

## Quantitative analysis of nanoparticles with EPMA

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Quantitative element analysis of single nanoparticles (less than 1µm) is very important in research on e.g. mineralogy, environmental pollution, and catalysis.

Usually, nanoparticles are analysed in a transmission electron microscope (TEM) with Energy Dispersive X-Ray-Spectroscopy (EDS). Since it is a standardless analysis, the resulting element concentrations are normalised to 100 Wt%. Unfortunately, the standardless analysis fails, if not all elements of the sample are known and are considered. Moreover the precision is low for the case of interfering peaks, e.g. overlapping peaks, which do not have a simple Gaussian shape.

On the contrary, the Electron Probe Micro Analysis (EPMA) uses crystal spectrometers (i.e. Wavelength Dispersive X-Ray-Spectroscopy, WDS), which may discover all elements of the sample, due to its higher spectral resolution. Moreover, the X-ray interaction cross section is larger compared to TEM-EDX, since the EPMA works with a considerably smaller acceleration voltage resulting in a higher X-ray signal.

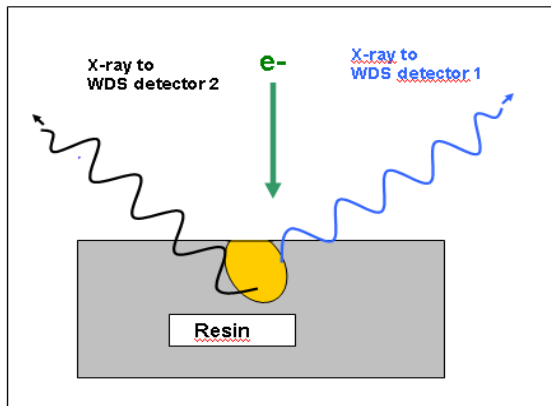
Since the spectrometer signal in EPMA is very sensitive to tilted sample surfaces, the nanoparticles are normally included in resin (**fig.1**). Then, the sample is polished and coated with graphite for better conductivity. But this sample preparation has the disadvantage that most of the X-rays from the sample have to pass through the resin (83 Wt% C, 14 Wt% O, H and Cl) causing problems by more or less unknown absorption and fluorescence. Therefore, high precision measurements are hardly possible.

In this paper, we present a new preparation and analysis procedure for the high precision element analysis of nanoparticles with EPMA. The particles are not included in resin but suspended in methanol. After a short dispersing in ultrasonic device, a liquid drop is deposited on a well polished carbon glass surface (**fig. 2**). During the analysis, the X-rays are detected by two opposite spectrometers. The two opposite signals are used by simple summation to compensate for the changes of the X-ray intensities due to the tilted surface of the nanoparticles.

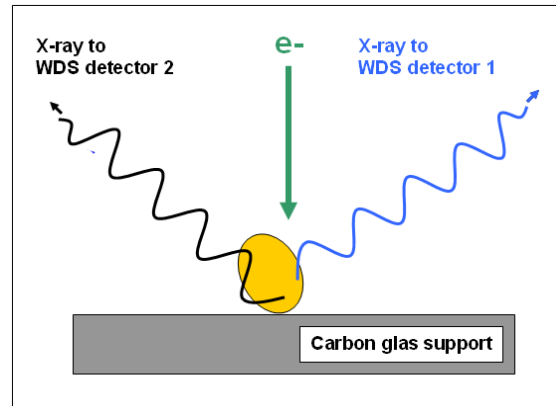
This method is tested with nanoparticles (400nm to 4 µm) scraped from a well known and homogeneous olivine mineral (50.51 Wt% MgO, 40.85 Wt% SiO<sub>2</sub>, 8.26 Wt% FeO, 0.38 Wt% NiO). For small nanoparticles, the beam diameter may exceed the particles size. In this case, the sum concentrations obtained from the EPMA analysis with standards is smaller than 100%. However, this sum is a measure for the particle size.

Fig. 3 shows the MgO-concentration (dots and squares) of several nanoparticles with different sizes measured with both opposite spectrometers. As usual, there is a strong variation due to fluctuations typical for EPMA and due to irregular 3D-shape of the particles. The mean values are shown by a straight line showing a clear trend different for both spectrometers. The promising result is that the sum of both mean values gives a constant MgO-concentration corresponding to the value of a bulk olivine sample very well. The advantage of the method is the experimental result that the MgO-concentration is determined with a 2% higher relative precision, which is important for most users of EPMA.

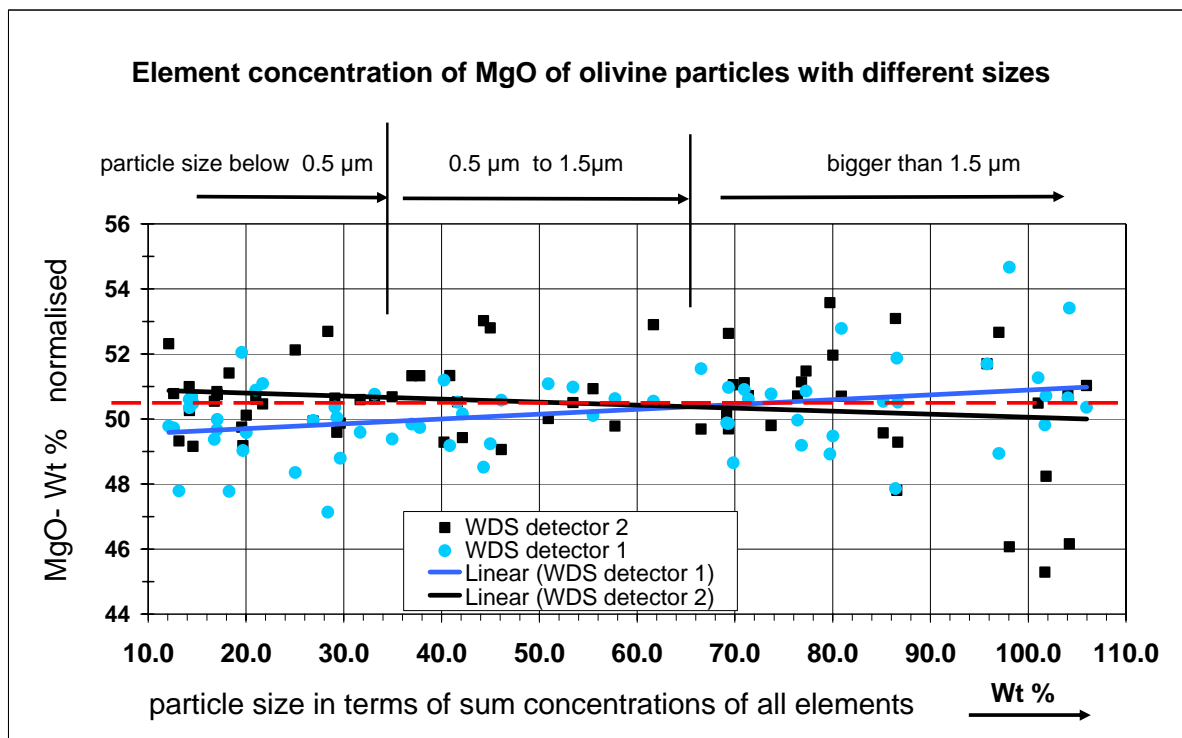
The measurements were performed on EPMA CAMEBAX MICROBEAM (Company CAMECA ) with SAMx programs (WWW.samx.com).



**Figure 1.** Standard preparation of nanoparticles for the analysis in EPMA having the disadvantage of strong X-rays interaction with the resin .



**Figure 2.** New sample preparation and analysis method using freestanding particles combined with the sum signal of two opposite detectors.



**Figure 3.** MgO-concentration in olivine nanoparticles with different sizes measured with EPMA with standards and two opposite detectors (black and blue); the straight lines show the mean values of the statistically fluctuating values; the red dashed line depicts the expected MgO-concentration equal to bulk olivine.