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Occupational exposure to metal nanoparticles: a pilot biomonitoring study

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AIM

The increase of exposure to **Metal Nanoparticles (MNPs)** during their synthesis, use and disposal presents new risks and uncertainties both for the general population and workers in nanotechnology companies and research institutions. To assess human exposure to MNPs, we collected urine (pre- and post-shift) during a working week and blood at the end of the same week from workers of **two different companies (A and B) that use different metal-based nanotechnologies**, comparing the results with those obtained on control subjects.

SUBJECTS

COMPANY A

Growth of **InAs** semiconductor **nanowires** by chemical beam epitaxy technique, using organometallic precursors. In some cases the growth is catalyzed by **Au nanoparticles**.

COMPANY B

Synthesis of **PVP-Pt colloidal nanoparticles** prepared by ascorbic acid reduction.

Protection equipment: chemical fume hood, chemical protective clothing and goggles; disposable gloves; facial mask class FFP3

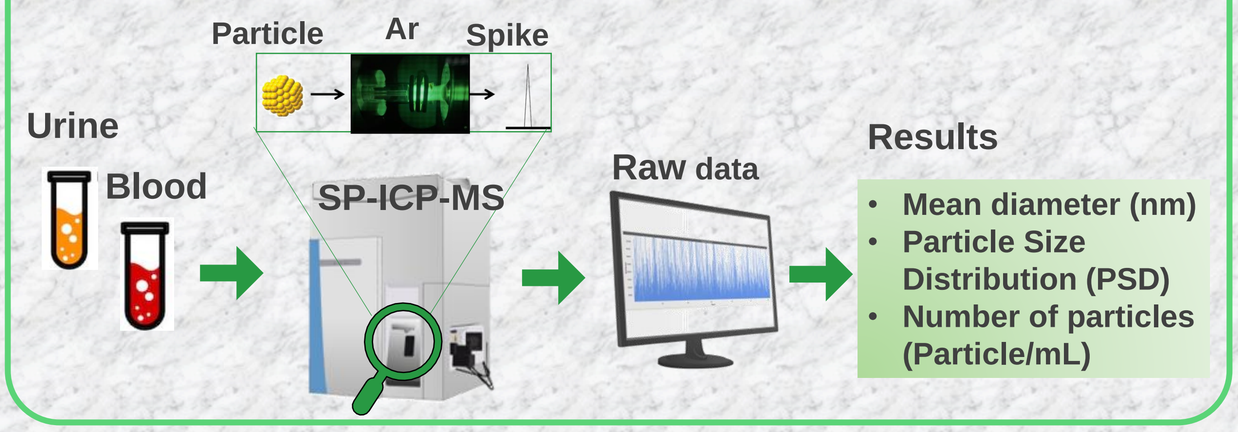
SAMPLE PRETREATMENT

Urine → 1:10 v/v water dilution

Blood → Alkaline extraction with TMAH 25% v/v → Sonication 10 min and 24 hours at room temperature → Dilution with 0.1% v/v Triton-X

ANALYSIS

Figure 1. Single Particle Inductively Coupled Plasma Mass Spectrometry



METHOD VALIDATION ON CERTIFIED REFERENCE MNPs

Figure 2. Calibration curves of Au and Pt NPs in urine and blood

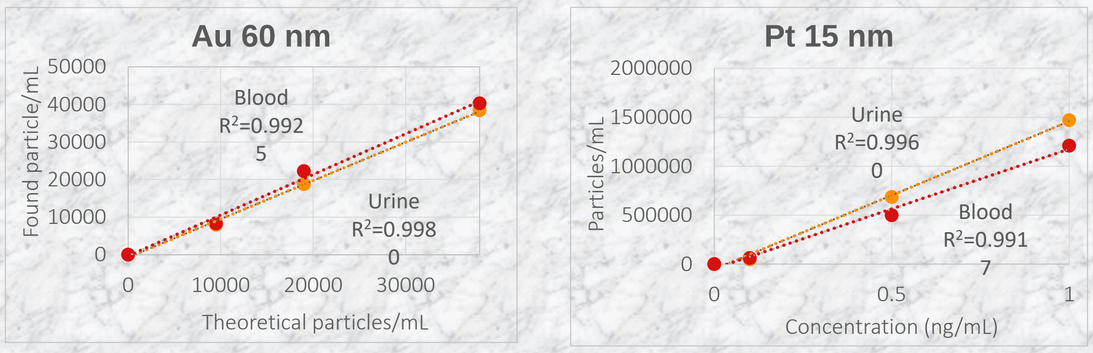


Table 2. Performances: all MNPs of interest in urine and blood

MNPS	Parameter (n=3)	Urine	Blood
Ag 40 nm 0.05 ng/ml	Concentration LoD	0.003 ng/mL	0.004 ng/mL
	Size LoD	12.1 nm	15.2 nm
	Found diameter (RSD)	32.9 nm (2.5%)	33.2 nm (0.8%)
Au 60 nm 19000 particles/mL	Concentration LoD	0.007 ng/mL	0.007 ng/mL
	Size LoD	9.1 nm	13.0 nm
	Found diameter (RSD)	66.1 nm (1.2%)	72.0 nm (0.8%)
In_2O_3 20-70 nm 5 ng/mL	Concentration LoD	0.40 ng/mL	0.52 ng/mL
	Size LoD	12.3 nm	17.1 nm
	Found diameter (RSD)	42.8 nm (8.7%)	45.4 nm (4.6%)
Ir 15 nm 5 ng/mL	Concentration LoD	0.76 ng/mL	1.02 ng/mL
	Size LoD	6.6 nm	7.8 nm
	Found diameter (RSD)	27.7 nm (8.2%)	30.8 nm (8.4%)
Pd 15 nm 5 ng/mL	Concentration LoD	0.33 ng/mL	0.68 ng/mL
	Size LoD	23.8 nm	25.9 nm
	Found diameter (RSD)	32.9 nm (1.2%)	35.4 nm (2.1%)
Pt 15 nm 0.5 ng/mL	Concentration LoD	0.07 ng/mL	0.13 ng/mL
	Size LoD	16.1 nm	17.3 nm
	Found diameter (RSD)	17.5 nm (7.0%)	19.5 nm (5.7%)
TiO2 <100 nm 5 ng/mL	Concentration LoD	0.28 ng/mL	0.81 ng/mL
	Size LoD	45.2 nm	50.2 nm
	Found diameter (RSD)	89.6 nm (2.8%)	85.5 nm (4.6)

RESULTS: COMPANY A

Table 3. MNPs in urine of workers (pre- and post-shift) and controls

MNPs	Worker (no.)	Diameter (nm)		Particle Concentration (Particle/mL)		Concentration (ng/mL)	
		pre-shift	post-shift	pre-shift	post-shift	pre-shift	post-shift
Ag	1-2	nd	nd	nd	nd	nd	nd
	3	29.2±2.9	29.4±2.5	19180±9921	13955±4608	0.012±0.005	0.009±0.002
Au, In, Pt, Ti	1-3	nd	nd	Nd	nd	nd	nd
	Control (no.)	Diameter (nm)		Particle Concentration (Particle/mL)		Concentration (ng/mL)	
		pre-shift	post-shift	pre-shift	post-shift	pre-shift	post-shift
Ag	1	28.9±1.9	28.4±2.5	7680±12327	6630±4087	0.006±0.006	0.006±0.002
	2	28.6±2.1	28.2±2.6	12215±4916	10470±396	0.008±0.002	0.007±0.002
Au, In, Pt, Ti	1-2	nd	nd	nd	nd	nd	nd

Table 4. MNPs in blood of workers (post-shift end of week) and controls

MNPs	Worker (no.)	Diameter (nm)	Particle Concentration (Particle/mL)	Concentration (ng/mL)
Ag	1-3	nd	nd	nd
Au	1	15.3	251177	0.620
	2	15.5	62794	0.154
	3	15.1	65934	0.162
In	1	nd	nd	nd
	2	37.9	14020	1.00
	3	37.6	6722	0.41
Pt	1-3	nd	nd	nd
Ti	1	82.4	49092	4.90
	2	83.4	16709	1.87
	3	86.8	17315	1.93
MNPs	Control (no.)	Diameter (nm)	Particle Concentration (Particle/mL)	Concentration (ng/mL)
Ag	1-2	nd	nd	nd
Au	1	15.1	10989	0.026
	2	15.3	95838	0.236
In, Pt	1-2	nd	nd	nd
Ti	1	84.5±12.0	16245	1.83
	2	90.4±16.4	14334	1.65

Figure 3. Ag NPs in urine: raw data (left) and PSD (right)

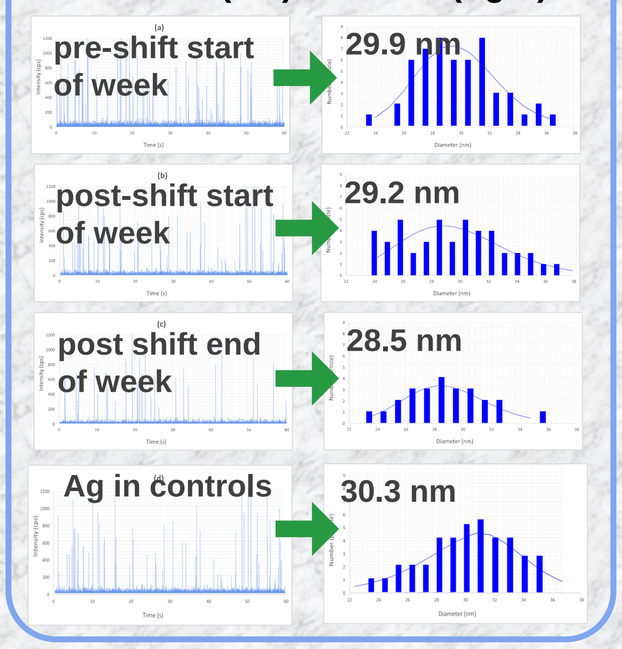
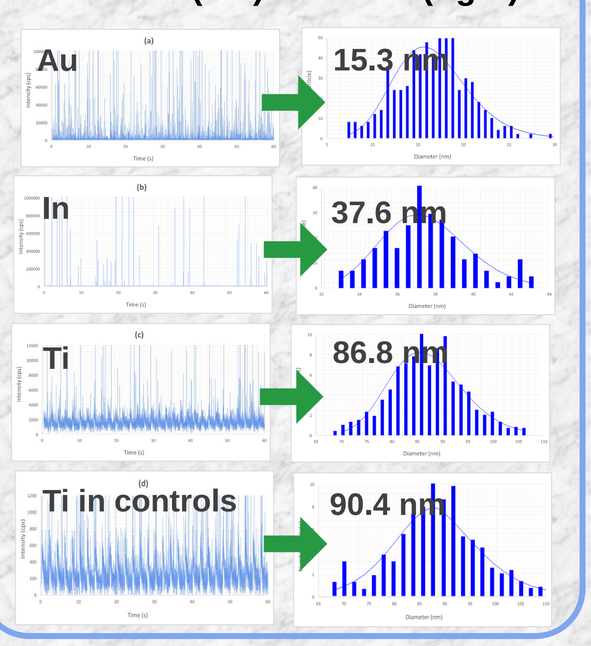


Figure 4. MNPs in blood: raw data (left) and PSD (right)



RESULTS: COMPANY B

The analysis of MNPs in workers from the Company B did not show presence of particles neither in urine nor in blood.

DISCUSSION

The SP-ICP-MS analysis showed that workers from the company A had measurable Ag NPs (29±0.5 nm) in urine and Au NPs (15±0.2 nm), In NPs (38±0.2 nm) and Ti NPs (90±3.2 nm) in blood.
There was no difference in diameter and number of particles between pre- and post-shift urine samples. In blood samples, the number of particles are higher respect to urine samples, even if a very low concentration was detected (0.1-5.0 ng/mL of MNPs).
In addition, Ag NPs in urine, and Au and Ti NPs in blood were also detected in control subjects.

CONCLUSIONS

Blood appeared a suitable biomarker for studying the human exposure to MNPs. The presence of MNPs in controls suggested that exposure through other daily-life sources may became relevant in the same way.