

eman ta zabal zazu



Universidad
del País Vasco

Euskal Herriko
Unibertsitatea



Ingeniaritza Goi Eskola Teknikoa
Escuela Técnica Superior de Ingeniería
Bilbao

LOS RETOS OCULTOS EN LA FABRICACIÓN DE ACEROS NANOALEADOS: SEGURIDAD Y MEDIO AMBIENTE

Punto de partida (1/2): Una innovación con antecedentes

13th-18th Centuries: “Damascus” saber blades contained carbon nanotubes and cementite nanowires that gave them strength, resilience, the ability to hold a keen edge, and a visible moiré pattern in the steel that give the blades their name.



(Left) A Damascus saber. **(Right)** High-resolution transmission electron microscopy image of carbon nanotubes in a genuine Damascus sabre after dissolution in hydrochloric acid, showing remnants of cementite nanowires encapsulated by carbon nanotubes (scale bar, 5 nm)

M. Reibold, P. Paufler, A. A. Levin, W. Kochmann, N. Pätzke & D. C. Meyer, Nature 444, 286, 2006.

Punto de partida (2/2): El contexto actual

- El desarrollo y comercialización de nuevos aceros nanoaleados requiere conocer y evaluar la exposición potencial a lo largo de su ciclo de vida.
- La evaluación de exposición ocupacional es un área activa en investigación, aunque se requieren resultados prácticos, al mismo tiempo.
- La ruta de exposición más probable es la inhalación (a la que se limita esta presentación).
- Actualmente, no hay límites de exposición específicos. Hay recomendaciones o valores de referencia para algunos materiales.
- No hay consenso sobre los procedimientos y técnicas instrumentales. No hay evaluación de incertidumbre de los diferentes procedimientos.

Los retos actuales para la evaluación de exposición a ENPs

- Métrica/s
- Limitaciones instrumentales
- Señal de fondo (Background)
- Evolución espacial y temporal del aerosol
- Estrategia de evaluación

Estrategias propuestas (1/2): OECD (2015), IUTA (2011):

Elementos base

- Proceso en condiciones reales o proceso simulado
- Emisión y/o aerosolización del nanomaterial
- Aproximación experimental multimétrica (Múltiples analizadores/muestreadores)
- Caracterización del aerosol on- y off-line
- Evaluación de la concentración de fondo (background) y reducción de la misma para obtener medidas/análisis significativos.



TIERED APPROACH, OECD 2015

Estrategias propuestas (2/2): NEAT (NIOSH, 2010):

- Combinación de técnicas e instrumentos
- DRI¹ portátil junto con un par de filtros (muestreo integrado temporalmente) en la PBZ² y en la fuente



Se considera esencial a efectos de identificación

¹ Direct Reading Instruments: Registros de PNC (Particle Number Concentration)

² Personal Breathing Zone

(NEAT 2.0) which distinguishes it from NEAT 1.0, places a stronger emphasis on time-integrated, filter-based sampling (i.e., elemental mass analysis and particle morphology) in the worker's breathing zone (full shift and task specific) and area samples to develop job exposure matrices. NEAT 2.0 includes a comprehensive assessment of emissions at processes and job tasks, using direct-reading instruments (i.e., particle counters) in data-logging mode to better understand peak emission periods. Evaluation of worker practices, ventilation efficacy, and other engineering exposure control systems and risk management strategies serve to allow for a comprehensive exposure assessment.

J Occup Environ Hyg. 2016 Mar 30:0. Refinement of the Nanoparticle Emission Assessment Technique into the Nanomaterial Exposure Assessment Technique (NEAT 2.0).

Eastlake AC, Beaucham C, Martinez KF, Dahm MM, Sparks C, Hodson LL, Geraci C

Un estudio de caso:

*Exposure assessment to engineered nanoparticles handled in industrial workplaces:
The case of alloying nano-TiO₂ in new steel formulations*

C. Vaquero, C. Gutierrez-Cañas, N. Galarza, J. M. López de Ipiña

Journal of Aerosol Science, (accepted) 2016

- Evaluación experimental de la exposición ocupacional a nTiO₂
- Abarca simultáneamente todas las estrategias, metodologías, técnicas
- Escenarios según etapa de procesado/producción
 - MSIS (Multi Source Industrial Scenarios). (López de Ipiña, J., Vaquero, C., Gutierrez-Cañas, C., & Pui, D. (2015). *Analysis of multivariate stochastic signals sampled by on-line particle analyzers: Application to the quantitative assessment of occupational exposure to NOAA in multisource industrial scenarios (MSIS)* Journal of Physics: Conference Series (Vol. 617, No. 1, p. 012003, 2015).

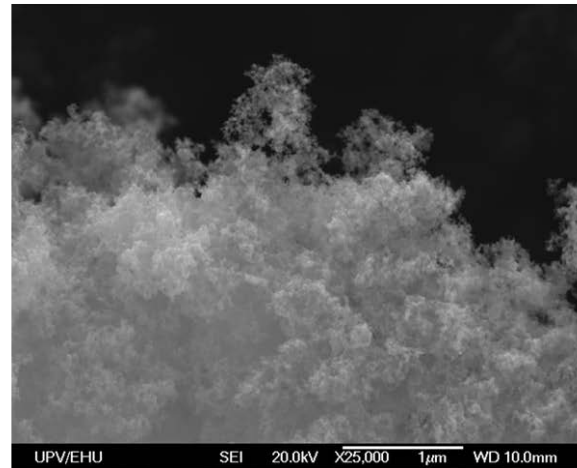
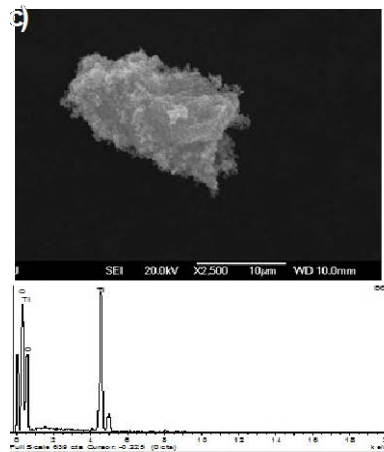
Un estudio de caso: La discusión sobre métrica/s

- Se miden todas las principales métricas propuestas: tamaño equivalente de partícula, concentración másica, concentración en desarrollo superficial, concentración en número y composición (ANALITICA DISPONIBLE PARA Ti).
- Algunas de estas técnicas plantean problemas de especificidad y/o de portabilidad en campo, otras son excesivamente caras o difíciles para medidas de rutina.

CUESTIONES A DEBATE (NANOSAFE)

- La evaluación de exposición debería ser un proxy para la dosis potencial recibida; sin embargo hay todavía diversas dudas sobre el parámetro idóneo para describir la dosis de nanomateriales.
- La concentración másica es adecuada para tamaños mayores, aunque no necesariamente sensible a nanomateriales.
- Resulta evidente que las funciones de superficie (forma, reactividad, solubilidad, ...) juegan un papel relevante en los efectos adversos de un material. ¿Cuál es la “dosis biológicamente activa” de un material/tamaño/cristalinidad ... específico?

Un estudio de caso: Superficie de un aglomerado de $n\text{TiO}_2$ muestreado como aerosol durante taladrado



Un estudio de caso: Limitaciones instrumentales

CUESTIONES A DEBATE (NANOSAFE)

- No toda la información se puede adquirir mediante un único instrumento (de la generación disponible comercialmente) por lo que deben combinarse un conjunto que produzca resultados significativos.
- Los análisis off-line (morfológicos, químicos o gravimétricos) complementan los registros de PNC pero no resuelven temporalmente en caso de transitorios o procesos discontinuos.
- No están resueltas cuestiones metrológicas fundamentales, como sensibilidad, derivas, límites de detección.

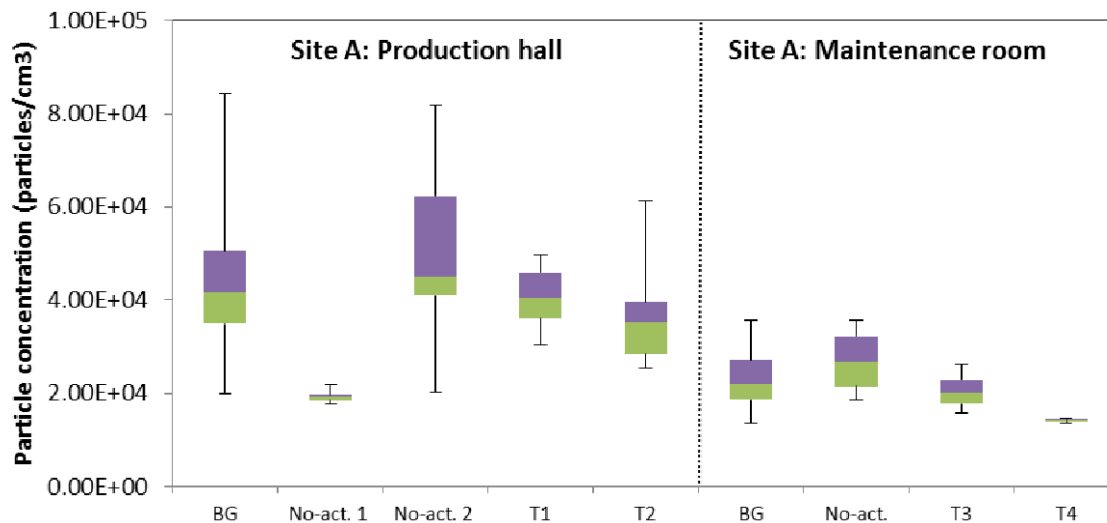
CONSENSO PROVISIONAL (NANOSAFE): VIABLE PARA MEDIDAS DE RUTINA?

“...multiple detection systems and complementary methods can build a good profile of a given aerosol to assess the potential for exposure and inform the selection and evaluation of control measures” (Kuhlbusch et al. 2011 and BSI 2010)

Un estudio de caso: NANOSAFE versus datos

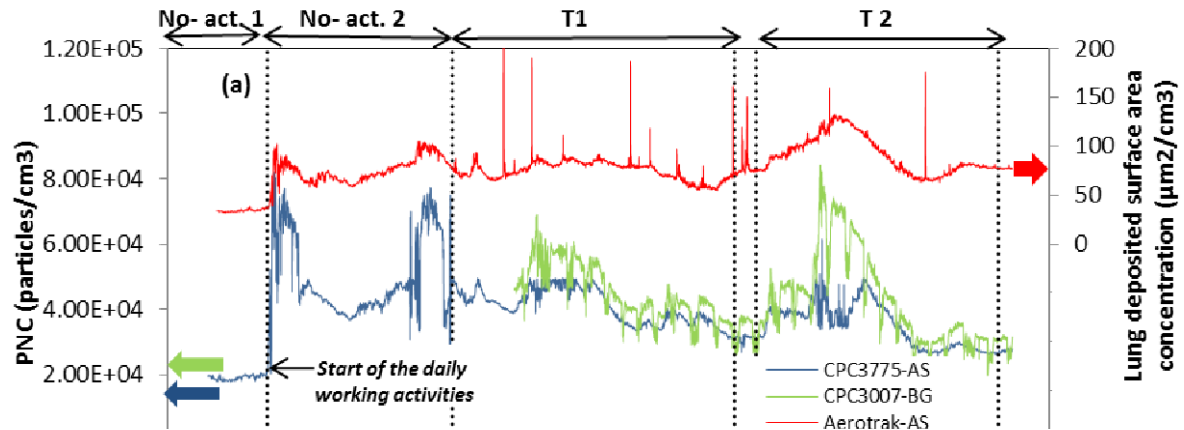
Strategies developed to address the background have been described by Kuhlbusch et al. (2011) and include time series, spatial, and comparative approaches based on studies with and without nanomaterials, and chemical and/or morphological analysis. Simulated approaches can also be undertaken using a “clean room” in order to study a specific process under controlled conditions. This simulation, although artificial, can give valuable information which can help the interpretation of complex data gathered from workplace measurements.

NANOSAFE APPROACH

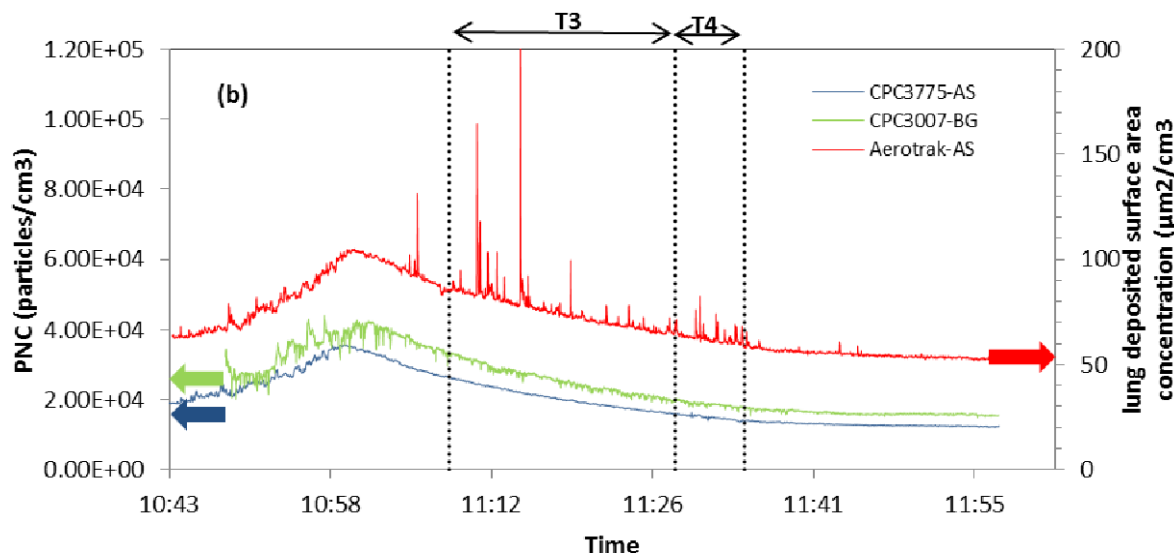


Time averaged PNC by task in Site A (two working positions). Data were not background corrected. Box plot represents minimum, 25th percentile, median, 75th percentile and maximum. Data from CPC3775 at work area, the BG-far distance was measured with the CPC3007.

Registros de PNC y LDSA en dos puestos de trabajo



Manufactura de tabletas
(compresión en frío)



Taladrado de tabletas

Para terminar:

The distinction of the MSIS dynamic background and its high interference level when using direct reading instruments not selective for nano-TiO₂ have been identified of utmost importance for both a quantitative exposure assessment and, eventually, to assess the efficiency of engineering controls of workplace atmosphere. Chemically selective on-line devices are critical to clearly distinguish the ENP sources from background particles. The use of promising techniques as Aerosol Mass Spectrometry or DMA coupled with selective chemical detectors may contribute to solve this gap.

Filter sampling and subsequent chemical analysis allows quantifying the mass concentration of nano-TiO₂. However, this strategy has several limitations. First, the time-integrated samples do not allow knowing the temporal evolution of the mass concentration, where high peaks of exposure may be hidden. Also, this strategy does not inform about the size distribution of the particles emitted, apart from the above cut-point used in the sampling (as respirable or PM2.5 range). From a health perspective these two factors may be quite relevant, especially the knowledge on the size of the particles that in last term will indicate in which part of the respiratory track the particles will deposit. Secondly, a well-known limitation of filter sampling is the need of high enough filter loading as required by the analytical procedure. This fact generally leads to longer sampling periods, eventually longer than the tasks to be performed with ENPs. Finally, the availability of a chemically selective analysis for the target material is a critical issue because of the need for a clear distinction of the ubiquitous background aerosol.

Para terminar:

The discussion about the usefulness of direct reading instruments versus filter based personal sampling is chemical as well as site-dependent. The right methodological choice for other scenarios could have been quite different. Specially, when the release of fine particles occurs in significant quantities of a well-defined chemical. For instance, (Demou, Peter, & ENP chemical can determine not only the characteristics size bins of the release size distribution, but also its potential interaction with gases or particles present in the work area. In this particular sequence of physical handling of nano-TiO₂ at room temperature, the eventual and temporary release of a low number of supermicronic particles is likely to be undistinguishable from the background concentration by the mere DRI output although these entities were clearly identified and measured by SEM/EDX and ICP-MS analysis of time-integrated samples.

The DRI, however, are of unquestionable applicability as real-time monitors to quantify engineering controls efficiency and, thus, for risk management activities and decision making. Unless real-time chemically-selective sensors for particular ENPs are developed, the information about PNC and size distribution can be of definitive importance, provided a previous understanding about the characteristics of airborne population and its relationship with operative task at a particular industrial site.

Para terminar:

New measurement devices that will solve the current gaps are expected in the near future, either as real-time chemically selective devices and/or the “universal aerosol sampler” able to a real-time description of the particle population in terms of surface, number and mass, as hypothesized by Maynard (2006). However, in the meantime it is necessary to reach a consensus, and therefore to develop an agreement on the feasible and reliable measurement protocols to be used in industrial environments. These standardized protocols are a key issue for a quantification of the repeatability and the reproducibility assessment, therefore enabling to a comparison of results from different studies and helping the industry to manage the potential nano-risks. The use of size- and chemical-selective real time approaches could help and avoid the otherwise required extrapolation to a full shift. Nevertheless, how widespread can be this approach depends on the development of cost-effective and robust instruments adapted to the routinely measure in such working environments.

Exposure assessment to engineered nanoparticles handled in industrial workplaces: The case of alloying nano-TiO₂ in new steel formulations
C. Vaquero, C. Gutierrez-Cañas, N. Galarza, J. M. López de Ipiña
Journal of Aerosol Science, (accepted) 2016

Esto es el resultado de un trabajo conjunto

Jesús López de Ipiña, Celina Vaquero, Nekane Galarza (Tecnalia)

Imara Ibarra, Gaizka Aragón, Iñaki Múgica, Miren Larrión, Cristina Gutierrez-Cañas (UPV/EHU)

BOSTLAN

Gerdau Reinosa

DYH Pui (Particle Technology Lab., U. Minnesota)

Y otros tantos

EHS-Advance (NanoMateriales IE14-396, 2014) <http://www.ehsadvance.com/web/guest>.

Gracias por su atención
