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ORIGINAL RESEARCH

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# Chemical and Physical Characterization of McIntyre Powder using Inductively Coupled Plasma Mass Spectroscopy and Electron Microscopy

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## ABSTRACT

**Aim:** The objective of this study was to determine the chemical and physical characteristics of McIntyre Powder, which was stated to be a mixture of aluminum oxide and elemental aluminum. The aim was to (i) confirm this with the current techniques and to see if there were any toxic metals present, which could contribute to health effects including neurological disorders and Parkinson's disease and (ii) obtain a precise particle size distribution. McIntyre Powder was inhaled by at least 27,500 gold and uranium miners of Ontario as prophylaxis to prevent silicosis during 1944–1979.

**Materials and Methods:** The chemical characterization involved analysis by inductively coupled plasma mass spectroscopy (ICP-MS) and scanning electron microscopy (SEM). The physical characterization was carried out using transmission electron microscopy (TEM).

**Results:** The chemical analysis results confirm that the McIntyre Powder contains mainly aluminum and only trace amounts of other metals. The physical characterization shows that it is about 12% of ultrafine (also referred to as nanoparticles) and 88% of fine particles. Approximate aerodynamic diameters of the particles are mean 321.5 nm (0.32 µm) and median 273.8 nm (0.27 µm) with a range from 9.5 nm (0.01 µm) to 1,314 nm (1.31 µm).

**Conclusions:** There are no metallic impurities in McIntyre Powder in quantities that could make a significant contribution to health effects. There is a 12% ultrafine particle content which could be important because of the apparent ability to translocate to the brain.

## ARTICLE HISTORY

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## KEYWORDS

McIntyre powder; particle size; ultra fine particles; inductively coupled plasma mass spectrometry; scanning electron microscopy; transmission electron microscopy

## Introduction

McIntyre Powder, which is no longer produced, was stated to be a mixture of finely ground aluminum and aluminum oxide. It was used as a prophylactic agent for treatment against lung disease silicosis in hardrock miners (gold and uranium) of Ontario, Canada from1944 to 1979 [1]. At least 27,500 miners inhaled the McIntyre Powder during that period according to the record in the Mining Master File of the Workplace Safety and Insurance Board (WSIB) of Ontario. The use of McIntyre Powder became known as aluminum therapy and was also taken up in Australia, the United States, and the United Kingdom [2–4], but its use was short-lived in those countries before the practice was abandoned, whereas in Canada, it was used for a prolonged period of time. The studies discussing the invention and use of McIntyre Powder for the prevention of silicosis have been described [5–7]. Several US patents were also granted for the manufacture of aluminum powder [8–10]. It has been claimed by workers/miners in Ontario that the McIntyre Powder may be responsible for the increased risk of developing adverse health conditions including neurological conditions such as Parkinson's and Alzheimer's diseases [11,12]. The WSIB of Ontario recently commissioned a review of scientific evidence to re-examine the issue. The report [13] did not find a link between aluminum and development of adverse health effects. In 2017, a systematic review [14] was conducted by the WorkSafeBC (an agency of the

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Government of British Columbia, Canada) on occupational exposure to aluminum (McIntyre Powder) by inhalation and the development of neurological disorders with similar conclusions. Their report stated that "the available epidemiological evidence does not support any potential (causal) association between occupational exposure to McIntyre Powder and death due to neurological disorder such as Parkinson's or Alzheimer's diseases." The Ontario WSIB has, however, commissioned and funded further investigations as referred to on their website (www.wsib.on.ca *occupational aluminum exposure and McIntyre powder update*).

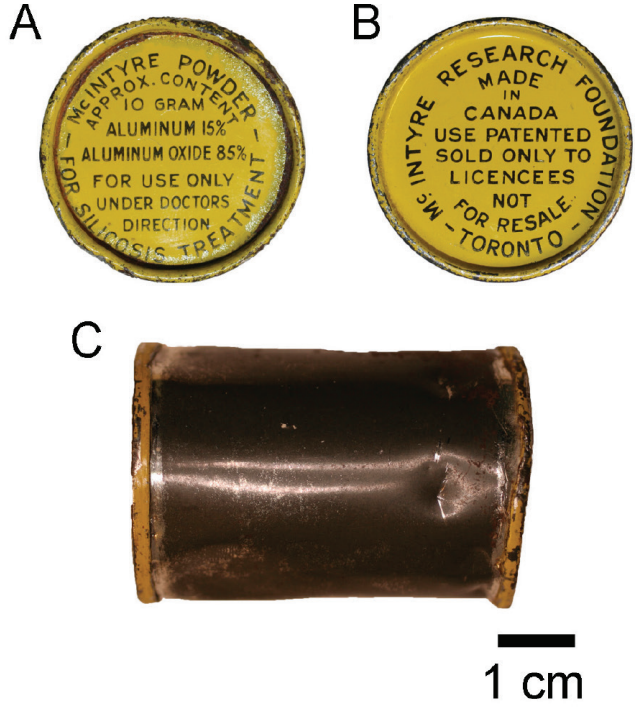
McIntyre Powder was produced by introducing small aluminum pellets of approximately 99.9% purity into a grinding mill. These pellets were grounded without the aid of any steel balls or pebbles in the mill under mill rotation [10]. The powder was stated to contain 15% of aluminum and 85% of aluminum oxide. The total metallic content was stated as 58%–60%. About 96% of the particles were reported to be less than 1.2 microns in diameter, with 88% less than 0.8 micron [10]. This would suggest that there could be a significant number of particles which, today, would be classified as ultrafine or nanoparticles. Ultrafines are the particles with a diameter less than 100 nm and are potential mediators of the well-documented cardiopulmonary and cardiovascular adverse health effects of $PM_{10}$ and $PM_{2.5}$ pollution in ambient air, which could also pose a problem in the occupational environment [15,16]. Furthermore, Oberdorster et al. [17] stated that "there are anecdotal data indicating a causal relationship between long-term ultrafine particle exposures in ambient air (e.g., traffic related) or at the workplace (e.g., metal fumes) and resultant neurotoxic effects in humans. More studies are needed to test the hypothesis that inhaled nanoparticles may be associated with neurodegenerative effects."

The toxicological significance of inhaled particles is dependent on the chemical and physical properties of the particles. The deposition of particles in the human respiratory system is governed by the size of the particles, whether the particles deposit in pulmonary, thoracic, or extrathoracic compartments. Since previously reported physical and chemical characterization data of McIntyre Powder were obtained by methods and techniques of the 1950s, we wished to confirm them by more current methodology. We thus undertook this study to characterize the chemical and physical properties of the McIntyre Powder using inductively coupled plasma mass spectroscopy (ICP-MS) and by both scanning electron microscopy (SEM) and transmission electron microscopy (TEM). One of us has also recently reported on the retained aluminum in the lungs of Ontario hardrock miners, who had inhaled McIntyre Powder for a significant number of years [18]. The objectives of this study were to determine: (i) the chemical composition of the powder, using a currently accepted methodology, to see if it contained metals other than aluminum and aluminum oxide, in amounts which may have toxicological significance and (ii) the physical characteristics of the McIntyre Powder to confirm more precisely the size distribution. This information would be useful for future health-related research on the exposed workers.

## Materials and Methods

### *McIntyre powder*

A canister of McIntyre Powder was obtained in 1979–1980 for the research purpose and was kept on hand until 2019. The canister is cylindrical, sealed at both the ends, with a diameter of 3.5 cm and length of 5.3 cm. Figure 1 shows the canister with identifying information on it. The sealed container held 10 g of powder. A hole was drilled into the container in 2018 to remove the powder for analysis. The powder is fine and grayish-white in color.




A = top, B = bottom, C = side view

**Figure 1.** McIntyre Powder canister.

### *Chemical composition characterization by SEM and ICP-MS*

Since the McIntyre Powder was supposed to be mainly aluminum, we analyzed the sample to determine the metal content to see if there are significant amounts of metals other than aluminum in the sample. A small aliquot of the powdered aluminum sample was dusted onto double-sided carbon tape which was adhered to an SEM stub. The powder was viewed in a Tescan Vega II LSU scanning electron microscope (Tescan USA, PA) operating at 20 kV. The SEM is equipped with an Oxford X-Max 80 Energy Dispersive Spectroscopy detector and Inca software (Oxford Instruments, UK), from which spectra and weight percentages were obtained. The chemical characterization was also performed by ICP-MS analysis. A sample was analyzed by an American Industrial Hygiene Association accredited Canadian laboratory for 12 metals. Approximately 500 mg of bulk sample was digested in the digestion tube with 5 ml of nitric acid ($HNO_3$), 1 ml of hydrochloric acid (HCl), and 100 µl of sulfuric acid ($H_2SO_4$). The sample was then heated for 3 hours at 100°C. It was then diluted and analyzed by ICP-MS.

### *Physical characterization by TEM*

A powdered aluminum sample was dispersed in 1 ml of 100% ethanol and sonicated for 1 minute. A 5 ml of droplet was placed onto a Formvar-coated Cu grid and allowed to dry. The grid was viewed in a JEOL JEM 1200 TEMSCAN transmission electron microscope (JEOL, Peabody, MA, USA) operating at an accelerating voltage of 100 kV. Images were acquired with an AMT 4-megapixel digital camera (Advanced Microscopy Techniques, Woburn, MA).

Particle size distribution analysis was performed on TEM images with magnifications between 40K× and 250K×. Larger particles had to be imaged at the lower magnification range, whereas smaller particles were imaged at higher magnifications in order to visualize them and to optimize the accuracy of measurements. ImageJ (National Institutes of Health, Bethesda, MD) [19] was used to convert grayscale images to binary images. Touching particles were segmented. Overlapping particles and particles touching the edge of images were excluded from measurement. A systematic search of the grid was made to find as many occurrences of separated particles as possible. Area measurements were calculated for 390 particles, and these area measurements were converted to area-equivalent diameters using the formula outlined in Rice et al. [20]. The software enables the outline of a particle to be drawn and then converts the irregular shape of the particle into an equivalent circle, and its diameter is given as area-equivalent diameter.

## Results

The result of chemical characterization by SEM is shown in Figure 2, where Figure 2A is at a magnification of 7k×, Figure 2B is at a magnification of

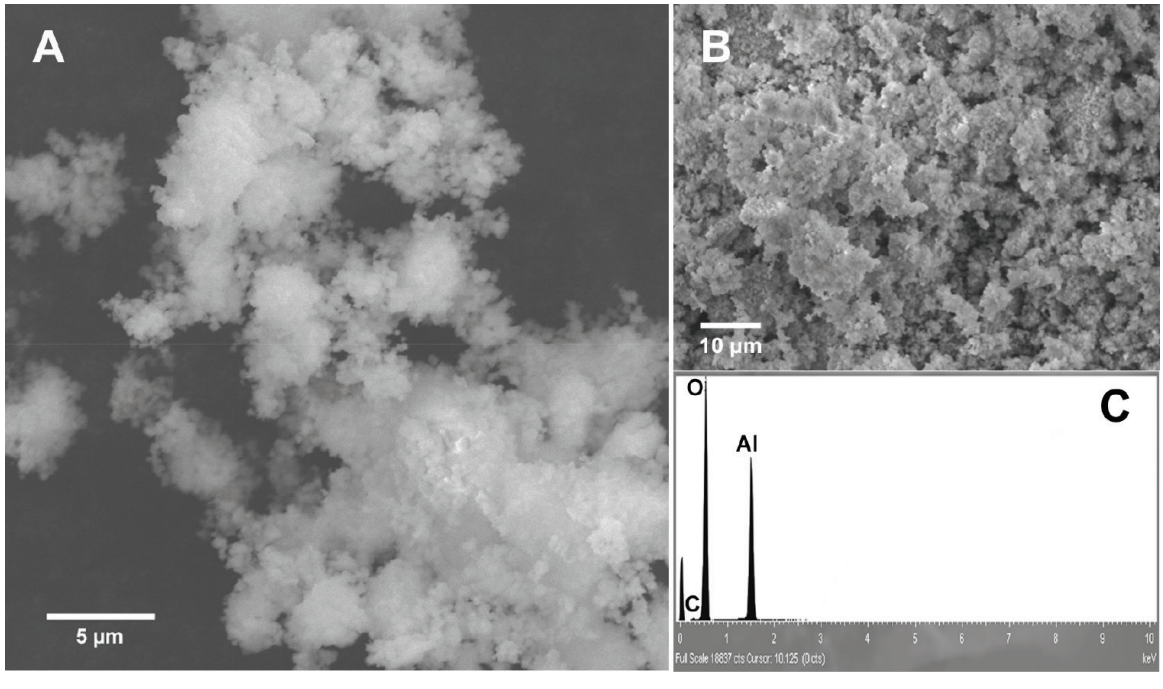



**Figure 2.** Scanning electron micrographs and energy dispersive spectrum.

2,000×, and Figure 2C shows the elemental distribution of Figure 2B. Only aluminum and oxygen peaks are predominant. The carbon peak is due to carbon tape used in the analysis. This confirms that the metal content of the powder is mainly aluminum.

The result of ICP-MS analyses as shown in Table 1 further confirms that it is mainly aluminum. Neurotoxic metals such as manganese and cadmium were not detected, and iron was presented only at the trace level. The overall precision and accuracy of the method of analysis as shown in Table 1 were not provided by the laboratory. The overall precision ($S_{rT}$) and accuracy (%) of the ICP-MS filter method are given in Table 4 of the method [21]. For example, in Table 4, the overall precision for aluminum by two different instrumental techniques is given as 0.0379 and 0.0419 and overall accuracy as 9.9 and 15.1, respectively. However, the modified method of analysis on bulk samples would likely have different precision and accuracy.

**Table 1.** Result of ICP-MS analysis.

| Analyte | Total Concentration (mg/kg) | Total Result (µg) | VMR (µg) |
|---|---|---|---|
| Magnesium | NA | <VMR | 100 |
| Aluminum | 350,000 | 35,000 | 500 |
| Vanadium | 30 | 3.0 | 0.50 |
| Chromium | NA | <VMR | 5.0 |
| Manganese | NA | <VMR | 5.0 |
| Iron | 810 | 80 | 50 |
| Cobalt | NA | <VMR | 0.20 |
| Nickel | NA | <VMR | 10 |
| Copper | 24 | 2.3 | 2.0 |
| Zinc | 110 | 11 | 5.0 |
| Cadmium | NA | <VMR | 0.25 |
| Lead | 9.5 | 0.94 | 0.50 |

NA = Not Applicable; VMR = Minimum Reported Values.

TEM provides two-dimensional images of particles that can be used to produce the number-based size distribution data. Figure 3 shows the typical micrographs of particles as viewed by TEM. Figure3A is at the magnification of 40k×, and Figure 3B is at the magnification of 200k×. A histogram of particle size distribution based on the size of 390 particles is shown in Figure 4. The results are in terms of area-equivalent diameter, which is the diameter of a circle that has an area equivalent to the area of the particle in question. The normal distribution pattern displayed in the histogram would suggest that we were able to obtain a good representation of particle size ranges comprising our sample. Table 2 shows the statistical characteristics of the particle distribution as calculated using Excel. The results of area-equivalent diameter can be approximately converted to aerodynamic diameter (da), which is more relevant in terms of deposition in the human respiratory system.

## Discussion

An assessment of particulate matters is defined by their particle size in discrete categories as coarse, fine, and ultrafine (also referred to as nanoparticles). Coarse particles are those which range between 2,500 and 10,000 nm (or 2.5 and 10 µm), fine particles are those between 100 and 2,500 nm (0.1 and 2.5 µm), and as defined earlier, ultrafine or nanoparticles are between 1 and 100 nm (0.001 and 0.1

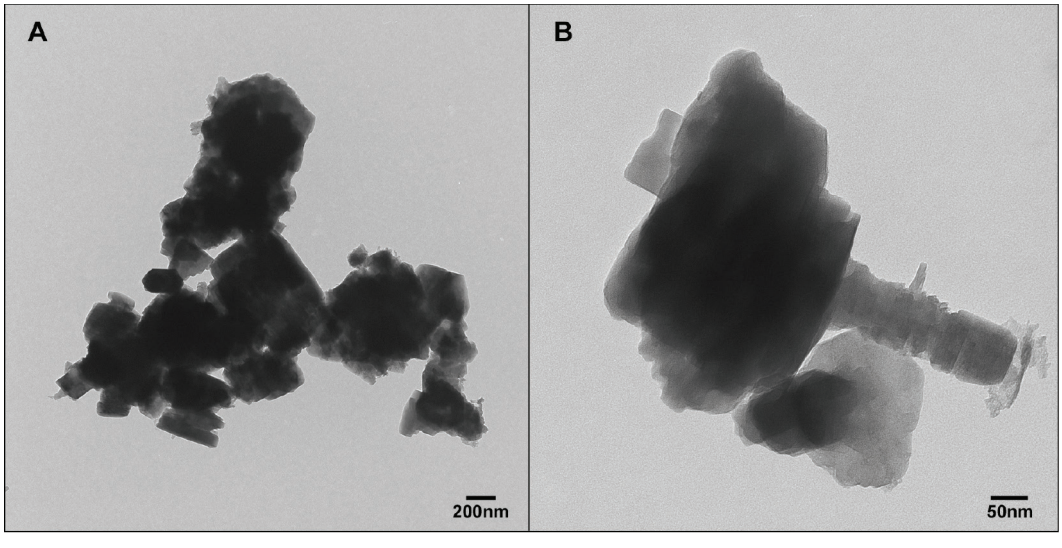



**Figure 3.** Transmission electron microscope micrographs.

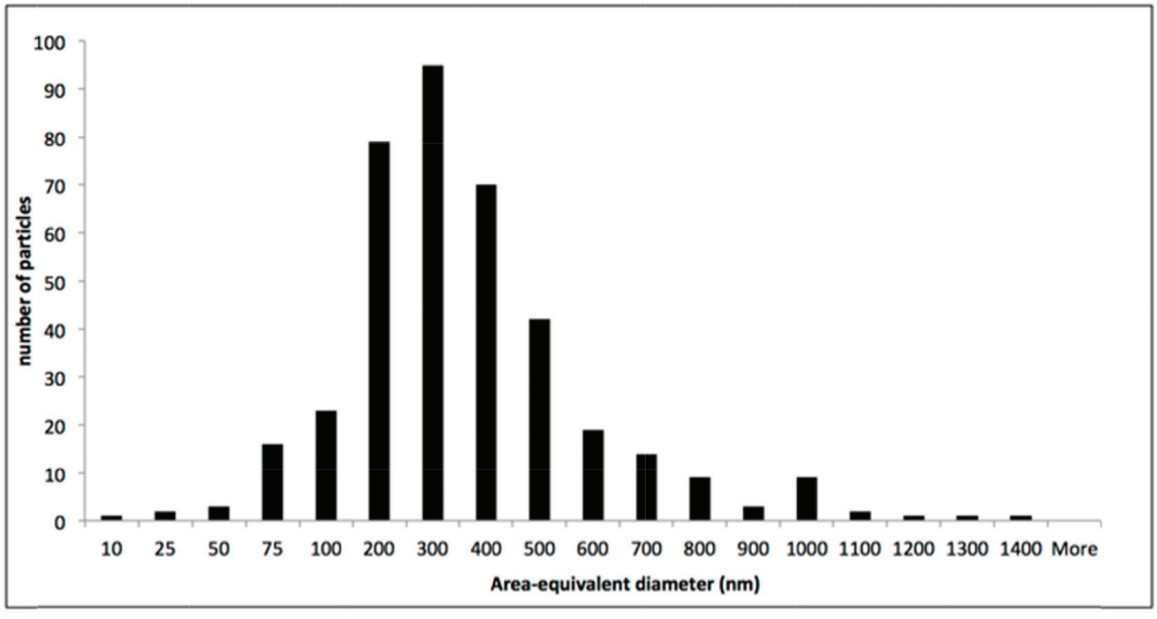



**Figure 4.** Histogram of particle size distribution by transmission electron microscope ($n$ = 390).

**Table 2.** Size distribution parameters, $n$ = 390 particles, and particle size in nanometer (nm).

| Statistic | Result |
|---|---|
| Mean | 321.5 |
| Standard Error | 11.2 |
| Median | 273.8 |
| Mode | 238.3 |
| Standard Deviation | 220.3 |
| Sample Variance | 48,526 |
| Kurtosis | 2.9 |
| Skewness | 1.5 |
| Range | 1,305 |
| Minimum | 9.5 |
| Maximum | 1,314 |
| Sum | 125,400 |
| Count ($n$) | 390 |

μm). In terms of health effects and deposition in the human respiratory tract, the aerodynamic diameter particle size is the most relevant parameter. Aerodynamic diameter (da) of a particle is the diameter of the unit density ($\rho$ = 1 gm/cm$^3$) sphere having the same settling velocity as the particle in question. The American Conference of Industrial Hygienists' (ACGIH) occupational exposure limits for particulate matters are defined for deposition as size-selective sampling based on aerodynamic diameter [22]. The aerodynamic diameter of the bulk powder can be directly measured by equipment such as an aerodynamic particle sizer, an expensive device [23]. Alternatively, aerodynamic diameter (da) can be approximately estimated from area-equivalent diameter obtained by microscopic technique using available data in the literature. Hinds [24] presented a table, where for mineral, dust ratio of da/dPA can be used to approximately convert area-equivalent diameter (i.e., dPA = projected area diameter) to aerodynamic diameter. He further stated that "this useful quantity combines the volume shape factor, dynamic shape factor, and particulate density into a single factor. Except for very heavy material, most minerals have a value close to 1." Assuming the ratio of aerodynamic diameter and equivalent area diameter given by TEM to be 1, the value of Table 2 can be approximately the aerodynamic diameter of a mean 321.5 nm (range 9.48–1,314 nm). The data in Figure 4 indicate that the particles that we examined from the McIntyre Powder were approximately 12% ultrafine (or nano) particles and 88% fine particles.

While the manuscript was under review, a paper describing the characterization of McIntyre Powder was published by Zarnke et al. [25]. The results are in broad agreement with the results of that paper, particularly those attributable to the light gray powder. For example, the aluminum content of the gray McIntyre Powder given in Table 1 at approximately 35% is similar to those reported by Zarnke et al. [25] of 32.4% ± 0.6% based on four light gray McIntyre Powders by ICP-MS/OES. This concentration, which was not what was expected based on the canister label, shows a mixture of elemental aluminum (15%) and aluminum oxide (85%). They were able to explain their finding using X-ray diffraction data which showed that the light gray powder consisted predominantly

of aluminum hydroxide polymorphs with hardly any elemental aluminum present. This would mean that the labels on the light gray canisters are not accurate. We do not have XRD data, but it appears likely that the gray powder is similar in composition to theirs.

## Conclusion

The chemical analysis of McIntyre Powder by the two methods such as ICP-MS and SEM confirms it to contain mainly aluminum. The physical characterization by TEM showed the powder to be mostly comprised of fine particles that were less than 1.3 µm in size but also contained a significant amount of ultrafine particles which may cause adverse health concerns. This information has not been previously available and should be useful in future toxicological and health studies, given the possibility that ultrafine particles may translocate to the brain. This maybe a useful line of research to follow in current consideration of health effects for those who had inhaled McIntyre Powder in the past.

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