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Chemical Substances and Biological Agents

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REPORT R-777



Characterization and Control of Occupational Exposure to Nanoparticles and Ultrafine Particles

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ABSTRACT

Many workers are exposed to a range of particles present on a nanometric scale. In occupational hygiene, it is common to differentiate manufactured nanoparticles (NP) from ultrafine particles (UFP) coming from natural, human or industrial sources. Given that major deficiencies exist in the usual risk assessment approaches for these particles, the objective of this research was to assess occupational UFP and NP exposures. The secondary objective was comprehensive testing of the assessment capabilities regarding occupational NP and UFP exposures in an industrial and laboratory context. Two main types of assessment were performed during this research. The first concerns the assessment of the fine and ultrafine particle concentrations with a particle counter (P-Trak, model 8525), and the second pertains to the assessment of fine and ultrafine particle size distribution with an electrical low pressure impactor (ELPI). The measurements were taken in two welding schools, an aluminium smelter, the research centre of a thermoplastics processing company, and three university laboratories producing and/or using nanoparticles.

The results revealed that aluminium smelter workers, people who perform welding tasks, and workers in the thermoplastic processing industry are exposed to UFPs. However, the assessments performed under this study do not reveal high NP concentrations in research laboratories. Only NP production by milling generated detectable NP concentrations. NP handling in glove boxes of two other laboratories seems to prevent worker exposure adequately.

There is currently no consensus concerning UFP and NP exposure evaluation measures. However, our findings suggest that the P-Trak is suitable for occupational assessment of UFP concentrations, whereas several uncertainties remain to assess NP exposure, particularly in their agglomerated form. In view of this research, it appears that a characterization and control study of occupational NP and UFP exposure should include assessment of the mass and particle number concentrations, measurement of granulometric distribution and electron microscopic characterization of nanoscale particles.

TABLE OF CONTENTS

ACKNOWLEDGMENTS	I
ABSTRACT	III
TABLE OF CONTENTS.....	V
LIST OF TABLES	VII
LIST OF FIGURES.....	IX
LIST OF ACRONYMS.....	XI
1. ORIGIN AND CONTEXT OF THE STUDY	1
2. STATE OF KNOWLEDGE OF THE PROBLEM OF OCCUPATIONAL EXPOSURE TO ULTRAFINE PARTICLES AND NANOPARTICLES	3
2.1.1 Effects on Health and Safety.....	3
2.1.2 Metrology.....	3
2.1.3 Nanoparticle Exposure.....	4
2.1.4 Ultrafine Particle Exposure.....	5
2.1.5 Means of Controlling Exposure.....	5
2.1.6 Risk Management	6
2.1.7 Regulation, Programs, Standardization and Guides	6
3. OBJECTIVE OF THE STUDY	8
4. METHODOLOGY	9
4.1 Metrology and Assessment Strategies	9
4.2 Study Environments.....	10
4.2.1 Welding Schools	10
4.2.2 Aluminium Smelter.....	11
4.2.3 Thermoplastic Processing Industry	11
4.2.4 University Laboratories Producing or Using Nanoparticles	12
5. RESULTS	15
5.1 Welding Schools	15
5.1.1 School A.....	15
5.1.2 School B.....	18
5.2 Aluminium Smelter.....	19
5.3 Thermoplastic Processing Industry	25
5.4 University Laboratories Producing or Using Nanoparticles	28

5.4.1	Laboratory A	28
5.4.2	Laboratory B	29
5.4.3	Laboratory C	30
6.	DISCUSSION	33
6.1	Welding Schools	33
6.2	Aluminium Smelter.....	34
6.3	Thermoplastic Processing Industry.....	35
6.4	University Laboratories Producing or Using Nanoparticles	36
6.4.1	Laboratory A	36
6.4.2	Laboratory B	36
6.4.3	Laboratory C	37
7.	GENERAL CONSIDERATIONS AND RECOMMENDATIONS.....	39
7.1	Occupational Exposures.....	39
7.2	Exposure Assessment Tools	39
8.	BIBLIOGRAPHY	41

LIST OF TABLES

Table 1 – Cutpoint diameters ($\square\text{m}$) for each ELPI stage, depending on the configuration used ...	9
Table 2 – Study environments	10
Table 3 – Mean concentrations (particles/cm ³) measured in the two welding schools	15
Table 4 – Descriptive statistics of the particle concentrations (particles/cm ³) measured with P-Trak particle counters during mapping of the Soderberg and prebaked anode processes and in the anode cooling rooms	20
Table 5 – Descriptive statistics of particle concentrations (particles/cm ³) measured with P-Trak particle counters during quasi-personal measurements in i) the Soderberg process and ii) the prebaked anode process	20
Table 6 - Proportions of particles in the ELPI stages (sampling without filter stage) for the Soderberg and prebaked anode processes.....	22
Table 7 – Main ultrafine elements detected during TEM/EDS analyses in the two electrolysis processes	23
Table 8 – Mean particle levels in the storage and processing rooms.....	26

LIST OF FIGURES

Figure 1 – Mean concentrations and typical errors measured with the P-Trak particle counters for the welding processes of Schools A and B (school indicated in parentheses).....	16
Figure 2 – Profile of concentrations recorded during one day of sampling for the SMAW process of Welding School A	16
Figure 3 - Profile of concentrations recorded during one day of sampling for the GMAW on aluminium process of Welding School A	17
Figure 4 - Profile of concentrations recorded during 30 minutes of sampling for the SMAW process of Welding School A	17
Figure 5 – Particle size distribution for the welding processes of School A	18
Figure 6 – Profile of concentrations recorded during one day of sampling for the SMAW process of Welding School B.....	18
Figure 7 – Particle concentrations in the Soderberg and prebaked anode processes.....	19
Figure 8 - Comparison of particle granulometric distributions based on opening of the potroom doors in the prebaked anode process	22
Figure 9 - Comparison of particle granulometric distributions based on the temperature of the anodes in the cooling rooms	23
Figure 10 – Prebaked anode process sample from the ELPI 28 nm stage.....	24
Figure 11 –Soderberg process sample from the ELPI 28 nm stage.....	24
Figure 12 – Prebaked anode process sample from the ELPI 93 nm stage.....	24
Figure 13 - Soderberg process sample from the ELPI 156 nm stage.....	25
Figure 14 – Prebaked anode process sample from the ELPI 156 nm stage.....	25
Figure 15 – Profile of particle concentrations measured in the research centre's different rooms	26
Figure 16 – Particle concentrations measured in the processing room.....	27
Figure 17 – Quasi-personal particle concentrations measured during CNT handling and extruder startup.....	27
Figure 18 – Particle concentrations in the aluminium/copper nanoparticle production laboratory (Laboratory A)	28
Figure 19 – Profiles of particle concentrations measured with P-Trak particle counters on the 3 rd day of sampling near the mill (i) and 3 metres from the mill (ii) (Laboratory A)	29
Figure 20 – Particle concentrations measured 1 metre from the glove box during CNT handling in Laboratory B	30

Figure 21 – Particle concentrations measured 3 metres from the glove box during CNT handling in Laboratory B	30
Figure 22 – Particle concentrations measured in the glove box during CNT handling in Laboratory C	31
Figure 23 – Aerosol concentrations measured in the glove box during CNT handling in Laboratory C	31
Figure 24 – Particle concentrations measured under the laboratory hood during polymer handling in Laboratory C	32
Figure 25 – Aerosol concentrations measured under the laboratory hood during polymer handling in Laboratory C	32

LIST OF ACRONYMS

CPC: Condensation Particle Counters

EEPS: Engine Exhaust Particle Sizer

ELPI: Electrical Low Pressure Impactor

FCAW: Flux Cored Arc Welding

FMPS: Fast Mobility Particle Sizer

GM: geometric mean

GMAW: Gas Metal Arc Welding

GSD: geometric standard deviation

GTAW: Gas Tungsten Arc Welding

NP: nanoparticles

NT: nanotechnologies

CNT: carbon nanotubes

SMAW: Shielded Metal Arc Welding

SMPS: Scanning Mobility Particle Sizer

TEM-EDS: Transmission Electron Microscopy coupled with Energy-Dispersive Spectrometry

UFP: ultrafine particles

1.ORIGIN AND CONTEXT OF THE STUDY

It is now recognized that workers are exposed to a whole range of particles present on a nanometric scale. Nanometric scale is defined as a size ranging from 1 to 100 nanometres (nm). In occupational health, it is common to differentiate manufactured nanoparticles (NP) from ultrafine particles (UFP), which originate from “natural, human or industrial sources, such as part of the smoke or fumes generated by forest fires, cigarettes, internal combustion engines or welding operations” [1]. NPs thus are produced for an industrial purpose, while UFPs are produced unintentionally during industrial activities. These are the definitions of NP and UFP used in this report.

Nanotechnologies (NT) are developing extremely rapidly. In 2008, the Agence française de sécurité sanitaire de l'environnement et du travail (AFSSET) (today called Agence nationale de sécurité sanitaire de l'alimentation, de l'environnement et du travail (ANSES)) identified several hundred mass market products containing nanomaterials: textiles, cosmetics, food, sporting goods, construction materials [2]. The IRSST also indicated, in 2008, that more than 650 products containing NPs were already commercially available [1]. In July 2011, the list published by the Woodrow Wilson Center for Scholars included 1317 commercially available products containing nanoparticles in its online inventory. A recent survey estimates that 21.2% of companies in the Swiss chemical industry use NPs; this percentage falls to 0.6% for the Swiss manufacturing industry as a whole [3]. Certain nanomaterials are also found in several construction products, particularly concrete, steel, ceramics, glass and paint [4]. According to Nano Québec, Québec's strengths in the NT field are concentrated in four priority sectors: 1) micro/nanosystems, particularly including the processes (micro/nanomanufacturing, electronic assembly, encapsulation, etc.) and development of devices (thin layers, electromechanical microsystems, etc.); 2) processing of materials, particularly including synthesis of materials (nanomaterials, thin layers, synthesis processes (plasma, etc.) and their integration (composites, coatings, sensors, etc.); 3) forestry and clean technologies, particularly including green materials (nanocellulose, recyclable materials, etc.) and energy production or storage techniques (photovoltaic, LED, batteries, etc.); and 4) nano-biohealth, particularly including devices (biosensors, biocompatible materials, etc.) and projects for the development of knowledge or techniques in the health/safety field [5].

Given the increased use of NPs in industrial applications, more and more workers thus are likely to be exposed to NPs. In addition, several studies suggest the possibility of health risks specific to these particles. There are also parallel concerns regarding the conditions which could generate exposure to these NPs and the means required to measure and control these conditions. Thus, there was a 124% growth in environmental, health and safety publications concerning this subject between 2004 and 2007, while this growth rate was only 29% for the same period for nanotechnology as a whole [6]. Faced with these situations of uncertainty, the IRSST recommends a preventive and even a precautionary approach to avoid any NP exposure [1]. AFSSET also recommends acting without waiting in the name of the precautionary principle, particularly by encouraging research in the exposure assessment fields [2]. The National Institute for Occupational Safety and Health (NIOSH) identified 10 critical fields concerning nanotechnology research. Among these fields, research on measurement methods and exposure

assessment strategies are necessary to improve occupational risk prevention [7]. These concerns also led the creation of numerous working groups, concerned about ensuring the safety of potentially exposed persons. Among these groups arising from national and supranational bodies, the United Kingdom Health and Safety Executive (HSE) [8], the Nordic Council of Ministers (NORDEN) [9] and the European Agency for Safety and Health at Work (EU-OSHA) [10]. Finally, in Québec, significant deficiencies remain regarding the exposure assessment and support offered to nanotechnology businesses. The IRSST also indicated, in 2008, that no NP assessment had been performed in the work environment by its researchers [1].

A problem also emerges with UFPs. It has long been known that these particles are present in many work environments, but it is only in the past few years that epidemiological research has suggested that UFPs can contribute to cardiovascular and respiratory problems [11-16]. However, there is little documentation of the UFP exposure levels in the work environments, even though certain data has been published in the past few years, for example, regarding smelters [17-20], welding processes [21-24], grinding processes [25] and metal machining processes [26]. However, no inventory of occupational UFP exposure sources currently exists, nor any consensus on exposure assessment tools. A project called MatPuf was deployed in France in 2010 to identify occupational situations generating UFPs, with the aim of producing a job-UFP exposure matrix. As in the case of NPs, there is a need for better understanding and better characterization of occupational UFP exposure.

2.STATE OF KNOWLEDGE OF THE PROBLEM OF OCCUPATIONAL EXPOSURE TO ULTRAFINE PARTICLES AND NANOPARTICLES

The NORDEN [9], IRSST [1] and EU-OSHA [10] literature review synthesis, produced in 2007, 2008 and 2009 respectively, served as a basis for the points presented in this section. For the purposes of this section, when it is desirable to group NPs and UFPs together, we refer to them as nanomaterials (NM).

2.1.1 Effects on Health and Safety

Several studies suggest cardiovascular and respiratory health effects for environmental and/or occupational UFP exposures [11, 14, 27, 28]. In addition, several synthesis documents have been published concerning the effects of nanoparticles. All the information in this section thus is derived from the documents by Kaluza et al. [10] and Ostiguy et al. [29]. Although there is still a debate on the mechanisms, “in animals, several effects have already been shown, including toxic effects on several organs (heart, lungs, kidneys, reproductive system...), as well as genotoxicity and cytotoxicity” [29]. Short-term animal studies are said to have shown reactions of inflammation, cytotoxicity and lung tissue damage. Distribution to other organs via the blood system or the brain directly via the nose is considered possible, but requires verification by other studies. Although cutaneous sensitization has already been observed, an intact skin seems sufficient to prevent any NM penetration into the body by this route. No human study to date has shown nanomaterials to have carcinogenic effects. While the current in vitro toxicity assessment methods need better validation before they are used in the case of nanomaterials, all in vivo methods would be applicable to the study of nanomaterials, with certain modifications, such as a detailed characterization of the particles.

The main NM-related safety risks are fire-explosion and the catalytic effect. The relative intensity of a fire or an explosion in relation to fine particles of the same material is variable; in the case of aluminium, this relative intensity is lower, due to the surface oxide layer, while it is similar for carbon black and carbon nanotubes (CNT). The increase in the specific surface of nanomaterials favours the catalytic effect and could lead to unexpected violent reactions.

2.1.2 Metrology

The “best practices guide favouring management of the risks related to synthetic nanoparticles” by Ostiguy et al. [1] serves as the reference for this section. In this document, the authors indicate that it is important to “characterize NP emissions and assess, as a minimum, the particle number concentration, granulometric distribution, specific surface and chemical composition”. The authors of the report thus indicate that “no instrument at the present time can produce a specific analysis of NPs to determine all the relevant characteristics of exposure to synthesized NPs.” A table showing examples of instruments and techniques allowing characterization of aerosol NPs is presented in the best practice guide. Condensation Particle Counters (CPC) particularly allow determination of the particle number concentrations and real-time concentrations of fine and ultrafine particles, while the Electrical Low Pressure Impactor (ELPI)

and the Scanning Mobility Particle Sizer (SMPS) can determine a set of parameters, such as numerical, mass and specific surface granulometric distributions. However, it remains that many technical constraints do not allow efficient measurement of all these parameters [1]. Other spectrometers are also available, notably the Fast Mobility Particle Sizer (FMPS), the Engine Exhaust Particle Sizer (EEPS) and the Universal NanoParticle Analyzer (UNPA) [30, 31]. These instruments, which are still being assessed [32-36] continue to be bulky, expensive instruments, difficult to use in a worker's respiratory zone. A recent review of the various instrument types is presented by Kuhlbusch et al. [37]. In the past few years, some miniaturized instruments, which can be placed in respiratory zone, have emerged for NM assessment, including the UNC passive dosimeter, perfected at the University of North Carolina at Chapel Hill [38], the Aerasense – Phillips NanoTracer® [35, 39, 40], the DiSCmini® Diffusion Size Classifier [35, 41, 42] and a thermal precipitator [43].

In addition to the NM concentration assessment, some studies seek to characterize the nature of the particles involved and the chemical and physical processes of their formation. Several studies thus have attempted to identify the chemical composition and morphology of UFPs in the manganese alloy fabrication industry [44], oil refineries [45] and stainless steel welding fumes [46]. Some have also addressed the mechanisms producing UFPs during abrasion [47, 48] and during laser ablation of paint films [49], while others have focused on the electrical discharge machining (EDM) die-sinking process [50] or the carbon nanotube industry [51-54]. Some authors present the need to establish NM generation potential by standardized tests [55, 56]. A last study analyzes the respective advantages of scanning electronic microscopy versus transmission electronic microscopy for NM characterization [57]. Finally, Hameri et al. [58] presented the main chemical and physical processes of NM formation and coagulation.

2.1.3 Nanoparticle Exposure

Three recent literature reviews on NP occupational exposure include many publications on the subject. These reviews are by Kaluza et al. [10], published in 2009, Brouwer [59] published in 2010, and Kuhlbusch et al. [37], published in 2011. Workplace studies and simulations of laboratory working conditions are listed in the reviews. These studies cover a wide range of materials, including carbon black, various metal and metalloid oxides (titanium, silicon, zinc, aluminium, cerium, manganese, etc.), silver, aluminium, organic clay, fullerenes and nanotubes (single-walled and multiwalled) and carbon nanofibres. Following these three publications, several others have been added on carbon nanotubes and the composites that contain them [60-63], metal and metalloid oxides [64-70], silver and aluminium NPs [71], carbon black [69], nanocellulose [72] and gold and cadmium selenide quantum dots (boxes) [73]. Whether in workplace exposure assessments or laboratory simulations, Kuhlbusch et al. raise several deficiencies that make it difficult to compare the results of the various studies, mainly including: 1) the lack of a harmonized approach concerning the strategies and instrument methods, the parameters measured, the dimensional ranges used and the data analysis procedures, 2) the absence of indication of uncertainty and the instrumentation detection limits, and 3) the absence of precision regarding the contribution of other sources to the concentrations measured [37].

2.1.4 Ultrafine Particle Exposure

The publication by Schneider et al. [9] is the only recent literature review listed on occupational UFP exposure. A summary of the different exposure levels associated with various activities, such as several types of soldering, machining and metal welding, some smelting activities, and even bread baking, are presented. Of greater interest to our research is the presentation of results of an assessment in an aluminium electrolysis plant or in welding processes. A preliminary study by the Oslo-based National Institute of Occupational Health clearly shows that several types of arc welding are major sources of UFP number concentration, reaching $1.6 \cdot 10^6$ particles/cm³ (measured with an SMPS). In the study by Thomassen et al. [19], fixed-station measurements also indicate high UFP number concentrations ($3 \cdot 10^5$ particles/cm³) during anode changes.

Since Schneider's literature review in 2007, many other publications have been released on UFP exposure. Thus, we find articles concerning metal machining and grinding [17, 74-76], firefighting [27], smelters [17, 18, 74, 77], precious metal refining [78], thermal spraying [79], the atmosphere inside automobiles [80, 81] or buses [82-85], bus garage mechanics and supervisors [85], pressurized metal casting [86, 87], restaurant cooking [86, 87], a diesel engine laboratory [86], sanding plywood and medium-density fiberboard (MDF) [88], asphalt production and spreading [89], polytetrafluoroethylene (PTFE) clothing manufacturing [90], operation of electric motors [91], the work of highway tollbooth attendants [92], commercial buildings [59, 93] operation of laser printers [94, 95], and school environments [96-98]. More interesting for our research are the various publications concerning metal welding [17, 99-102], in which the UFP number concentrations during MIG (Metal Inert Gas) welding of steel or aluminium range from $1.1 \cdot 10^4$ particles/cm³ to $7 \cdot 10^5$ particles/cm³, depending on the studies.

2.1.5 Means of Controlling Exposure

Ostiguy et al. "recommend that the means of control used allows NP dispersion in the air and on work equipment to be circumscribed as much as possible, in order to avoid exposing workers" [1]. According to one experiment in a testing booth, the capture efficiency of a suction source system would not vary for NP sizes between 4 and 100 nm. In addition, a study by the NIOSH conducted with suction nozzles, such as those used in welding, indicates a 74% to 76% reduction of the NP mass concentration between 15 and 50 nm [10].

Tsai et al. [103] and Cena et al. [62] indicate that handling of aluminium NPs, silver NPs or carbon nanotubes (CNT) under a hood can lead to high NP exposures. The turbulence created by the person's body in front of the hood would be at the origin of this exposure during the use of conventional hoods. Air curtain hoods would significantly reduce this type of exposure [71]. A suction nose used to clean tanks for a pilot project fabricating NPs of various metals (iron, copper, zinc, etc.) proved efficient in reducing exposure by 76% to 100% in the operator's respiratory zone [67].

The use of N95 and P100 filtering face pieces is very widespread in the NP industry. All the commercially available models are "Electret" models, in which the electrostatic effect is adding to the filtering mechanisms, such as diffusion, recognized as the most important mechanism for

nanosized particles. With these types of respiratory protective devices (RPD), the tests indicate that the particles penetrating the filtering materials more easily range in size between 30 and 70 nm [1]. However, the possibility that particles smaller than 10 nm also have high penetration due to the thermal rebound phenomena still has to be elucidated [104-106]. The need for better characterization of the penetration mechanisms and the leakage effects at the RPD contact points with the skin is recognized by several researchers [106-109].

The information concerning the efficiency of conventional skin protection for nanomaterials is much rarer. The use of protective equipment (suits and gloves) made of synthetic fibres is to be preferred, even if their efficiency is not yet proved for NPs [106].

2.1.6 Risk Management

Several NP risk analysis and management guides have been published in the past few years but, on the whole, these documents arrive at similar treatment as for fine particles or toxic materials in general [1, 10, 108, 110-112]. Control banding methods are proposed by several authors [10, 113-115], while an information gathering model, which should accompany every NP exposure measurement, is presented by Woskie et al. [116]. An analysis of the NP Material Safety Data Sheets (MSDS) seems to indicate that information varies greatly from one manufacturer to another and that, in general, the information found in these MSDS is similar to that of analogous materials (graphite for CNT or fine particles of the same molecule) [9]. More generally, based on the precautionary principle and the deliberations of the European NanoCap¹ project, van Broekhuizen proposes a six-step risk management approach: 1) reporting of the quantity and type of NPs in the products, 2) creation of a national register of workers potentially exposed to nanomaterials, 3) transparency in communication of known and uncertain risks, 4) establishment of exposure limit values, 5) deployment of an early warning system for the first signs of occupational diseases, and 6) approval before marketing of any application of nanotechnologies and nanomaterials as a central element of a regulatory oversight policy [117]. A similar approach, but more specific to NP use in pesticide manufacturing, is presented by Stone et al. [118].

2.1.7 Regulation, Programs, Standardization and Guides

To date, no government seems to have specific environmental health and occupational health regulations concerning NPs and UFPs. In Europe, the laws and regulations applicable to these particles are those associated with hazardous materials such as REACH, Seveso II and various environmental directives [10]. In the United States, in addition to the current scientific uncertainty regarding the properties of these particles, various administrative and legal constraints would prevent this government from establishing such regulations and laws in the near future [115, 119, 120]. There is the EPA's voluntary participation program, the Nanoscale Materials Stewardship Program [121], but in view of the participation rate and the confidentiality needs of the participating companies, there are strong doubts regarding its credibility [115, 122]. However, some European proposals exist for exposure limit values (ELV), one coming from the

1 www.nanocap.eu

Organisation for Economic Cooperation and Development (OECD), two from Germany's Federal Institute for Occupational Safety and Health (BAuA), four from the Institute for Occupational Safety and Health of the German Social Accident Insurance (IFA), and four from the British Standards Institution (BSI) [113, 123, 124]; all these proposals are preliminary due to the incomplete nature of the available information. The NIOSH has also made preliminary proposals for carbon nanotubes and nanofibres [125] and titanium dioxide [126]. All these ELVs are mass concentration values except for two from the IFA for biopersistent granular materials [113].

While the U.S. Government's financial support for NP-associated health research is often considered insufficient [122, 127] by the American scientific community, the European Commission subsidizes many research programs, such as NANEX and NANODEVICE, under its 7th Framework Programme [10]. Other agencies, such as the World Health Organization (WHO) and the OECD are interested in the subject and offers their support to several initiatives [10]. OECD work [128], such as "Report of the Workshop on Risk Assessment of Manufactured Nanomaterials in a Regulatory Context" and "Preliminary Analysis of Exposure Measurement and Exposure Mitigation in Occupational Settings: Manufactured Nanomaterials" can be consulted on that body's website².

The European Committee for Standardization (known as CEN), via its committees, CEN/TC137 and CEN/TC352, and the International Standards Organization (ISO), via its committees ISO/TC229 and ISO/TC146/SC 2, are working on the creation of standards concerning NPs. Currently, among those already published, two are related to exposure measurement [129, 130], while a third presents a risk analysis process [131], a fourth deals with safe work methods [132], and a fifth deals with terminology and definitions of nano-objects [133].

Among the European projects in progress that are more NP-specific, NANODEVICE is seeking to design and perfect portable, easy-to-use devices for NP measurement and characterization³, while NANEX intends to produce a list of exposure scenarios for manufactured nanomaterials, covering their life cycle and including work scenarios. A summary of NANEX's approach is presented in a series of documents called "Work Packages - (WP2-Development of Generic Exposure Scenario Descriptions, WP7-Scientific Integration and Gap Analysis et WP3-Occupational Exposure Scenarios)"⁴, and examples of work exposure scenarios are presented on the same website⁵.

2 http://www.oecd.org/findDocument/0,3770,en_2649_37015404_1_119666_1_1_1,00.html

Consulted 2011-06-21

3 <http://www.nano-device.eu/> Consulted 2011-06-21

4 http://www.nanex-project.eu/index.php/public-documents/cat_view/43-dissemination-reports/74-wps-reports Consulted 2011-06-21

5 <http://www.nanex-project.eu/index.php/exposure-scenarios-db> Consulted 2011-06-21

3.OBJECTIVE OF THE STUDY

The main objective of this research was to assess occupational UFP exposures in welding schools and aluminium smelters. In addition, the research examined exposure levels among NP producers and users.

The secondary objective was to examine the overall capabilities for assessing occupational NP and UFP exposures in an industrial and laboratory context.

4. METHODOLOGY

4.1 Metrology and Assessment Strategies

Two main types of assessment were performed during this research: assessment of NM particle number concentrations and granulometric distributions.

The fine and ultrafine particle concentrations were assessed with particle counters (P-Trak, model 8525) made by TSI Inc. These are portable condensation particle counters for particles ranging from 20 nm to 1 µm in a concentration range of 0 to 500,000 particles/cm³. This instrument presents the advantage of providing real-time information and being easy to use and transportable.

The second assessment concerns fine and ultrafine particle size distribution with an Electrical Low Pressure Impactor (ELPI), made by the Finnish company Dekati Ltd. This low pressure impactor with real-time electrical detection allows analysis of aerosols in the 7 nm to 10 µm range. These limit sizes can vary according to the configuration used. The ELPI data is expressed in standardized concentrations dN/dlogDp. The ELPI also allows collection of the particles deposited in the impactor for microscopic characterization analysis. Three different configurations were used in this study. Table 1 presents the cutpoint diameters for each stage, according to the configurations 1) sampling with filter stage, 2) sampling without filter stage, and 3) collection. In particular, these real-time granulometric measurements will allow confirmation and assessment of the presence of nanomaterials in aerosols.

The P-Trak particle counters were supplied by the occupational hygiene laboratory of the Université de Montréal and the ELPI was supplied by the IRSST.

Table 1 – Cutpoint diameters (µm) for each ELPI stage, depending on the configuration used

Configuration n	Sampling with filter stage	Sampling without filter stage	Collection
Stage	µm		
1	5.982	6.351	6.710
2	2.937	3.796	4.010
3	1.861	2.272	2.400
4	1.172	1.524	1.610
5	0.725	0.902	0.953
6	0.433	0.583	0.616
7	0.262	0.321	0.384
8	0.145	0.214	0.263
9	0.070	0.098	0.156
10	0.039	0.050	0.093
11	0.027	0.030	0.055
12	0.018	0.024	0.028

Different assessment strategies were used in this project, depending on certain requirements of the sampled environments and the measuring instruments. Fixed-station assessments and “quasi-personal” assessments thus were performed for both types of measurements. “Quasi-personal” measurements are defined in this report as measurements taken as close as possible to the workers’ breathing zone, by a technician or a hygienist.

4.2 Study Environments

Table 2 presents the list of study environments, the particle types assessed and the types of measurements taken.

Table 2 – Study environments

Description	Particle type	Types of measurements
Welding school A	UFP	Concentration/Distribution
Welding school B	UFP	Concentration
Aluminium smelter	UFP	Concentration/Distribution/TEM-EDS
Thermoplastic	UFP and CNT	Concentration
Laboratory A/NP production	Aluminium/copper NP	Concentration
Laboratory B/nanocomposites	CNT	Concentration
Laboratory C/nanocomposites	CNT	Concentration

UFP: ultrafine particles

NP: nanoparticles

CNT: carbon nanotubes TEM-EDS: Transmission Electron Microscopy coupled with Energy-Dispersive Spectrometry

4.2.1 Welding Schools

Exposure level assessments were performed in two welding schools in the Montréal region (Schools A and B). These assessments were spread over a 16-month period. For School A, particle size concentration and distribution assessments were performed for the following five processes: Shielded Metal Arc Welding (SMAW), Flux Cored Arc Welding (FCAW), Gas Metal Arc Welding (GMAW), Gas Tungsten Arc Welding (GTAW) and oxygen cutting. For School B, particle concentration assessments were performed for the following three processes: SMAW, FCAW and GMAW. In both schools, the arc welding processes were performed under inert gas (MIG/TIG) and the students worked in booths of about 1.50 m by 1.80 m, equipped with a local ventilation system. The number of students per group varied, but ranged between 15 and 25 students. Several groups could also work at the same time in different sections of the premises, without any physical separation between them.

The particle size concentration and distribution measurements were performed directly in the students’ booths, at a distance within 50 cm of the welding zone. Although non-personal, the sampling method can be considered as quasi-personal assessment because of close confines of the zone.

4.2.2 Aluminium Smelter

Two sampling campaigns were conducted in an aluminium smelter in the Province of Québec. Particle size concentration and distribution measurements were taken. Two primary aluminium production processes were assessed, the Soderberg process and the prebaked anode process. These are two Hall-Héroult electrolytic reduction processes. The Soderberg process uses a paste of petroleum coke and pitch, placed in hoppers with their ends submerged in molten alumina-cryolite bath, while the second process uses prebaked anodes [134].

The plant assessed under this project is being converted and has begun dismantling the Soderberg potlines to replace them with prebaked anode production lines. The two types of processes assessed are located in contiguous buildings separated by physical barriers, rendering the processes independent. The workers were grouped by similar exposure group according to the trade titles. The Soderberg process groups assessed were: 1) drivers who deposit the briquettes; 2) frame lifters; 3) employees who break the crusts of the electrolytic baths; 4) pressurized overhead crane operators; 5) maintenance employees. The prebaked anode process groups assessed were: 1) pressurized overhead crane operators; 2) anode transport truck (“Berger”) drivers; 3) auxiliary truck (“mule”) drivers; 4) maintenance employees. The carbon anodes from the prebaked anode process are assembled directly in the plant. In our study, this department, called the Anode Sealing Department, was also assessed and classified in two sections: hexapod cleaning (spent anode), and hexapod and carbon section sealing. The workers in these departments are the hexapod cleaning and sealing attendants. In connection with these facilities, the two spent anode cooling rooms (“cemetery”) were also studied.

The particle concentrations in the potrooms were mapped for both processes and for the two anode cooling rooms. Stationary measurements representative of the exposure of the truck drivers and overhead crane operators were also taken during work periods of 1 to 2 hours. Quasi-personal measurements were performed in the Anode Sealing Department for the cleaning and sealing attendants, in the Soderberg process for the maintenance attendants and the employees who break the crusts of the electrolytic baths, and in the prebaked anode process for the maintenance employees. All these measurements were taken during periods of 1 to 2 hours.

A UFP analysis was performed on a JEOL Transmission Electron Microscope (TEM), model JEM-2100F, in both processes. This microscope is equipped with a Field Emission Gun (FEG), operating at 200 kV. It has maximum image resolution of nearly 1 Angstrom. Polycarbonate filters and analysis grids were used on the five finest stages of the ELPI. The analysis grids were glued to the substrates with a standard liquid adhesive. The particles were photographed without any modification to the grids that served to collect the nanoparticles. Chemical composition analyses were also performed with an Oxford Energy Dispersive Spectrometer (EDS).

4.2.3 Thermoplastic Processing Industry

Assessments were performed in the materials innovation research centre of a thermoplastics processing company. The plant evaluated under this study is not yet at the stage of producing materials incorporating NPs, because it is a research centre with the goal of developing products containing nanoparticles that give plastics certain interesting properties, such as thermal

conductivity and strength. The research centre is composed of offices, a meeting room, a quality control laboratory and two rooms, one of which is used for plastics manufacturing. This first room is divided into two parts (storage and processing), separated by an unsealed physical barrier. The other room, called the “pool”, is not currently used by the research centre. The two rooms are not ventilated mechanically, while the rest of the premises are.

The process tested was a twin screw extruder fed with polyethylene granules. Multiwalled CNT fractions were injected into the single screw as additives to the polyethylene. Baytubes® Carbon Nanotubes (C150HP) made by Bayer Material Science (BMS) were used [135]. These agglomerated nanotubes were larger than 100 micrometres, giving them limited potential inhalation exposure, according to the company [136].

Background measurements were taken with three P-Trak particle counters, model 8525, made by TSI, in the centre's different rooms. Measurements were taken on Monday morning after a shutdown of several days, and then new measurements were taken during operation of the extruder, with and without CNTs. Stationary and quasi-personal measurements were taken.

4.2.4 University Laboratories Producing or Using Nanoparticles

Measurements were taken in three university research laboratories producing or using NPs.

Laboratory A

The process used by the first laboratory mills aluminium/copper particles in liquid nitrogen. The objective of the process is to reduce the size and spacing of the particles. A 10-litre mill operating by attrition with a continuous flow of liquid nitrogen is used. The mill consists of stainless steel balls, particles and liquid nitrogen. Thermocouples control the mill temperature (-195°C) and the liquid nitrogen level. The evaporated liquid nitrogen is routed into a hood equipped with a particle filter. An operator collects a sample every hour, necessitating partial dismantling of the mill. The initial particles have a mean diameter of 100 µm. After the first day, the particles were flattened but the size remained the same. It was only after the second day that the mean diameter diminished to a size of 10 to 20 µm, and then by 15 nm after the 3rd day of milling.

Stationary measurements of fine and ultrafine particle concentrations were taken near the mill (< 1 m) and 3 metres from the mill. Three days of sampling covering the entire milling process were performed.

Laboratory B

The second laboratory is a nanocomposite fabricating laboratory. Several tasks are performed in this laboratory. The assessed process consists of placing a CNT suspension in a solvent, styrene. The solution is mixed in a glove box (main chamber) equipped with a transfer box. The nanoparticle weighing steps and the incorporation of the nanoparticles into the styrene are performed in the main chamber.

Stationary measurements of the fine and ultrafine particle concentration were taken near the glove box during CNT handling (<1 m) and 3 m away from the glove box, with two P-Trak 8525 particle counters.

Laboratory C

The third laboratory uses CNTs to reinforce and modify the electrical properties of certain polymers. Nanoparticles are handled at two distinct locations in the laboratory. The CNT powders are handled in a glove box equipped with a vacuum. When the nanotubes are integrated into the polymer, the handling operations are performed under a hood. General ventilation is present in the laboratory. Multiwalled Baytubes® Carbon Nanotubes (C150P) made by Bayer Material Science (BMS) were used [135]. Background measurements were taken with two P-Trak 8525 particle counters and one DustTrak 8520 particle counter in the two locations where NPs are handled. The concentrations were measured inside the glove box and under the laboratory hood during certain tasks related to NP integration into the polymer (weighing, handling powders) and related to different tests on the polymers formed (breaking, polishing, scratching, drying).

5.RESULTS

5.1 Welding Schools

5.1.1 School A

The concentrations in School A before the welding operations began were lower than 10,000 particles/cm³. Concentrations over 50,000 particles/cm³ were measured for all processes combined (Table 3 and Figure 1). The oxygen cutting process generated the most particles (300,000 particles/cm³ on the average), followed by GMAW on aluminium (160,000 particles/cm³), GTAW on aluminium (117,000 particles/cm³), FCAW on aluminium (116,000 particles/cm³), GTAW on stainless steel (94,000 particles/cm³), GMAW on steel (89,000 particles/cm³) and SMAW (61,000 particles/cm³). For the same process, concentrations differences were measured, depending on the metal used, for GTAW and GMAW. In both cases, when aluminium was used, the highest particle concentrations were measured.

For each measurement, concentration profiles were obtained. Three of these profiles are presented in Figures 2, 3 and 4. These profiles tell us that the students essentially are exposed to peak concentrations. Figure 3, recorded during the GMAW on aluminium process, also indicates that the maximum of 500,000 particles/cm³ was reached many times.

The particle size distribution assessments, presented in Figure 5, show differences among the processes. The GMAW process generated the biggest particles and FCAW essentially generated nanoscale particles. However, for the four processes tested, over 60% of the particles were nanoscale and bimodal distributions were identified, with the first mode between 20 and 30 nm and the second between 200 and 300 nm.

Table 3 – Mean concentrations (particles/cm³) measured in the two welding schools

Processes	School A	School B
GMAW	Aluminium: 160,000 (7)	-
	Steel: 89,000 (10)	Steel: 92,000 (26)
FCAW	116,000 (6)	114,000 (31)
GTAW	Aluminium: 117,000 (15)	-
	Stainless steel: 94,000 (6)	-
SMAW	61,000 (16)	177,000 (14)
Oxygen cutting	300,000 (6)	-

(x): Number of samples for each process and for each school. Each sample is a mean concentration over a period ranging from 30 minutes to 2 hours.

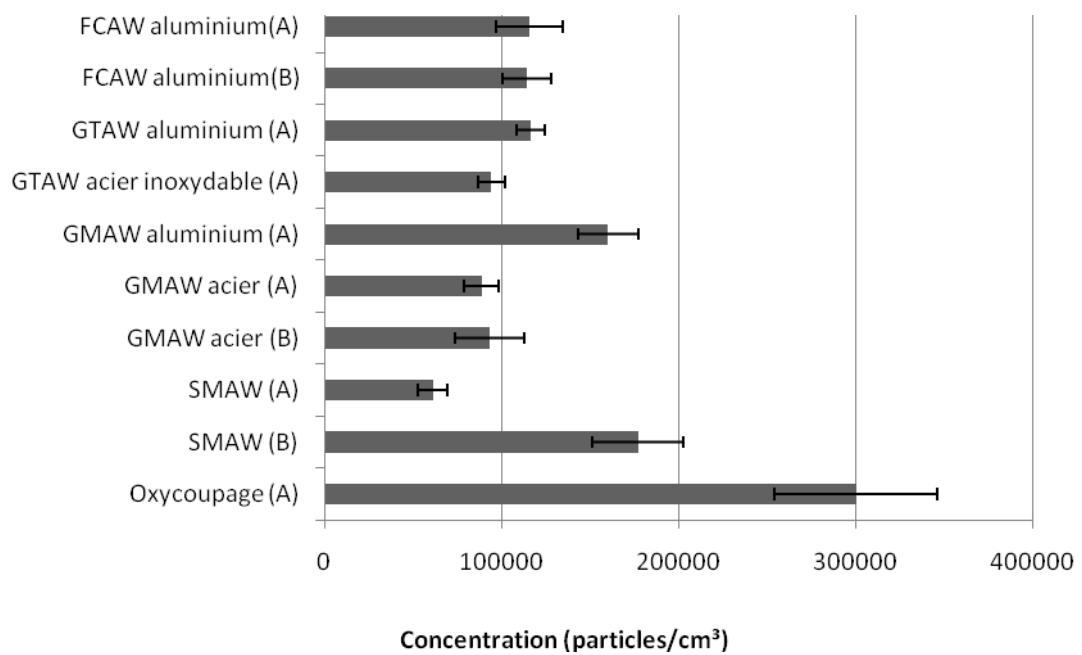


Figure 1 – Mean concentrations and typical errors measured with the P-Trak particle counters for the welding processes of Schools A and B (school indicated in parentheses)

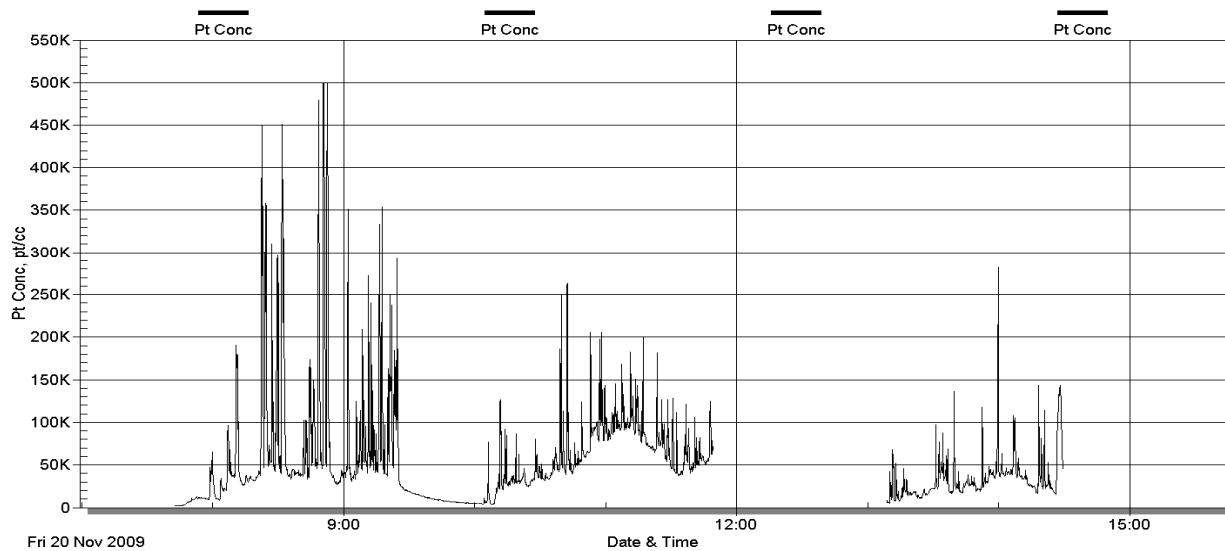


Figure 2 – Profile of concentrations recorded during one day of sampling for the SMAW process of Welding School A

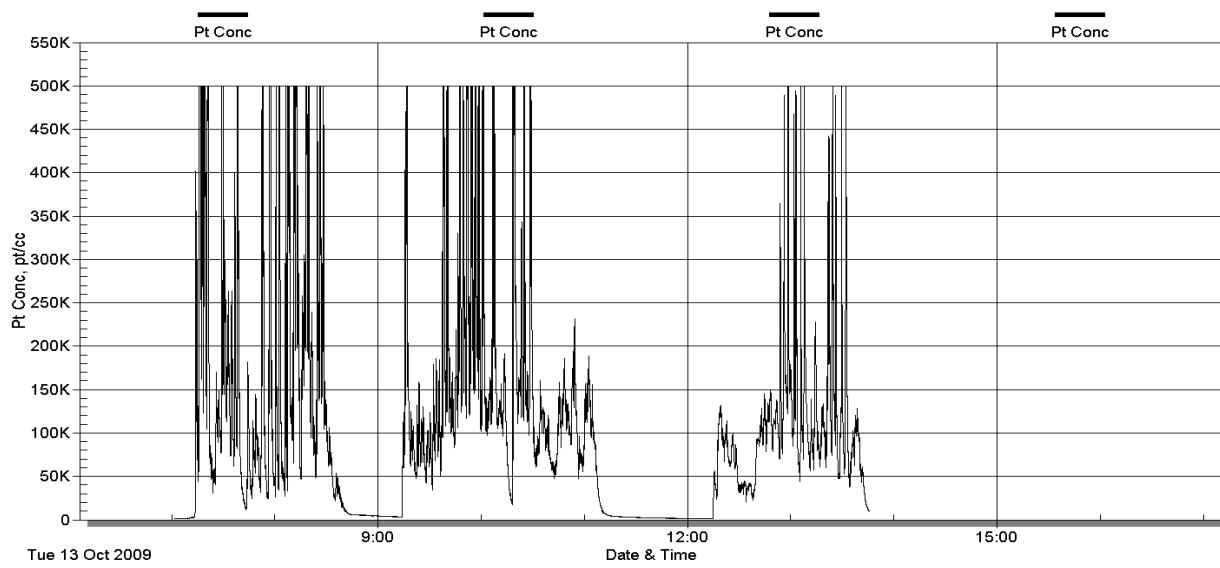


Figure 3 - Profile of concentrations recorded during one day of sampling for the GMAW on aluminium process of Welding School A

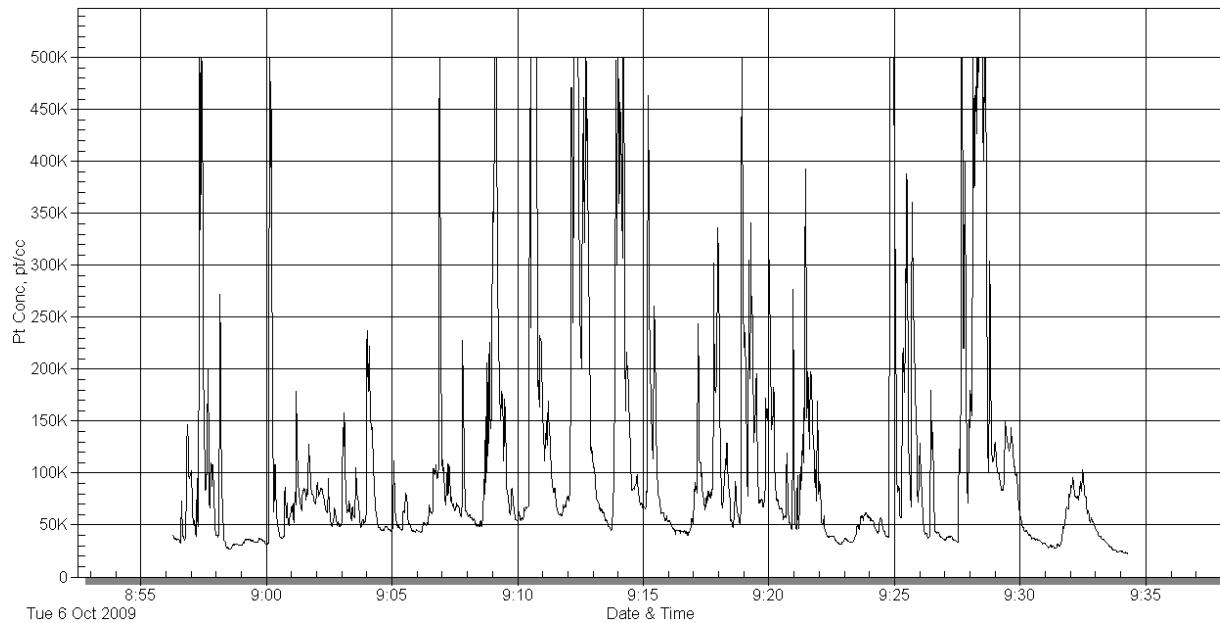


Figure 4 - Profile of concentrations recorded during 30 minutes of sampling for the SMAW process of Welding School A

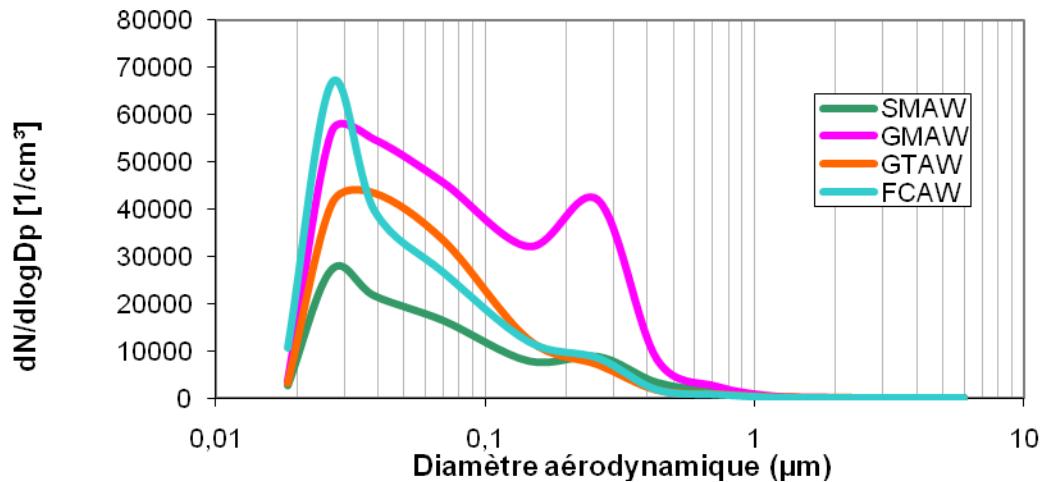


Figure 5 – Particle size distribution for the welding processes of School A

5.1.2 School B

The concentrations measured in School B before the welding operations began were lower than 10,000 particles/cm³. Concentrations higher than 50,000 particles/cm³ were measured for the three processes assessed (Table 3 and Figure 1). Contrary to School A, the concentrations measured during the SMAW processes (177,000 particles/cm³) were the highest, followed by FCAW (114,000 particles/cm³) and GMAW on steel (92,000 particles/cm³). The concentration profiles also show many peak concentrations, even though these peaks are less prominent for the SMAW process, with concentrations always higher than 100,000 particles/cm³ during the welding periods (see black lines, Figure 6).

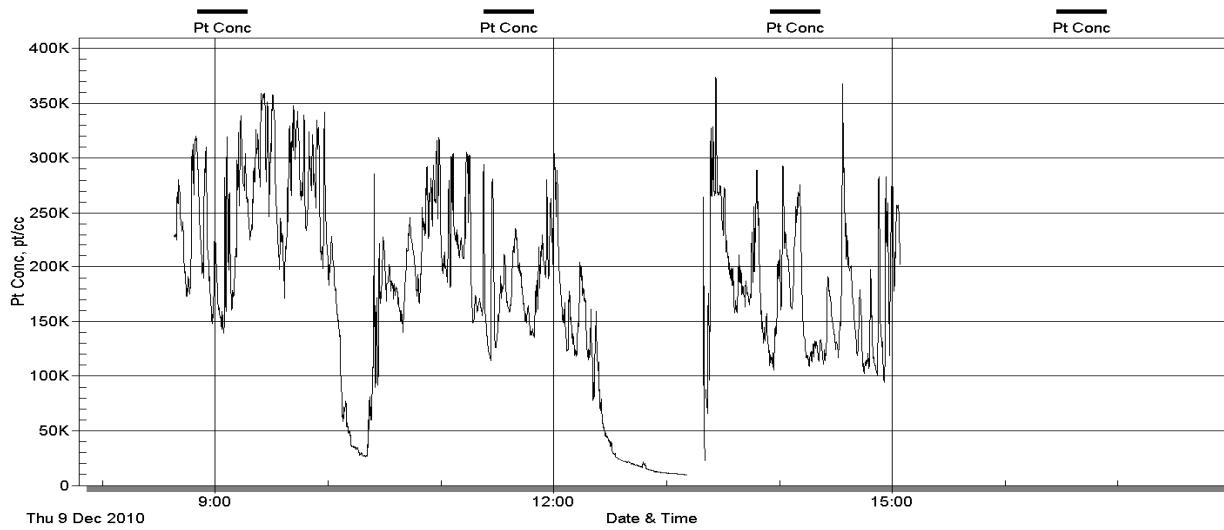
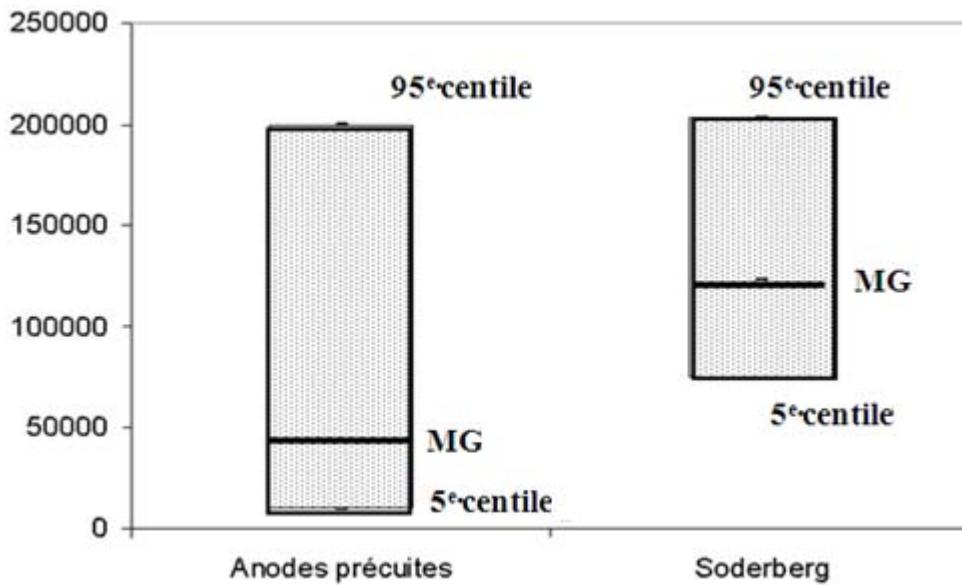


Figure 6 – Profile of concentrations recorded during one day of sampling for the SMAW process of Welding School B

5.2 Aluminium Smelter

The particle concentrations outside the plant were also lower than 7,000 particles/cm³. The mean particle concentrations measured with the P-Trak during mapping were 144,000 particles/cm³ in the Soderberg process, 70,000 particles/cm³ in the prebaked anode process and 238,000 and 44,000 in the anode cooling rooms (Table 4). It should be noted that in Anode Cooling Room B, there were anodes coming out of the electrolytic baths; these were hot anodes. In Room A, some anodes had been in this room for at least 12 hours; these were lukewarm or cold anodes. Figure 7 presents the geometric means (GM) of the same background measurements for the two processes. The GM of the Soderberg process in Room A is about three times higher than the GM of the prebaked anodes, and the 5th and 95th measurement percentiles indicate a wider range in the prebaked anode process, a sign of greater variability. The geometric standard deviation (GSD) for the prebaked anodes is 2.6, while the GSD of the Soderberg process is only 1.7.



GM: Geometric mean

Figure 7 – Particle concentrations in the Soderberg and prebaked anode processes

Table 4 – Descriptive statistics of the particle concentrations (particles/cm³) measured with P-Trak particle counters during mapping of the Soderberg and prebaked anode processes and in the anode cooling rooms

	Soderberg process	Prebake d anode process	Cooling Room A	Cooling Room B
n	137	205	24	20
Mean	144,000	70,000	44,000	238,000
Maximum	450,000	500,000	120,000	500,000
Minimum	7,000	15,000	22,000	76,000
GM	123,000	42,000	37,000	213,000
GSD	1.7	2.6	1.7	1.6

* The background noise concentrations were lower than 7,000 particles/cm³

GM: geometric mean

GSD: geometric standard deviation

Table 5 – Descriptive statistics of particle concentrations (particles/cm³) measured with P-Trak particle counters during quasi-personal measurements in i) the Soderberg process and ii) the prebaked anode process

i		Soderberg				
Trades	Overhead crane operator	Maintenance	Crust breaker	Frame lifter operator	Briquette driver	
N	4	11	3	5	4	
Mean	16,000	123,000	186,000	100,000	67,000	
Maximum	22,000	209,000	251,000	131,000	159,000	
Minimum	14,000	53,000	125,000	70,000	14,000	
GM	16,000	113,000	178,000	97,000	47,000	
GSD	1.2	2.0	1.4	1.3	2.7	

ii						
Trades	Overhead crane operator	Mainte-nance	Mule driver	Anode transport driver	Sealing	Hexapod cleaner
N	3	12	6	5	10	7
Mean	29,000	99,000	74,000	17,000	62,000	79,000
Maximum	46,000	217,000	113,000	31,000	131,000	133,000
Minimum	10,000	16,000	28,000	6,000	27,000	25,000
GM	24,000	83,000	66,000	14,000	55,000	70,000
GSD	2.2	2.0	1.7	1.9	1.7	1.8

* The background noise concentrations were lower than 7,000 particles/cm³

GM: geometric mean

GSD: geometric standard deviation

Concerning quasi-personal measurements, the concentrations were also higher in the Soderberg process than in the prebaked anode process. The GM of the concentrations for the workers who break the crusts of the electrolytic baths was 178,000 particles/cm³, followed by maintenance employees with 113,000 particles/cm³ and then frame lifters with 97,000 particles/cm³. The exposure of overhead crane operators was lower than for the other workers in the Soderberg process (Table 5).

Anode transport drivers (GM=14,000 particles/cm³) had the lowest concentrations in the prebaked anode process, followed, in ascending order, by pressurized overhead crane operators (GM=24,000 particles/cm³), the workers who seal the anodes (GM=55,000 particles/cm³), mule drivers (GM=66,000 particles/cm³), hexapod cleaners (GM=70,000 particles/cm³) and maintenance employees (GM=83,000 particles/cm³).

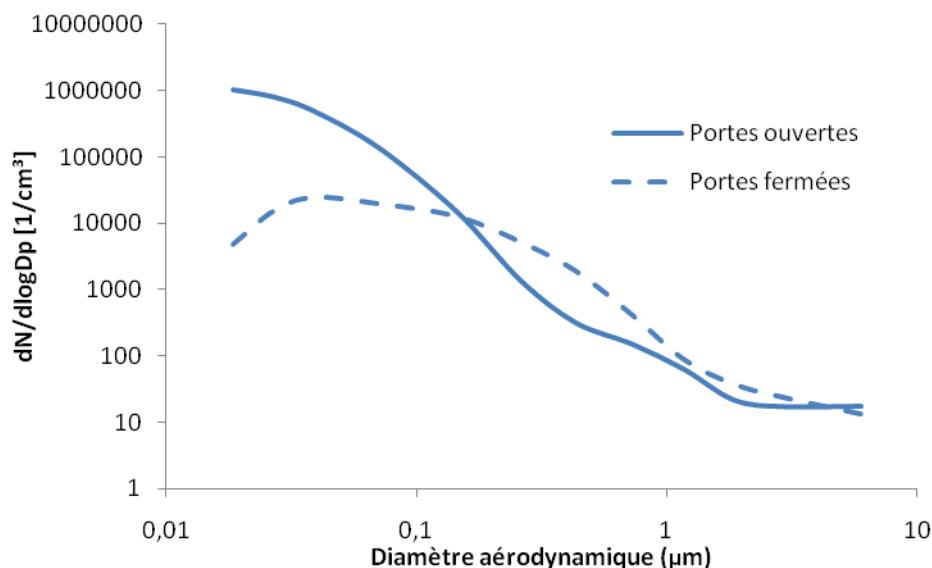
Table 6 presents the proportions of particles measured for each of the 12 stages of the ELPI impactor for the Soderberg and prebaked anode processes. The mean aerodynamic diameter of the particles collected in the two processes was smaller than 30 nm. In addition, very high proportions (>97%) of the particles had an aerodynamic diameter smaller than 98 nm in the two processes.

Figure 8 indicates that the fine fractions were bigger in the prebaked anode process when the doors were open. In addition, Figure 9 shows granulometric distribution differences depending on the temperature of the anodes in the cooling rooms. The curves cross each other, which indicates that, despite the concentration differences measured, granulometric distribution differences were also identified. Thus, when the anodes came out of baths, as very hot anodes, they generated high concentrations of airborne nanoscale particles, while when they were cold, larger particles had been measured (>100nm).

The results of the analyses performed on the TEM/EDS are presented in Table 7. The main elements detected are ranked in descending order for the five smallest stages of the ELPI. Overall, Al, Na and F are the elements found most often in the analyses, and particles simultaneously containing the elements Al, Na and F are the most common in both processes, with respective proportions of 69% in the prebaked anode process and 54% in the Soderberg process. Particles containing Ti were also identified, with proportions of 9% (prebaked anodes) and 33% (Soderberg). We should also note the presence of arsenic in both processes. In addition, 25% (prebaked anodes) and 31% (Soderberg) of the particles examined were fibres and were identified in the five stages of the ELPI. Fibrous particles are presented in Figures 10 and 12; they contain the elements Al and Na (the C, Si, O and Cu peaks are specific to the substrate and the grid). Other spherical or irregularly shaped particles are presented in Figures 11, 13 and 14. These particles contain the elements Ti (Figure 11), Al, F, Na, S (Figure 13) and Al, Na, S, As (Figure 14).

Table 6 - Proportions of particles in the ELPI stages (sampling without filter stage) for the Soderberg and prebaked anode processes

Cutpoint stages in nm	Proportion of particles (%)	
	Soderberg process	Prebaked anode process
24	42	77
30	32	18
50	19	3
98	4	<1
214	1	<1
321	<1	<1
583	<1	<1
902	<1	<1
1524	<1	<1
2272	<1	<1
3796	<1	<1
6351	<1	<1

**Figure 8 - Comparison of particle granulometric distributions based on opening of the potroom doors in the prebaked anode process**

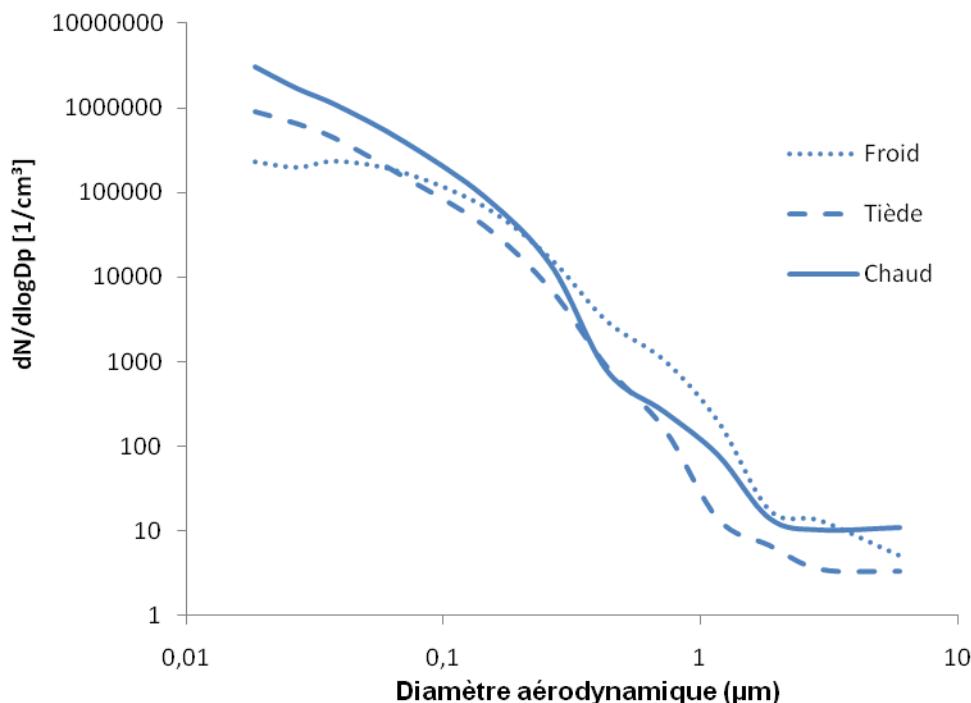


Figure 9 - Comparison of particle granulometric distributions based on the temperature of the anodes in the cooling rooms

Table 7 – Main ultrafine elements detected during TEM/EDS analyses in the two electrolysis processes

ELPI, cutpoint diameters in nm (setup in “collection” mode)					
	28	55	93	156	263
Soderberg process	Ti, Fe, Al, Na, K, S, F, Ca, Al, K, Na, Ca, Cl, Ti, As, Fe, Ti, As, Cl, V, Au, Pb, Zn	Al, Na, K, Al, Na, F, K, Al, Na, F, K, Al, Na, F, K, Na, Al, F, K, S, K, S, Fe, S, Ti, As, S, Fe, Ti, Ti, S, Fe, Mn, Ti	Al, Na, K, Al, Na, F, K, Al, Na, F, K, Al, Na, F, K, Na, Al, F, K, S, K, S, Fe, S, Ti, As, S, Fe, Ti, Ti, S, Fe, Mn		
Prebaked anode process					

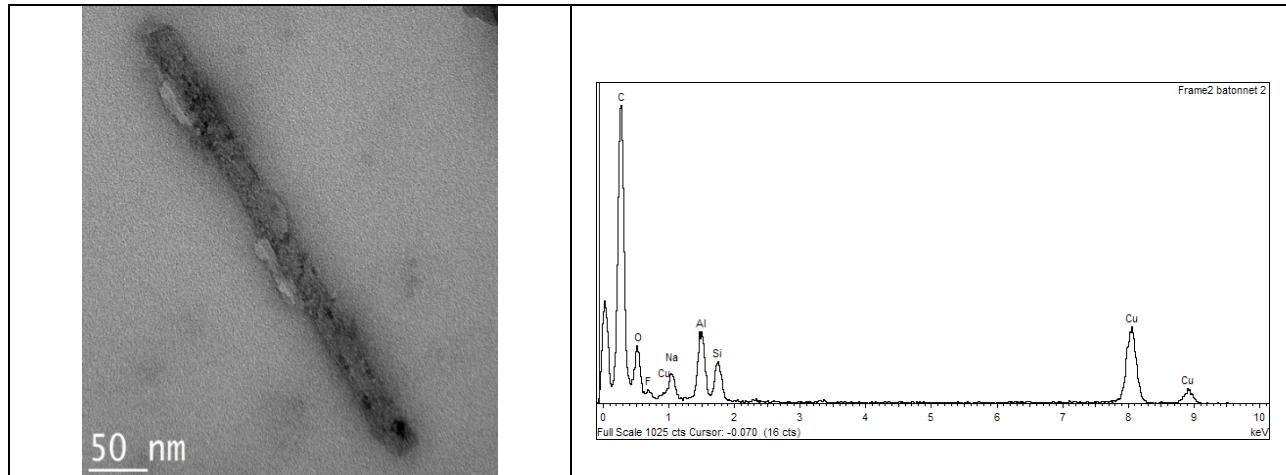


Figure 10 – Prebaked anode process sample from the ELPI 28 nm stage

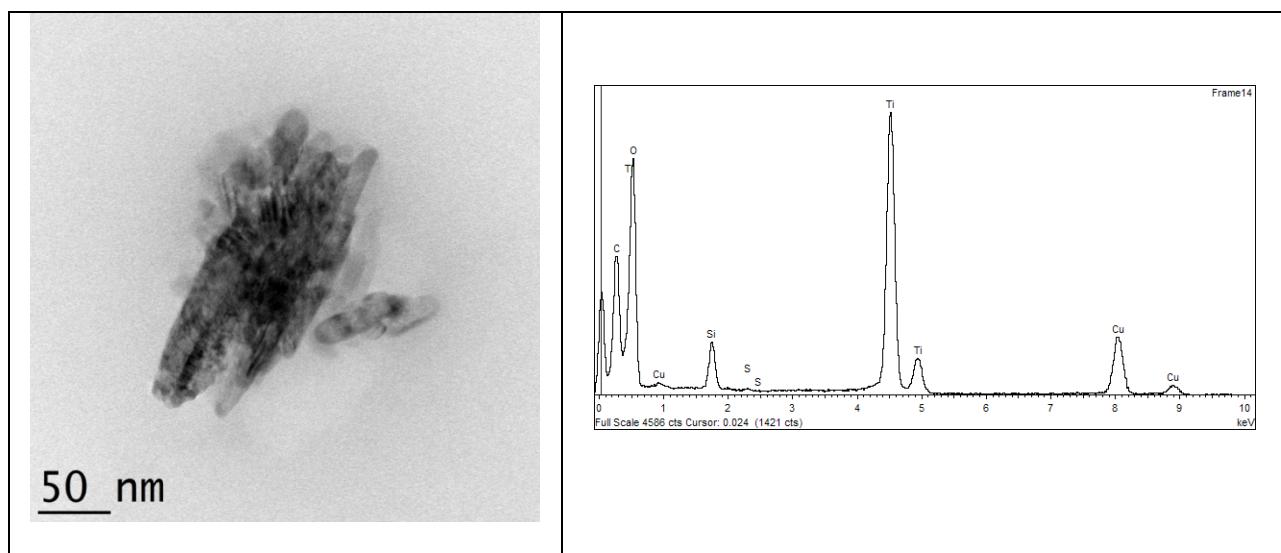


Figure 11 –Soderberg process sample from the ELPI 28 nm stage

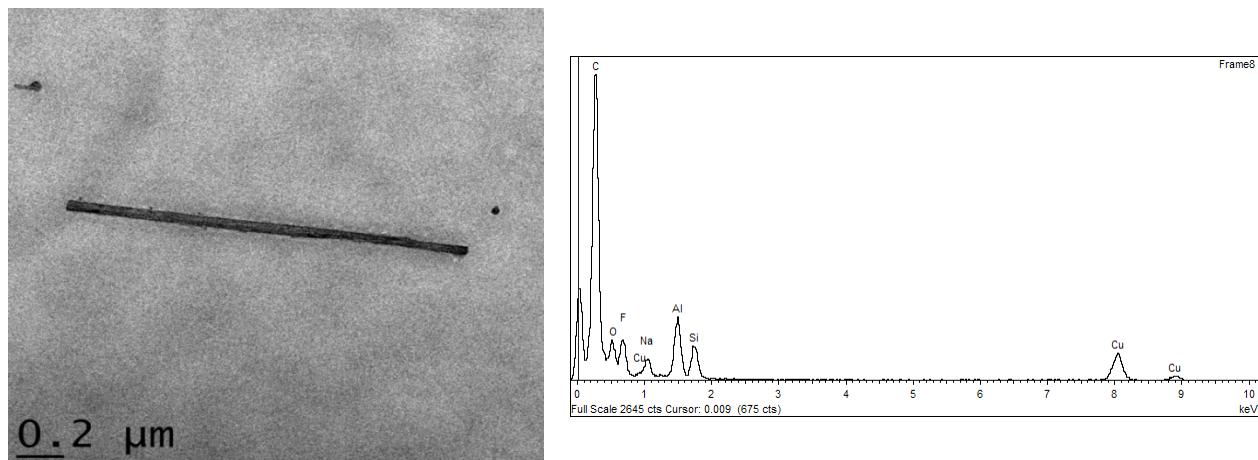


Figure 12 – Prebaked anode process sample from the ELPI 93 nm stage

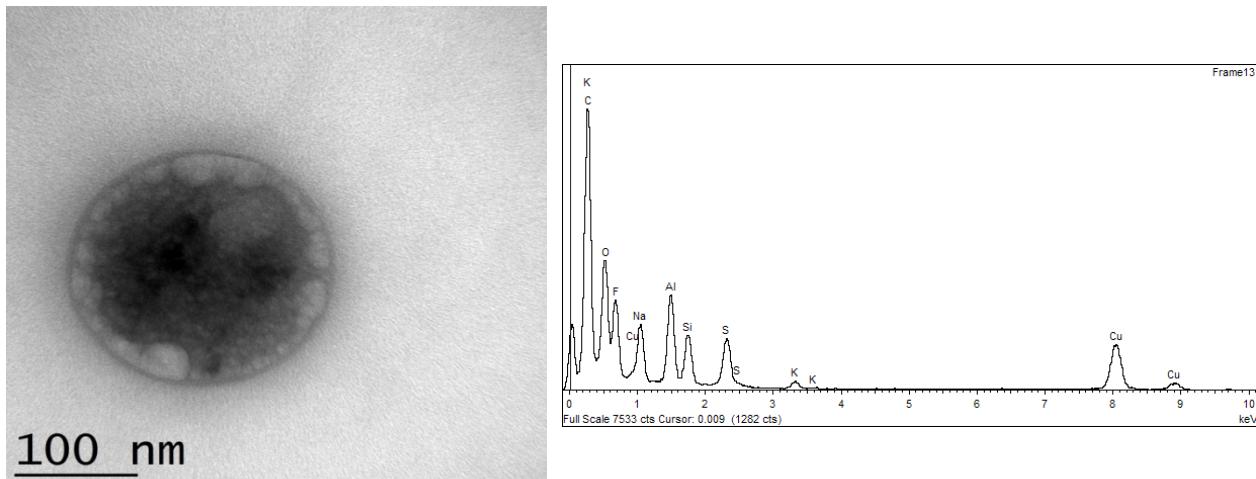


Figure 13 - Soderberg process sample from the ELPI 156 nm stage

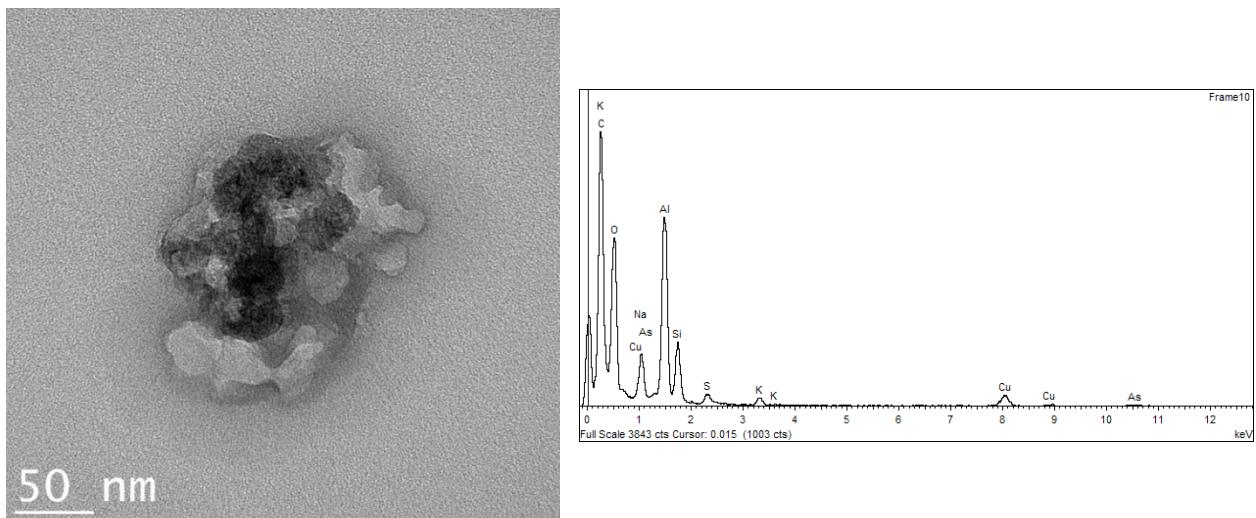


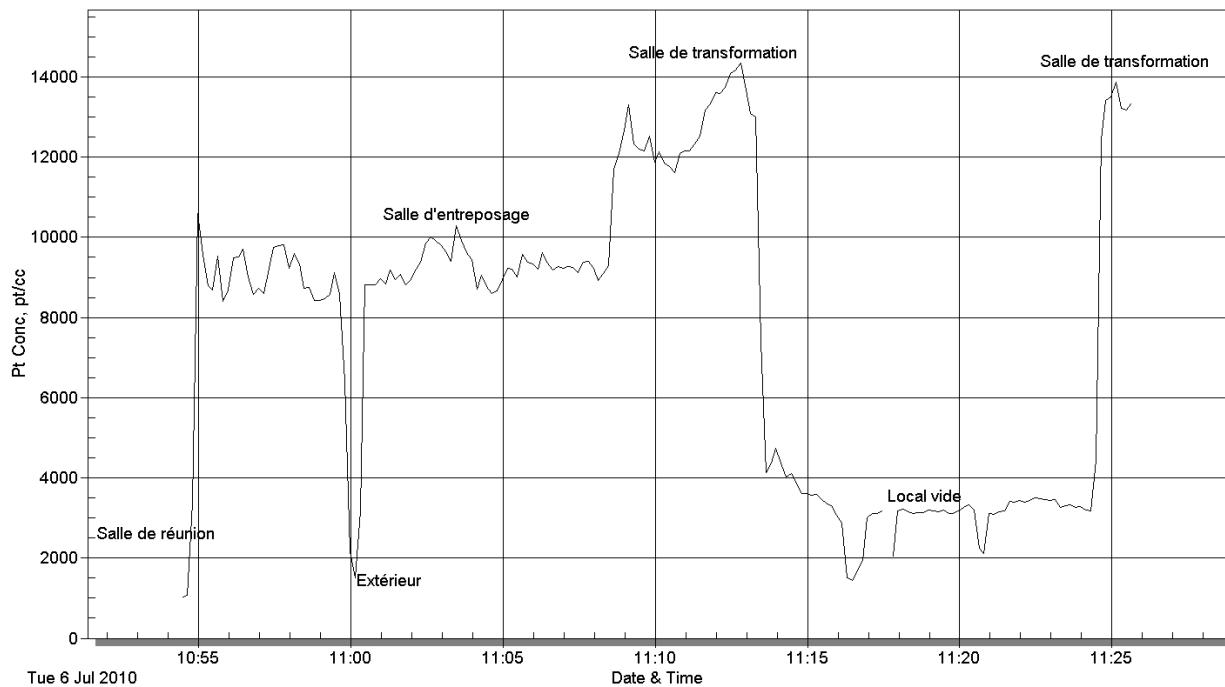
Figure 14 – Prebaked anode process sample from the ELPI 156 nm stage

5.3 Thermoplastic Processing Industry

High particle levels were measured in the storage and processing rooms, even after several days of shutdown of the facility. Table 8 presents the concentration results from mapping of the premises and indicates mean concentrations of 8,100 (P-Trak#1) and 9,160 (P-Trak#2) particles/cm³ in the storage room and 11,200 (P-Trak#1) and 13,500 (P-Trak#2) particles/cm³ in the processing room. By way of comparison, the concentration was around 1,500 particles/cm³ outside the building, 1,200 particles/cm³ in the meeting room and 900 particles/cm³ in the ventilated quality control laboratory. Figure 15 presents the continuous profile of particle concentrations measured during the visit to the premises before operation of the extruder.

Table 8 – Mean particle levels in the storage and processing rooms

	Mean [min-max] particle concentrations (particles/cm ³) in the storage room (n)	Mean [min-max] particle concentrations (particles/cm ³) in the processing room (n)
P-Trak #1	8,100 [7,800-8,900] (8)	11,200 [10,000-12,500] (9)
P-Trak #2	9,160 [8,500-9,500] (8)	13,500 [12,000-14,000] (9)

**Figure 15 – Profile of particle concentrations measured in the research centre's different rooms**

During operation of the extruder, a substantial increase in particle levels was observed in the storage and processing rooms, with concentrations reaching 100,000 particles/cm³ at a distance of 3 metres from the extruder. Figure 16 presents the particle concentrations measured from 11 a.m. to 3 p.m. with extruder startup at 1:50 p.m. During this recording period, a reduction in the concentrations was also recognized between 11:30 a.m. and 1:30 p.m., resulting from provoked aeration (opening of the windows) of the storage and processing rooms, where the levels fell from 13,000 to 3,500 particles/cm³.

Figure 17 presents the recording of the quasi-personal particle concentrations during CNT preparation and during extruder startup. There was no change in the particle concentrations

during CNT handling, while a net increase in the concentrations was observed during extruder startup.

The mean particle concentration measured in the absence of CNTs at a one-metre distance from the extruder was 288,912 particles/cm³, while a mean concentration of 227,430 particles/cm³ was measured during operation of extruder with CNTs.

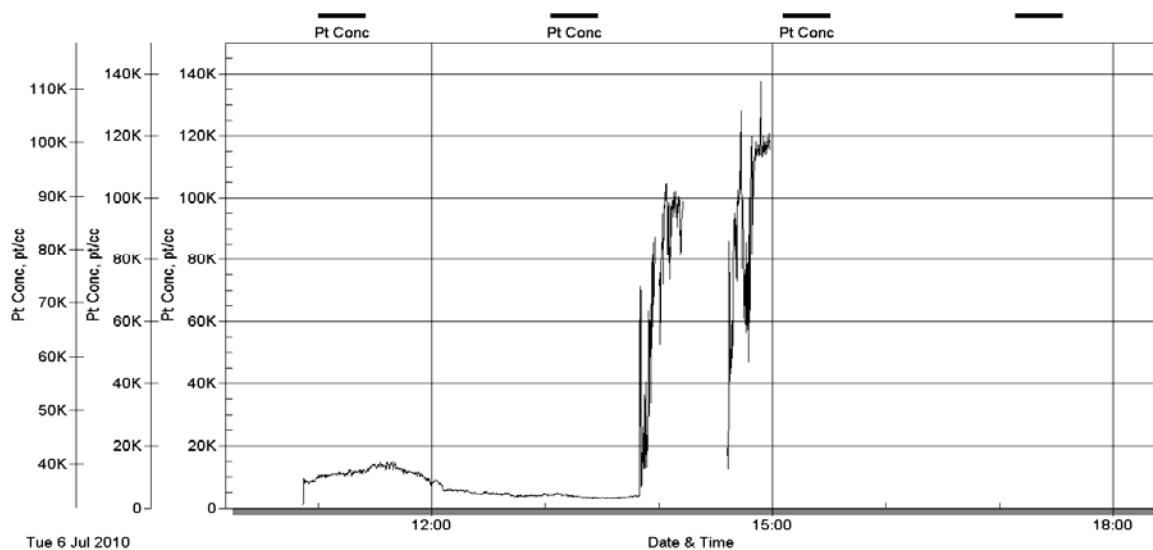


Figure 16 – Particle concentrations measured in the processing room

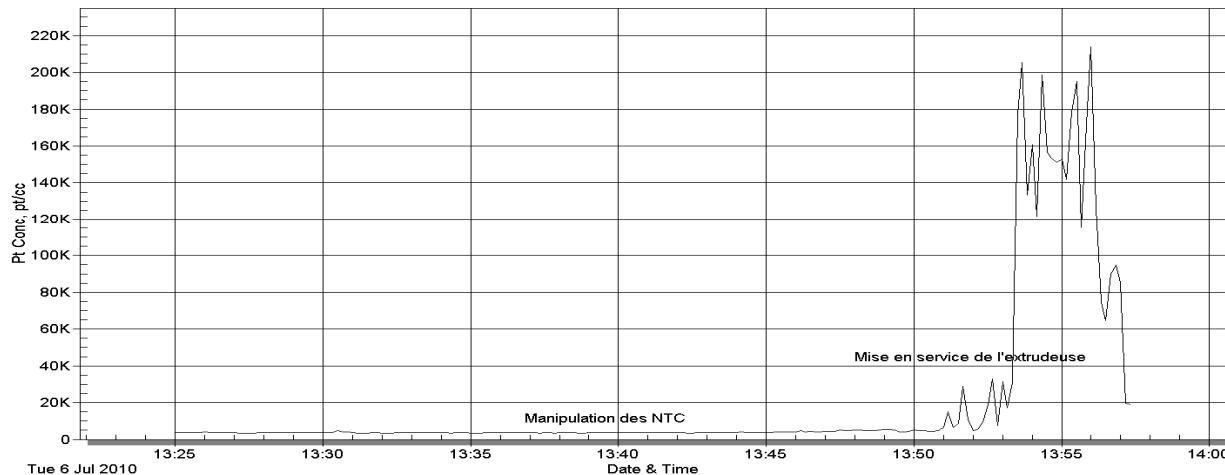


Figure 17 – Quasi-personal particle concentrations measured during CNT handling and extruder startup

5.4 University Laboratories Producing or Using Nanoparticles

5.4.1 Laboratory A

The levels measured in the cryomilling process are low and are identical or close to the laboratory's background noise concentrations (between 4,000 and 6,000 particles/cm³). Figure 18 presents the concentrations measured during milling, dismantling of the mill and handling of the powders, and in the gas plume released by the liquid nitrogen. The highest concentrations were measured in the gas plume concentrations of liquid nitrogen, at more than 10,000 particles/cm³. Slightly higher concentrations were also measured on the 3rd day of sampling.

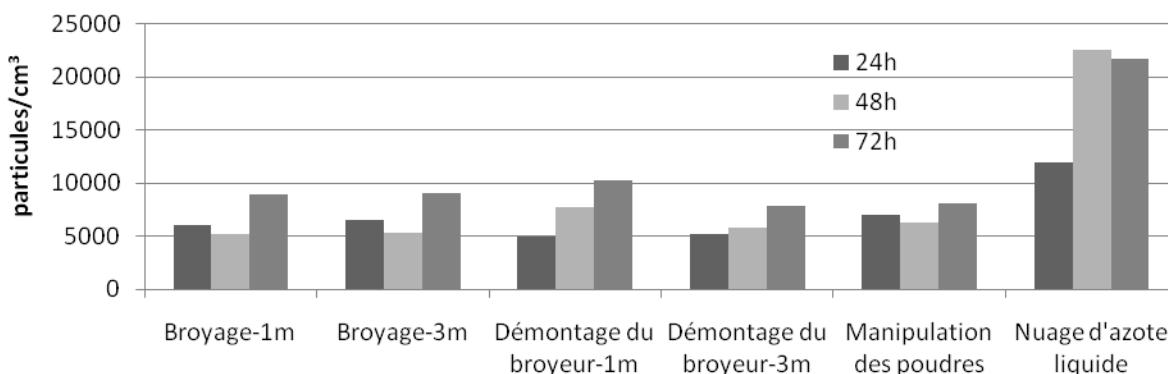


Figure 18 – Particle concentrations in the aluminium/copper nanoparticle production laboratory (Laboratory A)

Figure 19 presents the particle concentration profiles near the mill (i) and 3 metres from the mill (ii), measured with the P-Trak particle counters on the 3rd day of sampling. Short peak concentrations are visible in the two profiles during each collection, i.e. at 10:50 a.m., 12 noon, 1 p.m., 2 p.m., 3 p.m. and 4 p.m. Only the complete dismantling stage (between 5 p.m. and 5:30 p.m.) shows differences between the two sampling stations, with peak concentrations close to the source but none 3 m away. It must be noted that the hourly collections were placed on the floor between the two measuring zones. A decrease in concentrations is also recognized during the day in Figures i and ii, attributable to an overall reduction of the laboratory background noise.

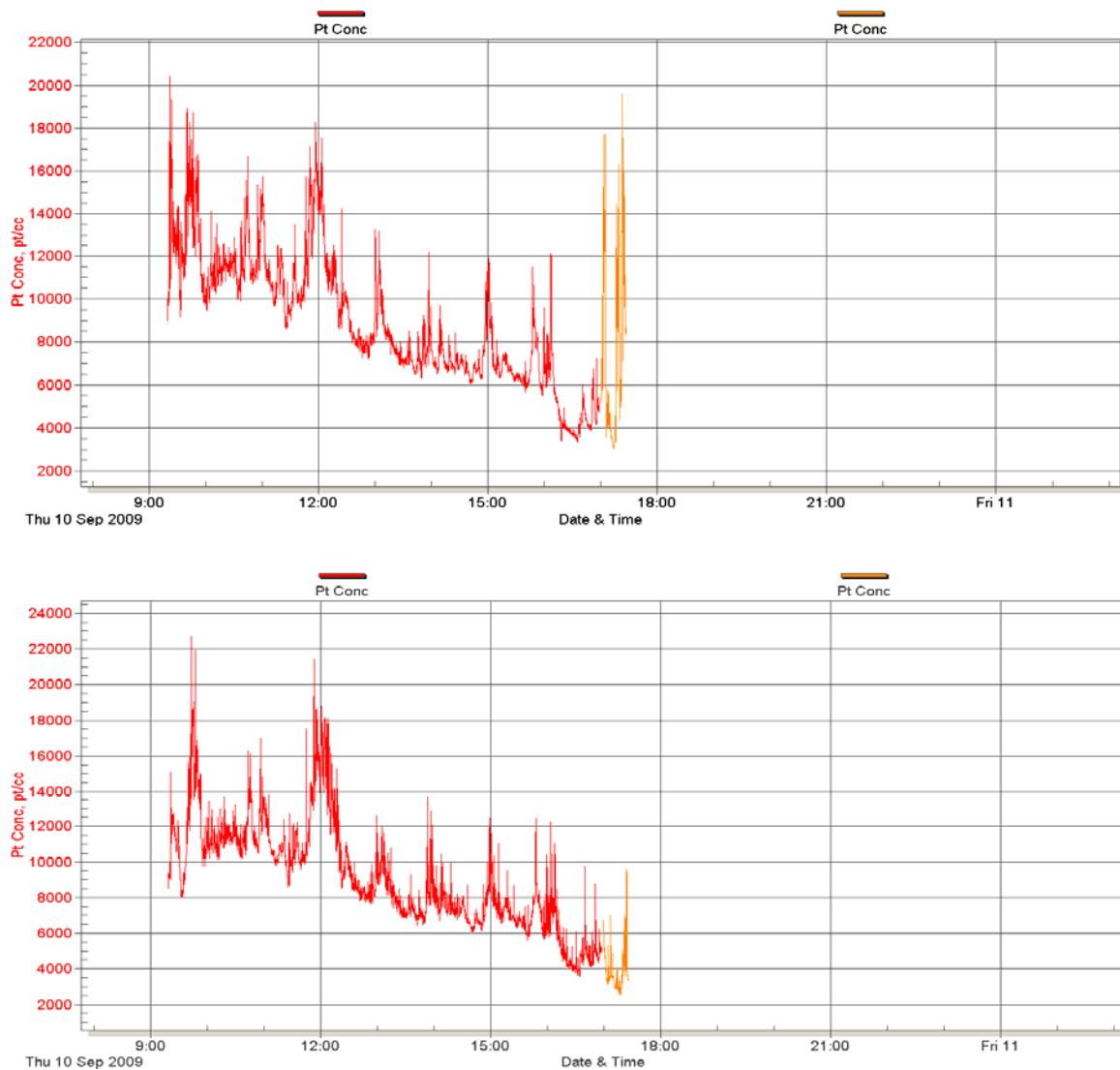


Figure 19 – Profiles of particle concentrations measured with P-Trak particle counters on the 3rd day of sampling near the mill (i) and 3 metres from the mill (ii) (Laboratory A)

5.4.2 Laboratory B

Figure 20 presents a profile of particle concentrations measured during CNT handling in the laboratory glove box at a 1 metre distance, while Figure 21 presents the same data at a 3 metre distance. There is no significant difference between the concentration profiles, while the weighted mean concentrations measured are also very similar, at 3,832 particles/cm³ for the zone near the glove box and 3,974 particles/cm³ for the zone farther away. The background noise concentration corresponds to the initial concentrations of Figures 20 and 21, about 4,000 particles/cm³.

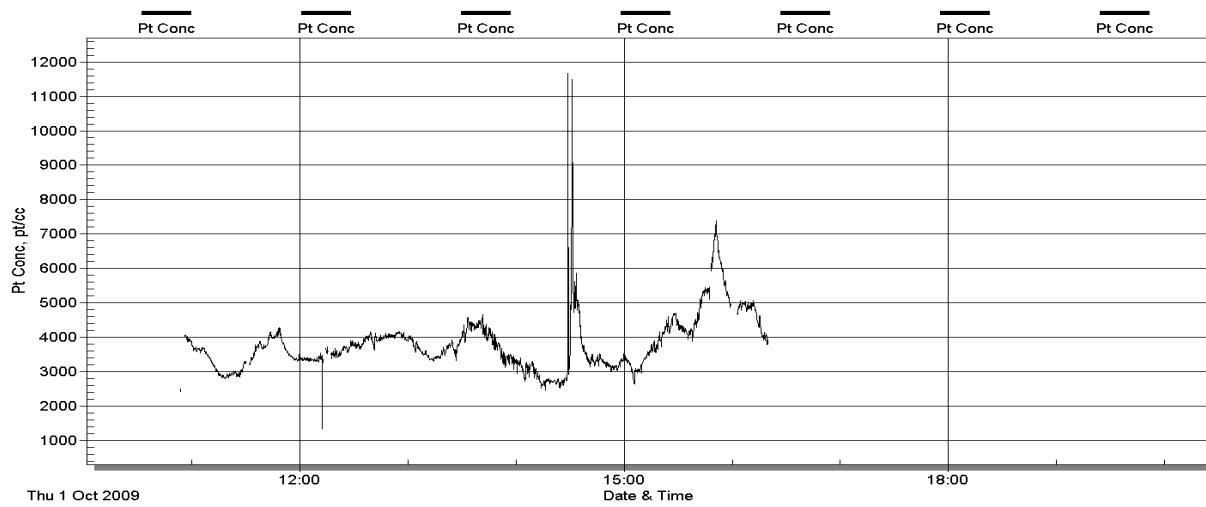


Figure 20 – Particle concentrations measured 1 metre from the glove box during CNT handling in Laboratory B

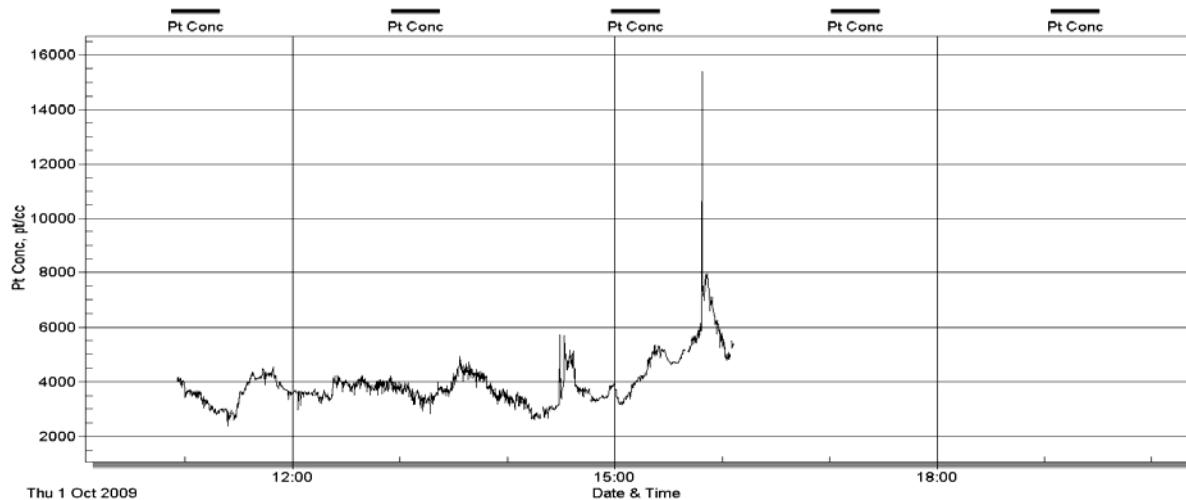


Figure 21 – Particle concentrations measured 3 metres from the glove box during CNT handling in Laboratory B

5.4.3 Laboratory C

Figures 22 and 23 present the continuous profiles of the particle concentrations ($\text{particles}/\text{cm}^3$) and aerosol concentrations (mg/m^3) measured in the glove box during CNT handling. The particle concentrations in the laboratory were about 900 $\text{particles}/\text{cm}^3$ and the mass concentrations were 0.016 mg/m^3 on average. In the glove box, much lower concentrations were measured, between 20 and 30 $\text{particles}/\text{cm}^3$ and between 0.001 and 0.005 mg/m^3 . No particle level increase was measured with the P-Trak (Figure 22), while two peaks were recorded with the DustTrak during CNT handling (Figure 23). However, these peaks indicate relatively low concentrations of 0.02 and 0.04 mg/m^3 .

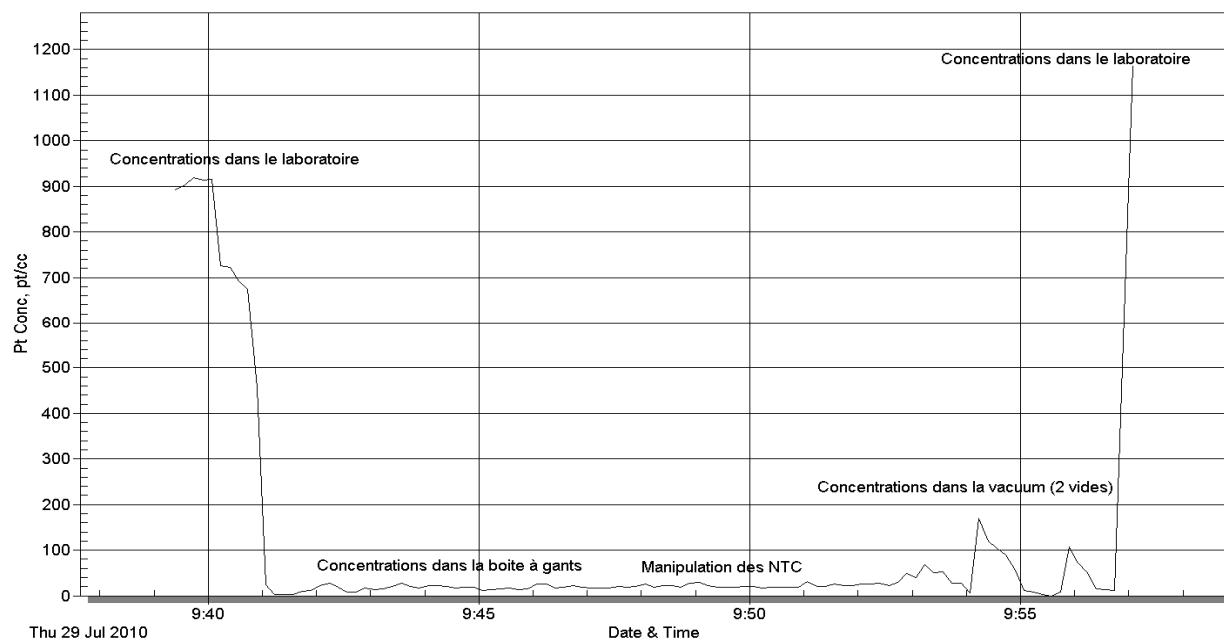


Figure 22 – Particle concentrations measured in the glove box during CNT handling in Laboratory C

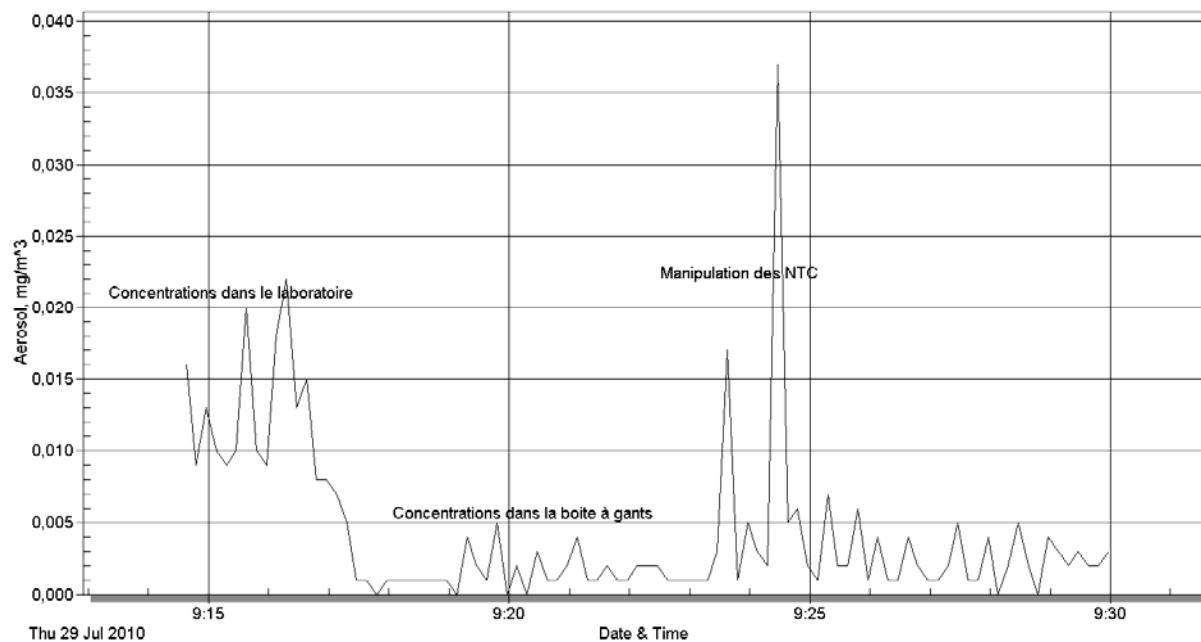


Figure 23 – Aerosol concentrations measured in the glove box during CNT handling in Laboratory C

Figures 24 and 25 present the continuous profiles of the particle concentrations (particles/cm³) and aerosol concentrations (mg/m³) measured during polymer handling under the laboratory hood. The particle and aerosol concentrations are similar to those measured in the laboratory, i.e. between 800 and 1,000 particles/cm³ and between 0.01 and 0.02 mg/m³, respectively. However, a peak is noted in each figure, referring to two distinct tasks, polymer polishing for the numeric concentration (Figure 24) and polymer breaking for the mass concentrations (Figure 25).

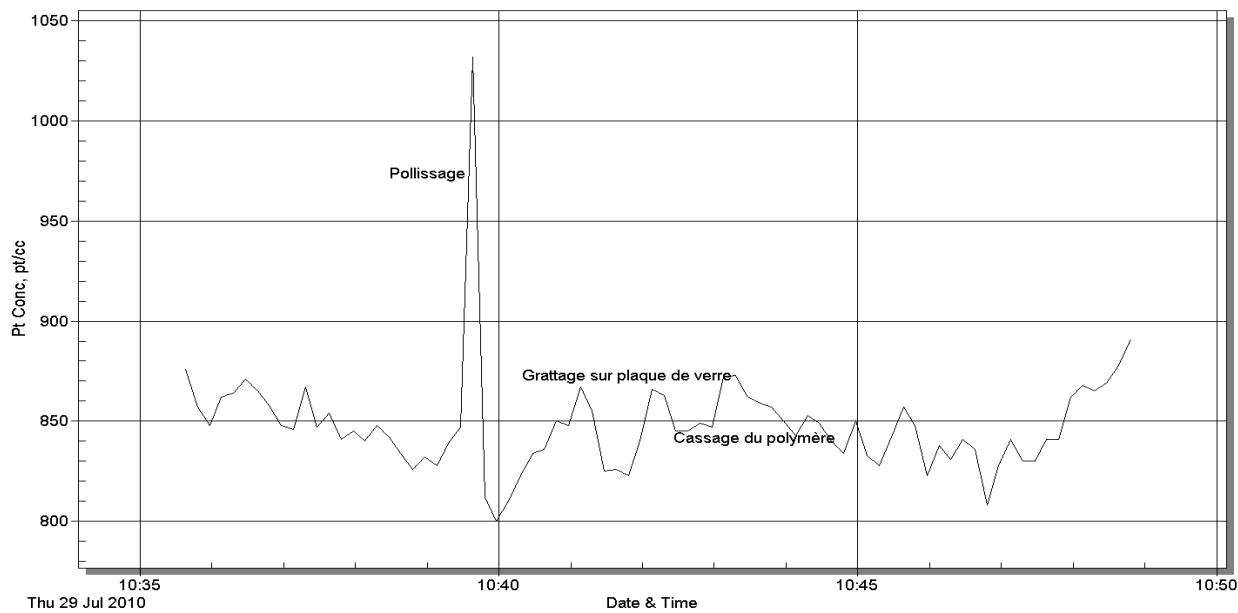


Figure 24 – Particle concentrations measured under the laboratory hood during polymer handling in Laboratory C

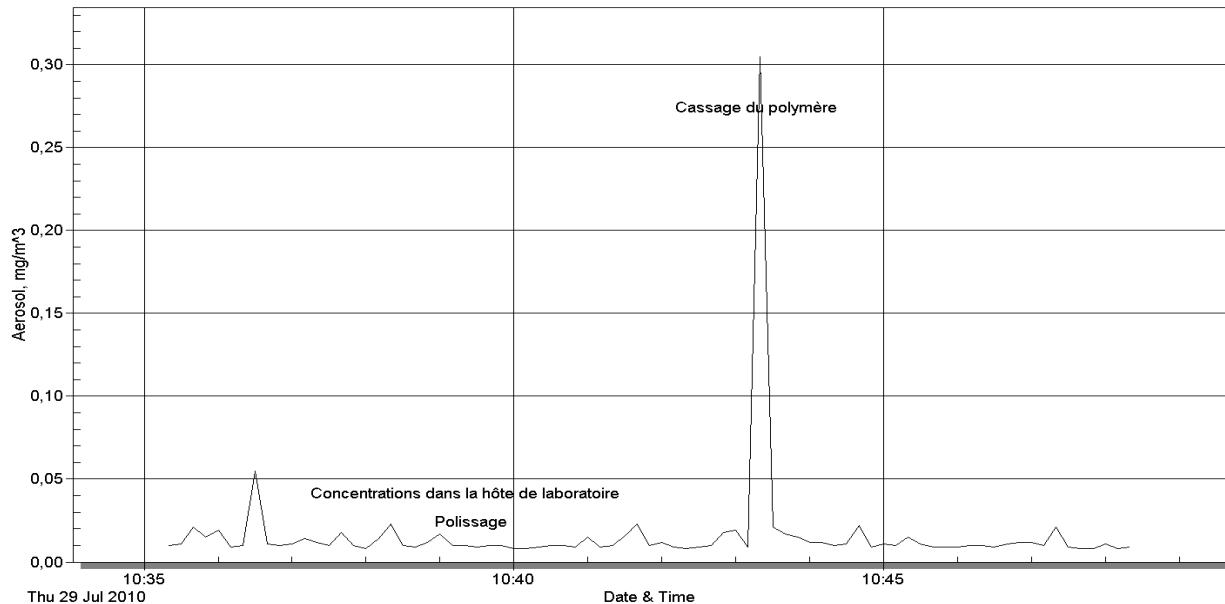


Figure 25 – Aerosol concentrations measured under the laboratory hood during polymer handling in Laboratory C

6. DISCUSSION

6.1 Welding Schools

The measurements taken in the two welding schools indicate that the apprentice welders are exposed to high particle concentrations (between 61,000 and 300,000 particles/cm³). Most of these particles have an aerodynamic diameter smaller than 100 nm. In addition, the granulometric distribution profiles of the four assessed processes show bimodal distributions, with the first mode between 20 and 30 nm and the second mode between 200 and 300 nm. Pfefferkorn et al. [100] also showed a bimodal distribution for an aluminium friction stir welding process, with the first peak at about 30 nm and the second at 550 nm, measured with an EEPS. The same authors indicate that two particle types are found in the aerosols of this process: particles generated mechanically by tearing at the material, and metal particles produced by condensation, mostly spherical, with a unit diameter of 30 nm. Particles of this second type form agglomerated particle chains [100]. In our study, the processes used did not result in tearing of the particles as in the friction stir welding process. The two modes identified then essentially would result from the effect of agglomeration of the unitary metal oxide particles formed by nucleation [58]. A new characterization study by TEM/EDS using the ELPI's impactor for selective collection of the particles would allow validation of this hypothesis.

The results indicate that the welding processes and the metal used may be key determinants of exposure to fine and ultrafine particles. Other determinants are also reported in the literature. Thus, in the SMAW process, Soward et al. [137] showed that the electrode type was a determinant of particle exposure concentrations. Hovde and Raynor showed that the voltage used for welding was also a key determinant of exposure to fumes and that the particle concentrations were three times higher at 23.5 V than at 16 V for a GMAW welding process [23]. In our study, the students were followed over several work weeks, spread over several months, during which many exercises were performed. Only the work environment, the process and the metal being welded were controlled, but different voltages, different electrodes (e.g. E7018, E4918, E6011 for SMAW) or different wire electrode types could be used by the students. These parameters could not be controlled within the framework of this study. These unconsidered parameters could explain in part the differences obtained for the concentrations of the SMAW process between the two schools, i.e. 61,000 particles/cm³ for School A and 177,000 particles/cm³ for School B. On the other hand, in our measurements, very close concentrations were measured in both schools for the FCAW and GMAW on steel processes, with concentrations of 116,000 (School A) and 114,000 particles/cm³ (School B) for the first process and 89,000 (School A) and 92,000 (School B) particles/cm³ for the second process. These results suggest that, despite the above-mentioned uncontrolled parameters, the process itself appears to be a key determinant of exposure. Schoonover et al. [138] showed that the exposures to metal welding fumes of workers performing the GMAW and SMAW processes were higher than those of the GTAW process. Those measurements were taken in mass units with 37 mm cassettes, while the measurements taken in our study only considered particle number concentrations with diameters smaller than 1 µm. These conceptual differences do not allow a comparison between the two measurement methods, but suggest differences based on them.

Four concentrations profiles were presented in this study (Figures 2, 3, 4 and 6). The results indicate that the apprentices are exposed to high peak particle concentrations during welding activities. However, a difference was noted between the SMAW profiles of Schools A and B. Indeed, the concentrations in School B remain at relatively high levels, above 100,000 particles/cm³, between welding activities. This could reflect insufficient local ventilation in this school, then partially explaining the differences obtained for the SMAW process concentrations. However, in general, the peak concentrations indicate good efficiency of the local ventilation installations, because the peak concentrations are short term. This implies that if a respiratory protection program is established, it should focus directly on the welding periods. The P-Trak and the ELPI are direct reading instruments with a very good response time, allowing precise characterization of these peaks. However, on several occasions, the results underestimated the actual exposure, because several peak particle concentrations exceeded the instrument's limit of 500,000 particles/cm³. Other authors recognized the importance of proceeding with assessments of welding fume exposures with direct reading instruments to characterize these peaks [138].

Finally, the data presented in this study allows characterization of the apprentices' exposures to fine and ultrafine particles and a better understanding of the different determinants of these occupational exposures. This data is especially important, given that epidemiological studies suggest that apprentice welders can develop early respiratory symptoms, a warning sign of the possibility of developing occupational asthma [139].

6.2 Aluminium Smelter

The results confirm the major presence of nanoscale particles in the two aluminium production processes. On the average, the prebaked anode process generates fewer particles than the Soderberg process, although high particle levels were measured during specific activities, such as changing anodes. High particle concentrations were also measured in the anode cooling rooms and in the prebaked anode fabricating processes, with concentrations reaching 500,000 particles/cm³. These results indicate that it is important to consider the occupational exposures in these rooms. We also showed in this study that the workers most exposed were those who manually broke the crusts on the electrolytic baths. Gylseth et al. [95] already indicated that these workers were exposed to high fibrous particle levels, but without quantifying them in terms of number of particles.

The granulometric distribution assessment confirms the major presence of UFPs in this work environment. Our results indicate that over 90% of the particles are nanoscale, and thus smaller than 100 nm. These results agree with the measurements taken with SMPS in other studies [17, 19]. More specifically, Thomassen et al. [19] reported that the electrical mobility diameters were about 40 nm in the Soderberg process and 20 nm in the prebaked anode process.

Several UFP exposure determinants were identified in this study. The finest particles thus are found in high concentrations near the pots, when the doors are open, and/or during handling of hot anodes. These results confirm that the longer the life of the particles, the more they gather by agglomeration and thus increase in size, while the overall numerical concentration decreases. These phenomena are known but still have little documentation in the work environment. Finally, understanding these determinants is essential to proceeding with occupational UFP

exposure assessments, because the collection locations and the instrument response time then become crucial factors in these assessments.

The microscopic (TEM/EDS) studies presented in this report only concern fine and ultrafine aerosol fractions, and thus are not representative of the workers' overall exposure. Furthermore, the elements C, Si, O and Cu could not be assessed, because they are part of the background noise (substrate and analysis grid). However, the TEM/EDS study indicates that most of the workers are exposed to particles containing the elements Al, Na and F, with proportions of 69% (prebaked anode process) and 54% (Soderberg process). These results agree with the study by Höflich et al. [140], who indicate that sodium β-alumina ($\text{NaAl}_{11}\text{O}_{17}$) and cryolite (Na_3AlF_6) were the oxides and fluorides most present in aluminium smelters. Other similar compositions were reported in the studies by Gylseth et al. [95] and Thomassen et al. [19].

Several fibrous particles were identified during TEM assessment. The fibre proportions were 25% in the Soderberg process and 31% in the prebaked anode process, which corresponds to the 30% rate mentioned by Thomassen et al. [19]. Some of these particles were identified in the prebaked anode process when there had not been any anode change in progress, suggesting again that the workers can be exposed to these fibres in all potrooms at any time. Gylseth et al. [95] already reported that high fibre concentrations ranging from 9 to 720 fibres/cm³ had been measured in the Soderberg and prebaked anode processes. These fibres were described as smaller than 0.1 µm in diameter and shorter than 5 µm. Voisin et al. [141] also confirmed the presence of short aluminium fibres (with mean lengths of 1 to 2 µm) in the bronchoalveolar fluid of four aluminium smelter workers, and the authors considered these fibres to be different forms of aluminium oxides. These same authors [141] also indicated that these fibres were highly biopersistent in the airway, because they were found in biological samples more than five years after the end of exposure. Our study showed that these fibres can have nanoscale aerodynamic diameters, because several fibres were observed by TEM in the ELPI's finest stages.

Finally, the high Ti rates observed and the presence of arsenic in the samples are new data. Höflich et al. [140] already indicated the presence of Ti oxides in their characterization of potroom dusts. However, the proportions were clearly lower than those obtained in this study. These differences could be explained by the fact that only the fine and ultrafine aerosol fractions were considered in this study. The small number of particles analyzed by TEM/EDS (about 170 particles) could also explain this discrepancy and further evaluation is required. Indeed, since our study is the first to have performed a TEM/EDS analysis by preselection of fine and ultrafine aerosol fractions, new studies are necessary to confirm these results.

6.3 Thermoplastic Processing Industry

The results indicate the major presence of fine and ultrafine particles in the extrusion process studied. The high particle levels measured when there was no operation, and the progressive and significant increase in the concentrations presented in Figures 16 and 17, result from a lack of general ventilation in the storage and processing rooms. Provoked aeration of the premises (opening the doors and windows) for approximately two hours reduced the concentrations to arrive at levels close to the outdoor concentrations.

Assessment of the workers' exposure during CNT handling did not show an increase in the concentrations measured with the P-Trak particle counters. This is probably explained by the fact that the CNTs used appear in the form of large agglomerates (>100 micrometres), which are far above the P-Trak upper detection limit (1 micrometre). It is then possible that high levels of larger particles can be measured by mass methods. Mass measurements are also proposed by the NIOSH to assess carbon nanotubes and nanofibre exposures, based on the measurement method for diesel particulate matter (NIOSH Method 5040) [125]. However, no equivalent method exists at the IRSST, although a synthesis document on the Diesel Emissions Evaluation Program (DEEP) was published in 2001 on the subject [142].

Levels exceeding 200,000 particles/cm³ of air were measured during extruder startup (1 metre), with or without nanotubes. Some authors report exposures to complex mixes of vapours and fumes during different processes in the plastics processing industry [143-145]. In particular, they found short-chain hydrocarbons (C2-C6), long-chain hydrocarbons (C9-C11) and aromatic and cyclic hydrocarbons [144]. Forrest et al. [143] also indicate that extrusion processes generate large quantities of fumes, in comparison with injection moulding processes. However, to our knowledge, no specific study exists on the UFP exposures of this sector's workers. The preliminary data presented in this report thus constitutes new information.

6.4 University Laboratories Producing or Using Nanoparticles

6.4.1 Laboratory A

The levels measured in this laboratory are low and well below the levels reported in other nanoparticle synthesis processes, which can reach concentrations of 106,000 particles/cm³ [64]. The process studied is a closed process and milling is performed in liquid nitrogen, which greatly limits the powdering and explains why the particle levels are relatively stable and similar at the two sampling stations. However, slight increases are noted in the particle concentrations during experimentation for all the sampled tasks. In addition, the concentrations measured in the gaseous phase of nitrogen show that particles exit the liquid phase, drawn by the flow of gas towards the floor. Maynard et al. had also proposed that certain nanoparticles (CNT) could be drawn by air movements [146]. Finally, during dismantling of the mill, concentration differences appear between the zone near the mill and the zone farther away. The most noticeable difference was recorded on the third day, when the particles were nanoscale. These results indicate the possibility of NP exposure during specific opening and NP collection stages in the mill and during the dismantling and cleaning stage. This process requires in-depth assessment, but it appears at this stage that specific means of prevention should be put in place.

6.4.2 Laboratory B

Assessment of the concentrations during CNT handling in the glove box did not show an increase in the particle number concentrations in the laboratory at the two sampled stations. Although this data does not allow a conclusion on the potential particle generation in the glove box's air, it shows that no particles are generated outside it. These conclusions are valid for particles within the P-Trak detection range from 20 nm to 1,000 nm.

6.4.3 Laboratory C

Assessment of the concentrations during CNT handling, whether in the glove box or under the laboratory hood, did not show an increase in particle number concentrations. This is probably explained by the fact that the CNTs used appear in the form of large agglomerates (>100 micrometres), which are far above the P-Trak detection limit (<1 micrometre). These results also go in the same direction as other measurements taken in the laboratory during CNT handling [146, 147]. Furthermore, Maynard et al. indicated that mere handling of CNT powders did not generate enough energy to overcome the van der Waals forces present in these particles [146]. However, the authors also indicated that uncertainties remained for more energetic processes that could generate high NP concentrations.

Although the concentrations measured are low, two peak aerosol mass concentrations were measured during nanotube handling in the glove box with the DustTrak. These results suggest that larger particles, with a diameter $>1,000$ nm, corresponding to the P-Trak detection limit, could be airborne momentarily. These results necessitate in-depth assessments in order to confirm the effectiveness of mass measurements in assessing CNT exposure, but it appears that the prevention method in place in this laboratory, CNT isolation in a glove box, is suitable.

7.GENERAL CONSIDERATIONS AND RECOMMENDATIONS

The NM concentration assessments performed in this project on real occupational exposure cases are the first published by the IRSST. The results presented in this report will make it possible to complete certain data on occupational NM exposure and to specify the tools for assessing exposure to these products based on certain “field” parameters.

7.1 Occupational Exposures

Aluminium smelter workers, persons who perform welding tasks and thermoplastic processing industry workers are exposed to high UFP concentrations. Since several authors recognize UFPs as possible causes of respiratory and cardiovascular problems [11-16], it is important to continue assessing the nature of UFP exposure and the UFP exposure levels of the groups of workers at risk. This data is essential to the success of the epidemiological surveys on the health effects of these contaminants.

The assessments performed within the context of this report do not show high NP concentrations in the research laboratories. Only the milling process generated detectable NP concentrations. CNT handling in the glove boxes of the other two laboratories seems to prevent occupational exposure adequately. In Laboratory C, peak particle concentrations were measured during polymer polishing. Characterization studies could allow identification of the nature of these particles and their agglomeration state.

7.2 Exposure Assessment Tools

There is currently no consensus concerning UFP and NP exposure assessment measurements. However, this study showed that the P-Trak was suitable for assessment of UFP concentrations. In a comparative field study, Zhu et al. [148] also showed that the P-Trak is an effective instrument to compare UFP exposures in relation to other more perfected but non-portable instruments. However, the authors indicate that special attention must be paid to measurements near combustion sources. Park et al. state that the P-Trak could overestimate certain exposures to high concentrations by a factor of 3 [86]. This device's quick response time also let us show the peak exposures during welding operations. Finally, all the “field” studies that seek to assess UFP exposures should integrate a granulometric aerosol distribution assessment to confirm the presence of UFPs. The P-Trak's detection limits let it measure fine and ultrafine particles simultaneously.

The assessments performed during CNT handling did not show an increase in the particle concentrations measured with the P-Trak devices, whether during handling of powders in an open environment (thermoplastic), in a university laboratory (Laboratory B) or even in a glove box (Laboratory C). Bello et al. [147] also showed that in a chemical vapour deposition (CVD) laboratory, no detectable quantity of NPs is generated in the laboratory. The measurements had been performed with CPCs and an FMPS. Tsai et al. also indicate that the particle number concentrations measured during different nanopowder handling activities were close to the background noise levels [69]. These results do not indicate that the workers are unlikely to be

exposed to NPs, but that the P-Trak cannot measure these particles. In Laboratory C, when a DustTrak had been placed in the glove box, peaks had been recorded in relation to the CNT handling operations. The CNTs used in the thermoplastic processing plant and in Laboratory C were the same, Baytubes® Carbon Nanotubes (C150HP) made by Bayer MaterialScience (BMS) [135]. These nanotubes have agglomerated sizes over 100 micrometres, giving them limited inhalation exposure potential, according to the company [136]. Our results indicate that measurement with the P-Trak particle counters then is inappropriate for these raw powder handling stages. However, it remains possible that high agglomerated particle levels can be measured by other sampling methods. Mass measurements are proposed by the NIOSH to assess exposures to carbon nanotubes and nanofibres [125]. Tsai et al. also conclude from their study that mass measurement of respirable dusts is necessary for assessment of occupational NP exposure [69]. Finally, the results presented confirm that mass assessments should be considered when handling nanopowders.

In view of this research, it appears that a characterization and control study of occupational NP and UFP exposure should include an assessment of the mass and particle number concentrations, a measurement of the granulometric distribution and an electron microscopic characterization of the nanosized particles [149].

The conclusions and recommendations presented in this report are only one aspect of assessment of the human health risks posed by UFPs and NPs. The toxicity aspect, but also the scientific uncertainty, should be considered when pronouncing on the risk and the means of prevention to be deployed.

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