



Quasi-On-Line Mass Size Distribution Measurements of Aerosol Particle Chemical Composition

The characterization of size distributions relating to the different chemical constituents of airborne particles is an essential step for many applications including:

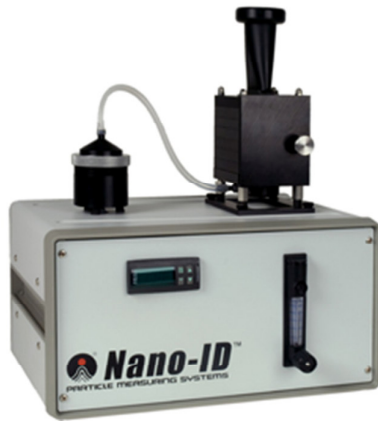
- Occupational hygiene
- Environmental research
- Automotive industry
- Atmospheric science
- Nanotechnology
- Microelectronics

One method commonly used to obtain size-resolved chemical composition data is to collect the airborne particles using a cascade impactor, and then analyze the fractionated samples using an off-line technique such as Atomic Absorption Spectroscopy (AAS), Gas Chromatography-Mass Spectrometry (GC-MS), and ICP-MS (Inductively Coupled Plasma Mass Spectrometry). However, the time requirements and expense of such off-line techniques can be a major drawback.

An alternative method for obtaining size-resolved chemical composition data involves using a time-of-flight mass spectrometer (e.g., from TSI, Inc.), but this kind of instrument is large and expensive and has very limited applications for laboratory research.

To date, there are no affordable techniques available for the size-resolved chemical composition characterization of airborne particles.

Recently a novel fractionating sampling system, the **Nano-ID Select** (Figure 1), has been developed by Naneum Ltd. and Particle Measuring Systems. The **Nano-ID Select** can be combined effectively with various on-line analytical techniques to enable chemical characterization, such as X-Ray fluorescence (XRF) spectroscopy with a handheld device and Raman Spectroscopy using a portable Raman spectrometer.



The **chemical analysis** of particles collected can now be done almost **instantly** employing recently-developed analytical techniques!

Figure 1: The **Nano-ID Select** wide-range aerosol particle sampling system.

Benefits of the **Nano-ID Select** include:

- A high aerosol sampling flow rate of 20 l/min ensures that sufficient mass can be collected for chemical characterization
- Particles are fractionated into 12 separate stages over a wide range of sizes between 2 nm and 30 μm
- The first instrument to allow nanoparticles to be size-selectively collected.
- Samples are compatible with Transmission Electron Microscopy and Scanning Electron Microscopy
- Provides the ability to quantify Engineered Nanoparticles (ENP) at a mass level below the atmospheric background.

Examples of size distributions obtained using the **Nano-ID Select** are shown in Figures 2 and 3.

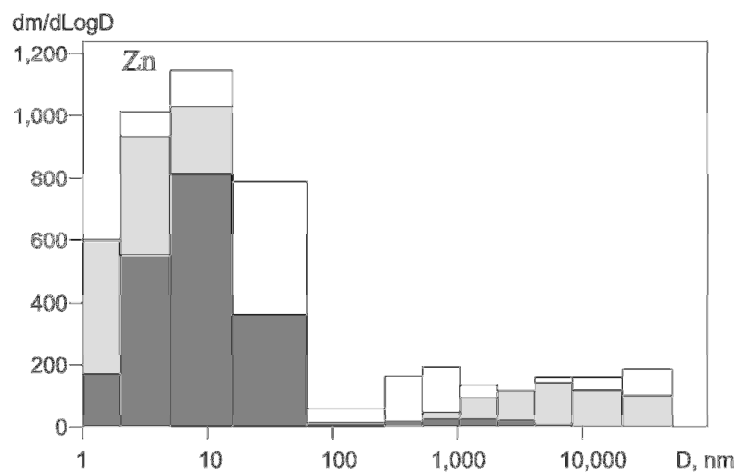


Figure 2: Particle mass-size distributions (dm/dLogD in ng/m^3) of zinc obtained at a welding site.

White bars represent airborne zinc, grey bars represent particles deposited in the entire respiratory system (calculated using the ICRP [International Commission of

Radiological Protection] lung deposition model), and dark bars represent particles deposited in the alveolar and trachea bronchial regions.

The health risk of exposure to aerosols depends on the fraction of aerosol particles that are deposited in the respiratory system. Not all airborne particles entering the respiratory system are deposited in the respiratory tract. As can be seen from Figures 2 and 3, the concentration corresponding to particles deposited in the respiratory system is considerably lower than the concentration of particles in the air. This means that the accumulated dose calculated based on the airborne particle concentration (i.e., exposure) overestimates the actual amount of the particulate matter deposited in the respiratory system, and therefore overestimates the health risk.

Deposition in the alveolar and trachea bronchial regions is important for assessing health risk, especially for nanoparticles since it is known that nanoparticles can cause harm to these parts of the respiratory system.

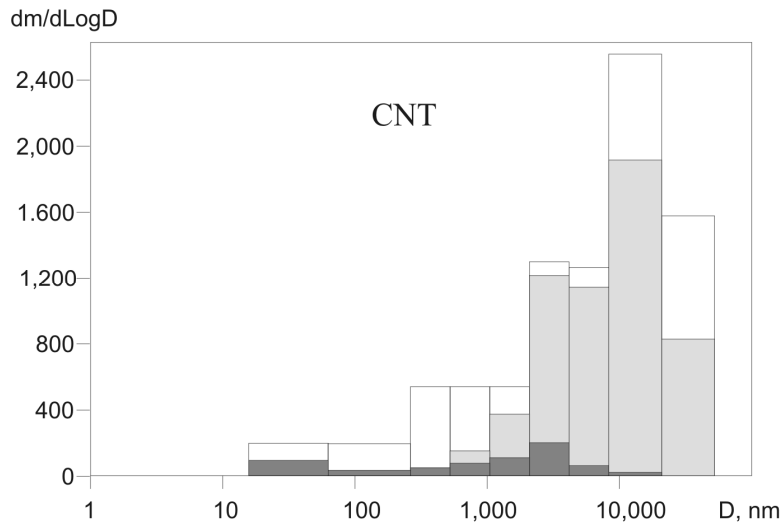


Figure 3. Particle mass size distributions ($dm/dLogD$ in ng/m^3) of carbon nanotubes (CNTs) obtained at a welding site. White bars represent airborne CNTs, grey bars represent particles deposited in the entire respiratory system (calculated using the ICRP lung deposition model), and dark bars represent particles deposited in the alveolar and trachea bronchial regions.

In response to customer preference for on-line or quasi-on-line analysis, Naneum Ltd. Particle Measuring Systems have developed interfaces to allow the Nano ID Select to be used in combination with modern handheld and portable devices for the chemical analysis of sampled aerosol particles.

Nano-ID MR250 Mass Reader used with Nano-ID Select

For quick measurement of the total mass-size distribution of aerosol particles, the **MR250 Mass Reader** can be used in combination with the **Nano-ID Select**.

The mass-size distribution of aerosol particles is normally obtained by gravimetric analysis using microbalances. This is a very time consuming and labor intensive procedure, especially when the samples only contain very small amounts of material. Naneum has developed a novel technique to enable the mass-size distribution to be obtained very quickly without tedious gravimetric analysis.

The Nano-ID Mass Reader **MR250** is a companion product for the **Nano-ID Select** used to quickly determine mass-size distributions without the need for laboratory analysis. The **MR250** provides seven channels of resolution in the microparticle range from 250 nm to 20 µm, with sensitivity for sample masses less than 10 nanograms. Used in combination with the **MR250**'s user-friendly software, histograms showing the total mass-size distributions of aerosol samples collected by the **Nano-ID Select** can be obtained in minutes.



Figure 4: The **Nano-ID MR250** allows the mass of aerosol particles deposited onto substrates to be quantified in minutes.

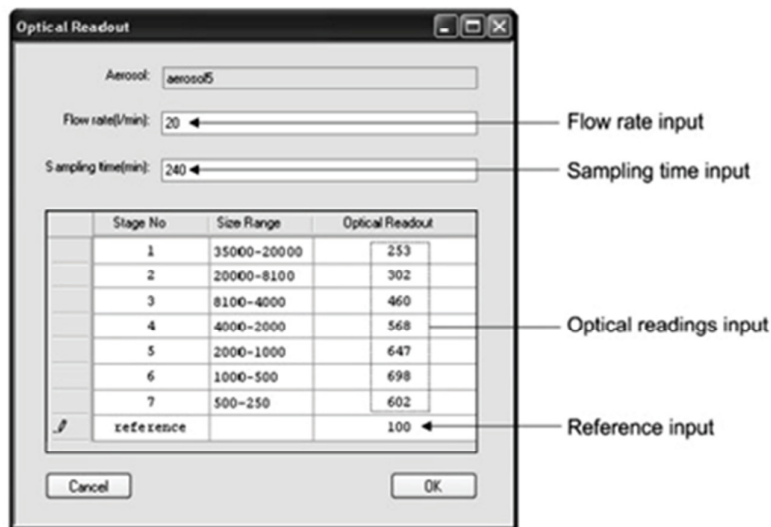


Figure 5: Example dialog box in the **MR250 Mass Reader's** user-friendly software.

MR250 Case Studies

Case Study 1 – Mass-size distribution of pure titanium dioxide (TiO₂).

A small amount (less than 0.5 g) of titanium dioxide powder (Aeroxide® TiO₂ P 25)

was atomized using a Naneum **Powder Aerosolizer (PA100)**, and samples of the resulting aerosol were collected using a **Nano-ID Select** over a period of about 4.5 minutes. The aerosol samples were then analyzed in the **MR250** to obtain the mass-size distribution shown in Figure 6.

The TiO₂ mass-size distribution shows a much greater contribution from larger particles than is seen in atmospheric aerosol, with an obvious peak in the 4 - 8 μm range. The average primary particle size for this TiO₂ powder is specified by the manufacturer as 21 nm so clearly this material exhibits a strong tendency to form large agglomerates or aggregates of particles. The total mass concentration over the range of 250 nm to 35 μm is 827 μg/m³.

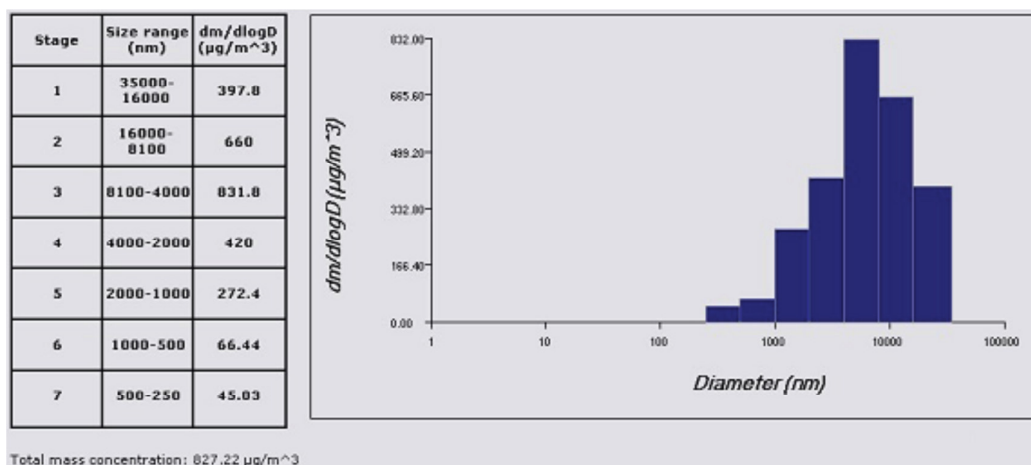


Figure 6. Mass-size distribution of TiO₂ obtained using the **MR250**.

Case Study 2 – Mass-size distribution of pure multi-walled carbon nanotubes (MWCNTs)

Samples were taken using the **Nano-ID Select** from an aerosol consisting of pure multi-walled carbon nanotubes (Arkema Graphistrength[®] C100) generated using the **PA100 Powder Aerosolizer**. The samples were analyzed in the **MR250** and the resulting mass-size distribution is shown in Figure 7.

Clearly there is a much greater contribution to the mass-size distribution from large particles than is seen in a typical atmospheric aerosol. The mass-size distribution appears to peak at around 10 μm, however, since the **Nano-ID Select** cascade impactor separates particles based on their aerodynamic diameter (defined as the diameter of a sphere of density 1g/cm³ with settling velocity identical to that of the particle in question), and carbon nanotubes have a strong tendency to form large, low density (~ 0.15 g/cm³) agglomerates of particles, the Stokes diameter will be even larger. The total mass concentration in the size range 0.5 – 8.1 μm is 4277 μg/m³.

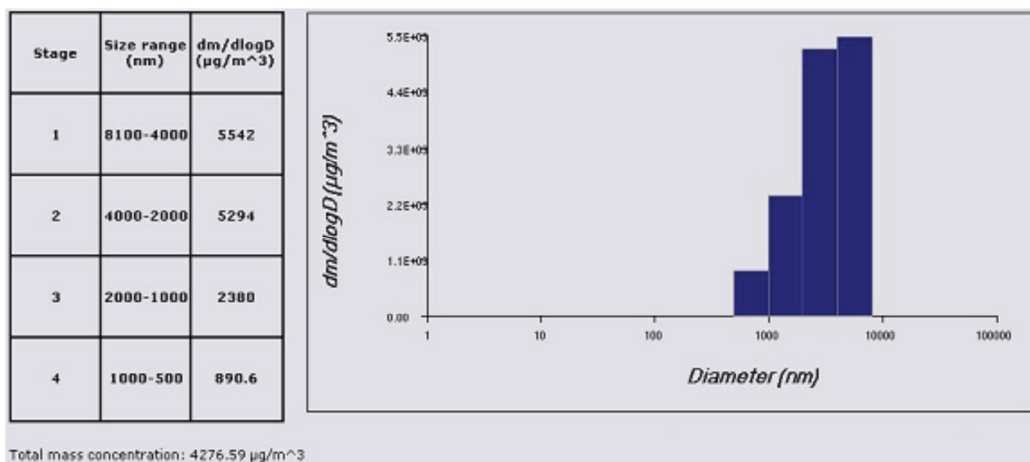


Figure 7: Mass-size distribution of MWCNTs obtained using the **MR250**.

Raman Spectroscopy used to Quantify Compounds

Raman spectroscopy was used to quantify organic and inorganic compounds (including carbon nano-tubes) collected with the **Nano-ID Select**.

Raman spectroscopy is another analytical technique that can be particularly useful in the characterization of organic and inorganic compounds, and CNTs present in an aerosol particle sample. The Raman spectroscopic technique involves directing a monochromatic light source (such as a laser) onto a sample and detecting the scattered light. Most of the light is scattered elastically (known as Rayleigh scatter), but a small fraction is scattered inelastically (Raman scatter).

Raman scatter involves the interaction of incident electromagnetic radiation with the vibrational frequencies of the molecule (n_m) to cause a shift in the frequency of the scattered light away from the excitation wavelength ($n_{ex} \pm n_m$). Raman spectroscopy is a powerful tool used to identify and characterize the structure of molecules.

A portable Raman spectrometer (for example the Ocean Optics Laser Raman System shown in Figure 8) can be used with samples collected by the **Nano-ID Select** to quantify the amount of organic compounds, CNTs, and many other chemical constituents present in the aerosol samples.



Figure 8: Ocean Optics portable Raman system

A suitable Raman instrument can be supplied by Naneum Ltd., along with user-friendly software to enable graphs of size distributions to be prepared from Raman data on chemical composition. Use of the Raman spectrometer does not require any special sample preparation. Substrates can be taken out from **Nano-ID Select** and

analyzed instantly. Once routines have been established, the Raman data can be applied to identify and quantify the mass-size distribution of specific compounds in a relatively short time.

Raman spectrometry can provide a wealth of information related to the chemical nature of aerosol particles. For example, the Raman spectra of TiO₂ particles change depending on the size of particles present, and therefore can be used to reveal differences in the nature of the TiO₂ particles – for example changes in the crystal structure. Figure 9 shows a collection of Raman spectra taken using the Ocean Optics portable Raman system from size-fractionated samples of TiO₂ aerosol particles collected using the **Nano-ID Select**. The four peaks clearly observed at ~150, 402, 520, and 643/cm are characteristic of TiO₂ particles.

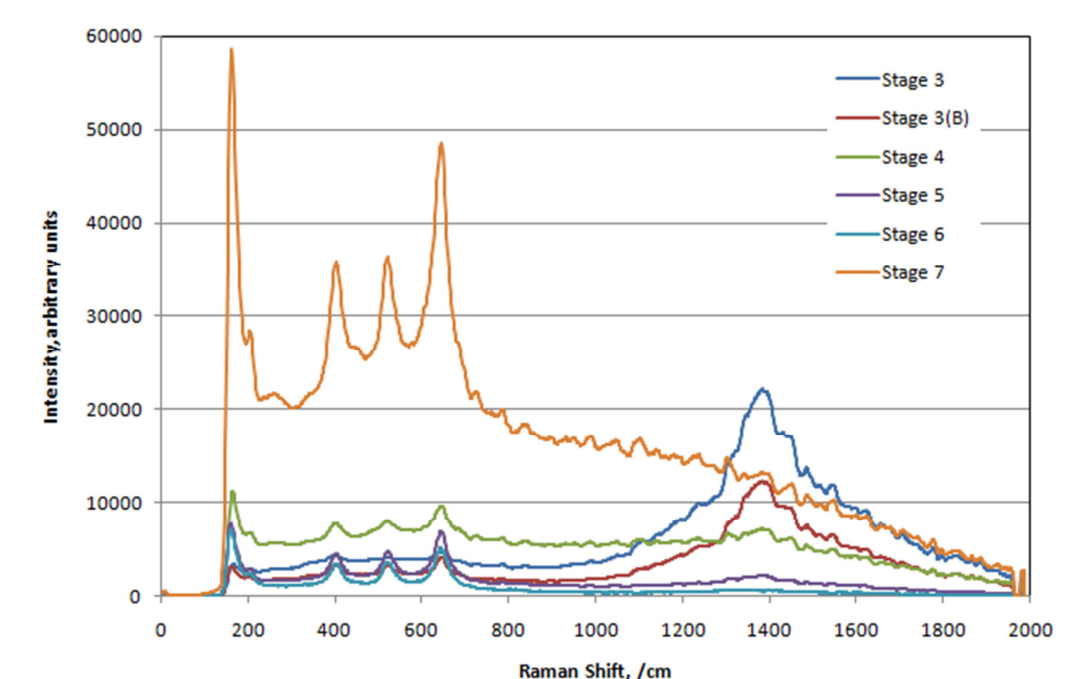


Figure 9: Raman spectra of TiO₂ aerosol particles sampled using a **Nano-ID Select**. The spectra were obtained using an Ocean Optics portable Raman system without any sample preparation.

The numbered stages in Figure 9 correspond to the following particle size fractions:

Stage	3	4	5	6	7
Size range, μm	4.0 – 8.0	2.0 – 4.0	1.0 – 2.0	0.5 – 1.0	0.25 – 0.5

Carbon Nanotube Detection and Quantification

Raman spectroscopy is widely used for CNT detection and identification. Raman spectra of multi-walled carbon nanotubes reveals two distinctive peaks, with Raman shifts at around 1320 and 1600 cm^{-1} . The peak at 1600 cm^{-1} is known as the “G-peak” and is a characteristic feature of graphite layers arising due to tangential vibrations of the carbon atoms. The peak at 1320 cm^{-1} can be attributed to the “D-peak” and is atypically an indication of defects in the graphite structure. By comparing the ratio of

the intensity of the D-peak to the G-peak it is possible to get an indication of the quality of the sample (Figure 10). The amplitudes of the D-peaks are large compared to the G-peaks, which indicates that the CNT sample may contain a high proportion of defects. This is to be expected for a sample consisting mostly of multi-walled carbon nanotubes.

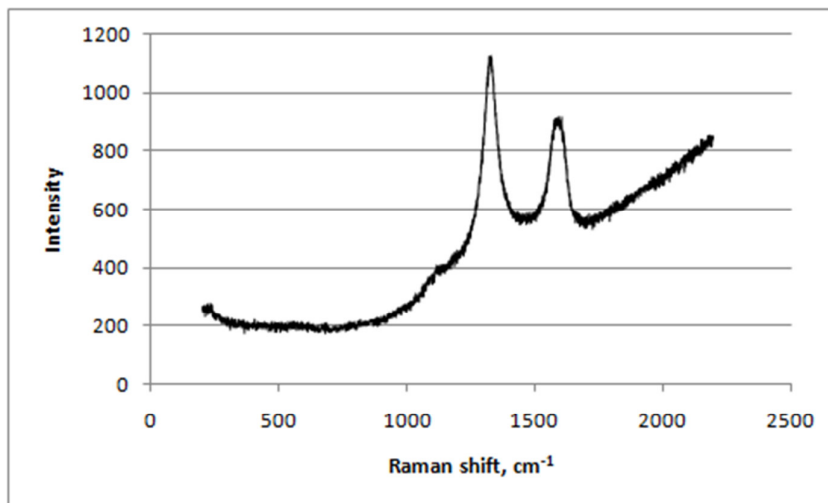


Figure 10: Raman spectra of CNT samples of aerosol particles sizes from 1 to 2 μm collected with **Nano-ID Select**.

The spectra were obtained without any sample preparation.

Raman Spectra of Atmospheric Aerosol

Figure 11 reveals the complicated spectra of atmospheric aerosol particles collected in the summer of 2010 at the University of Kent in Canterbury, UK. The spectra were taken from a sample containing particles in the size range 0.5 – 1 μm , and contain a number of features that can be attributed to a variety of organic and inorganic compounds.

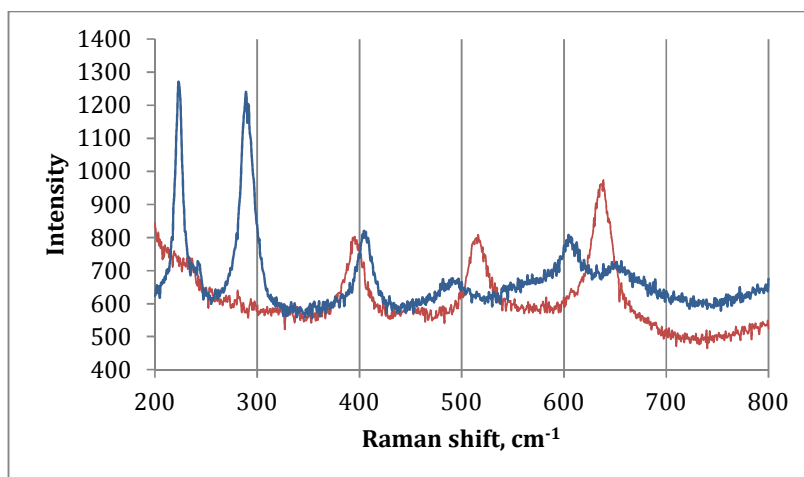


Figure 11: Raman spectra of atmospheric aerosol samples (particle sizes from 0.5 – 1 μm) collected with **Nano-ID Select**.

The spectra were obtained without any sample preparation.

Quantifying Metals and Other Elements in Aerosol Samples

Metals and other elements present in aerosol samples collected by the **Nano-ID Select** were quantified using X-Ray Fluorescence spectroscopy (XRF).

A handheld XRF instrument of the kind shown in Figure 12 can be used with samples collected by the **Nano-ID Select** to quantify the amount of metals, sulphur and other elements present. XRF is based upon a phenomenon that is similar to light fluorescence but occurs when atoms are excited by an X-ray source. When an atom in the sample is illuminated by an X-ray beam it emits a specific wavelength of radiation that is a signature of that particular element. The wavelength of emitted radiation is indicative of the element(s) present, and the signal intensity can be used to quantify the elemental constituents of the sample.



Figure 12: A Thermo handheld XRF spectrometer

Naneum is able to supply an XRF instrument suitable for use with samples collected by the **Nano-ID Select** along with user-friendly software to enable size distributions to be obtained from XRF data on elemental composition.

- There is no need for any special sample preparation.
- Substrates can be removed from the **Nano-ID Select** and placed into the interface unit (supplied by Naneum Ltd.).
- Readings can be taken following the standard procedure for the XRF instrument.
- XRF readings can usually be obtained in a matter of minutes.

Using the **Nano-ID Select** in combination with XRF eliminates a major obstacle in aerosol particle chemical composition analysis, enabling size-resolved data to be obtained almost immediately after collecting the samples.

Figure 13 shows an example of an XRF spectrum taken from a sample of **carbon nanotubes** collected using the **Nano-ID Select**. The XRF instrument used was a DELTA Alloys & Metals Handheld XRF Analyzer (see Figure 12).

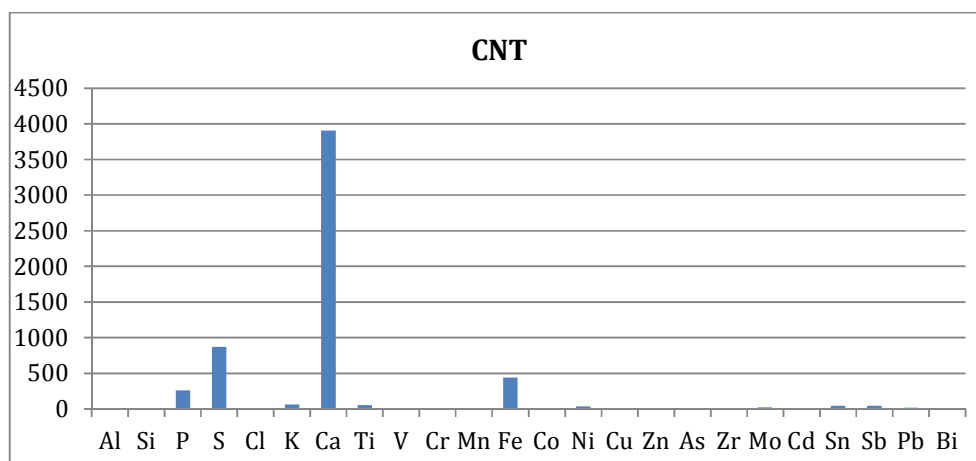


Figure 13: An XRF spectrum of CNT particles in the size range 0.5 – 1 μm collected using the **Nano-ID Select**.

The XRF spectrum in Figure 13 reveals the presence of four metallic elements: phosphur, sulphur, calcium and iron, although traces of potassium and titanium can also be seen. The CNTs used for these tests were supplied by a leading European CNT manufacturer, and the elements seen in the spectrum are most likely to be remnants of the catalyzers used to grow the nanotubes. The signal intensity from these catalyzer elements can be used to quantify the amount of CNTs in the sample based on the known relationship between the mass of CNTs and catalyzers.

Figure 14 shows an XRF spectrum taken from **diesel exhaust** particles sampled using the **Nano-ID Select**. The most significant peak in the spectrum comes from sulphur, which is a well known component of fossil fuels. The XRF method is very sensitive to sulphur, making it is a good choice when using XRF to quantify the mass concentration of particulate matter emitted by a car diesel engine. Another prominent signal comes from calcium, and there are also signals from potassium, chlorine, titanium, vanadium, chromium, iron, and zinc. These elements may have been either present in the fuel or generated as a result of fuel combustion in the engine.

The XRF spectrum reveals a wealth of information regarding the chemical composition of the exhaust particles generated by a diesel engine. A handheld instrument of this kind is a very convenient tool that can be used in combination with the **Nano-ID Select** to obtain information on chemical composition and size distributions of the various constituents of complex aerosols. Chemical analysis of complicated and unpredictable aerosols such a car's diesel exhaust can be a time-consuming and labor-intensive process. With a handheld XRF instrument meaningful data can be obtained almost **instantly** without the need for any kind of sample preparation. In addition, XRF is a **non-destructive method**, so samples can be kept and examined again using other complimentary techniques.

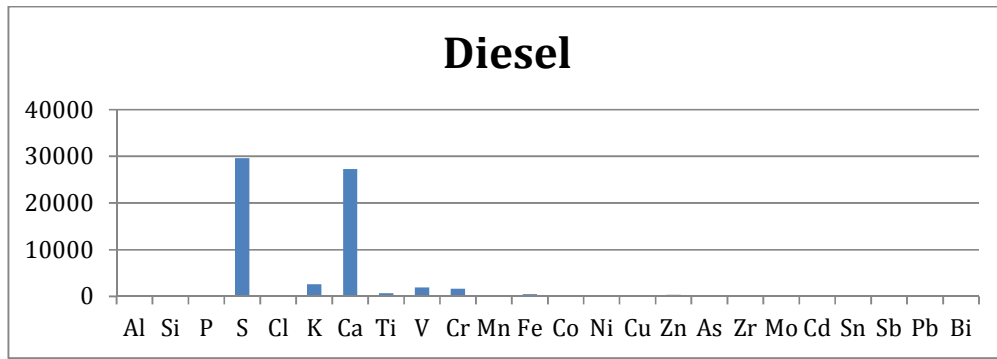


Figure 14: XRF spectrum of particles from a car’s diesel exhaust sampled using the **Nano-ID Select**.

The particle size-range in this sample was 250 – 500 nm.

Arizona test dust is a widely used test dust for aerosol instrument calibrations. It is a typical aerosol of the kind that can be found in abundance in the atmosphere. Similar aerosols may be generated by winds in arid areas such as Sahara desert, for example. The spectrum in Figure 15 was obtained using a DELTA Alloys & Metals Handheld XRF Analyzer.

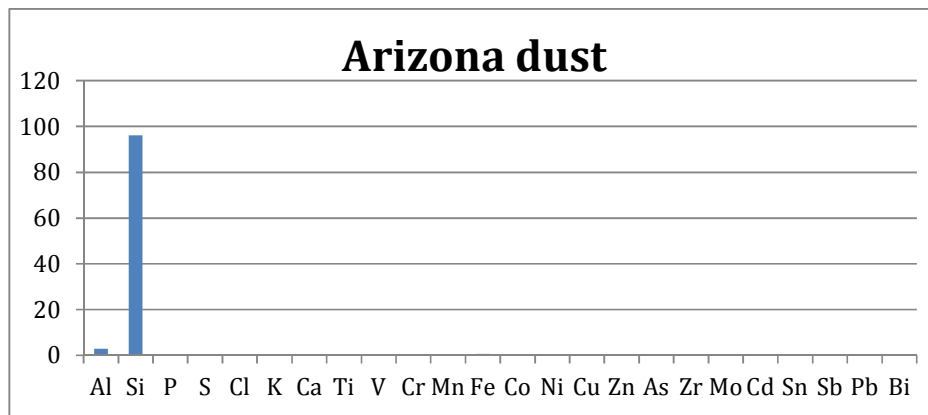


Figure 15: An XRF spectrum of Arizona test dust particles sampled with the **Nano-ID Select**. The size-range of particles in this sample is 2 – 4 μm .

Commercially-available Arizona dust was atomized using a **PA100 Powder Aerosolizer**, and the resulting aerosol was fractionated and collected using a **Nano-ID Select**. After sampling the substrates were analyzed using a DELTA Alloys & Metals Handheld XRF Analyzer. By far the largest signal represents silicon, with a smaller second signal coming from aluminium, which is what one would expect to see for Arizona test dust. However, the absence of other elements was rather surprising. Only two other elements (iron and zinc) were detected at low levels not visible in the spectrum shown in Figure 15. From this we concluded that commercially available Arizona test dust is relatively clean and contains very few impurities.