# Purchasing Metal Oxide Nanopowders for Research: Buyer Beware!

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SESSION 1 - Measurement and characterization of nano-objects

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# Introduction

**Eight metal oxides were selected for research on solubility of engineered nanomaterials (ENMs) dispersed in water and cell culture media. Focus of this ongoing research is on the relationship between solubility and toxicity.**

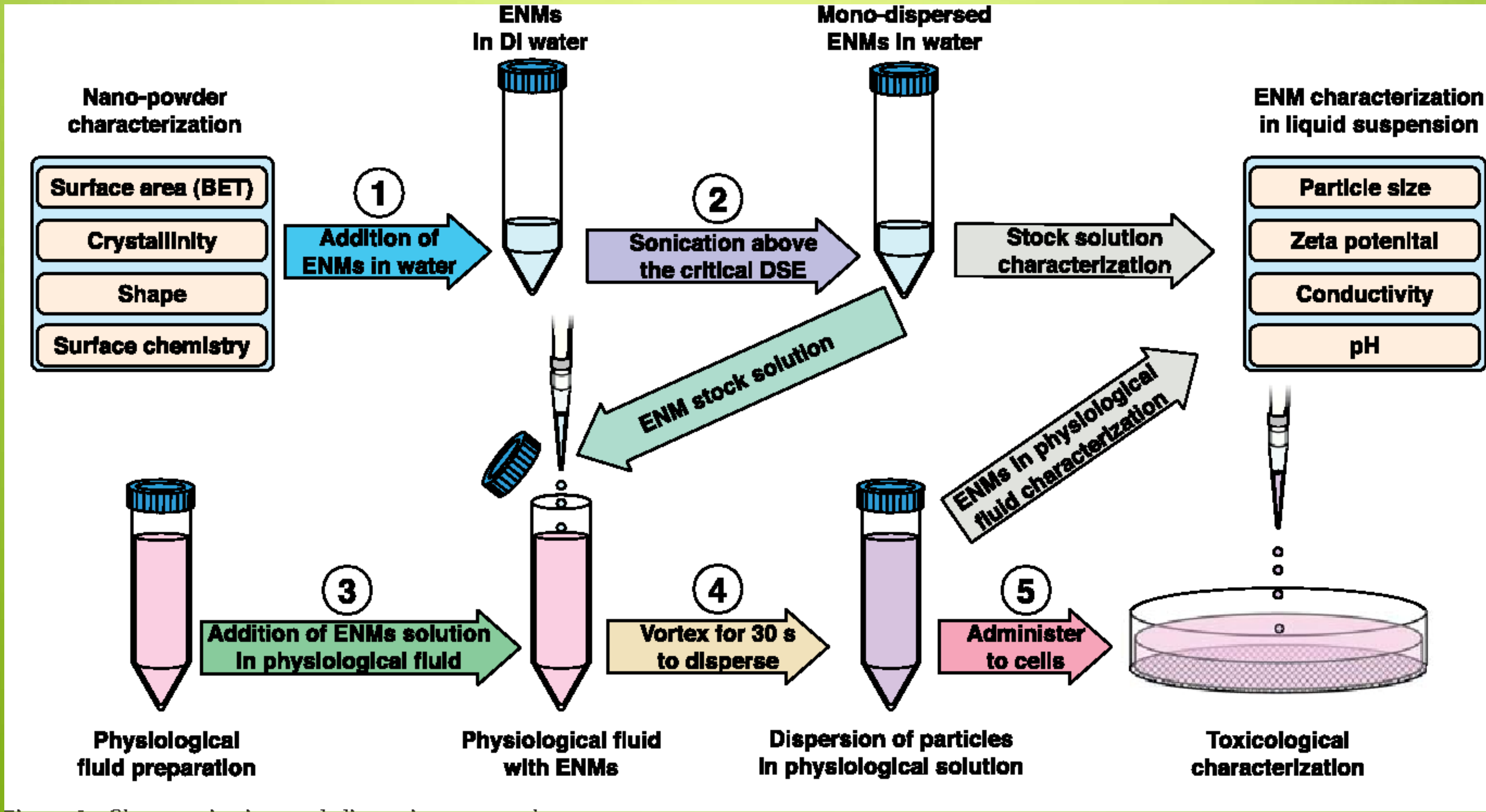
**Suppliers of metal oxide nanopowders were identified by internet search, and products were selected based on particle size (≤50 nm using TEM).**

**The following ENMs were obtained in dry nanopowder form:**
**ZnO, NiO, $TiO_2$,$CeO_2$, CuO, $Al_2O_3$, $Mn_2O_3$ and $Fe_2O_3$**

**BUYER BEWARE:**

- **Two out of the eight metal oxide ENMs obtained for this project did not meet the manufacturers' claims ($Mn_2O_3$ and $Fe_2O_3$).**
- **Different lots of the same nano-CuO product required different sonication protocols.**

# Nano-powder sample preparation for toxicity studies (from Cohen et al. 2013)




Cohen et al. (2013) Nanotoxicology, 7(4):417-31

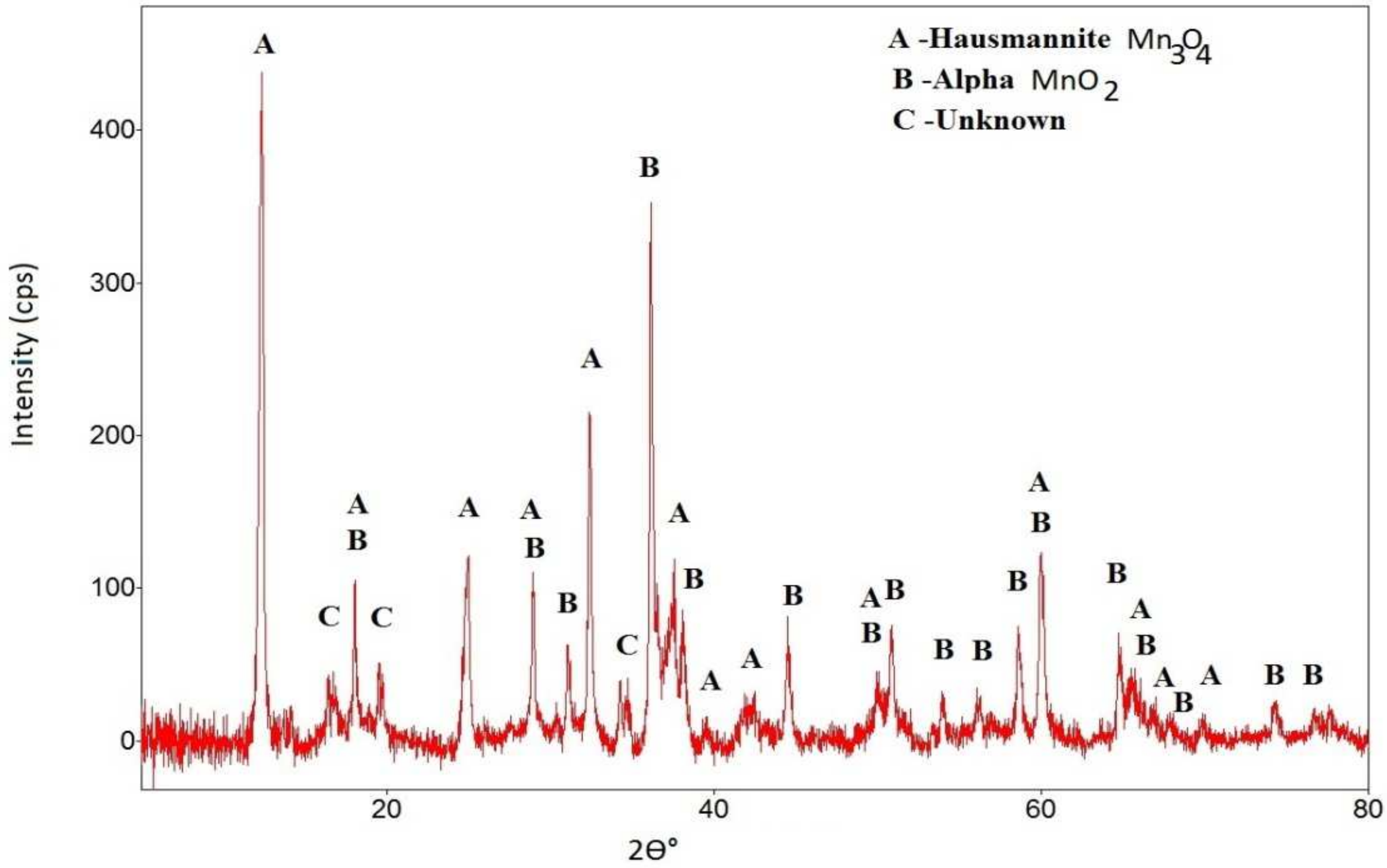
# Confirmation of compounds present in purchased nanopowders

- **$Mn_2O_3$ was purchased from two suppliers but neither contained $Mn_2O_3$ according to XRD analysis.**
- **One nanopowder sold as $Mn_2O_3$ contained two $MnO_2$ compounds: akhtenskite (83 wt %; 20 nm) and ramsdellite (17 wt %; 32 nm).**
- **The second nanopowder sold as $Mn_2O_3$ consisted mainly of alpha $MnO_2$ (21 nm) and hausmannite ($Mn_3O_4$; 46 nm), with a small fraction of an unidentified compound (55 nm).**


**Rigaku Ultima IV X-ray diffractometer (Bragg-Brentano geometry)**

Photo credit www.rigaku.com

# X-ray diffractogram of nanopowder incorrectly identified as $Mn_2O_3$ by the supplier




**Product consists mainly of alpha $MnO_2$ (avg crystal size 21 nm) and hausmannite ($Mn_3O_4$; size 46 nm), with a small fraction of an unidentified compound (size 55 nm).**

# XRD confirmation cont'd

- **XRD analysis of the purchased $Fe_2O_3$ nanopowder indicated the presence of two different compounds: gamma $Fe_2O_3$ (88 wt%) and synthetic hematite (12 wt%).**

- **This mixed $Fe_2O_3$ product was likely to yield inconsistent solubility results. (Solubility of a metal oxide depends on the crystalline form.)**

- **Also the crystalline form must be known so that the correct refractive index is entered into the DLS (next slide).**

- **A different supplier was selected whose $Fe_2O_3$ product was determined to contain >98% synthetic hematite.**

# Correct refractive index of nanopowder is needed for DLS

- **DLS = dynamic light scattering**

- **Used for measurement of particle size distribution (extent of agglomeration), polydispersity, zeta potential etc**

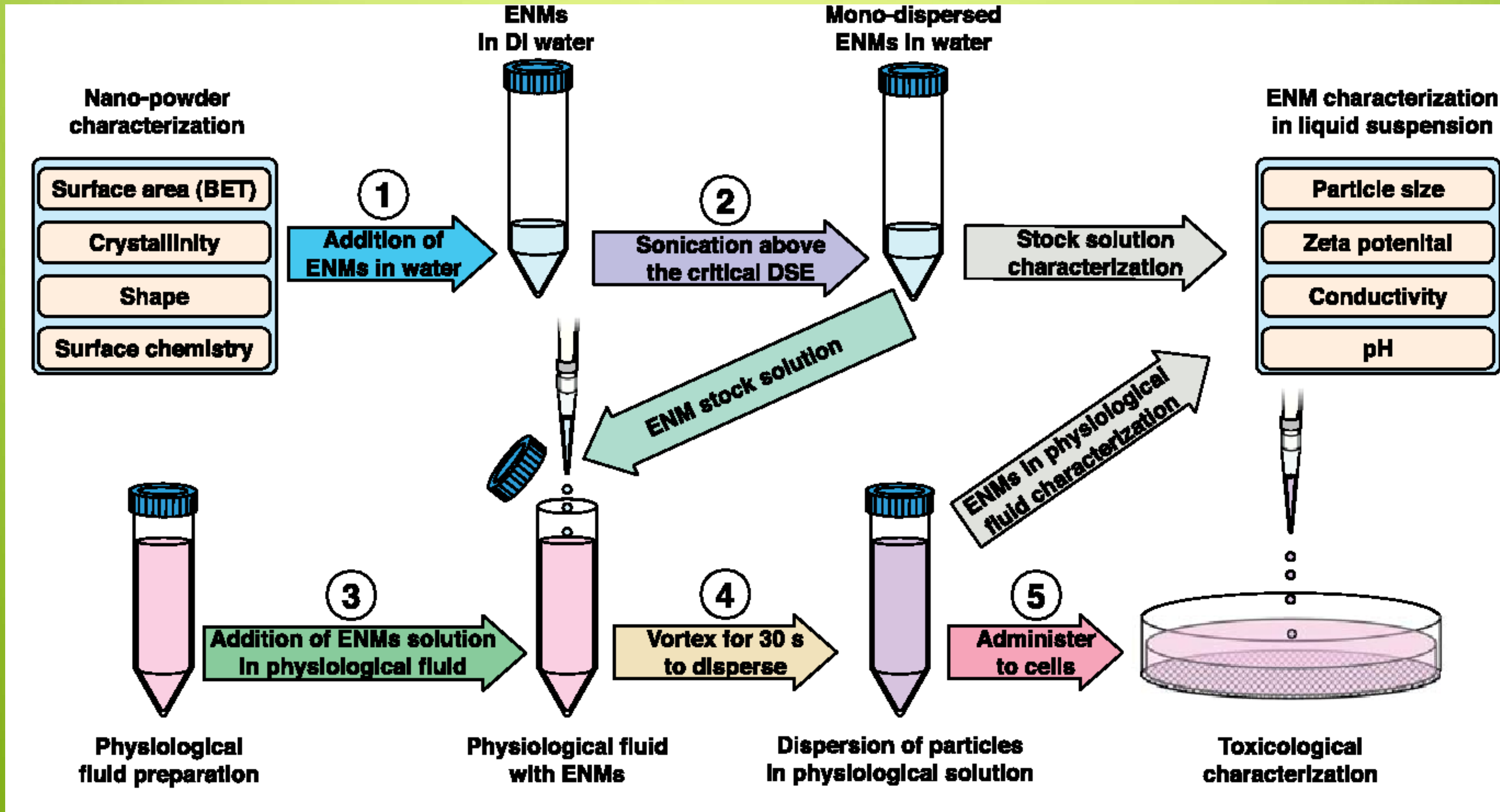
- **Accurate refractive index information is needed for ENM compound being measured.**

- **Example: MnO = 2.16; $MnO_2$ = 2.4; $Mn_3O_4$=2.46**


**Malvern Zetasizer and Titrator**

Photo credit www.cnsi.ucsb.edu

# Nano-powder sample preparation for toxicity studies (from Cohen et al. 2013)



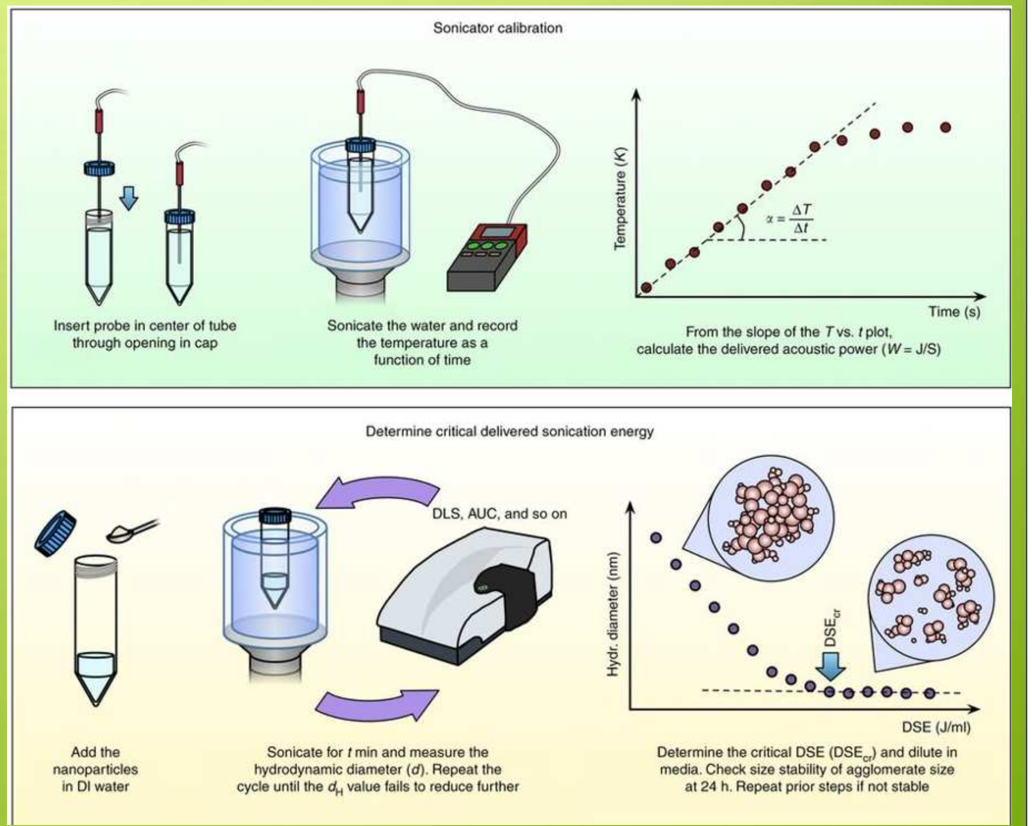

Cohen et al. (2013) Nanotoxicology, 7(4):417-31

# Determination of critical delivered sonication energy (DSE) from Deloid et al. (2017)

- **To optimize the critical DSE (J/mL):**
  - **first vary the power (W) while keeping sonication time constant,**
  - **then vary the sonication time (min) while keeping power constant.**

- ***Note that OECD (2018) Test Guideline 318 specifies 40W/10 min sonication to prepare stock dispersion.***

- **But critical DSE is "material-specific" according to Deloid et al. (2017).**




Deloid et al.(2017) *Nature Protocols*, 12:355–371

# Optimized sonication energy for CuO nanopowder: an unexpected result

| Aldrich Catalogue # | Lot # | Optimized DSE (J/mL) | Smallest Attainable $D_h$ (nm) |
|---|---|---|---|
| 544868 CuO <50 nm | MKBH9047V | 384 | 365 |
| 544868 CuO <50 nm | MKAAA0633 | 24 | 186 |
| 544868 CuO <50 nm | MKBT8894V | 72 | 289 |

**DSE = delivered sonication energy; $D_h$ = hydrodynamic diameter**

**The critical DSE had to be optimized separately for each lot of the same nano-CuO product (Aldrich # 544868)!**

**Why would it be necessary to customize the sonication protocol individually for each lot?**

# Mystery solved…the different lots were actually different ENMs

| Aldrich Catalogue # | Lot # | DSE (J/mL) | $D_h$ (nm) | From CofA Particle size (nm) | From CofA SSA ($m^2/g$) |
|---|---|---|---|---|---|
| 544868 CuO <50 nm | MKBH9047V | 384 | 365 | <50 | 25-40 |
| 544868 CuO <50 nm | MKAAA0633 | 24 | 186 | 28 | 33 |
| 544868 CuO <50 nm | MKBT8894V | 72 | 289 | 40 | 25-40 |

DSE = delivered sonication energy; $D_h$ = hydrodynamic diameter

**Certificates of Analysis (CofA) on supplier's website indicated different particle size and specific surface area (SSA) for each lot.**

# Conclusions

**These results underscore the importance of double-checking information about nanopowders obtained for research:**

- **Compounds must be correctly identified so that subsequent measurements are conducted properly**
  - **critical DSE is ENM-specific**
  - **correct refractive index must be entered into the DLS**
- **The crystalline form must be known to understand dissolution behaviour**
  - **different forms of the same compound are likely to have different solubility**
  - **solubility is a key parameter for hazard assessment**
- **Adequate physical-chemical characterization of the ENMs being studied is <u>critical</u> for meaningful toxicology assessments.**
  - **see Krug HF. Nanosafety research-are we on the right track? Angew Chem Int Ed 2014;53(46):12304-12319.**

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# ***Thank you!***