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PROOF-OF-CONCEPT EXPERIMENT REPORT

MORPHOLOGY AND COMPOSITION OF ZIRCONIA PRIMERS

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Proof-of-Concept experiment details

Received sample: Four vials with Zirconia powder called ADT10, ADT16, ADT18 and ADT21

Planned analysis:

* SEM imaging of ADT powder dispersed on a suitable substrate

* SEM/EDX analysis of selected primers

* X-Ray Fluorescence (XRF) spectroscopy of selected ADT powders dispersed on a suitable substrate

Sample preparation:

For SEM/EDX: the powder has been dispersed in ethanol (absolute), sonicated for 10 minutes and then dropcasted on a thoroughly clean SiO_2/Si susbtrate kept at 80 C.

For XRF: the powder has been dispersed in ethanol (absolute), sonicated for 15 minutes (following the same sample prepratation procedure for SEM/EDX) and then dropcasted on a thoroughly clean Au TEM grid covered with formvar film.

Measurement author, dates and place:

SEM/EDX: the sample preparation and the reported measurement has been performed by dr. Mattia Fanetti in the period from 18/08/20 to 26/10/2020 at University of Nova Gorica (campus of Ajdovščina).

XRF: the sample preparation and the reported measurements have been performed by dr. Alessandra Gianoncelli in the period from 24/11/20 to 26/11/20 at TwinMic beamline of Elettra Sincrotrone Trieste (Trieste, Italy).

Preliminary measures: dispersion has been attempted with ultrapure water, but agglomeration of particles was higher and single crystallites were not found. For XRF: the dispersed powder were firstly deposited on 100nm thick Si_3N_4 membranes and analysed; however Si emission line appears so strong that it creates a large background preventing detection of trace elements.

Observation conditions:

SEM Imaging: beam energy 10-25 KeV; secondary electron detector, backscattered electron detector.

EDX mapping and spectroscopy has been performed with the beam energy: 10 KeV, 20 KeV and 25 KeV; Probe current: ~ 1 nA

XRF Imaging: beam energy 2.209 KeV; X-ray Fluorescence and absorption imaging.

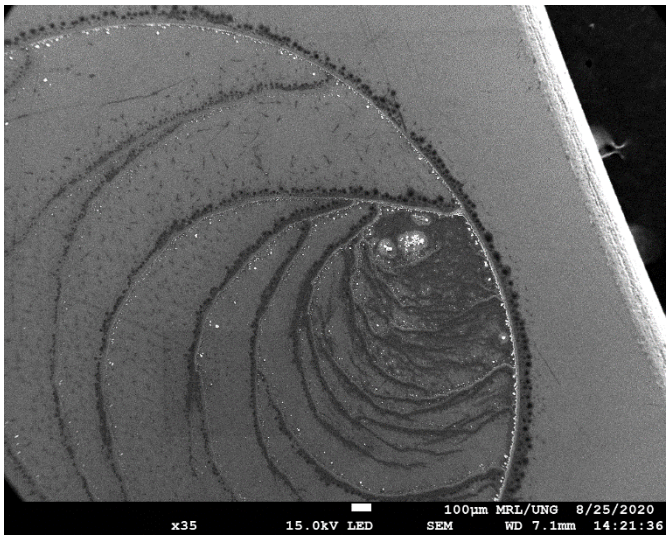
XRF mapping and spectroscopy: Beam energy: 2.209 KeV; Probe size: 600nm, step size 500nm

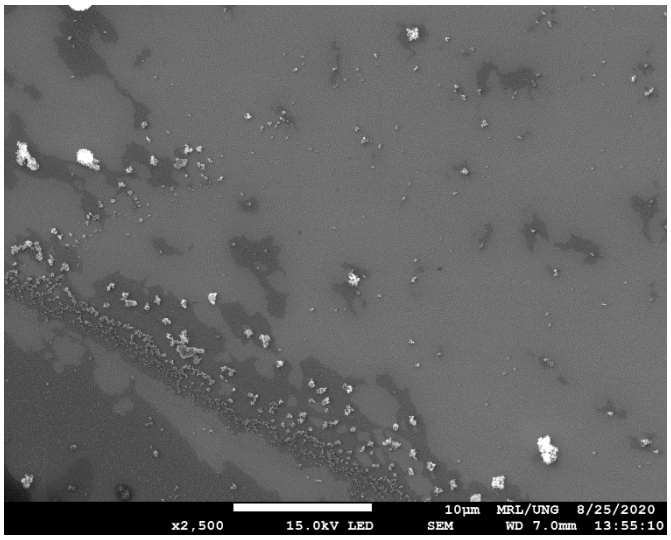
The main aim of the experiment is to verify if SEM/EDX analysis are effective in the investigation of the morphology and in the composition of the different primers. In particular, SEM is used to investigate the morphology of the primer nano-powder. EDX analysis is meant to show if elements present as dopant in the nominal composition (Cu, Ce, Y) are detected in the primer particles. XRF analysis is meant to show which elements are present in the nanoparticles agglomerates.

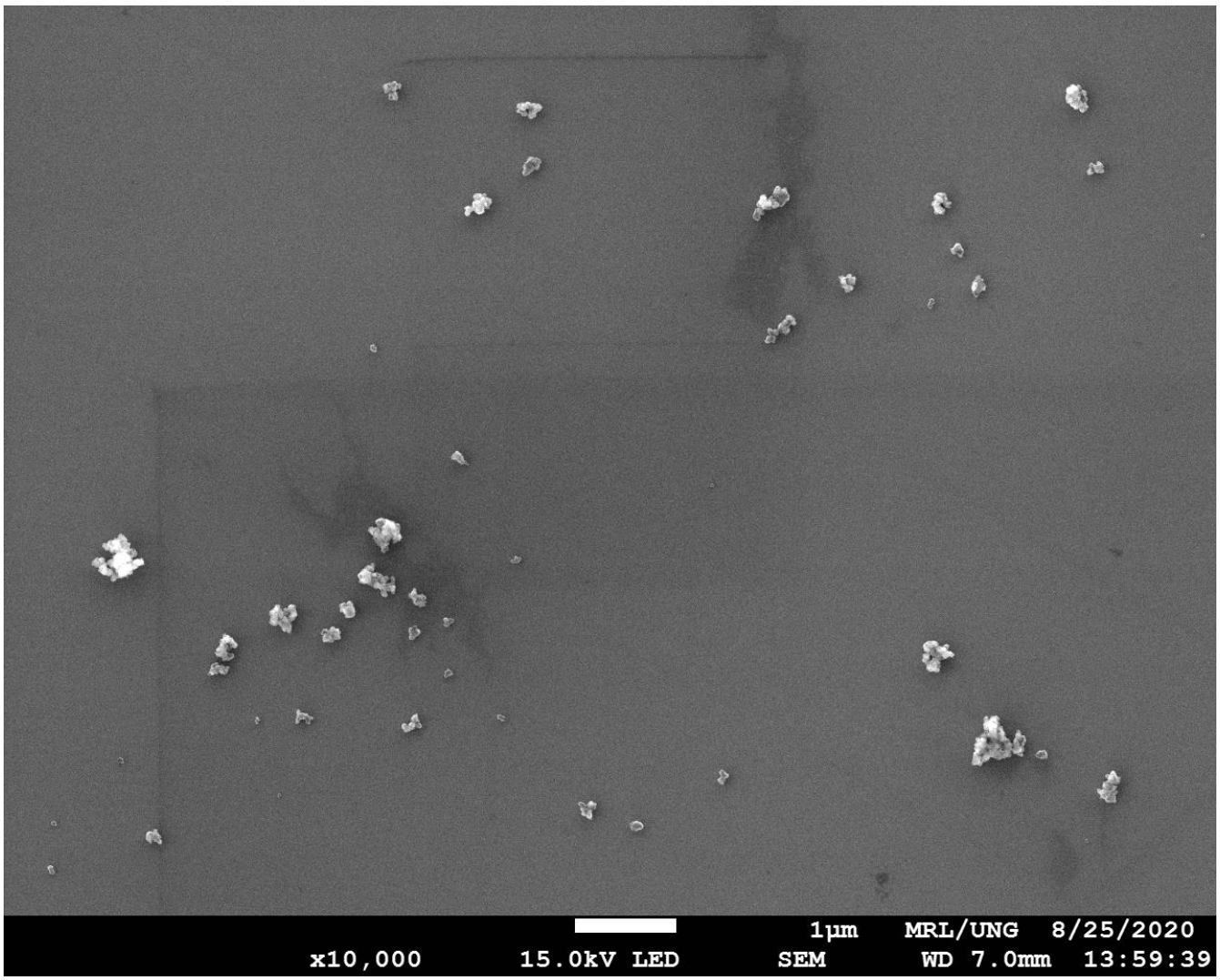
Results - morphology

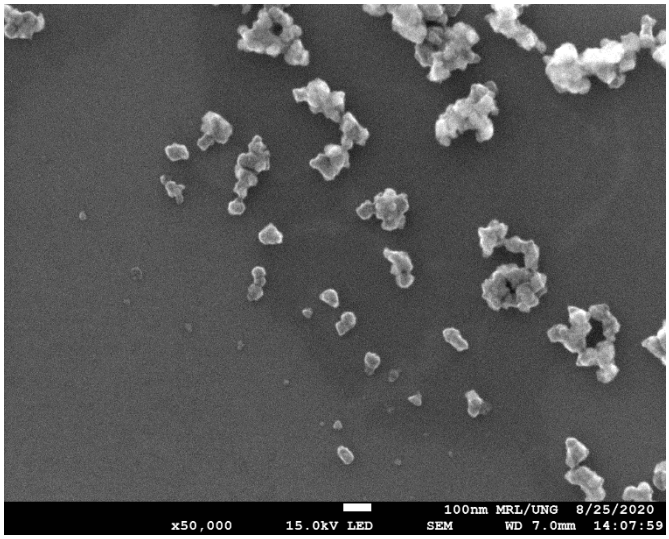
ADT10

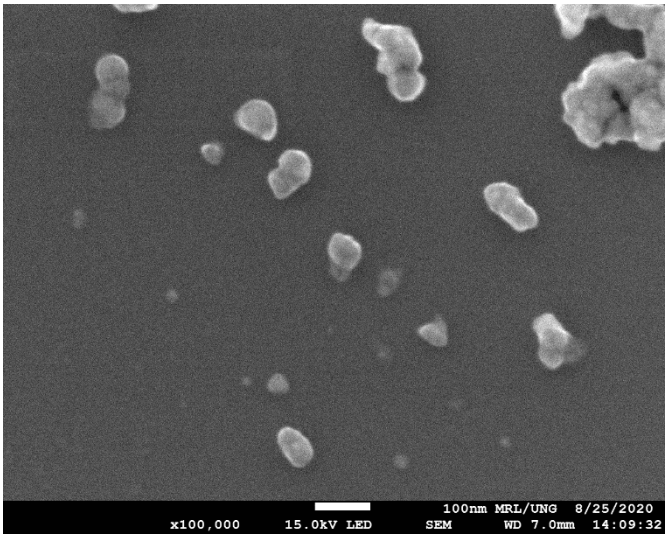
After dropcasting of ADT10 dispersed in ethanol on Si substrate, the particles are not homogeneously covering the Si surface. Instead, they mostly agglomerate in clusters of particles. Still, some of them are found isolated on the substrate.



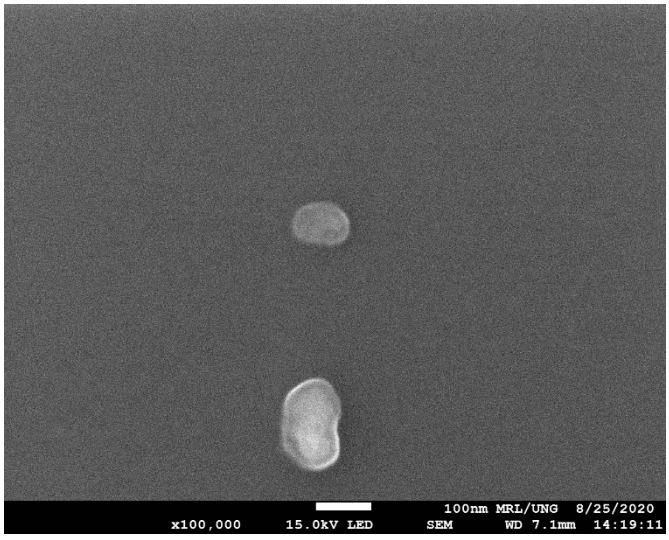


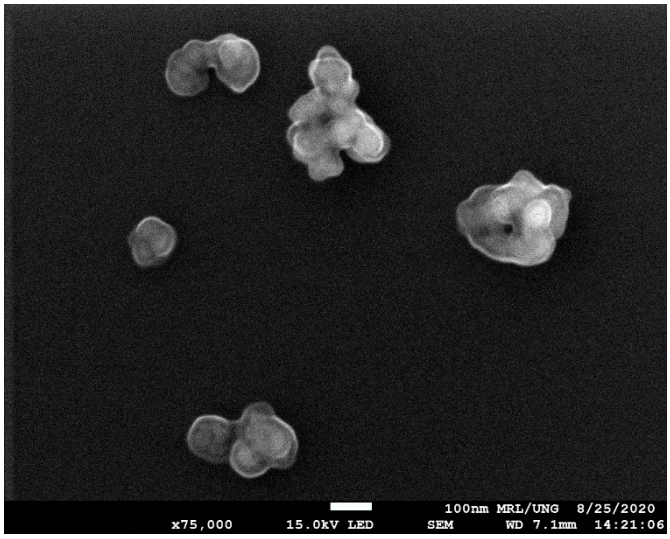






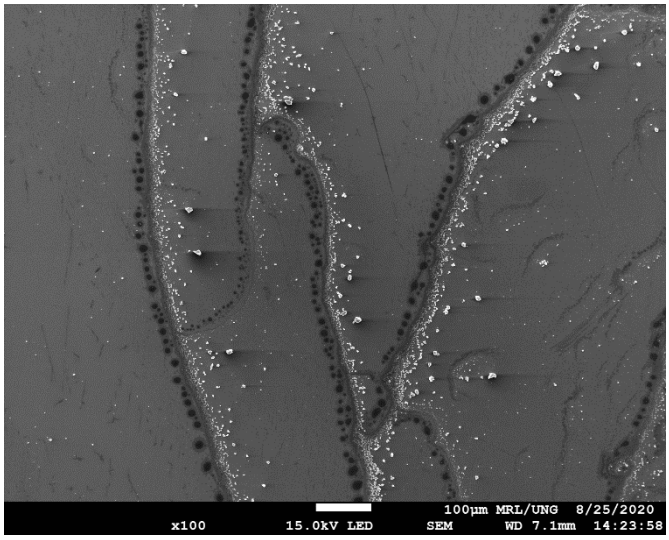
The cluster size typically is in the range from 80 nm to 2 micrometers. The objects recognized as single particles have size typically from 10 to 80 nm. In some cases a coating is observed surrounding the particles, as shown in the images below. This may be due to residuals of synthesis additives (tannins, phytic acid).

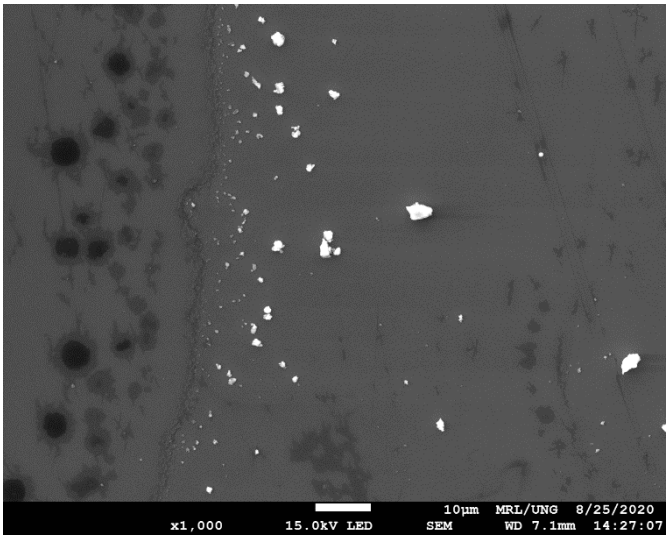


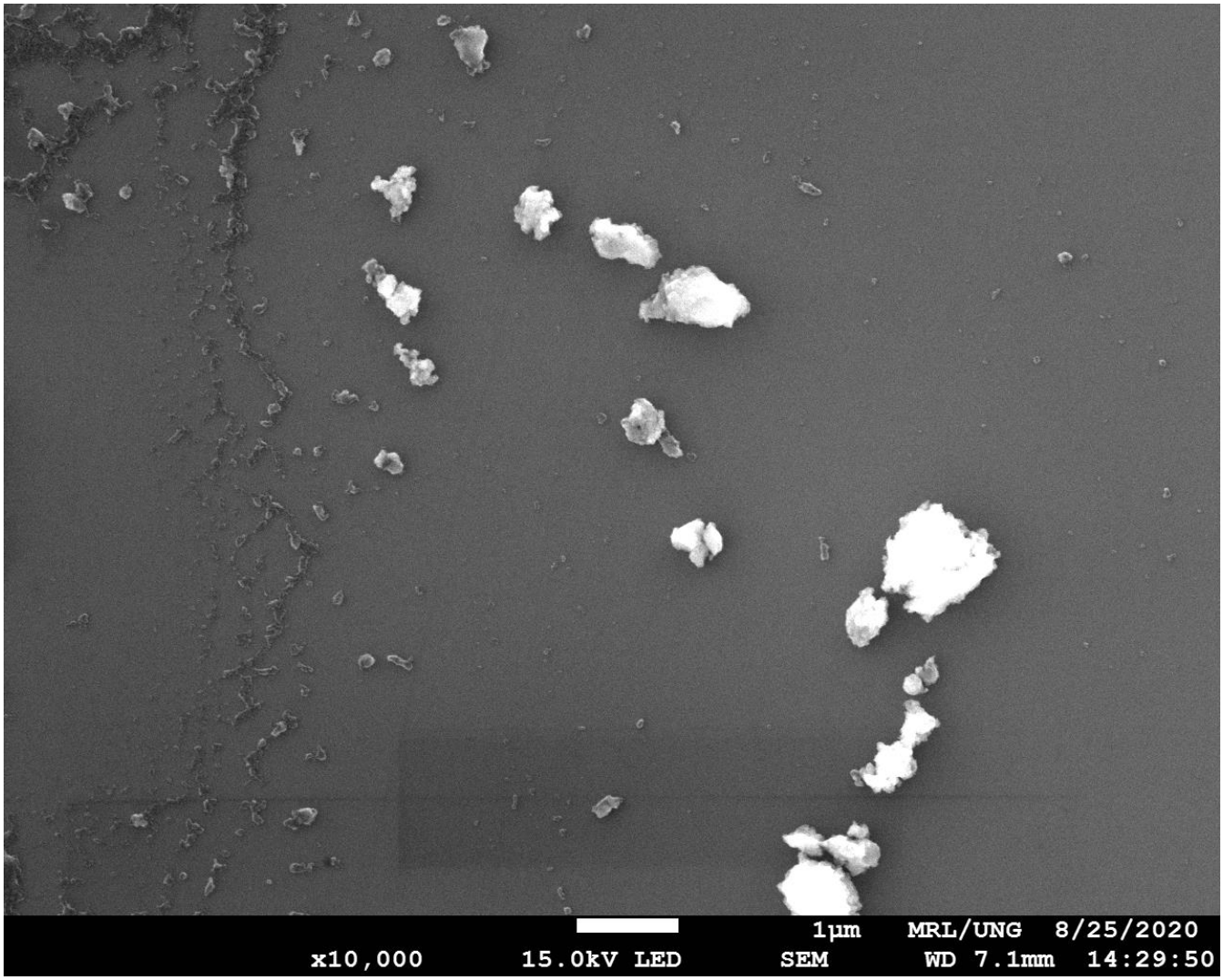


ADT16

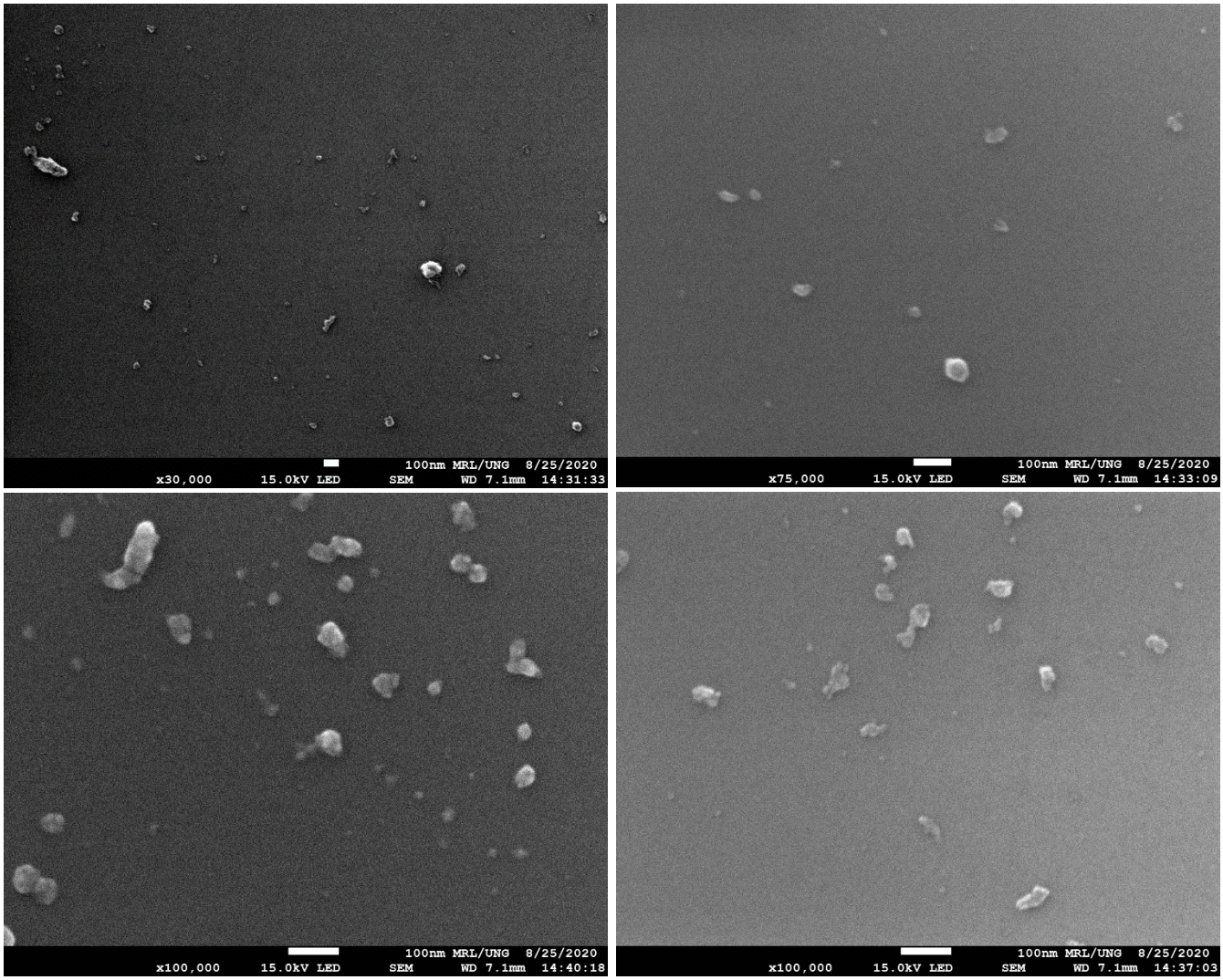
After dropcasting of ADT16 dispersed in ethanol on Si substrate, the particles are not homogeneously covering the Si surface. Instead, they mostly agglomerate in clusters of particles. Still, some of them are found isolated on the substrate.





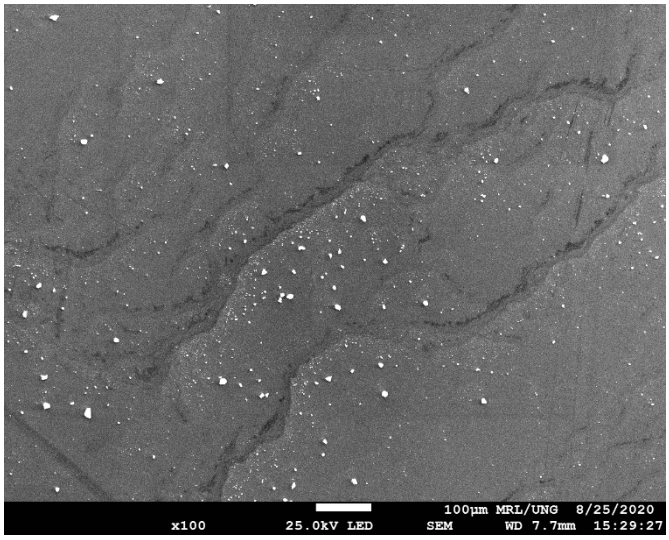


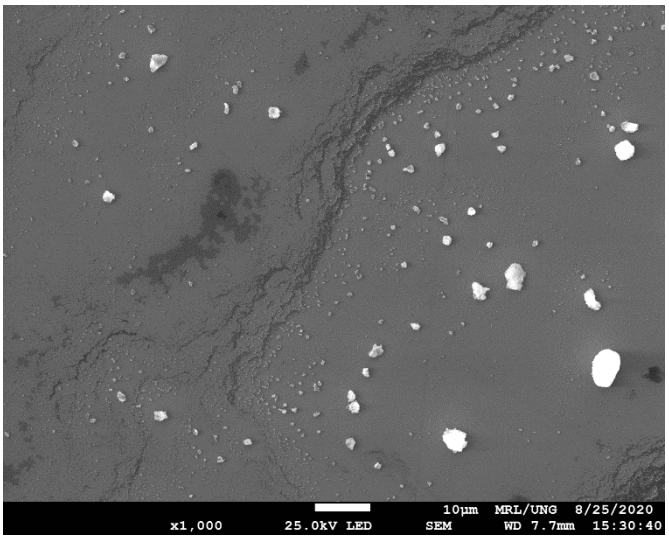
As for ADT10, the most of the particles are agglomerated in clusters with very variable size, roughly from 80 nm to 3 µm. Beside agglomerates, isolated particles are detected, with size mostly in the range 10 - 50 nm.

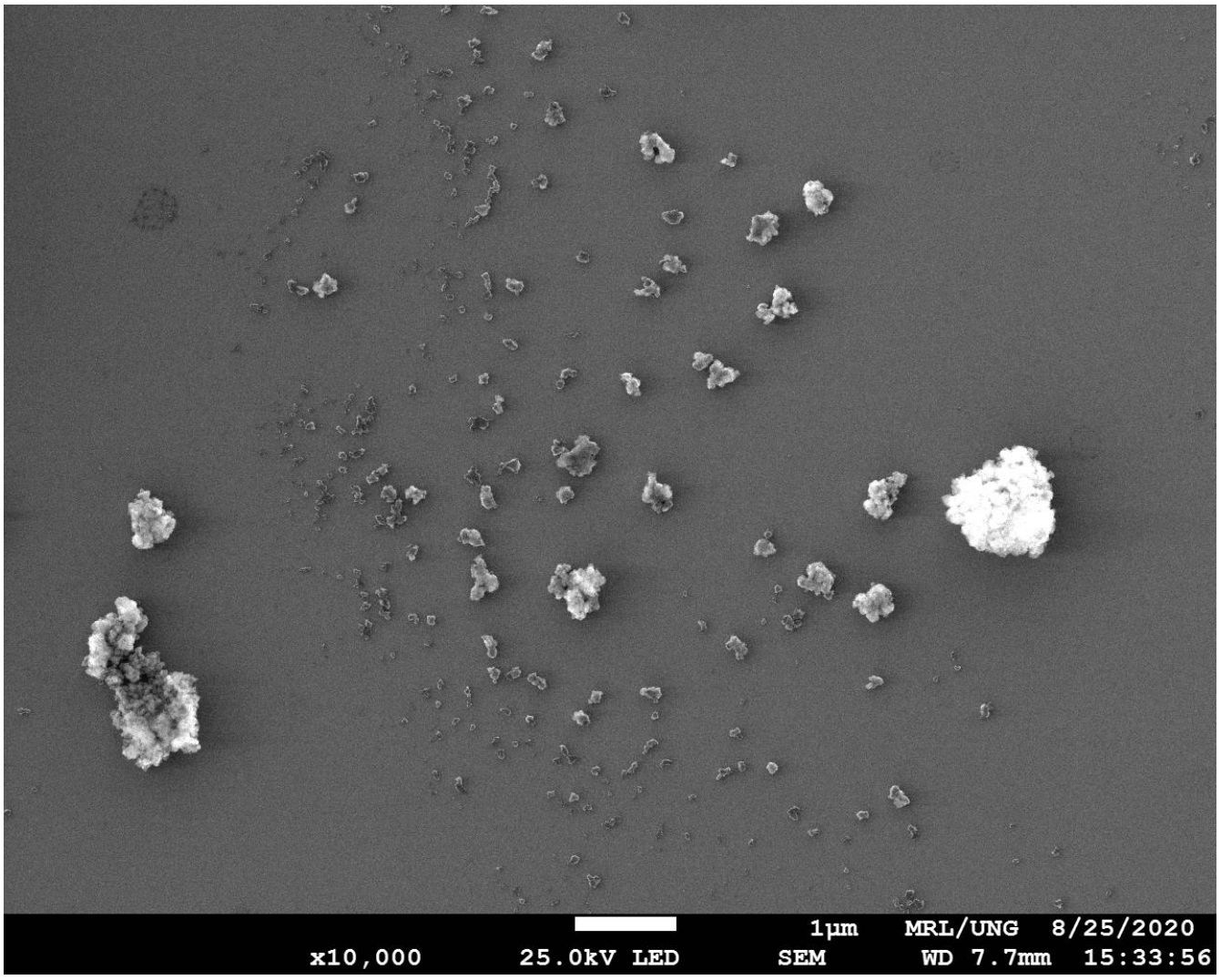


ADT18

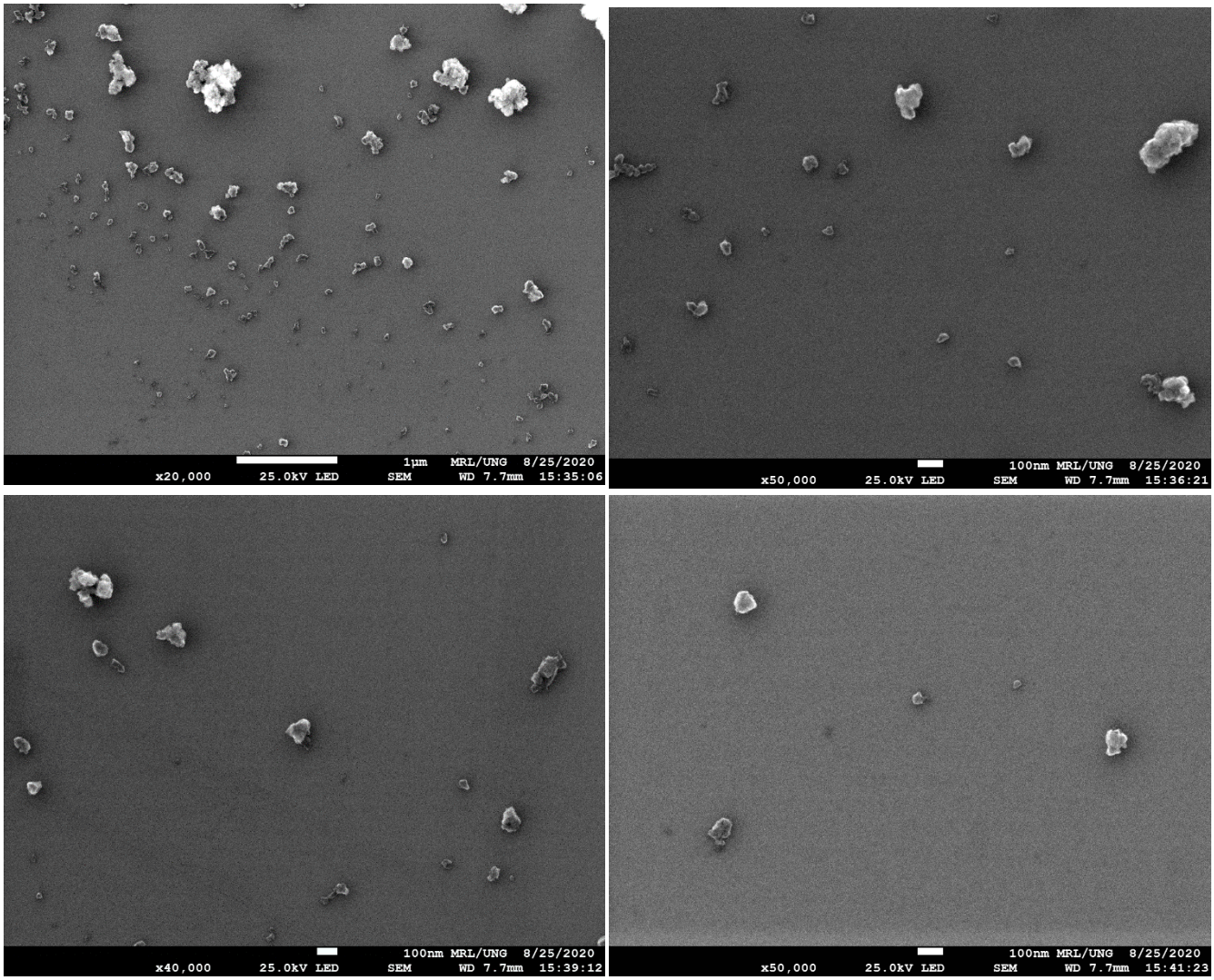
After dropcasting of ADT18 dispersed in ethanol on Si substrate, the particles are not homogeneously covering the Si surface. Instead, they mostly agglomerate in clusters of particles. Still, some of them are found isolated on the substrate.





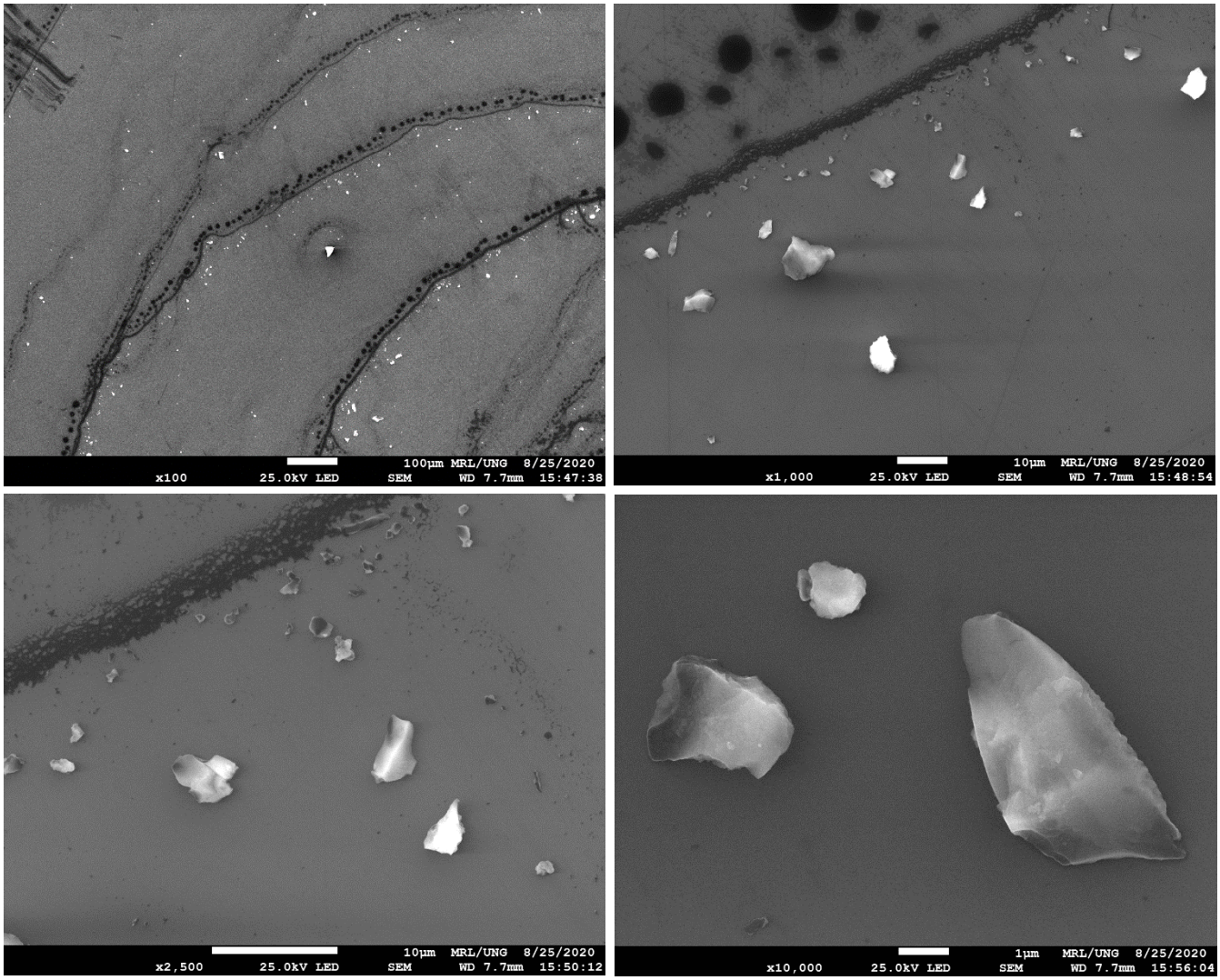


The clusters have size mostly in the range 100 nm – 5 μm. The isolated single particles have size in the range 10-90 nm.

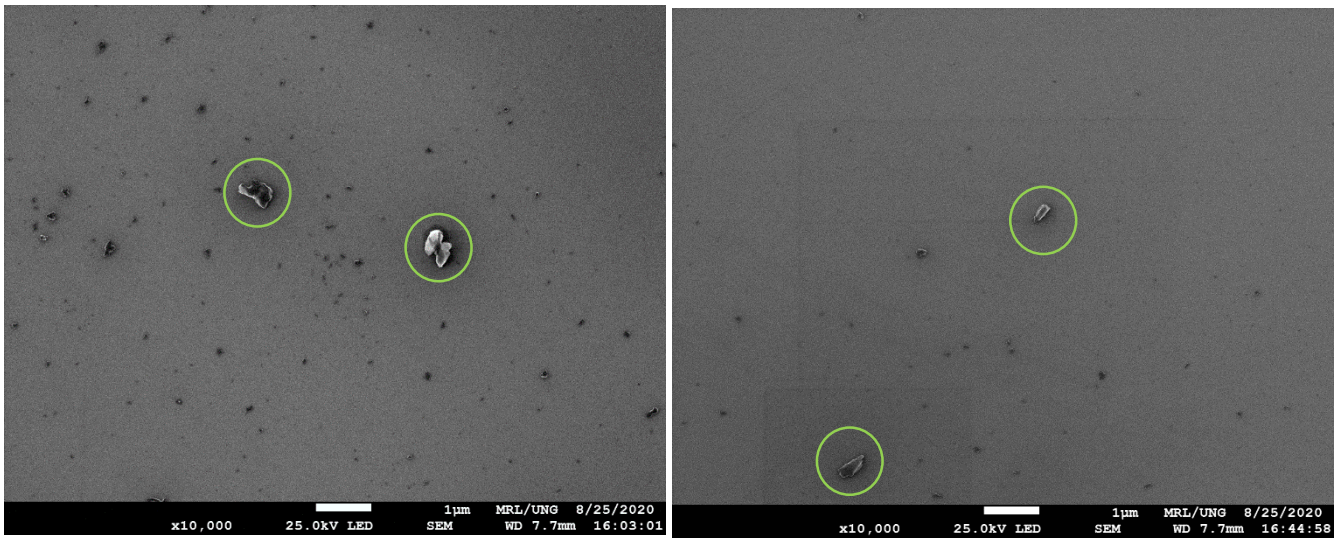


ADT21

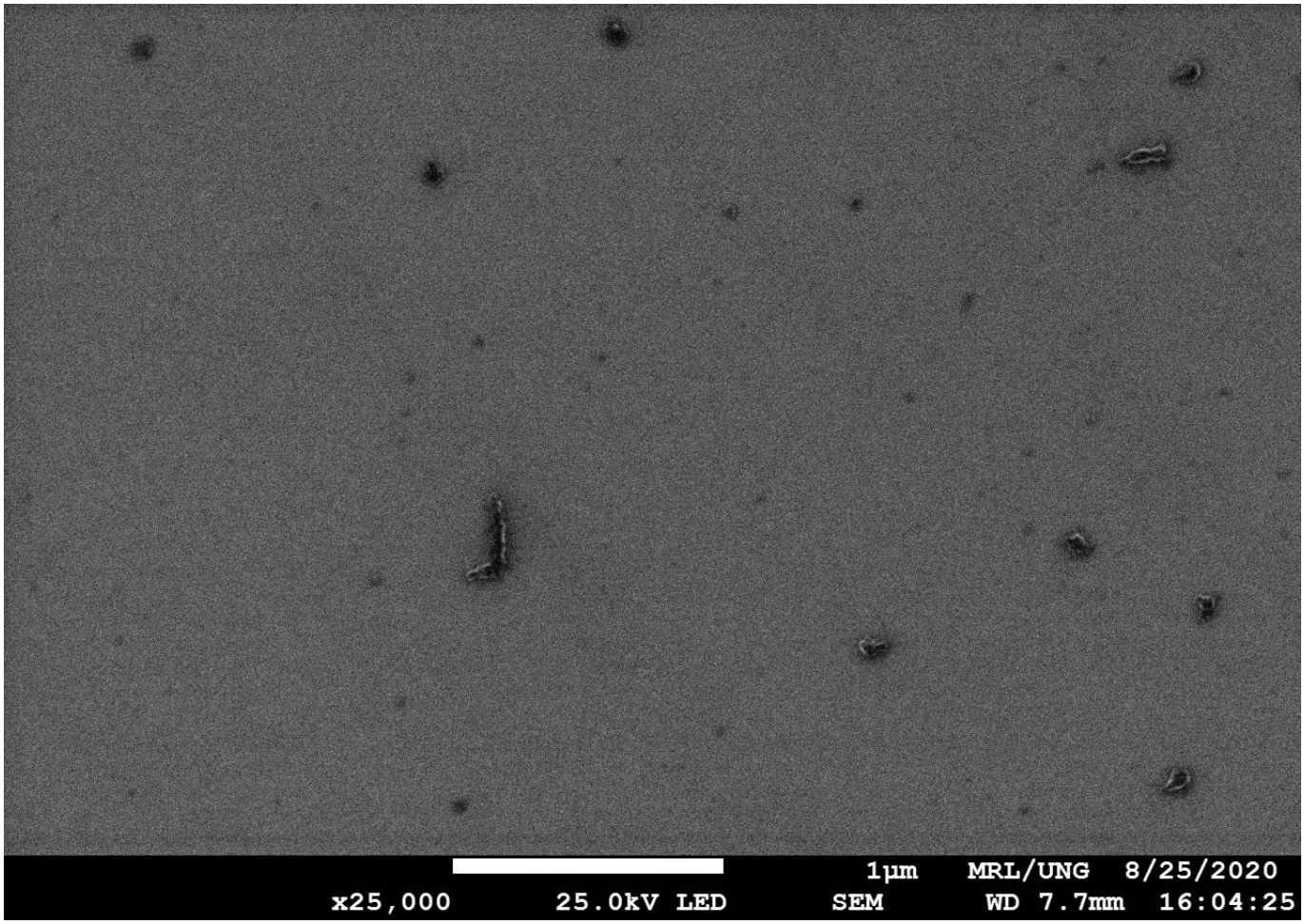
After dropcasting of ADT21 dispersed in ethanol on Si substrate, the particles are not homogeneously covering the Si surface. On contrary to the previous samples, in ADT21 the difference between large objects and single particles is more evident. Large objects in many cases display sharp edges and flat faces, and are not simply agglomerate of particles, but they look more like larger solid particles. Their typical size is mostly in the range 1 – 10 μm, but larger can also be found. Some images are below:



Beside the large objects, small particles are found on the substrate, which can be divided into two types. The first type are particles with size in the range 100 – 700 nm. Some of them are circled in green.



The second type are smaller, mostly less than 100 nm (see image below).



Results – Microanalysis

EDX microanalysis has been performed on the same specimens for ADT16 and ADT 21. The aim is to verify if EDX is effective in determining the nature of the particles and to detect the dopants.

ADT16

ADT16 Zr oxide based and doped with Cu and Ce. It should also contain phytic acid.

For quantification, the following lines have been used: Cu k (8.04 KeV), Ce L (4.84 KeV) P K (2.01 KeV), Na K (1.04 KeV). For Zr, see below.

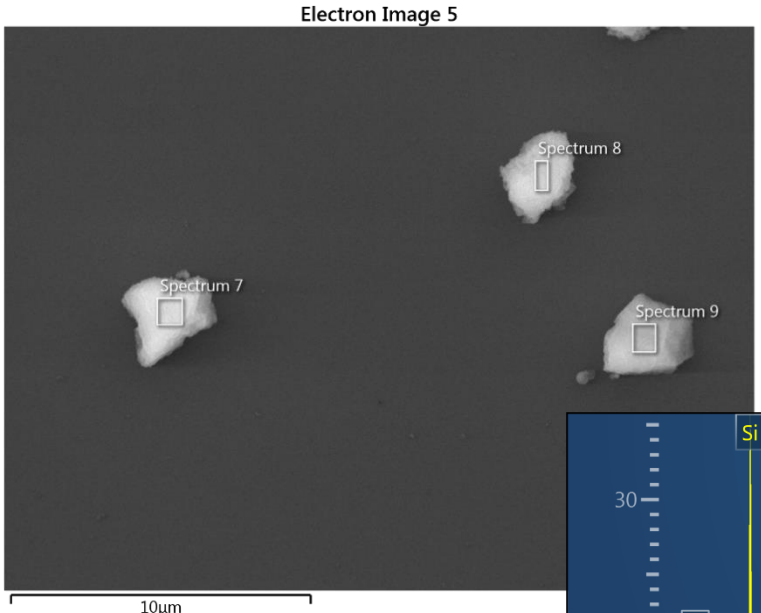
The analysis has been carried out both on large cluster and small NPs, in two different conditions:

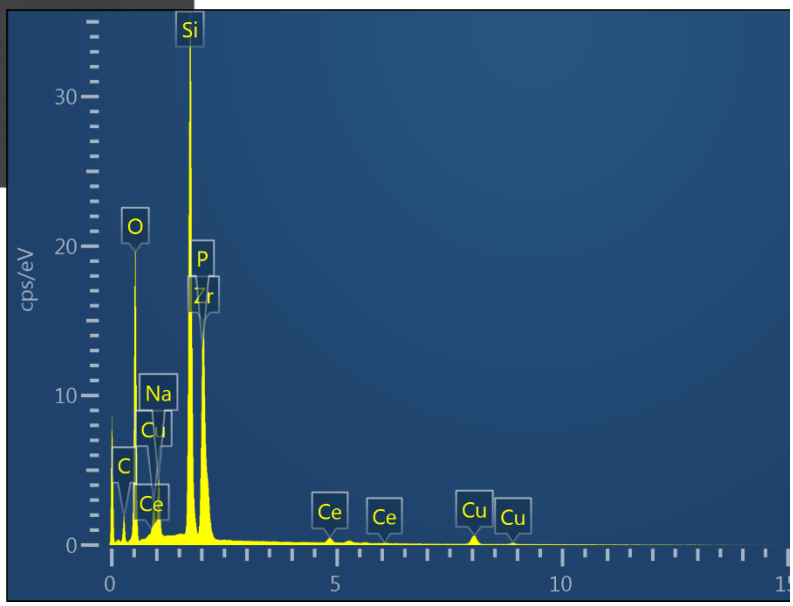
- at 20 KeV beam energy, considering Zr K line (15.75 KeV)

- at 10 KeV beam energy, considering Zr L line (2.04 KeV)

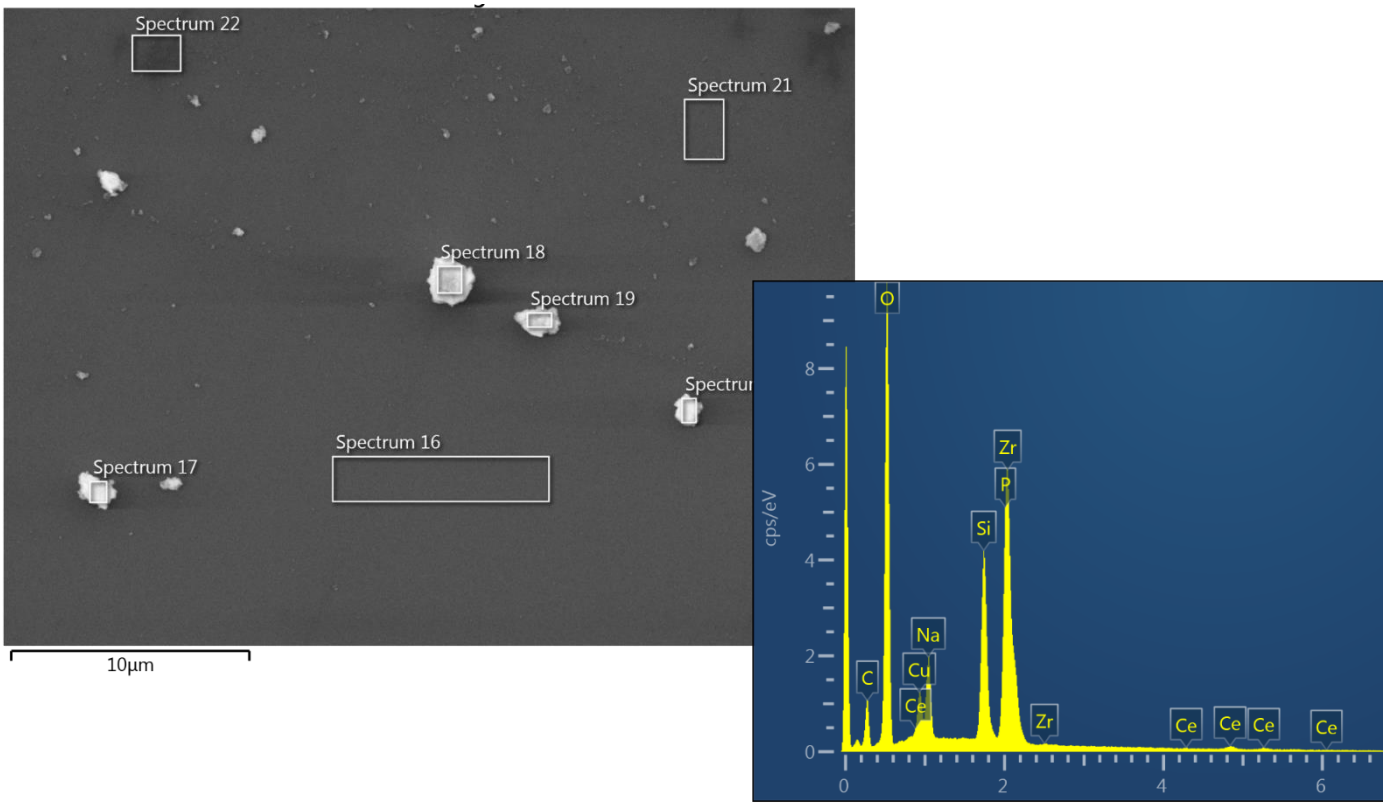
<u>Large clusters</u>

A typical EDX spectrum acquired on a large cluster (ca. 3 μm) with **20 KeV beam energy** is shown below, together with acquisition area:



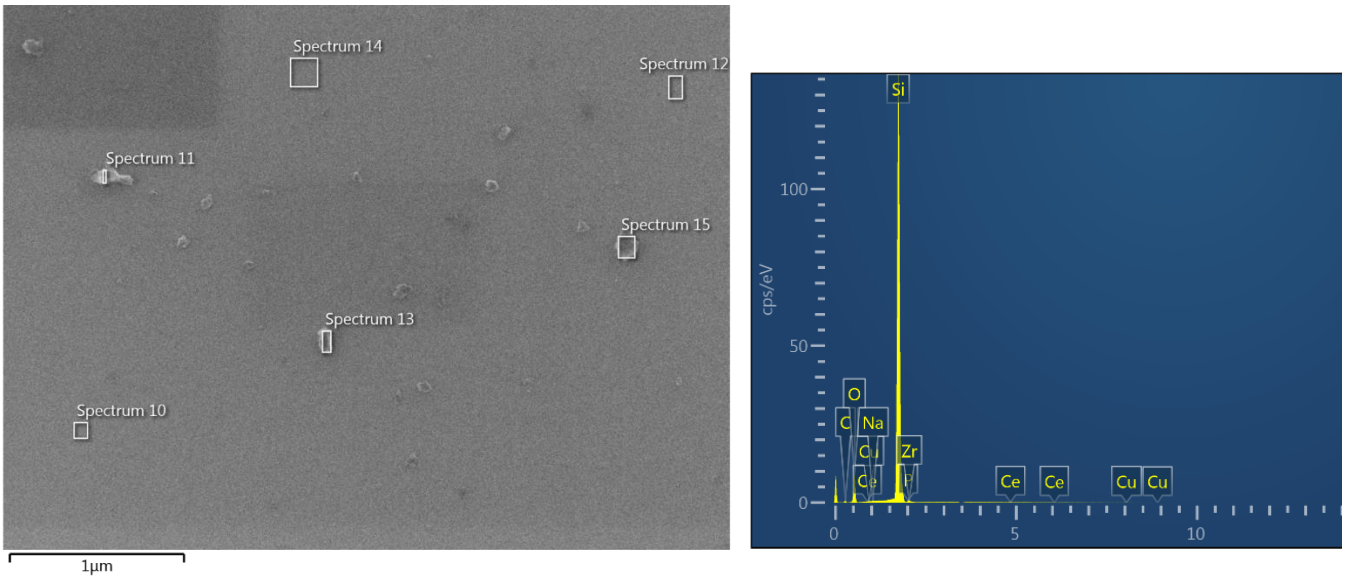


The microanalysis on large clusters has been performed also **at lower beam energy (10 KeV)**. In this case Zr L line is used, which overlap with P K line. A typical spectrum is shown below:



Small clusters or single NPs (50 - 100 nm)

A typical EDX spectrum acquired on NPs with **20 KeV beam energy** is shown below, together with acquisition area:



The highest peak is obviously Si, which is excluded from quantification. After that O and C are the most abundant. Zr signal is clearly present at low energy (Zr L) and typically observed also at high energy (Zr K).

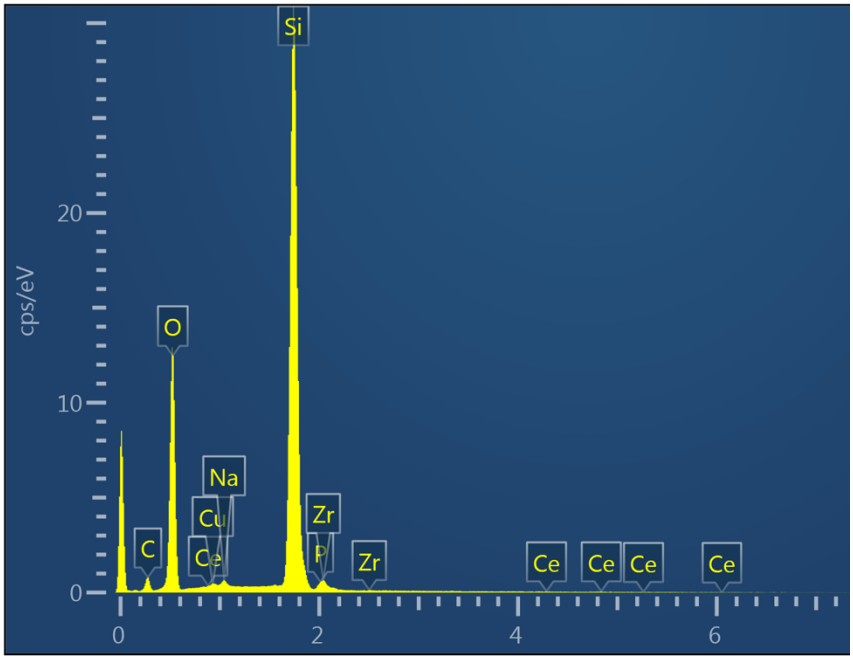
P signal is also detectable, with concentration lower than Zr.

Cu signal is many times not visible, but for some NP is detectable. Ce signal is not detected.

Hence, the information obtained in these conditions for the NPs are the following:

- they contain Zr and P
- in few cases, they contain Cu
- nothing can be said for Ce

By performing EDX **at lower beam energy (10 KeV)** the typical spectrum is shown below:



As before, the highest peak is Si, which is excluded from quantification. After that O and C are the most abundant. Zr signal is clearly present at low energy, together with P. By fitting the (Zr L + P K) peak, it is clear that both P and Zr are present.

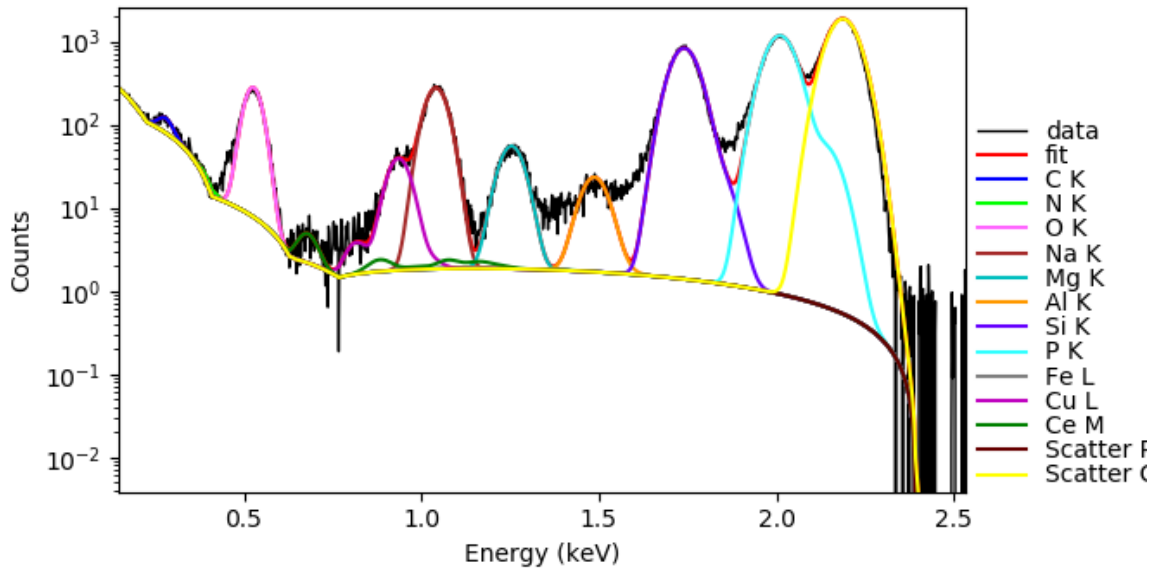
In the case of NPs the quantification is not reliable, not only for the absolute values, but in some cases a non zero concentration is assigned to elements with a non observable peak.

Na K peak is usually observed. Cu K is not observed, but Cu L is sometimes weakly detected. Ce is not detected.

In summary, in these conditions the information about NPs are the following:

- they contain Zr and P
- they contain Na
- In few cases, Cu is present
- nothing can be said for Ce

The detection of elements in the powder has been performed also by XRF. The spectra have been acquired on agglomerates with few μm size. A spectrum obtained from ADT16 powder is shown below:



In ADT16 we could clearly detect P, Si, Na and Mg. Traces of Al, Cu and Ce are detected. The used excitation energy (2.209 KeV), at the limit of the TwinMic energy range, did not allow to excite and detect Zr.

The detection of P and Cu is in agreement with what observed in EDX, and confirm their presence in the powder. The significant presence of Na is also confirmed. Two novelties are observed: 1) the presence of Mg, that was not detected before. 2) The presence of Si, which was not possible to characterize by EDX due to the substrate.

In summary, for ADT 16:

- for large clusters (80 nm – 3μm): beside C and O, they contain Zr, P, Na, Cu and Ce. Zr, P and Na are detected with concentration in the same order of magnitude. Cu and Ce concentration is lower, and Cu/Ce ratio is typically compatible with the expected nominal value.

The results obtained with the two beam energies (10 and 20 KeV) are substantially in agreement. If one wishes to avoid the fit of the (Zr L + P K), which can be source of larger uncertainty, one should select 20 KeV.

- for small clusters and single NPs (about 50-100 nm): beside C and O, they contain Zr, P, Na. Cu is in few cases weakly detected, while Ce is not detected. This doesn't mean that Cu and Ce are not there, but just that their signal, if there, is too low to be distinguished from noise.

- XRF spectroscopy, in addition to what observed by EDX (Cu and P), reveals the presence of Si and Mg in the powder.

ADT21

ADT21 is Zr oxide based and doped with Ce and Y. It should also contain lignosulfonates.

For quantification, the following lines have been used: Ce L (4.84 KeV), , P K (2.01 KeV), Na K (1.04 KeV), S K (2.31 KeV). For Zr and Y, see below.

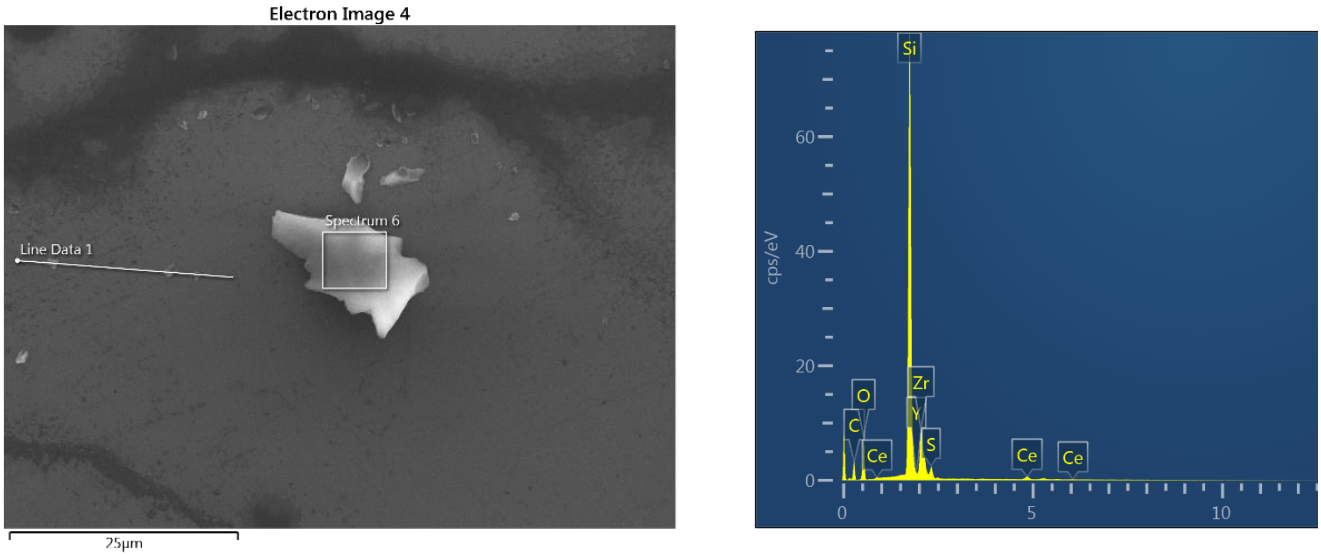
The analysis has been carried out both on large cluster and small NPs, in two different conditions:

- at 25 KeV beam energy, considering either Zr K line (15.75 KeV) or Zr L (2.04 KeV). Also for Y both Y L (1.92 KeV) and Y K (14.93 KeV) has been used, with very similar results.

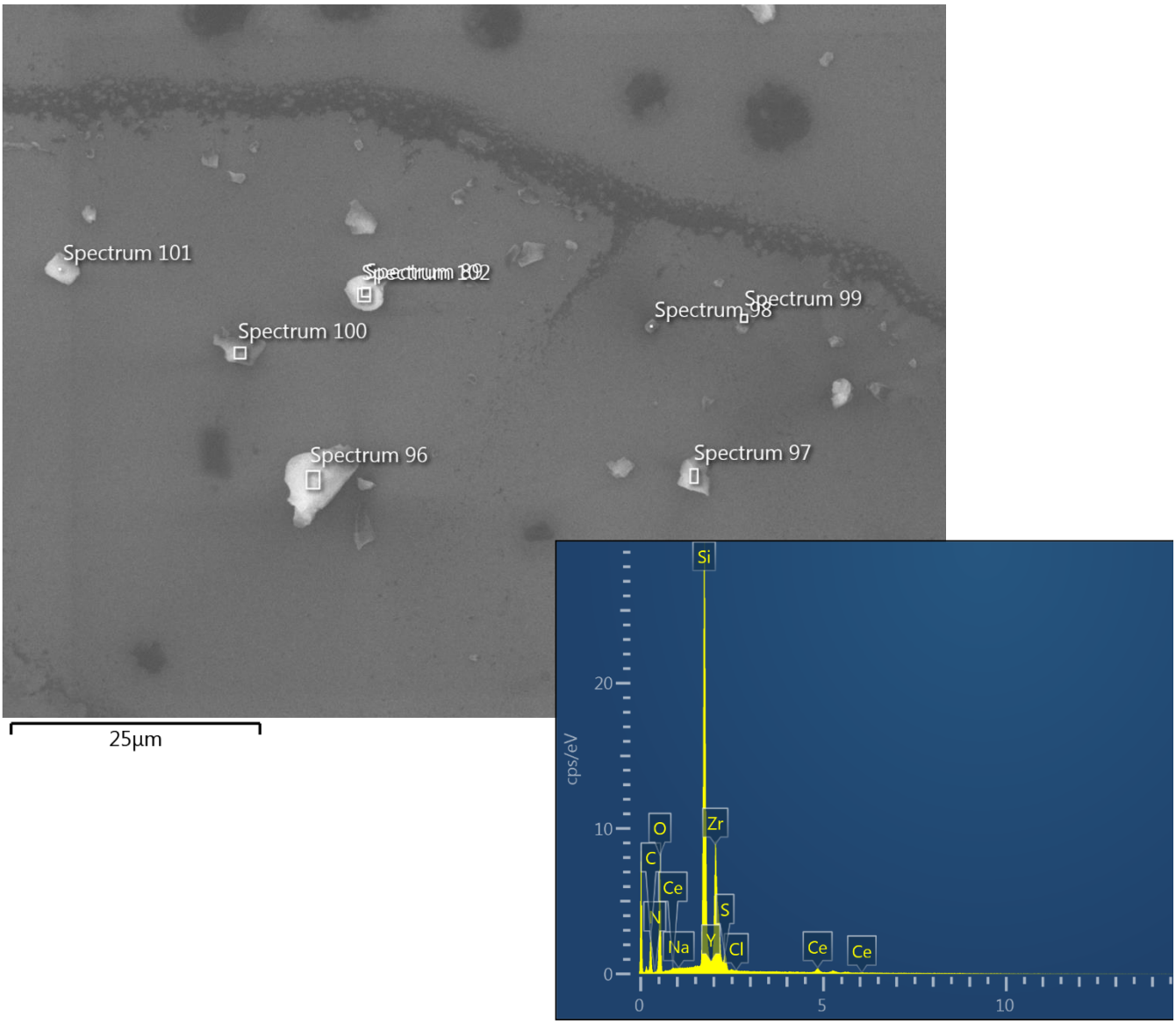
- at 10 KeV beam energy, considering Zr L and Y L lines

Large clusters

An EDX spectrum acquired on a very large chunk with **25 KeV beam energy** is shown below, together with acquisition area:



This exceptionally large cluster is not typical. As described before, in the sample large clusters are found, with size in the range 1-10 µm. In the following a typical spectrum acquired on one of these is shown, together with the acquisition area:



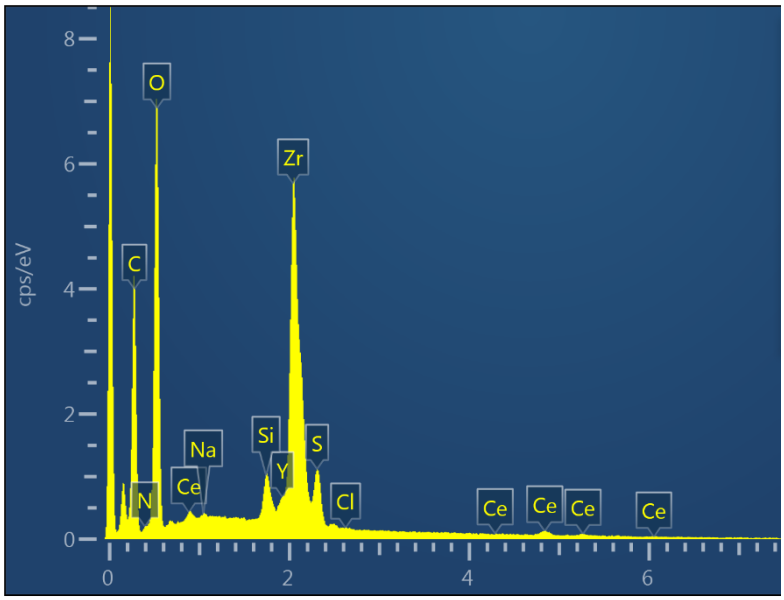
Beside Si, O and C, the following element are usually observed: Zr, Ce, Y, S. Traces (<0.1 at%) of Na, Cl are sometimes observed. N is also generally observed, with concentration about 1%.

Y concentration is problematic to quantify. The line at high energy (Y k, 14.93 KeV) is very poor in signal (consider that Y concentration is very low), while the low energy line (Y L, 1.92 KeV) is sitting between Zr L and Si K. Still, the Ce/Y ratio is in many cases close to the expected value.

At high beam energy (25 KeV) it is possible to quantify eithr with Zr K or Zr L. To analyze the differences in the result, some spectra acquired on large clusters have been compared.

The only relevant difference is the concentration of Zr itself, which can varies significantly. Zr L line is much more intense, but suffers of overlapping with S and Y. For large clusters (e.g. spectrum 96, above) the two results are similar. For small cluster is not possible to conclude which one is more reliable.

The EDX analysis on large clustershas been conducted also with **low beam energy (10 KeV).** One example is shown below.



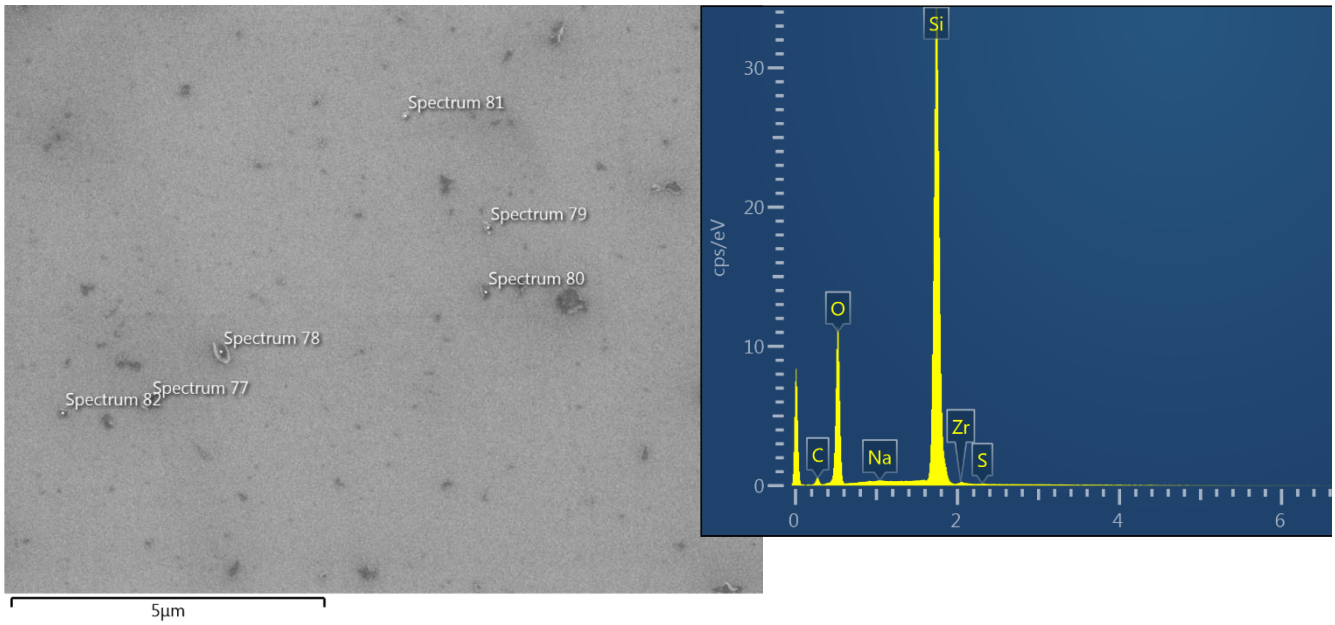
Medium particles

The analysis of medium particles (100 – 700 nm) has been conducted at 10 and 25 KeV. It brings to similar results:

- Zr is present, together with S.
- Ce is mostly not observed, with few exceptions
- Y is not detectable. The high energy line Y K, which is accessible at 25 KeV, has too low intensity for particle with this size. On the other hand, the low energy line Y L is strongly overlapped with Zr and on the tail of the Si K line from the background, which for particles of this size is very strong.

Small particles

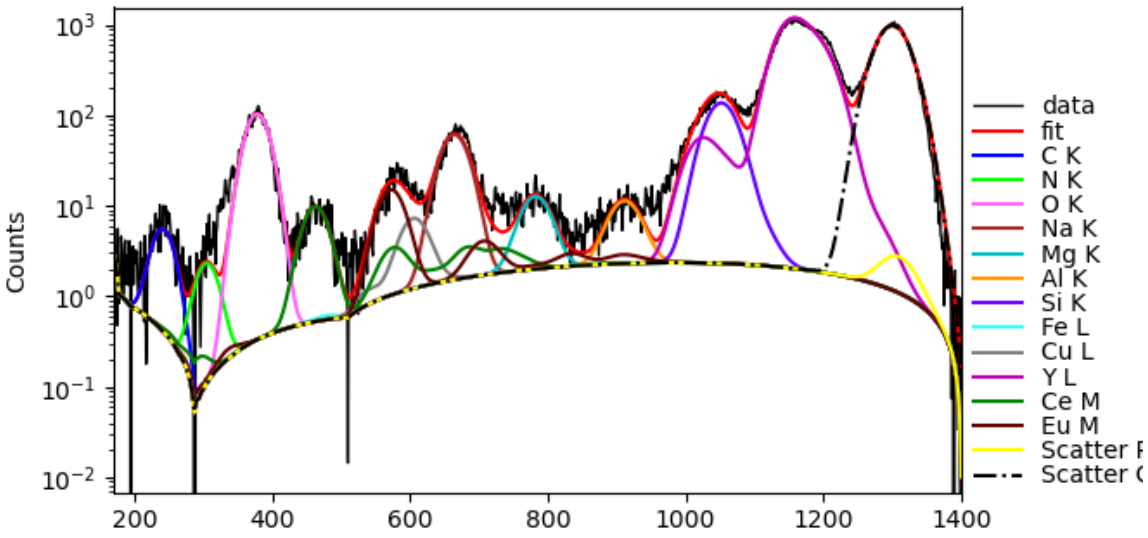
For small particles (<100 nm) the EDX analysis has been carried out only at 10 KeV, with the aim to verify if they are made of Zr. An example is given below:



The results show that:

- on the most of them Zr signal is detectable, as well as S signal. This means that most of them contains Zr, and are probably belonging to the same phase of larger particles.
- Ce and Y are not detected. However, considering that the signal intensity of the major element (Zr) is already very weak, they are not expected to be detectable.

XRF analysis has also been used to characterize the composition of ADT21. The spectra have been acquired on agglomerates with few μm size. A representative spectrum is shown below:



In ADT21 we could detect Y, Si, Mg, Na, traces of Al, possibily traces of Eu and Cu, Ce and O. The used excitation energy (2.209 KeV), at the limit of the TwinMic energy range, did not allow to excite and detect Zr.

Beside the confirmation of the presence of Y and Na, we remark again the detection of Mg (not observed by EDX) and of Si. Moreover, it is interesting the high sensitivity to Y, which does not suffer for overlapping with Zr in the case of XRF. This can be a great advantage if the main point of the analysis is the Y concentration.

In summary, for ADT 21:

- for large clusters (1 – 10 μm): beside C and O, they contain Zr, S, Ce and Y. Ce and Y are usually found with similar concentrations, in agreement with the nominal.

- for medium (100-700 nm) particles: Zr and S are clearly detected. Ce is detected only in few cases, while Y is not.

- for small particles (<100 nm): Zr is still detected, at least the low energy line Zr L. S is also detected. Ce and Y are not detected.

- The presence of Zr in medium and small particles is compatible with the hypothesis they belong to the same phase of large clusters.

- XRF spectroscopy, in addition to what observed by EDX (Y and Ce), reveals the presence of Si and Mg in the powder.

Summary about the analytical capability of SEM, EDX and XRF in these experimental conditions:

- dipersion of these powders in ethanol is better than in water. The dropcasting onto SiO_2 substrate allows for observation of isolated particles.

- SEM is effective in the analysis of particle morphology

- EDX is effective in detecting the presence of the major element (Zr) in the particles, also for the ones <100 nm. XRF at TwinMic is not suitable for Zr, due to the accessible photon energy limited at 2.209 KeV.

- The dopants (Cu, Ce, Y) can be recognized by EDX on the largest particles (1 – 10 μm). A semi-quantitative analysis on the dopant concentration is possible in some cases.

- For the sub-micrometric particles the detection is possible for dopants with high concentration (e.g. Cu in ADT16) but difficult or impossible for dopants with lower concentration (e.g. Ce or Y)

- XRF has lower lateral resolution than EDX (ca 0.5 μm), but due to its high sensitivity for low energy X-ray emission, it gives some advantages for light element detection (e.g. Mg). Moreover, it is significantly suitable for analyis of Y L low energy line, which for EDX is made difficult by overlapping with Zr.

Advices for future analysis:

- XRF can be used on other beamlines, where the energy range is more extended. In this case, Zr detection is allowed.

- for submicrometric particles (also <100 nm) EDX in a TEM apparatus will allow for chemical analysis with higher spatial resolution and more accuracy in the quantification.

This report has been written by Mattia Fanetti and Alessandra Gianoncelli, 04/11/2021