithmar[1], S.A. Pergantis[2], C. Stephan[3], E.M. Siska[4], S.A. Beres[3], [1] US EPA, [2]University of Crete, [3]PerkinElmer, [4]Student Services Contractor to EPA, Transformations of silver Nanoparticles at environmentally relevant concentrations in fresh and saline surface waters, May16, 2011. Milan, Italy

"TGA – [GC] MS for analysis of Polyaromatichydrocarbons adsorbed on nano-TiO2"

"TGA [is a] powerful tool to study purity, structural changes with nanomaterials for with a well defined parameter and experimental condition. [and] environmental transformation [of CNTs] including sorption and oxidation of nanomaterials can be studied." *-- E. Sahle-Demessie[1], A. Zhao[1], A. W. Salamon[2], [1]U.S. EPA, [2]PerkinElmer , Integrated Thermal Analysis and Related Hyphenated Techniques for the Characterization of Multi-Walled Carbon Nanotubes, March 16,2011. Atlanta, GA.*

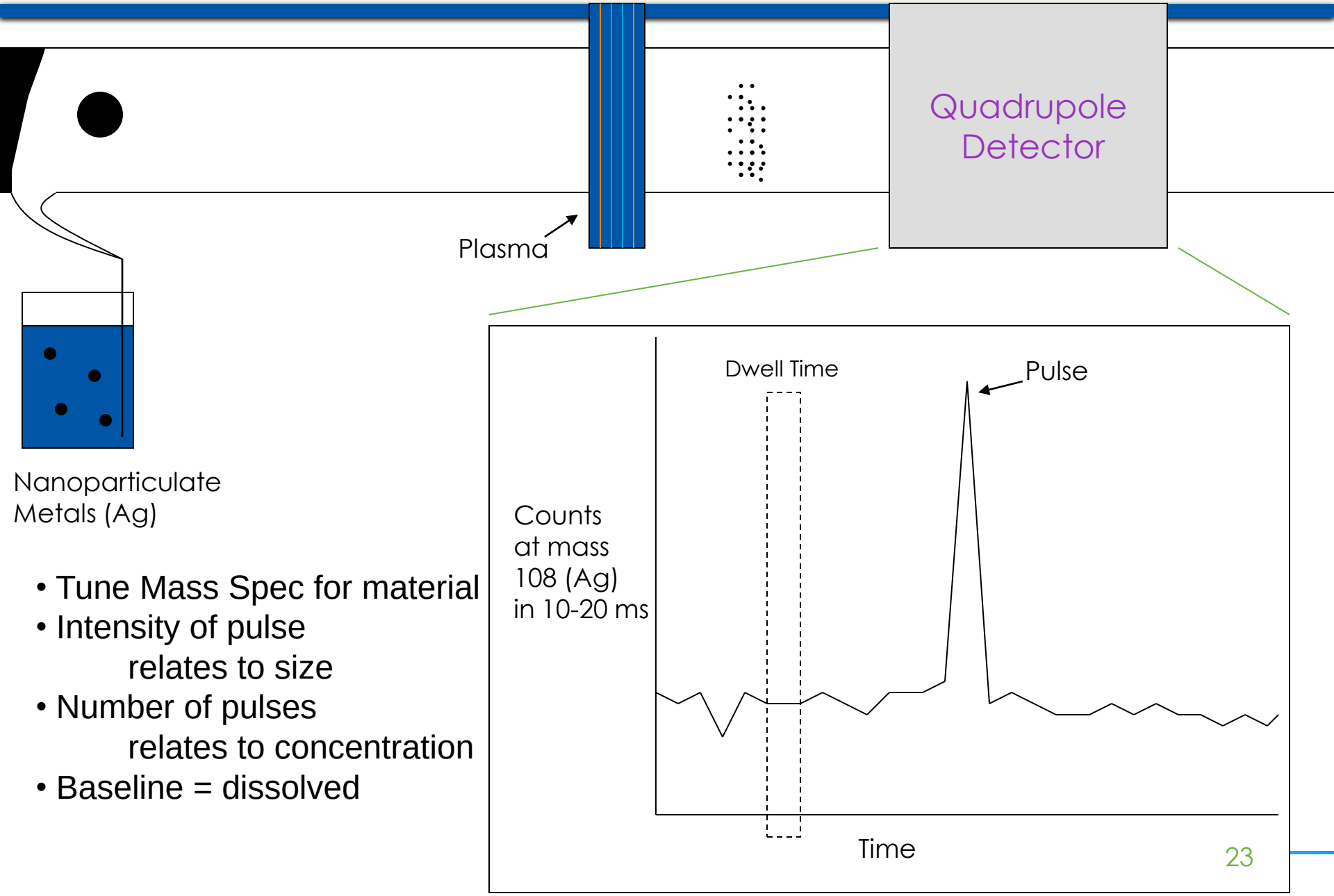
Multi-Walled Carbon Nanotubes; Significant New Use Rule - June 6th, 2011

40 CFR Parts 9 and 721 [EPA–HQ–OPPT–2009–0686; FRL–8865–4] RIN 2070–AB27

"This action requires persons who intend to manufacture, import, or process the chemical substance for a use that is designated as a significant new use by this final rule … "After the final SNUR is effective, any person intending to manufacture, import, or process the substance for a use other than as an additive/filler for polymer composites and support media for industrial catalysts "

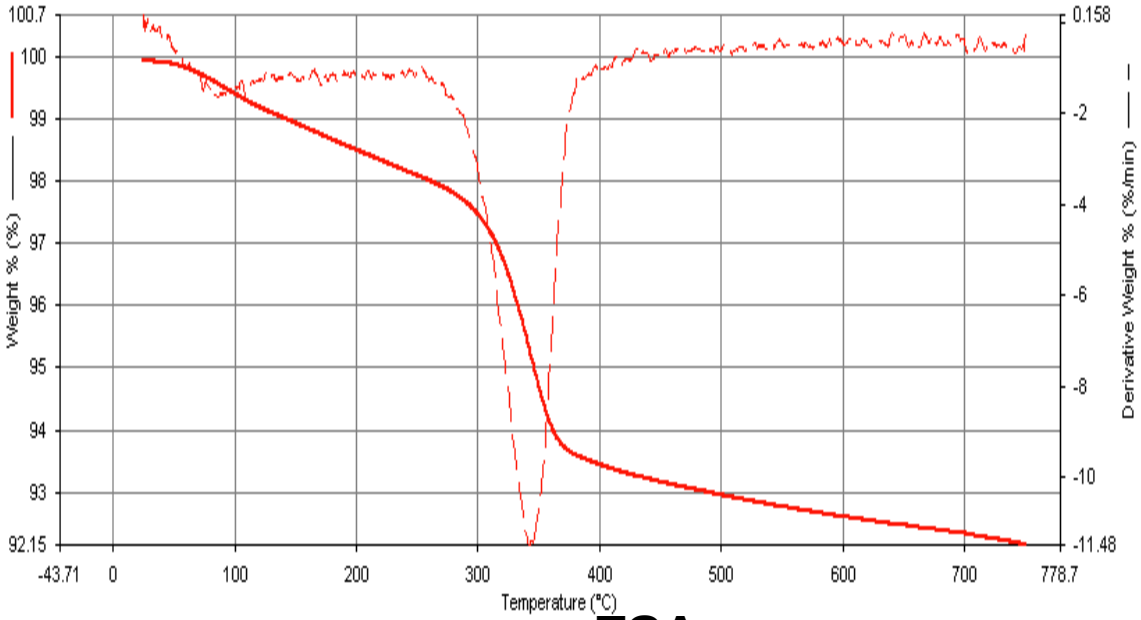
ICP-MS Schematic of General Analysis for Nano Metals

--courtesy of Dr. Chady Stephan



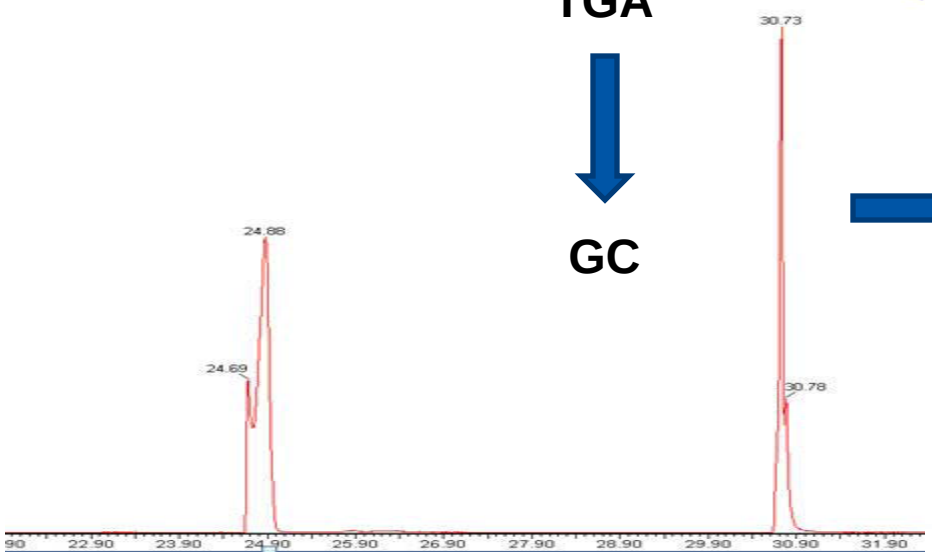
- Tune Mass Spec for material
- Intensity of pulse
  relates to size
- Number of pulses
  relates to concentration
- Baseline = dissolved

TGA --GC--MS for analysis of Polyaromatichydrocarbons adsorbed on nano-TiO2

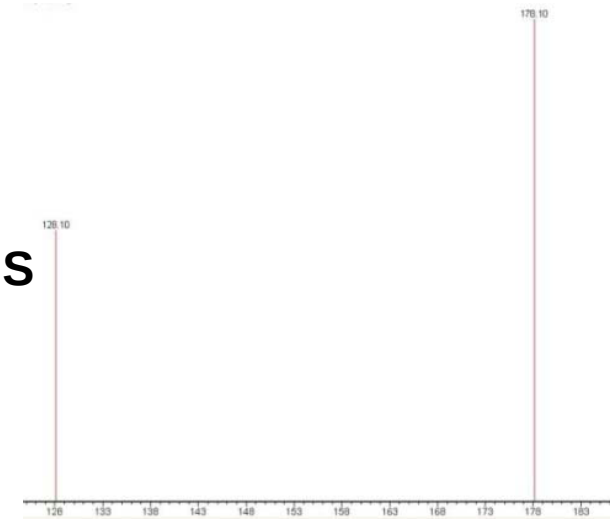


TGA

GC

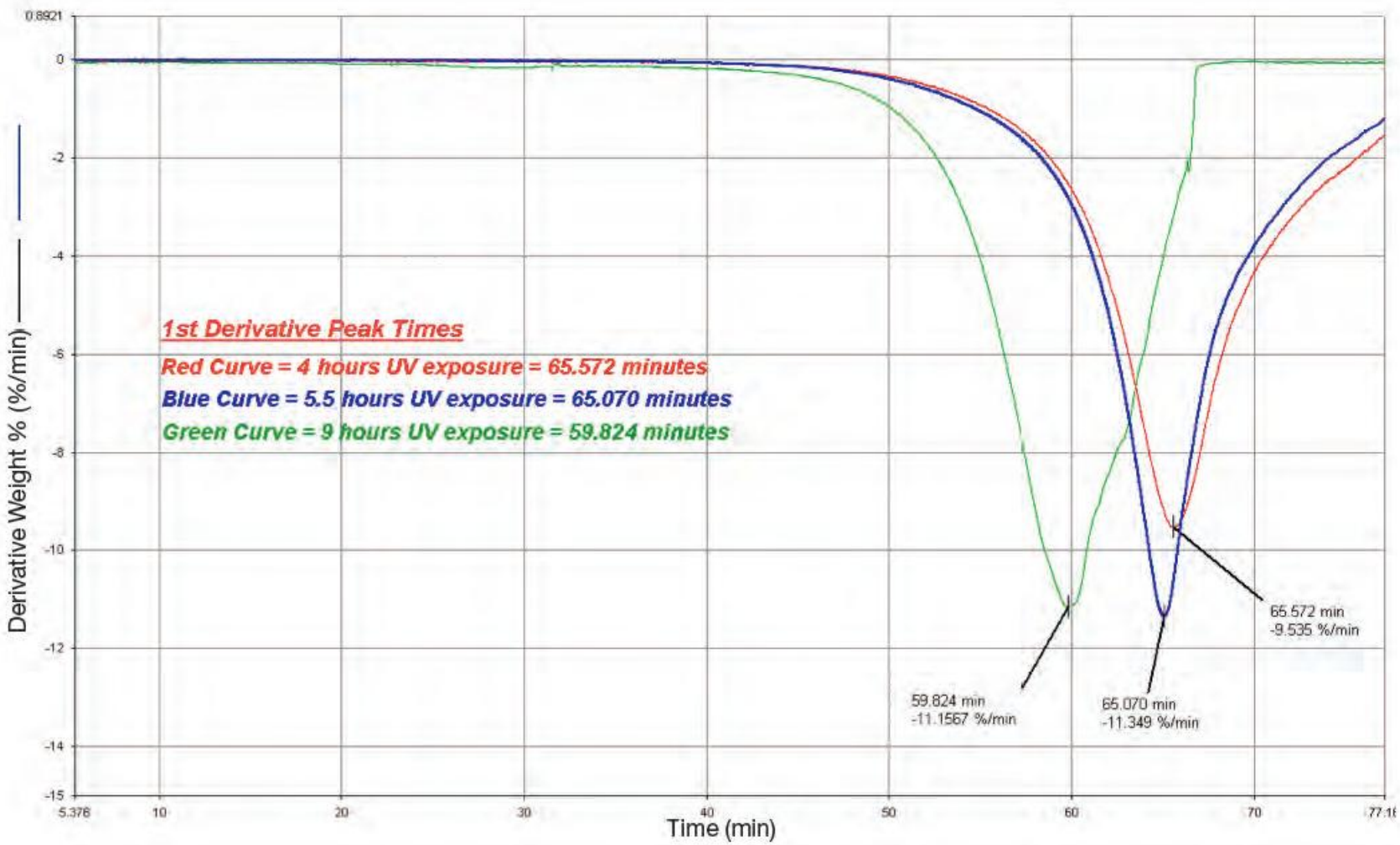


MS

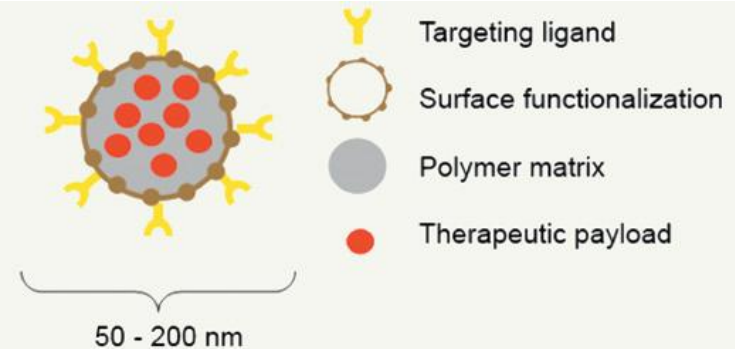


--Courtesy of the US EPA

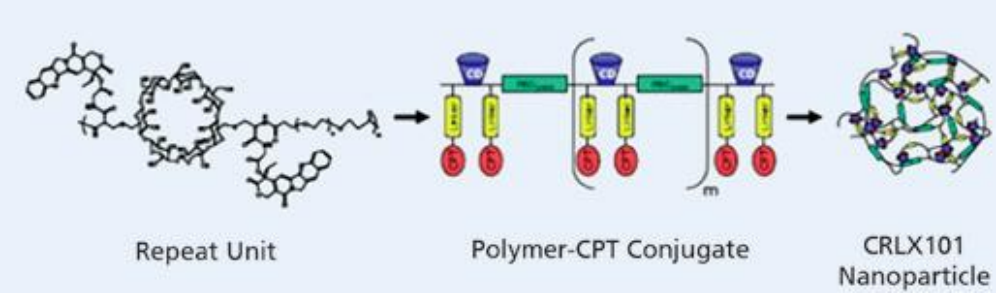
Aged CNTs characterized by TGA



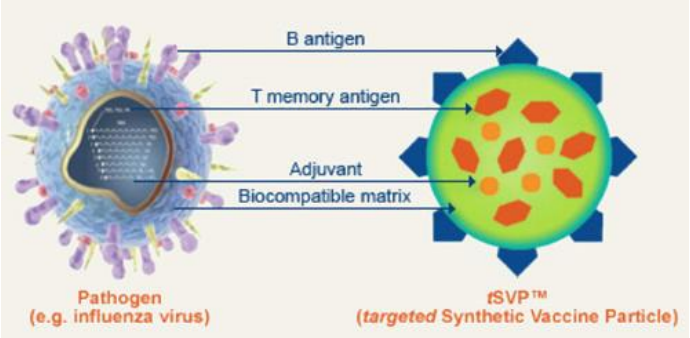
Complex Nanopharmaceuticals



Bind Biosciences, Inc. 2010, Accessed Jan 2011, http://www.bindbio.com/content/pages/technology/index.jsp



Cerulean Pharma Inc. Clinical Trials, Accessed Jan 2011, http://www.ceruleanrx.com/clinical_trials.html



Selecta Biosciences, 2011, Accessed Jan 2011, http://www.selectabio.com/product-platform/index.cfm

So where do we start?

- We start by identifying the most important new instrument need.
- We start by indentifying the most important method needed for an existing analytical technique.
- We begin dialogs with instrument manufacturers.
- We begin dialogs with NM manufacturers and end product formulators.
- We begin dialogs with ISO and ASTM.

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Thank you

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