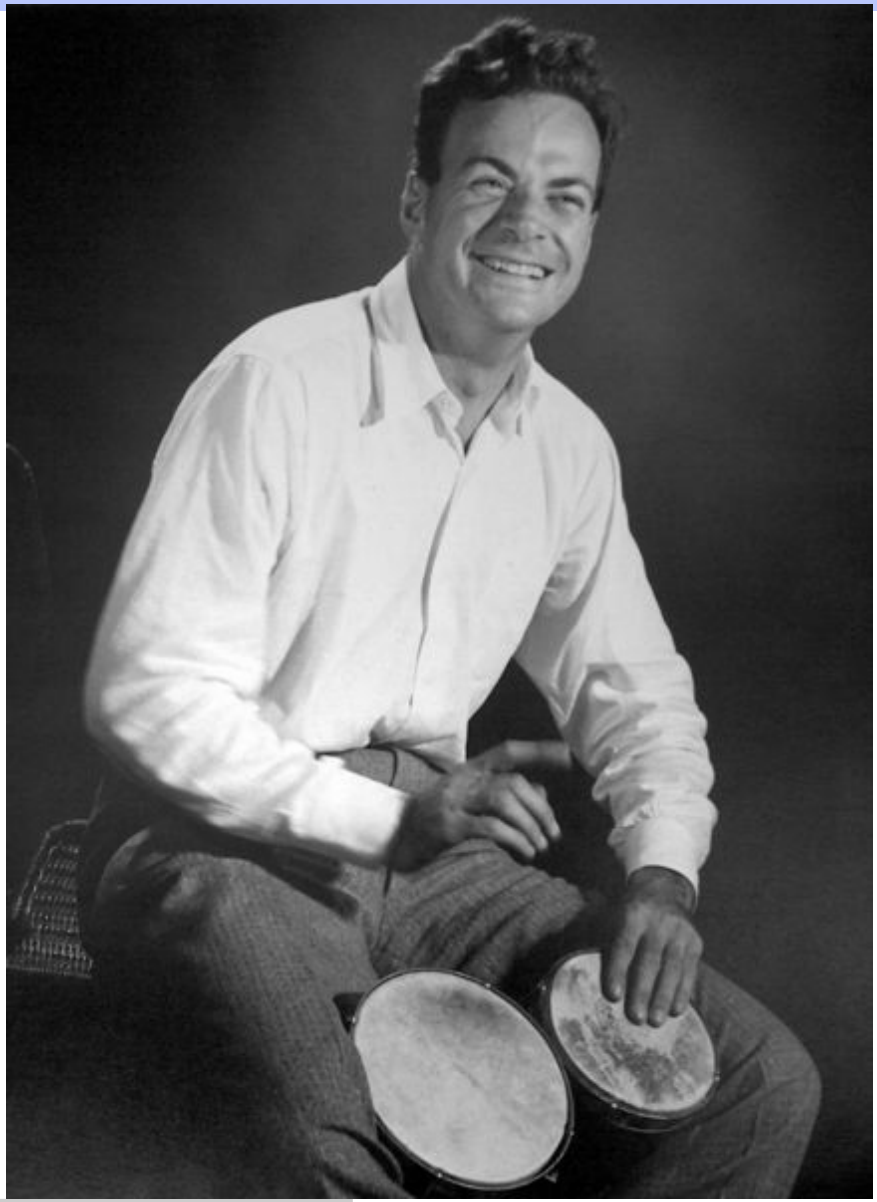
CENAM
CENTRO NACIONAL DE METROLOGÍA

*Second Tri-National Workshop on Standards for Nanotechnology*
**National Institute of Standards and Technology**

# PARTICLE SIZE MEASUREMENTS AND INTERLABORATORY COMPARISONS IN MEXICO

**José M. Juárez-García, José A. Salas-Téllez and Rubén J. Lazos-Martínez**
Centro Nacional de Metrología, México

Gaithersburg, Md., USA, February 6, 2008.



# *There´s Plenty of Room at the Bottom*

Richard P. Feynman
December 1959

*What I want to talk about is the problem of manipulating and controlling things on a small scale.*

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# WHAT IS THIS TALK ABOUT?

**Particle size (PS) measurements needs**

**Interlaboratory comparisons on PS measurements**

**Measurement uncertainty on PS measurements**

# PARTICLE SIZE MEASUREMENT NEEDS

n-particles are important either as elements

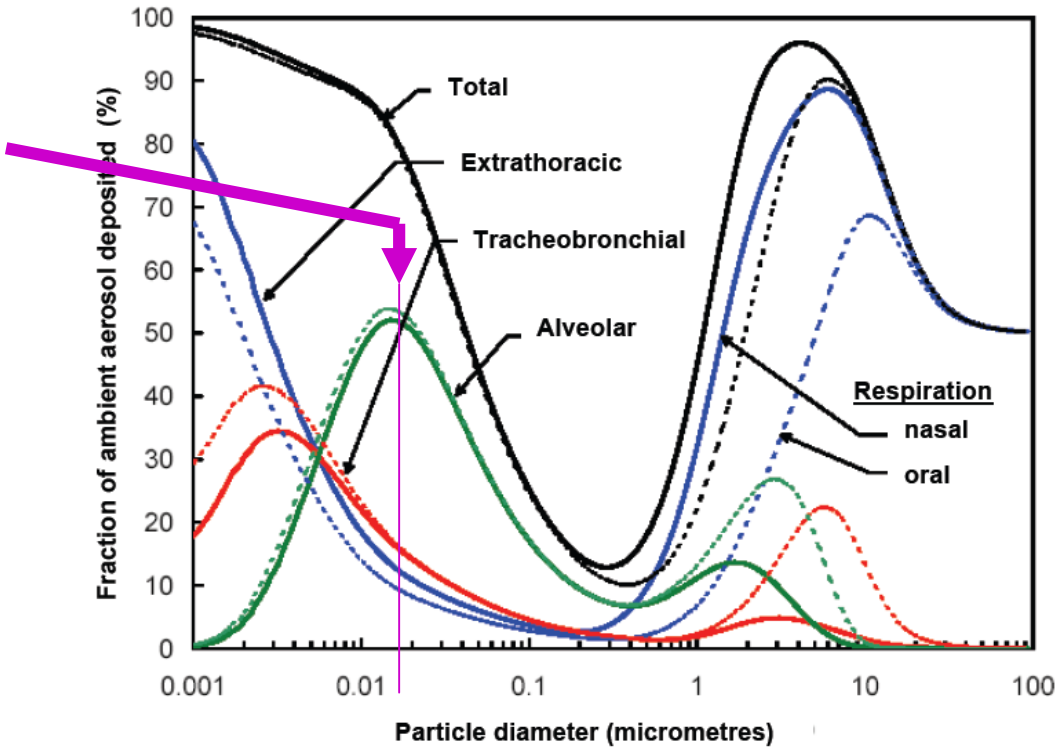
- to be seeked
  - silver n-particles as biocides
  - applications in chemical, food, automotive, oil, ceramics, … industries

- undesirable / pollutants
  - potential risk for health
    - byproducts of burning of diesel
    - application of coatings

# PARTICLE SIZE MEASUREMENT NEEDS

## Pulmonary deposition of nanoparticles and ultrafine particles

Particle size is important




*NRC Workshop, 7 February 2007*





irsst

***Ref: [1] C. Ostiguy, 2007.*** 5

# PARTICLE SIZE MEASUREMENT DRIVERS

**BSI PD 6699-2:2007 Nanotechnologies – Part 2: Guide to safe handling and disposal of manufactured nanomaterials**

**Asia Nano Forum some standardization activities related to n-technologies:**

| | | | |
|---|---|---|---|
| Metrology | China | GB/T 13221-2004 | Nanometer powder--Determination of particle size distribution--Small angle X-ray scattering method |
| | | GB/T 19587-2004 | Determination of the specific surface area of solids by gas adsorption using the BET method |
| | | GB/T 15445.2-2006 | Representation of results of particle size analysis - Part 2: Calculation of average particle sizes/diameters and moments from particle size distributions |
| | | GB/T 15445.4-2006 | Representation of results of particle size analysis - Part 4: Characterization of a classification process |
| | | GB/T 19627-2005 | Particle size analysis-Photon correlation spectroscopy |
| | | GB/T 20307-2006 | General rules for nanometer-scale length measurement by SEM |
| | | accepted | nano-powder seperation methods under liquid phase |
| | | under review | micro,nano crystal particles measurement- x ray method |

# CENAM IN PS INTERCOMPARISONS

***I. ANMET* 02-PT01 Particle Size Analysis*** *interlaboratory Comparison organized and conducted by CENAM an under demand by APEC, 1*μm.

***II. Interlaboratory Comparison on Nanoparticle Size Characterization 2005***
organized by *Asia-Pacific Economic Cooperation (APEC)* Particle size 100nm
Lead to certification of 2 reference materials.

**III.** ***APEC-ISTWG (Industrial Science and Technology Working Group) Project Nanoparticle Size Characterization 2006***. Particle size 100nm.

**IV. Proficiency test** ***610-C006-0002-PA Tamaño de Partícula Promedio***, in Mexico. Particle size 300nm, in colaboration with CINVESTAV.

* ANMET - APEC Network for Materials Evaluation Technology

# CENAM IN PS INTERCOMPARISONS

## *II. Interlaboratory Comparison on Nanoparticle Size Characterization 2005*

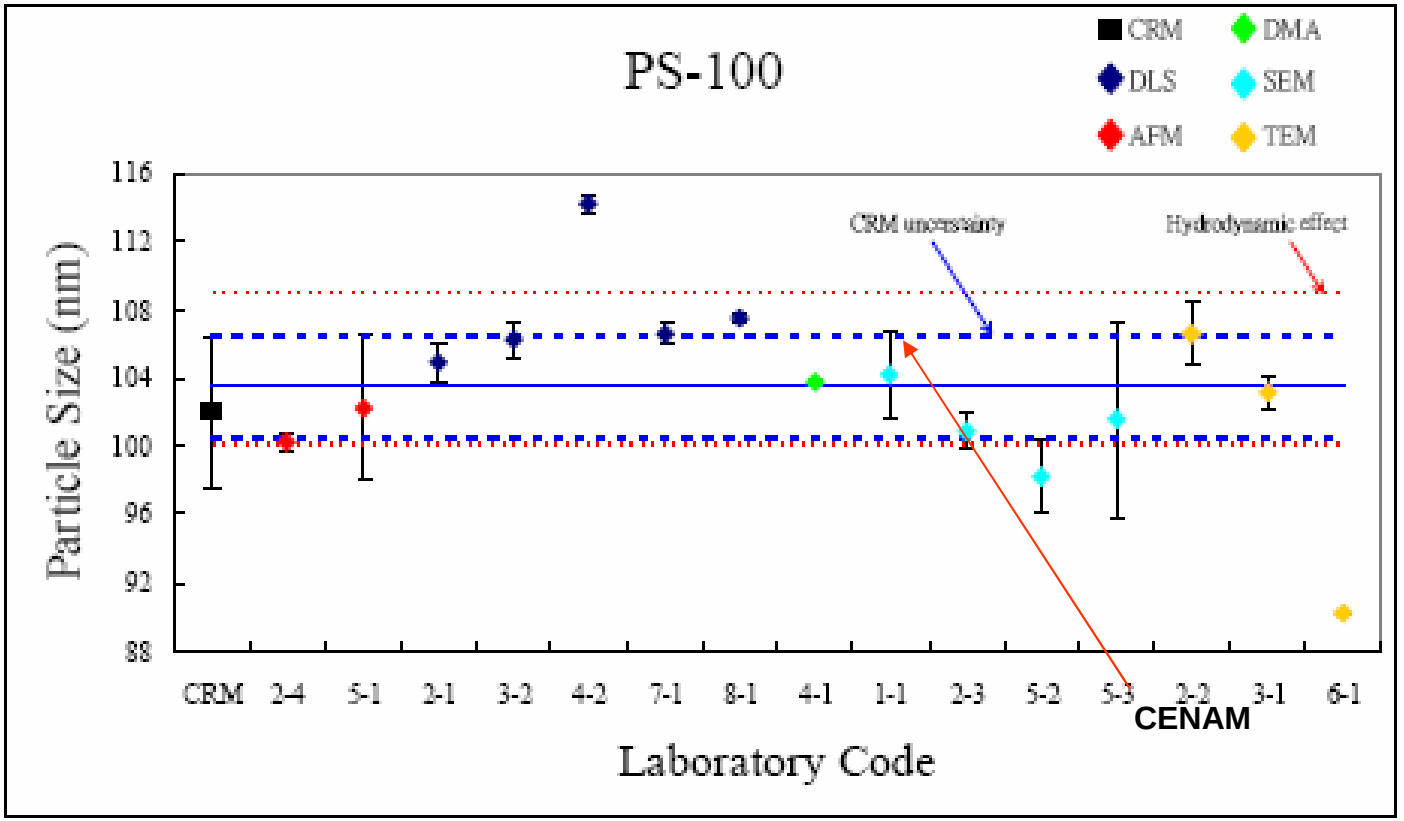


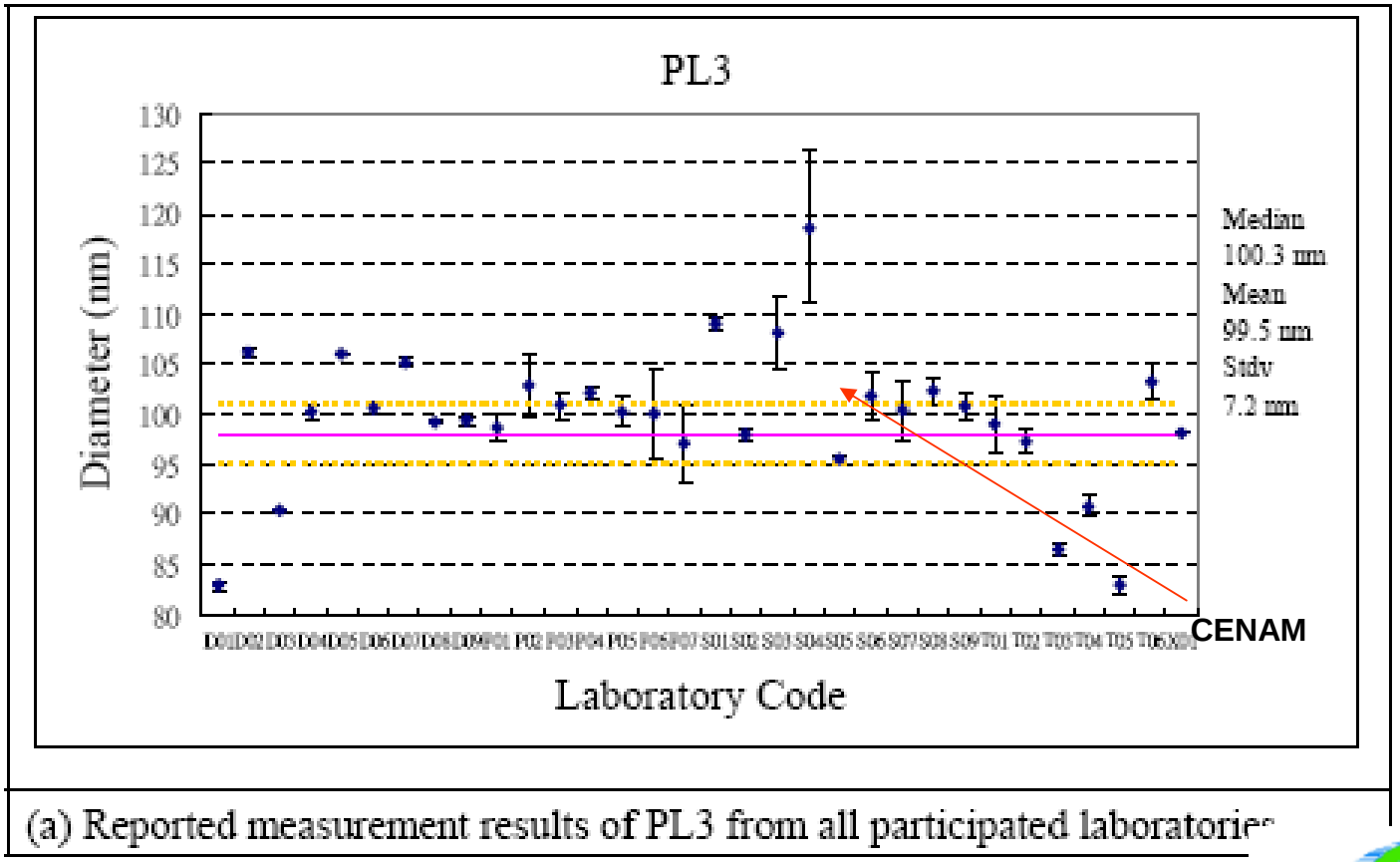

Figure 7: Measurement particle sizes from 15 participants

***Ref: [2] APEC Project***

Asia-Pacific Economic Cooperation

# CENAM IN PS INTERCOMPARISONS

## III. *APEC-ISTWG (Industrial Science and Technology Working Group) Project Nanoparticle Size Characterization 2006*.



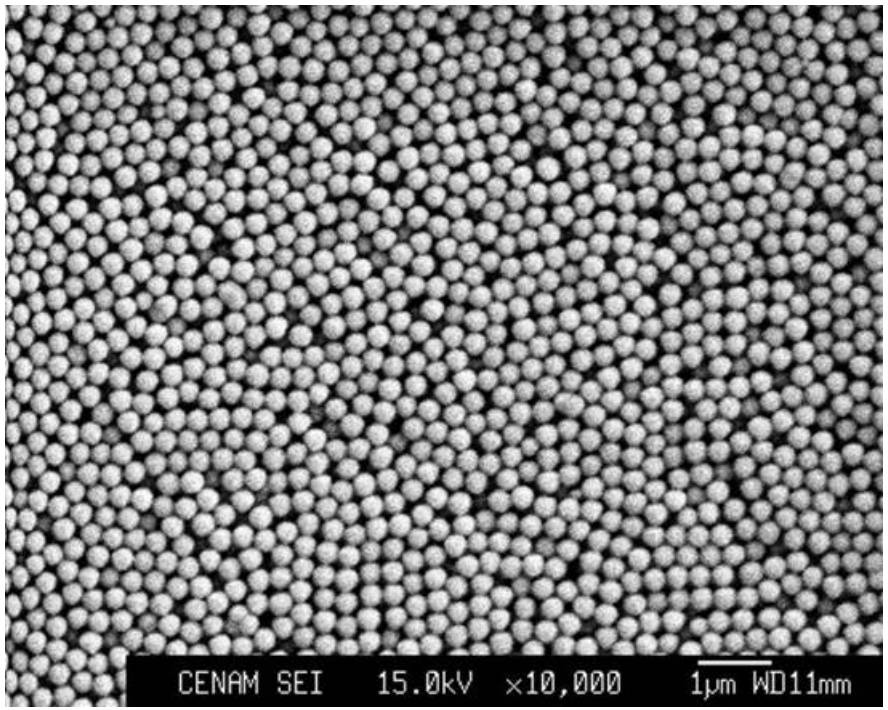

(a) Reported measurement results of PL3 from all participated laboratories

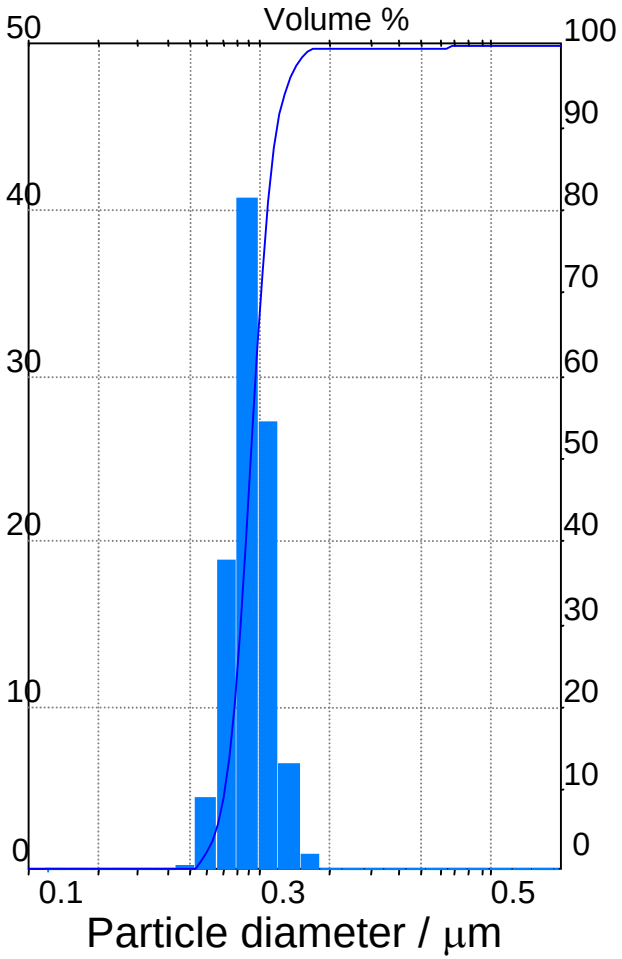
*Ref: APEC ISTWG Project Interlaboratory Comparison on Nanoparticle Size Characterization 2006 Report on Measurement Results*

Asia-Pacific Economic Cooperation

# SMALL LENGTH MEASUREMENT SERVICES

- **150 -300 nm (2005-2006)**



# EQUIPMENT


SEM JSM 6390 L UV

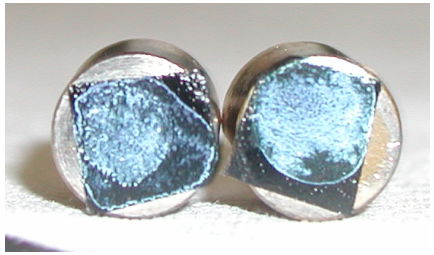


EPMA JEOL JXA 8200

# THE MEASUREMENT PROCEDURE

sample preparation

homogeneization
dilution
drying
coating



*Samples prepared for the SEM*

↓

sampling

↓

picturing in the SEM
@15 kV-25 kV, 100 pA

↓

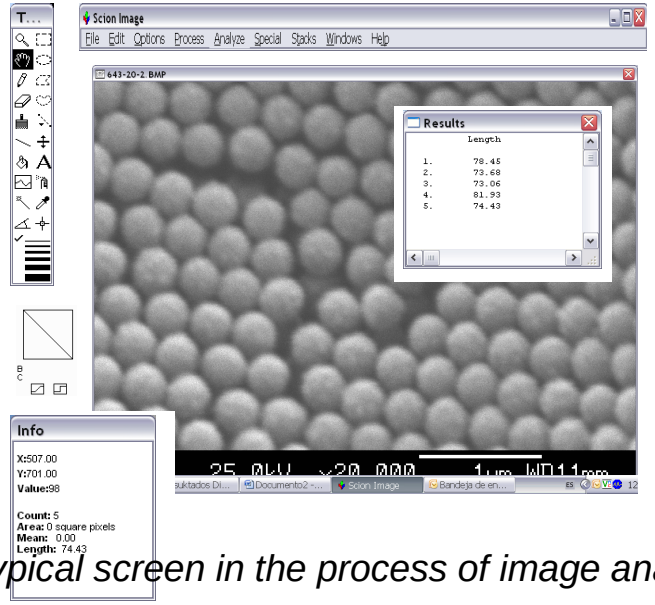
readings on the CRM by image analyzer software

↓

readings on the sample by image analyzer software

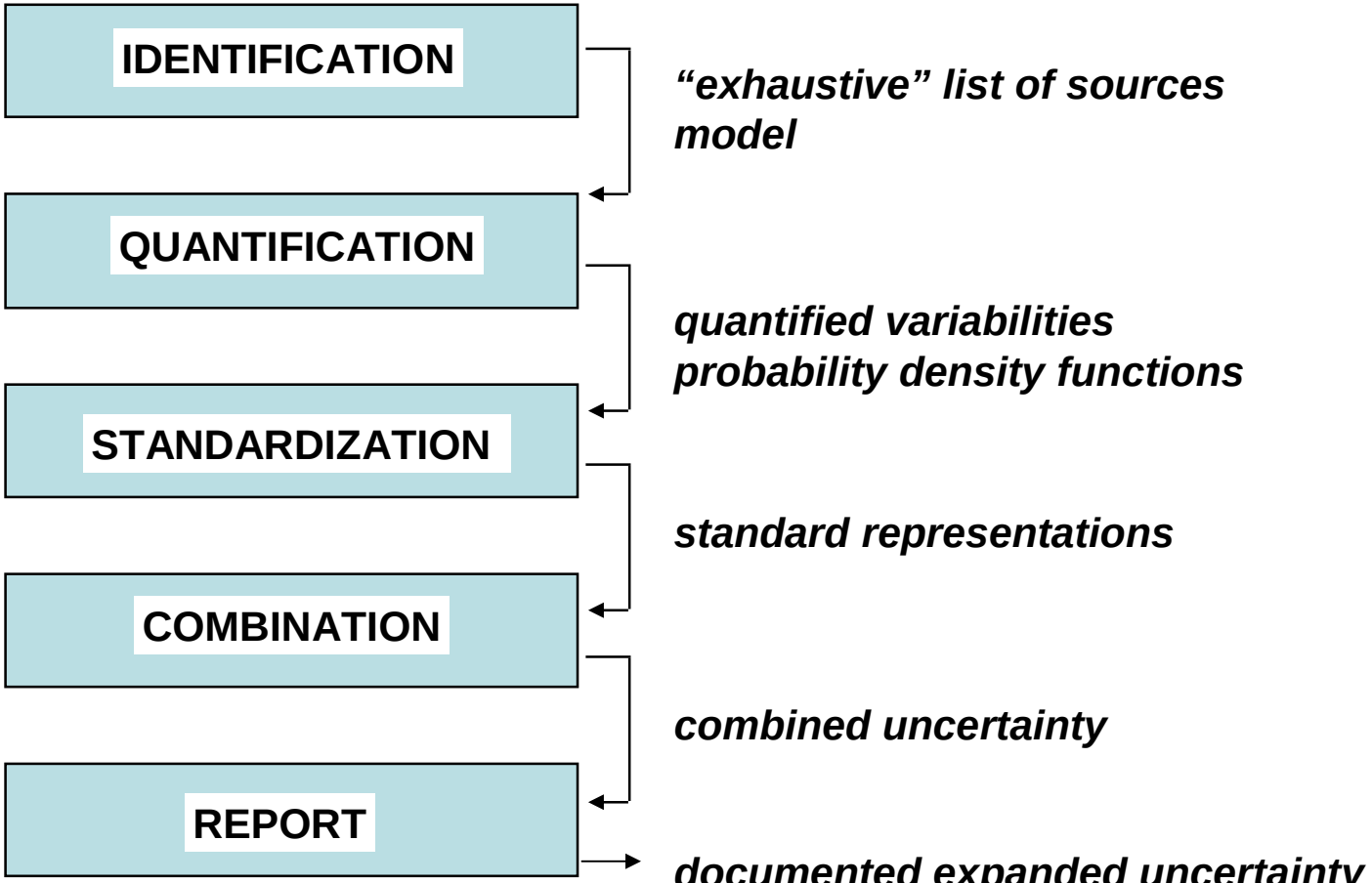
↓

determining particle size



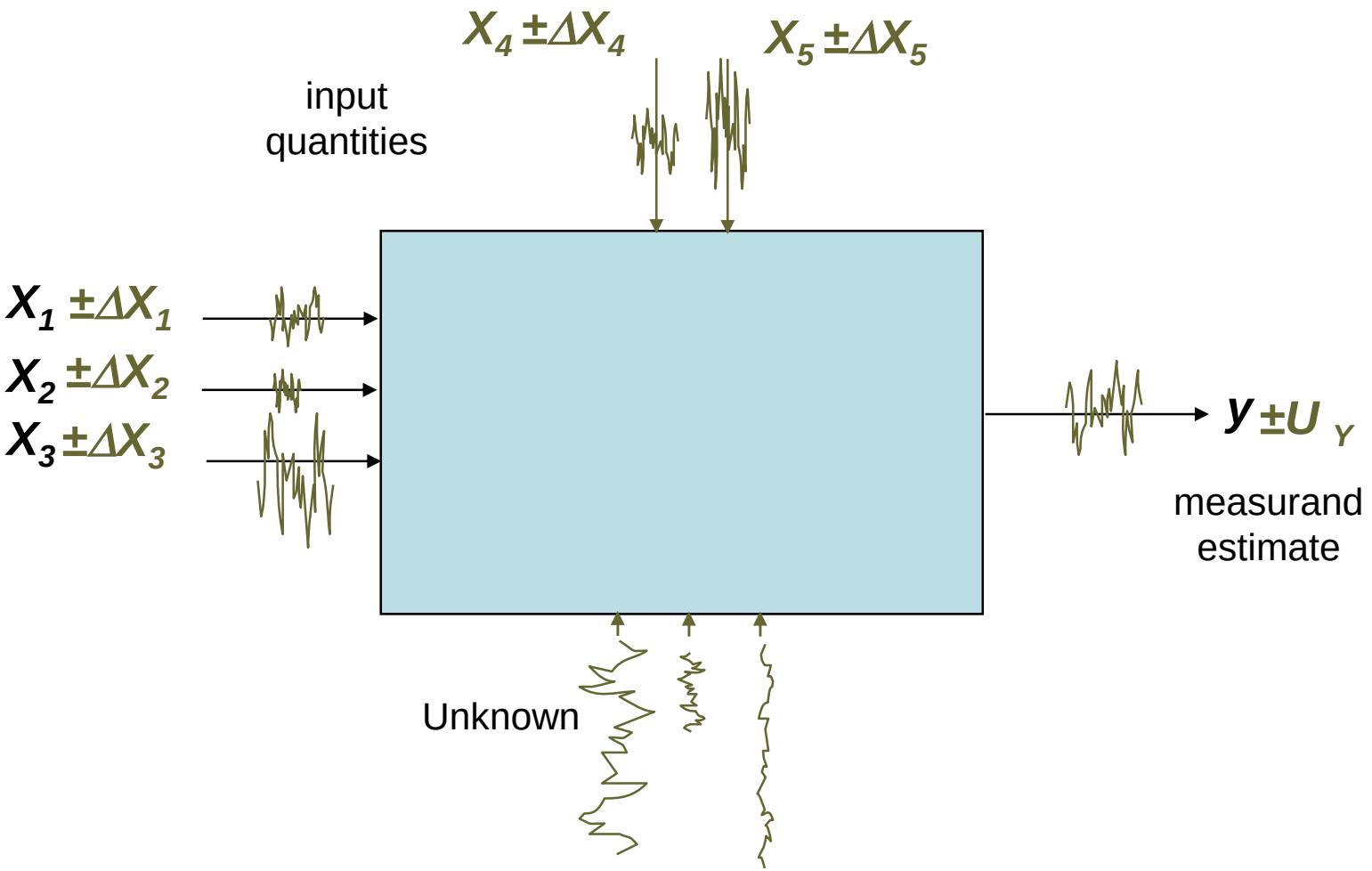

*Typical screen in the process of image analysis*

# GUM METHOD IN PRACTICE




*Ref: GUM [3]*

# REAL WORLD MEASUREMENTS




The random effects may be represented by probability density functions (***pdf***)

# THE MEASUREMENT MODEL

**Measurand**: mean diameter $y$ of N particles

$$y = f \cdot x$$

$$f = \frac{\delta}{d}$$

| | |
|---|---|
| $f$ | calibration factor |
| $x$ | average of the readings in pixels of N particles sizes |
| $\delta$ | diameter of particles according to the CRM value in units of length |
| $d$ | reading in pixels of a particle size of the CRM |

*Ref [4]: J. Juarez et al*

# DETAILED MEASUREMENT MODEL

$$y = \frac{\delta}{d + res(d) + repr(d)} \cdot \left[ x + res(x) + repr(x) \right]$$

$\delta$ *random variable associated to the value of the CRM: pdf gaussian with mean as the value stated in the CRM certificate, standard deviation = the combined standard uncertainty stated in the CRM certificate.*

$d$ *mean value of readings of diameter of particles of the CMR by means of the image analyzer*

$x$ *idem but of the sample*

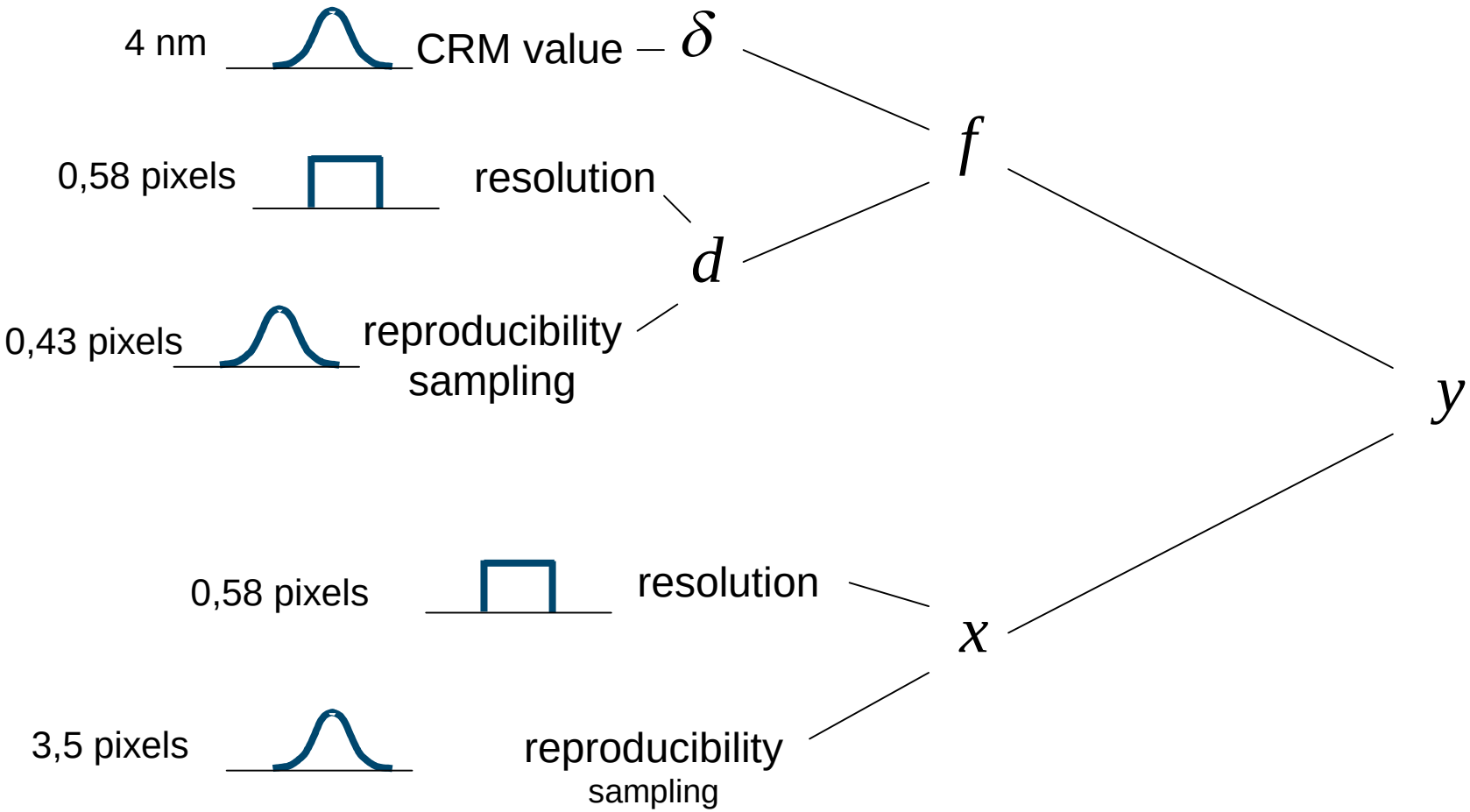
$res(d)$ *random variable associated to the lack of resolution of the image analyzer at measuring $d$: pdf uniform with mean = 0 and width = 2 pixels.*

$res(x)$ *idem but at measuring $x$*

$repr(d)$ *random variable associated to the lack of reproducibility of the readings of $d$, mainly due to sampling: pdf gaussian with mean = 0 and standard deviation = 0,43 pixels.*

$repr(x)$ *idem but at reading $x$:*
*pdf gaussian with mean = 0 and standard deviation = 3,5 pixels.*

# THE CONTRIBUTORS




All the values are expressed as standard uncertainties

# ADDING UP CONTRIBUTIONS

According to the linearization proposed by “classical” GUM:

$$u_c = \sqrt{\sum_{x_i}\left[\frac{\partial f}{\partial x_i}u(x_i)\right]^2 + 2\cdot\sum_{x_i,x_j}\frac{\partial f}{\partial x_i}\cdot\frac{\partial f}{\partial x_j}\cdot u(x_i,x_j)}$$

We assume negligible covariances.

# TAKING IN TRACEABILITY TO SI UNITS


National Institute of Standards & Technology

## Certificate of Analysis

### Standard Reference Material® 1690

Nominal 1 µm Diameter Polystyrene Spheres

(In cooperation with the American Society for Testing and Materials)

This Standard Reference Material (SRM) is intended for use as a particle size standard for the calibration of particle size measuring instruments including optical and electron microscopes. The SRM is an aqueous suspension of monodispersed polystyrene spheres at a mass concentration of about 0.5 %. A small amount of sodium azide (50 mg/kg) was added to the solution as a biocide.

Certified Number Average Diameter

0.895 µm ± 0.008 µm

0.895 ± 0.008 µm

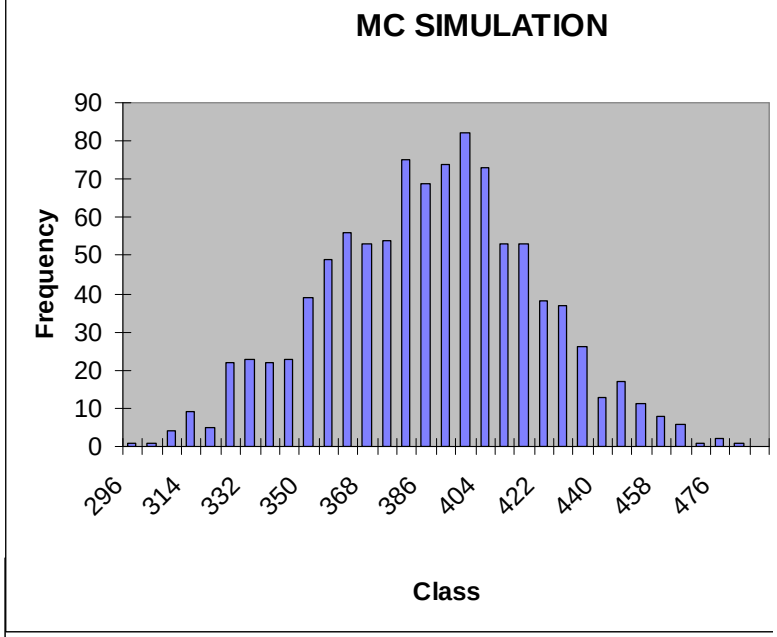
# PS MEASUREMENT UNCERTAINTY

(figures for a typical service)

| | Input quantity $X_i$ Source of uncertainty | estimated value | | source of information | original uncertainity | | | pdf | standard uncertainity $u(x_i)$ | sensitivity coefficient $C_i$ | | Contribution $u_i(y)$ | corre lation | Degrees of freedom $\nu$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | **Value of the CRM δ** | **895** | nm | certificate | ± | 8 | nm | gaus/2s | 4 | 0.43 | 1 | 1.7 | 0 | 200 |
| 2 | **reading of CRM d** | 94.38 | pixel | | | | | | | | | | | |
| 2a | Resolution | | | inspection | | 2 | pixel | uniform | 0.58 | -4.08 | nm/pixel | -2.4 | 0 | 50 |
| 2b | Sampling | | | experiment | | 0.43 | pixel | gaus/1s | 0.43 | -4.08 | nm/pixel | -1.8 | 0 | 8 |
| 3 | **reading of sample x** | 40.63 | pixel | | | | | | | | | | | |
| 3a | Resolution | | | inspection | | 2 | pixel | uniform | 0.58 | 9.48 | nm/pixel | 5.5 | 0 | 50 |
| 3b | Sampling | | | experiment | | 3.4 | pixel | gaus/1s | 3.40 | 9.48 | nm/pixel | **32.2** | 0 | 14 |
| | | | | | | | | | | | | | | |
| | | | | | | | | | | sum of squares | | 1081.123 | $\nu_{ef}$ | **15** |
| | | | | | | | | combined standard uncertainty | | | | **32.9** | $t_{Student}$ | **2.13** |
| | **Calibration factor *f*** | 9.483 | nm/pixel | | | | | **Expanded uncertainty (p = 95%)** | | | | **70** | **nm** | |
| | | | | | | | | | | | | | | |
| | | | | | | | | | **Particle diameter** | | | **385** | **nm** | |

# VALIDATING THE UNCERTAINTY ESTIMATION

(figures for a typical service)

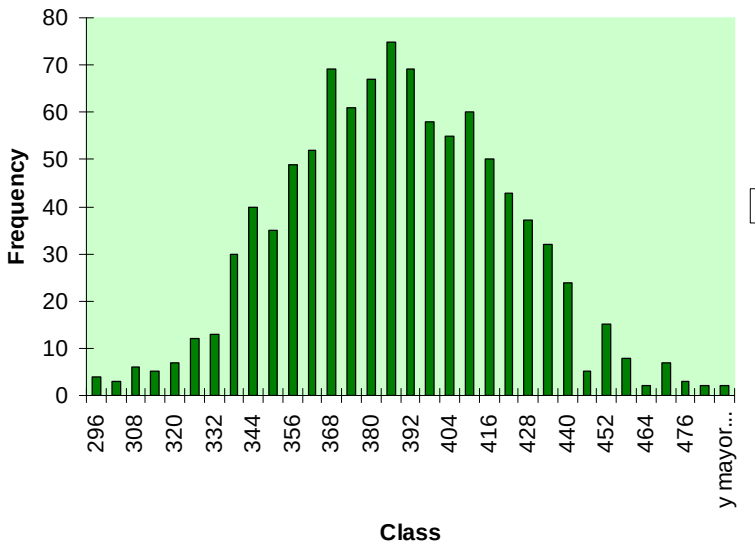



## MONTE CARLO SIMULATION 1000 points each *pdf*

| | |
|---|---|
| **Mean** | **384** |
| **Median** | **386** |
| **Standard Deviation** | **32** |
| Curtosis | -0.24 |
| Coeficiente de asimetría | -0.004 |

**Interval 95%** **(322, 448)**

Linear model and gaussian y-pdf can be accepted




“Classical” GUM APPROACH:

Best estimate: 385

Interval 95%: (315, 455)

| | |
|---|---|
| **Mean** | **384.5** |
| **Median** | **383** |
| **Standard Deviation** | **34** |
| Curtosis | 0.48 |
| Coeficiente de asimetría | 0.16 |

differences due to software and number of points limitations

Interval 95%: (321, 451)

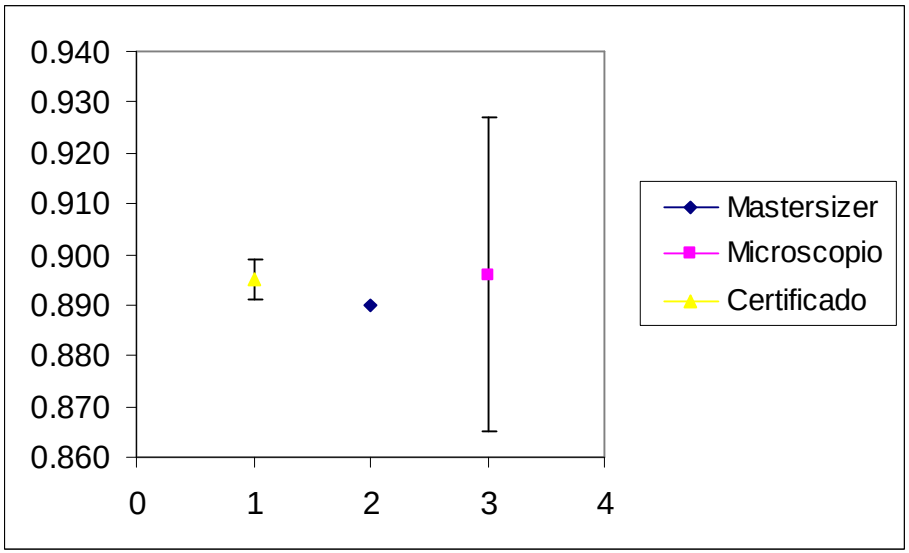
histogram representation 1000 points

# VALIDATING THE MEASUREMENT METHOD

Best estimates for the same sample:

| | |
|---|---|
| **Certificate** | **0.895** |
| **Laser dispersion Mastersizer** | **0.890** |
| **SEM** | **0.896** |

*Figures in micrometers*




**SEM method** seems to produce equivalent results to those by **laser dispersion**

# METROLOGICAL ELEMENTS OF MEASUREMENT PROCEDURES

## PROPOSAL

## In standards, method documentation should include:

| | |
|---|---|
| ✓ Measurand | suitably defined |
| ✓ Traceability | to SI preferantly |
| ✓ Measurement directions | detailed as necessary |
| ✓ Measurement model | |
| ✓ Uncertainty *U* estimation | the clearer the better |
| ✓ Validation of *U* estimation | |
| ✓ Method validation | |

# FINAL REMARKS

- Particle size measurements are important to support nanotechnology, either to promote industrial competitiveness as welll as to take care of the safety and health of the population, and protect the environment.

- By means of participations in intercomparisons, CENAM has demonstrated capabilities to measure particle size around 100 nm

- GUM classical method is applicable to estimate and express the measurement uncertainty of the particle size measurements by SEM.

- CENAM is under preparation to tackle particle size measurements down the nanometric scale

# REFERENCES AND ACKNOWLEDGMENTS

## REFERENCES

[1] C. Ostiguy, 2007 *Nanomaterials: Occupational Health and Safety.* Tri-national workshop on standards for nanotechnology, Ottawa, Canada. Feb 2007.

[2] *APEC Project: Preliminary Interlaboratory Comparison on Nanoparticle Size Characterization  Comparison Report First Draft.*

[3] *Guide to the Expression of Uncertainty in Measurement*. BIPM, IEC, IFCC, ISO, IUPAC, IUPAP, OIML. 1995.

[4] J. Juárez, F. Martínez, F. Juárez. *Medición y estimación de incertidumbre del tamaño de partícula utilizando un microscopío electrónico de barrido con electrones.* Proceeds. XXVII Congreso Nacional de la Sociedad Mexicana de Ciencias y Tecnología de Superficies y Materiales. Oaxaca, México. Sep 2007.

## ACKNOWLEDGMENTS

Froylán Martínez-Suárez
Fernando Rosas Gutiérrez

# I appreciate your attention

Ruben J. Lazos Martínez
Centro Nacional de Metrología
MÉXICO

Phone: +52(442) 211 0575
e-mail: rlazos@cenam.mx


# Mission

**Provide assistance to the various sectors of society in order to satisfy present and future demands in the field of metrology, establish national measurement standards, develop reference materials, disseminate their accuracy, provide technological services of the highest quality, increase the country's competitiveness, contribute to sustainable growth and improve the living standard of the population.**