LABORATOIRE NATIONAL DE MÉTROLOGIE ET D'ESSAIS

LABORATOIRE DE TRAPPES
29, avenue Roger Hennequin - 78197 Trappes Cedex
Tél : 01 30 69 10 00 - Fax : 01 30 69 12 34

TEST REPORT

Requesting party:	**ASS VEILLE INF CIV ENJ NANOSCI NANOT** Maison des associations 8, rue du Général Renault 75011 PARIS FRANCE
Order date and reference:	Proforma Invoice no. DEV2414082-V2 on 16 December 2024
Purpose:	Study of the potential release of pearlescent pigment (particle size and surface chemistry) on two samples. Characterization by SEM and elemental analysis (EDX) of 8 other samples of cosmetic products.

1 SAMPLES RECEIVED AND INFORMATION RECEIVED

1.1 OBJECTIVE OF THE STUDY

The aim of the study is to :

1) Study the potential release of nanoparticles (including particle size measurements and surface chemistry analysis) from pearlescent pigments contained in two cosmetic products.
2) Characterize by SEM and elemental analysis (EDX) of 8 other samples of cosmetic products.
3) XPS analyses performed by UVSQ (see appendix 2) on S7 and S8 to identify any silicate or aluminate coating around TiO_2 layers on mica.

From the received cosmetic products, this will involve:

1) Preparing the particle population so as to perform reliable measurements.
2) Identifying the chemical nature of the observed particles using elemental analysis by EDX (Energy-dispersive X-ray spectroscopy).
3) Carrying out measurements on the size, size distribution and shape (qualitative description) of the extracted population by SEM (Scanning Electron Microscopy).
4) Identifying the chemical nature of molecules present on TiO_2 particle surface using XPS (X-ray Photoelectron Spectroscopy).

Recommendation made in standard NF EN ISO 19749:2023 03 (T16-403) "Nanotechnologies - Determination of particle size and shape distribution by scanning electron microscopy" will be followed.

The minimum Féret diameter will be measured for each particle. This measurand is particularly well suited to the European commission recommendation on the definition of nanomaterial given in the next page. If the smallest dimension of the particle is in the size range 1 nm to 100 nm, then it is considered as a nanoparticle.

The Platypus™ software platform (POLLEN Metrology) will be used to extract information associated with particle size from the taken SEM images.

Test report continued on next page

1.2 REMINDER OF THE DEFINITIONS

- **European Commission Recommendation of 10 June 2022 on the definition of nanomaterial (2022/C 229/01)**:

  " 'Nanomaterial' means a natural, incidental or manufactured material consisting of solid particles that are present, either on their own or as identifiable constituent particles in aggregates or agglomerates, and where 50 % or more of these particles in the number-based size distribution fulfil at least one of the following conditions:
  (a) one or more external dimensions of the particle are in the size range 1 nm to 100 nm;
  (b) the particle has an elongated shape, such as a rod, fibre or tube, where two external dimensions are smaller than 1 nm and the other dimension is larger than 100 nm;
  (c) the particle has a plate-like shape, where one external dimension is smaller than 1 nm and the other dimensions are larger than 100 nm.

  In the determination of the particle number-based size distribution, particles with at least two orthogonal external dimensions larger than 100 µm need not be considered.
  However, a material with a specific surface area by volume of < 6 m^2/cm^3 shall not be considered a nanomaterial. "

  (11) The definition should not cover large solid products or components, even when they have an internal structure or a surface structure at the nanoscale, such as coatings, certain ceramic materials and complex nanocomponents, including nanoporous and nanocomposite materials. Some of these products or components may have been manufactured by using nanomaterials and may even still contain them.

- **Cosmetic Regulation No. 1223/2009**: defines a nanomaterial as an "*insoluble or biopersistant and intentionally manufactured material with one or more external dimensions, or an internal structure, on the scale from 1 to 100 nm*".

1.3 SAMPLES RECEIVED

10 samples have been received at LNE on December 2024 and February 2025.

Table 1 gives information about these samples. According to the labels, 9 samples contain mica.

Reminder:

The general formula of the mica can be chemically given by $X_2Y_{4-6}Z_8O_{20}(OH, F)_4$,

in which

X is K, Na, or Ca or less commonly Ba, Rb, or Cs;

Y is Al, Mg, or Fe or less commonly Mn, Cr, Ti, Li, etc.;

Z is mainly Si or Al, but also may include Fe^{3+} or Ti.

Structurally, micas can be classed as dioctahedral (Y = 4) and trioctahedral (Y = 6). If the X ion is K or Na, the mica is a common mica, whereas if the X ion is Ca, the mica is classed as a brittle mica.

Table 1 : *information about samples received. Ingredients of interest indicated on the label are reported.*

n°	Reception	Reference	Description	Ingredients declared by supplier						
				Mica	Iron Oxide	Titanium Oxide	Silica	Other oxides	Organic Pigments	Others
S1	19/12/2024	NOCIBE, poussières d'étoiles, lot Q122	Glitter powder	yes	CI 77491	CI 77891,	Yes	Tin Oxide (SnO_2)		
S2	19/12/2024	SEPHORA, 02 SPICY SUNSET, lot 42780	Bronzing powder	yes	CI 77491 CI 77492 CI 77499	CI 77891		Tin Oxide (SnO_2)	Yellow 5 CI 19140 Red 7 Lake CI 15850	
S3	19/12/2024	AROMA ZONE, nacre minérale ref: 03052	Golden powder	yes	CI 77491	CI 77891				
S4	06/01/2025	René Furterer, OKARA blond	Brightening spray for hair	yes	CI 77491	CI 77891				
S5	06/01/2025	L.A. Girl Shimmer spray gold réf GFS918	Finishing spray for face & body	-		CI 77891		Tin Oxide (SnO_2) Alumina		
S6	06/01/2025	Adopt Wonderful Intense	Glittery eau de parfum	yes	CI 77491	CI 77891				
S7	06/01/2025	SI SI la paillette	Glitter powder (hair & body)	yes	CI 77491	CI 77891				
S8	06/01/2025	MaCosmetoPerso, MICA OR	Pigment for homemade cosmetics	yes	Fe_2O_3	CI 77891				
S9	06/01/2025	SLA SUN BAY Terre de soleil	bronzing powder	yes	CI 77491 CI 77492 CI 77499	CI 77891			Yellow 6 Lake CI 15985 Ultramarines CI 77007	Talc Zinc Stearate
S10	11/02/2025	Le Petit Marseillais	Pearly moisturizing milk	yes		CI 77891	yes		Yellow 5 CI 19140 Yellow 6 Lake CI 15985	

2 EXPERIMENTAL PROTOCOLE

2.1 SAMPLE PREPARATION

The specific procedure "332TP0522 - Procédure de préparation des échantillons pour la microscopie électronique à balayage (MEB) » ("Procedure for preparing samples for scanning electron microscopy (SEM)") was followed.
The preparation of samples for SEM electron microscopy and EDX elemental analysis depends on the nature of the products being analysed. The protocol followed will be specified in the section “sample preparation”.

2.2 TESTS CONDITIONS

- SEM images

  The specific procedure "322TP0521 – Procédure d’acquisition des images MEB et d’identification chimique par EDX des nanoparticules" ("*Procedure for the acquisition of SEM images and chemical identification of nanoparticles by EDX*") was followed.

  SEM images were taken using a Zeiss Ultra-Plus scanning electron microscope (SEM) equipped with In-Lens detector or JEOL IT 800 SEM equipped with UHD detector. The JEOL low vacuum mode was also used in some cases.

  The accelerating voltage used was EHT = 3 kV and the working distance was WD = 3.0 mm.

- SEM measurements and data processing

  The specific procedures "322TP0523 – Mode opératoire pour la mesure des propriétés dimensionnelles de nanoparticules par MEB – Traitement des données" ("*Procedure for measuring the dimensional properties of nanoparticles by SEM - Data processing*"), "322TN0501 – Détermination des paramètres dimensionnels caractéristiques d’une population de particules à partir d’images de microscopie (AFM, MEB) " ("*Determination of the characteristic dimensional parameters of a population of particles from microscopy images (AFM, SEM)*") and "322TP0525 – Evaluation de l’incertitude de mesure associée aux paramètres dimensionnels caractéristiques d’une population de nanoparticules mesurées par MEB" ("*Evaluation of the measurement uncertainty associated with the characteristic dimensional parameters of a population of nanoparticles measured by SEM*") were followed.

  The measurements were carried out on the SEM images using Pollen Metrology's Platypus™ platform.

- Elementary analyses by EDX

  The specific procedure "322TP0521 - Procédure d’acquisition des images MEB et d’identification chimique par EDX des nanoparticules" ("*Procedure for the acquisition of SEM images and chemical identification of nanoparticles by EDX*") was followed.

  The elementary analysis, which provides information on the atoms constituting the particles, is carried out using the EDX technique: a detector installed on the electron microscope gathers the X-ray photons emitting from the particles. The electron microscope is equipped with an Oxford Instruments EDX system comprising one Ultim Max detector with a window.

3 STUDY OF RELEASE OF NANOPARTICLES FROM PEARLESCENT PIGMENTS

3.1 SAMPLE S5 : L.A. GIRL SHIMMER SPRAY GOLD REF. GFS918

A picture of the studied sample is shown in Figure 1.

Figure 1*: Picture of the sample S5 reference L.A. GIRL SHIMMER SPRAY GOLD REF. GFS918*

The presence of titanium dioxide (CI 77891), Tin oxide (SnO_2) and alumina is indicated by the producer on the label.

3.1.1 Preparation of the sample

The sample preparation protocol is as follows :

- The bottle is shaken as indicated on the label.
- The product is sprayed 10 cm away onto a silicon wafer for SEM observation and EDX analysis.

Test report continued on next page

3.1.2 SEM measurements and EDX analyses performed on particle deposition.

Some examples of SEM images performed at magnification x250 and x1500 are shown on Figure 2.

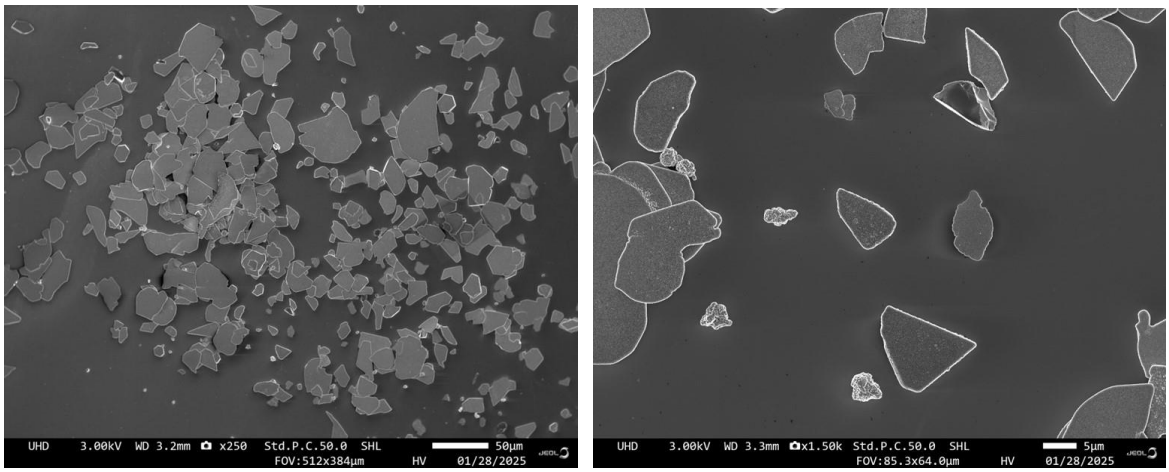


Figure 2*: SEM image of the sample reference S5 L.A. GIRL SHIMMER SPRAY GOLD REF. GFS918 (Magnification: x250 and x1500).*

The sample consists of typical platelet particles of mica pearlescent pigments. But agglomerates made up of constituent particles having near-spherical shapes are also observed. Platelets and agglomerates/aggregates have variable sizes.

Details on notions of constituent particles and agglomerates/aggregates are given in the appendix to this report.

Test report continued on next page

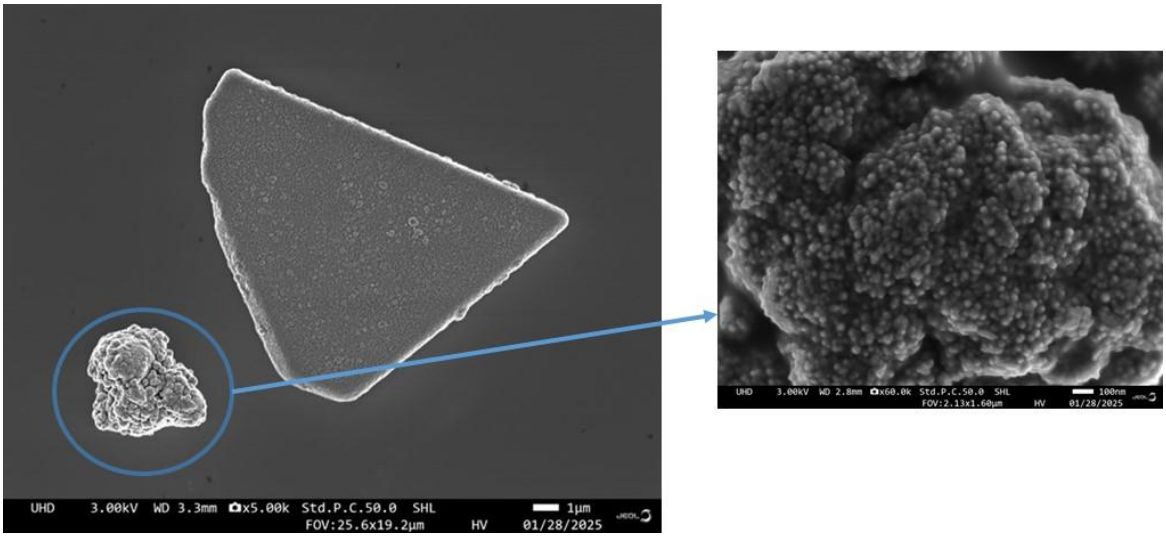


Figure 3 : *SEM images of particles (one platelet and one agglomerate/aggregate) extracted from sample L.A. GIRL SHIMMER SPRAY GOLD REF. GFS918 (sample S5), performed at magnification x5,000 and x60,000.*

Figure 3 shows one agglomerate and one platelet with on the right, a zoom of the agglomerate/aggregate.

Analysis providing information on the constituent atoms of each particle was carried out on the agglomerate/aggregate and the platelet imaged in Figure 3 using the EDX technique. This elementary analysis is performed on the sample prepared on a silicon substrate.

Figure 4 shows the EDX spectrum of the population of particles constituting the agglomerates/aggregate and mica platelet imaged in Figure 3.

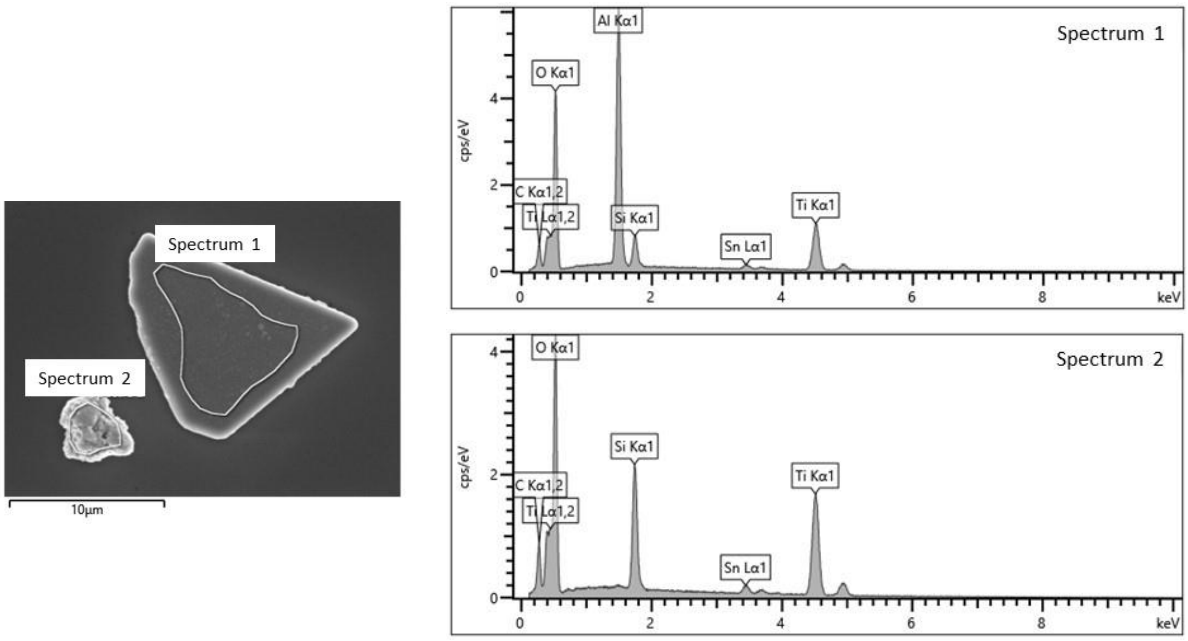


Figure 4 : *(on left) SEM image of particle agglomerates extracted from the sample S5 (magnification: x5,000). (on right) EDX spectra performed on the particle agglomerates/aggregates and mica platelet.*

In order to confirm the chemical composition of the agglomerates/aggregates and platelet, X-ray mapping was carried out on the both particles. The results are shown in Figure 5. They show that elements oxygen, aluminium, titanium and tin are present in all parts of the platelet imaged on Figure 3 and that the agglomerate/aggregate consists of oxygen, titanium and tin.

Table 2 : Information from EDX spectra and EDX mapping performed on S5, Figure 4.

	Peaks	Element	substance
Spectrum 1	O Kα1	oxygen	Mica platelets and oxides on mica platelets
	Al Kα1	aluminium	Mica platelets (see reminder section 1.3)
	Ti Kα1, Lα1,2	titanium	TiO_2 particles
	Sn Lα1	tin	Tin oxide
	Si Kα1	silicon	Silicon substrate and/or mica platelets
	C Kα1,2	carbon	contamination especially linked to the scanning of the electron beam
Spectrum 2	O Kα	oxygen	oxides within agglomerates
	Ti Kα, Lα1,2	titanium	TiO_2 particles within agglomerate/aggregate
	Sn Lα1,2	tin	Tin oxide within agglomerate/aggregate
	Si Kα	silicon	Silicon substrate and/or mica platelets
	C Kα	carbon	contamination especially linked to the scanning of the electron beam

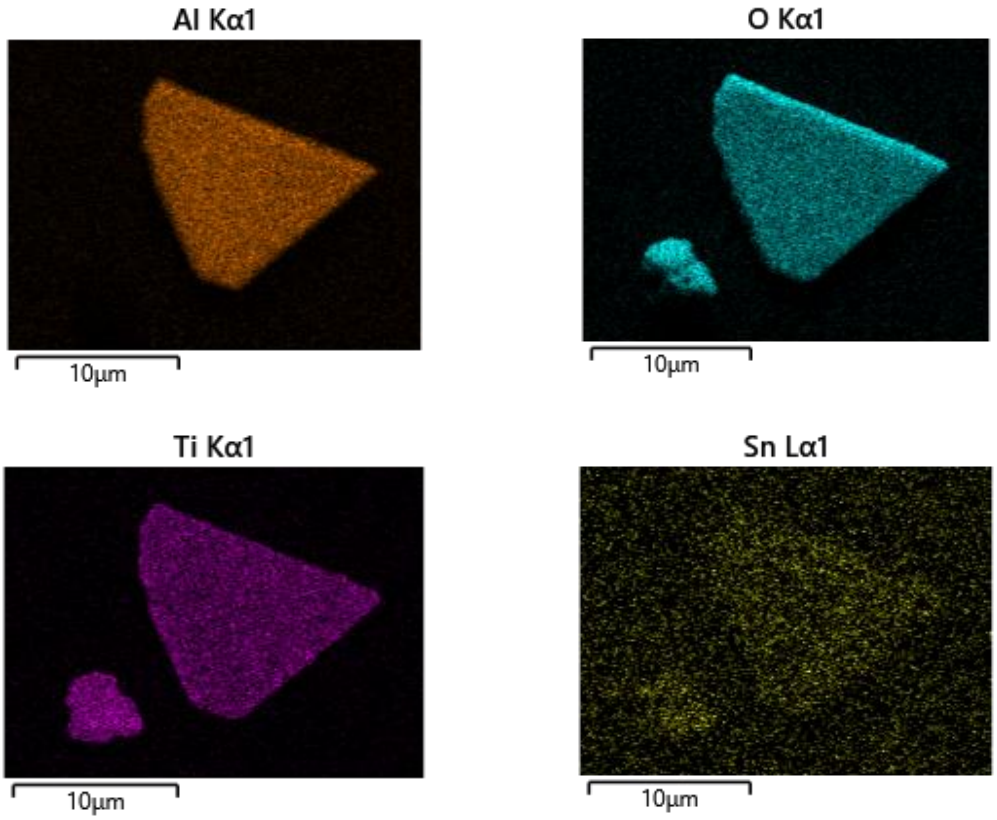


Figure 5 : *EDX mapping performed on the particle agglomerates (sample S5) of Figure 3 (left).*

The results combining EDX mapping and area elementary analysis indicates the presence of TiO_2 and SnO_2 on the mica platelet. As mentioned in the reminder of section 1.3, mica sheets contain Al. The agglomerate/aggregate is mainly made up of TiO_2 and contains Sn.

An image of agglomerate/aggregate is given in Figure 6 with a magnification x 15 000. The agglomerate consists of much smaller particles.

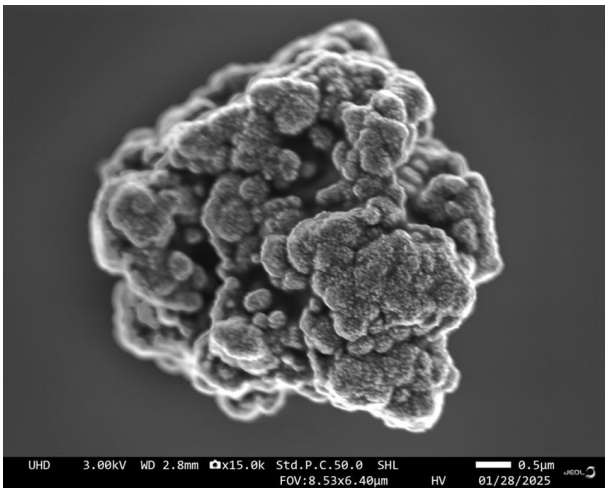


Figure 6 : *SEM image of an agglomerate/aggregate with a magnification x15 000 (sample S5).*

A EDX spectrum is carried out on the agglomerate/aggregate imaged in Figure 6. The measurements are given in Figure 7.

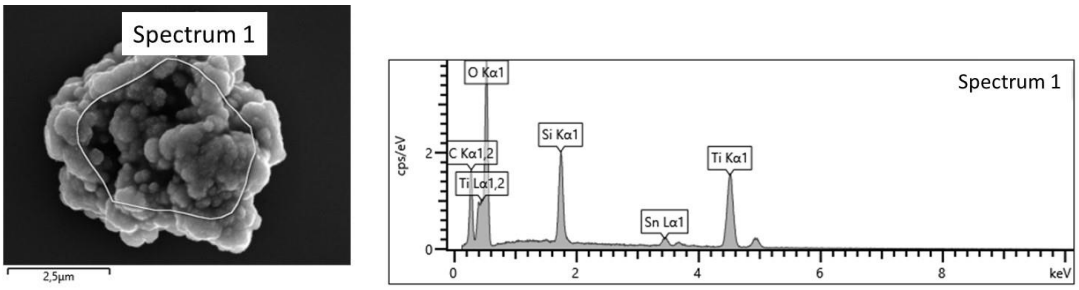


Figure 7 : *area analysed on the left image and obtained spectrum on the right (sample S5).*

Once again, we find the titanium, oxygen and tin peaks. As a result, the agglomerates/aggregates mainly consists of TiO_2 particles with SnO_2 traces. It is impossible to distinguish TiO_2 from SnO_2.

Table 3 : Information from EDX spectra and EDX mapping performed on S5, Figure 7.

	Peaks	Element	substance
Spectrum 1	O Kα1	oxygen	oxides within agglomerate/aggregate
	Ti Kα1, Lα1,2	titanium	TiO_2 particles within agglomerate/aggregate
	Si Kα1	silicon	Silicon substrate
	C Kα1,2	carbon	contamination especially linked to the scanning of the electron beam
	Sn Lα1	tin	Tin oxide within agglomerates

Small agglomerates/aggregates with sizes close to or less than 100 nm were observed. The SEM images of three examples of such agglomerates are given in Figure 8.

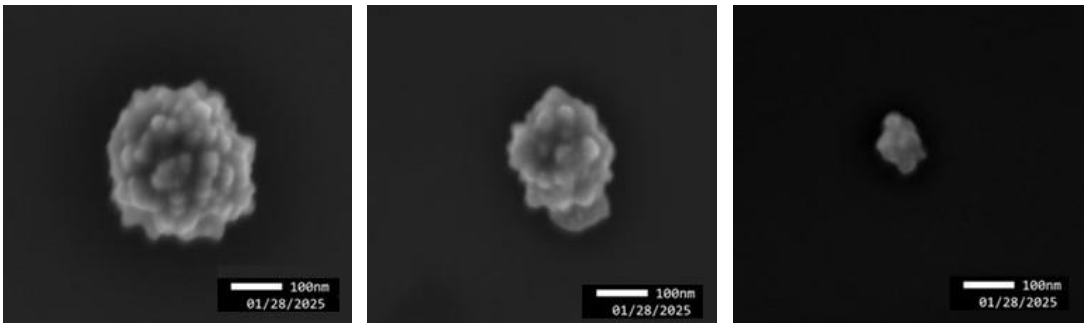


Figure 8 : *three examples of small agglomerates with sizes close to 100 nm (sample S5).*

3.1.3 Constituent particles size of the agglomerates and platelets

The sizes of the particles constituting the agglomerates and platelets were determined using the SEM image analysis. 300 particles were counted and measured to build each histogram of size distribution (Figure 9 and Figure 10). The results are reported in the Table 4.

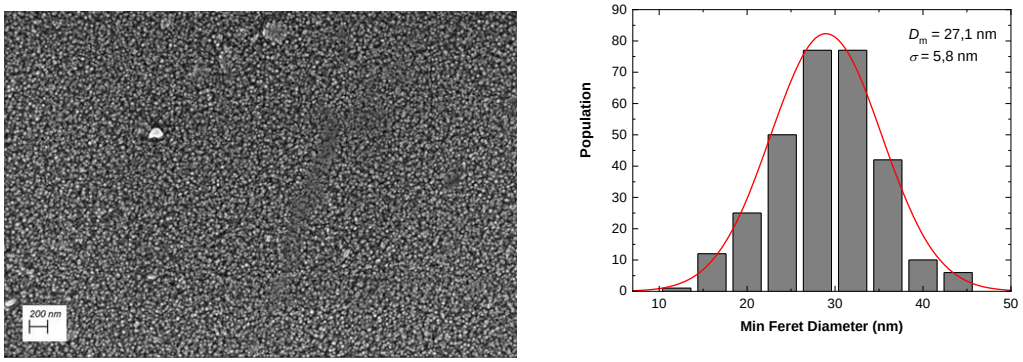


Figure 9 : *SEM image of mica surface (sample S5) with magnification x 20 000 (left) and size distribution histogram of the constituent particles (right).*

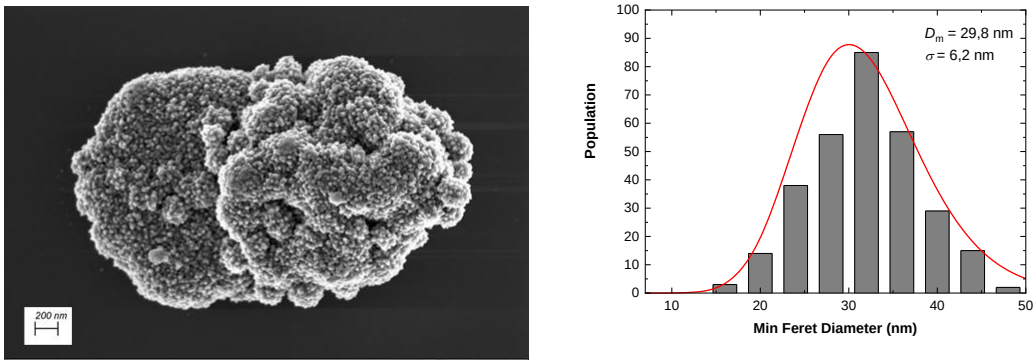


Figure 10 : *SEM image of agglomerate/aggregate (sample S5) with magnification x 25 000 (left) and size distribution histogram of the constituent particles (right).*

Test report continued on next page

Table 4 : *Results of constituent particle sizes obtained from the measurements carried out on agglomerates and platelets (sample S5).*

Objects	distribution	Mean Feret Diam. (nm)	Median (nm)	Mode (nm)	Polydispersity (nm)
Particle in agglomerate	Gaussian	29.5* ± 3.5	29.8	29.8	6.2
Particle in platelet	Gaussian	26.8* ± 3.5	27.1	27.1	5.8

*corrected value

The particles constituting the agglomerates/aggregate and platelets are similar in size (Table 4) and in chemical composition (mainly TiO_2, see Figure 4).

The median of particle size within agglomerates and platelets is smaller than 100 nm.

Consequently, 100 % of these particle populations are considered as nanoparticles.

3.1.4 Surface state of mica platelets

As mentioned in literature and observed in the previous sections, the mica platelets are covered by TiO_2 nanoparticles with sizes close to 30 nm. The surface state of some platelets were studied. Examples are given in Figure 11. The quality of the surface is quite poor. Agglomerates of TiO_2 nanoparticles are observed at the surface. The presence of these agglomerates/aggregates seems to result from degradation of the upper layers of particles, as observed in Figure 12. The interaction between platelet surface and these agglomerates/aggregates could be weak and explains the presence of isolated agglomerates/aggregates on the silicon substrate outside platelets.

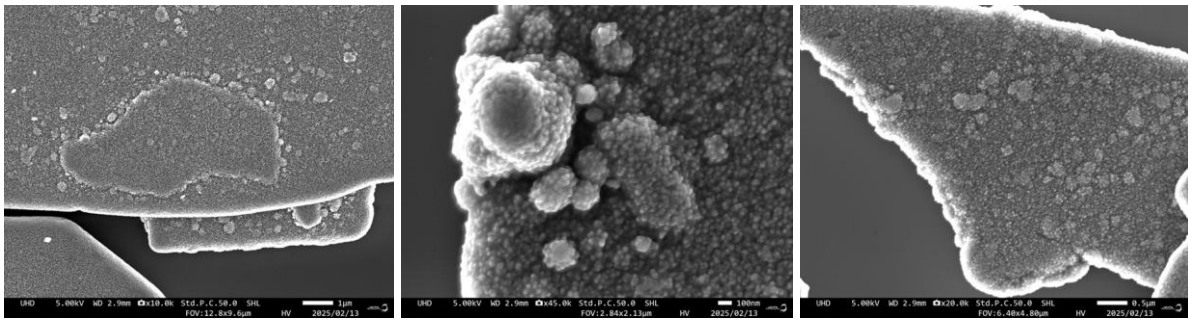


Figure 11 : *SEM images of the Surface state of a few platelets (sample S5).*

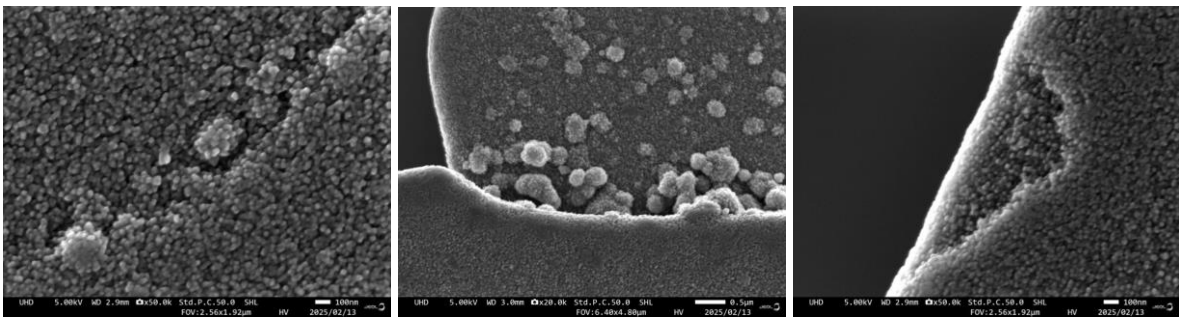


Figure 12 : *SEM images of platelets showing the potential degradation of their surface (sample S5).*

The example reported in Figure 13 shows a platelets with a part of the bare mica.

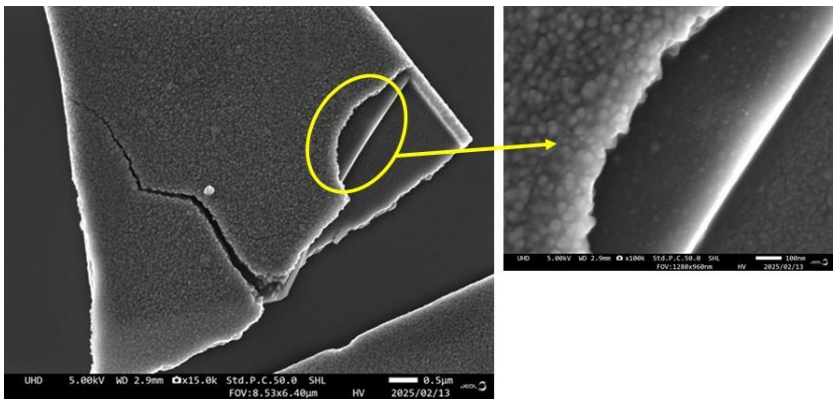


Figure 13 : *SEM images of a platelet showing a cracking (on the left part) of the TiO_2 nanoparticle upper layer and a bare part of the mica sheet (on the right corner). A zoom of the bare part is reported on the right (sample S5).*

The platelet given in Figure 13 is analysed by EDX. The spectra are reported in Figure 14. Two area scans (spestra 49 & 50) and one single-point analysis (spectrum 51) were performed. An EDX mapping carried out on the same platelets is given in Figure 15. The spectrum 50 area corresponds to the lower layer of the mica platelet. This layer does not contain mica sheet because no Al peak is observed.

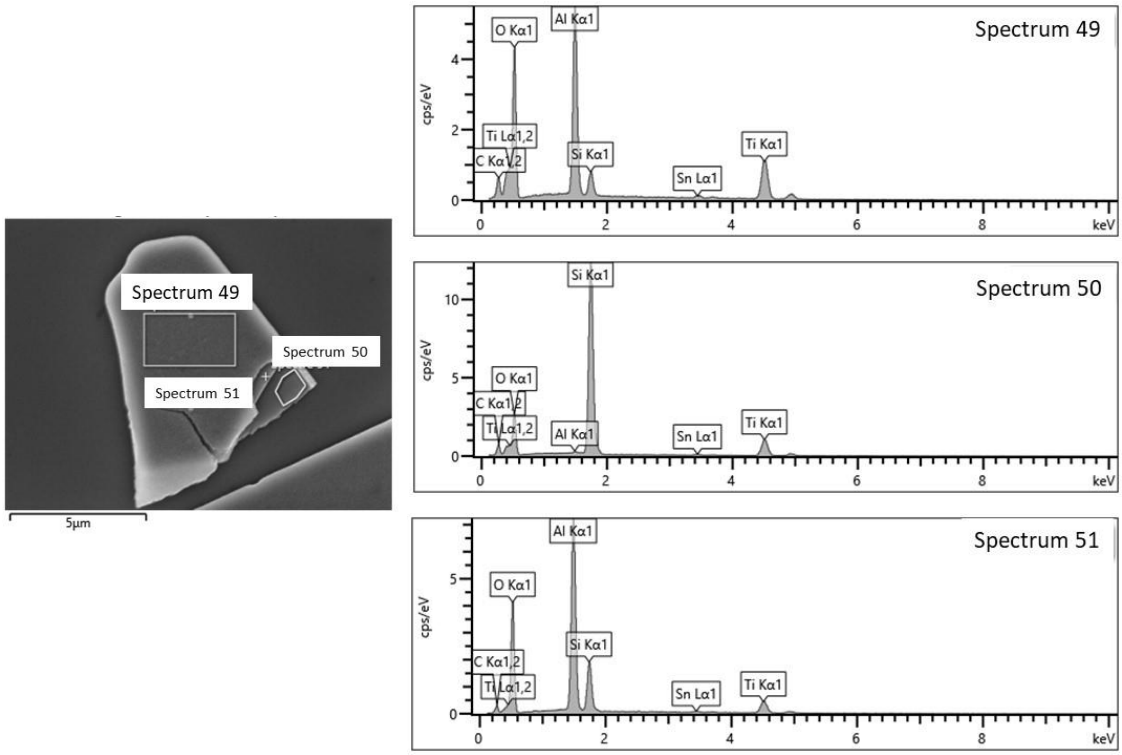


Figure 14 : Two *areas (spectrum 49 & 50) and one single-point (spectrum 51) analysed on the left image and obtained spectra on the right (sample S5).*

Test report continued on next page

Table 5 : Information from EDX spectra and EDX mapping performed on S5, Figure 14.

	Peaks	Element	substance
Spectrum 49	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminium	Mica platelets (see reminder section 1.3)
	Ti Kα1, Lα1,2	titanium	TiO_2 particles on mica platelet
	Sn Lα1,2	tin	Tin oxide on mica platelets
	Si Kα1	silicon	Silicon substrate and/or mica platelets
	C Kα1,2	carbon	contamination especially linked to the scanning of the electron beam
Spectrum 50	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminium	Mica platelets (see reminder section 1.3)
	Ti Kα1, Lα1,2	titanium	TiO_2 particles on mica platelet
	Sn Lα1,2	tin	Tin oxide on mica platelets
	Si Kα1	silicon	Silicon substrate and/or mica platelets
	C Kα1,2	carbon	contamination especially linked to the scanning of the electron beam
Spectrum 51	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminium	Mica platelets (see reminder section 1.3)
	Ti Kα1, Lα1,2	titanium	TiO_2 particles on mica platelet
	Sn Lα1,2	tin	Tin oxide on mica platelets
	Si Kα1	silicon	Silicon substrate and/or mica platelets
	C Kα1,2	carbon	contamination especially linked to the scanning of the electron beam

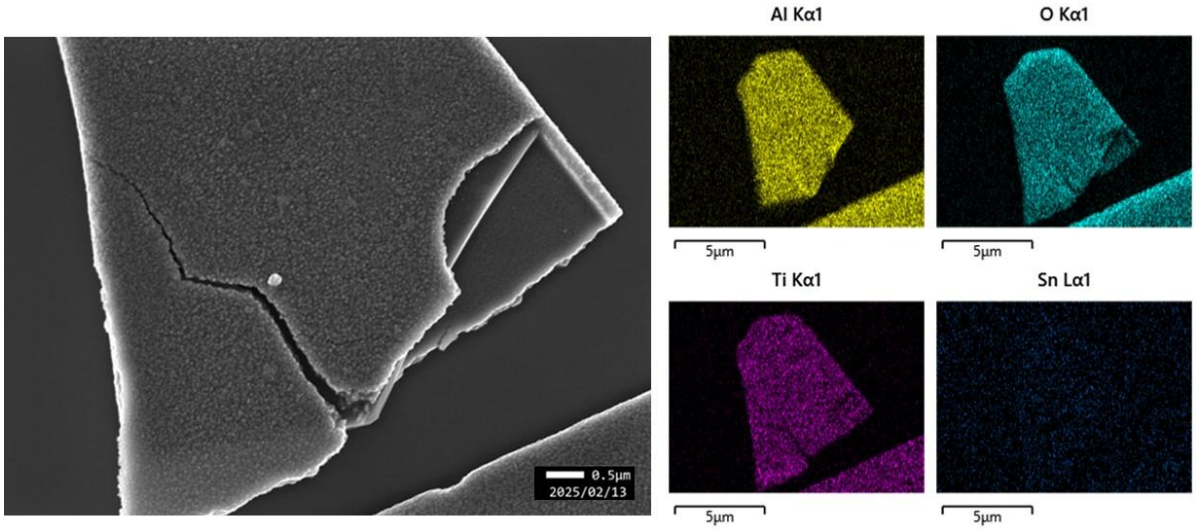


Figure 15 : *EDX mapping performed on the platelet imaged on the left (sample S5).*

Test report continued on next page

3.1.5 Surface state of mica platelets after sonication process

In a second stage, the suspension with mica platelets was sonicated with a gun before depositing on silicon substrate. SEM images of surface state are given in Figure 16.

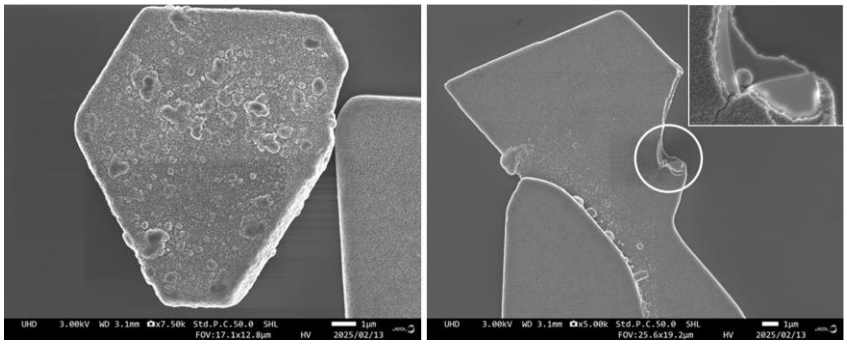


Figure 16 : *damaged surface of a few platelets after sonication process (sample S5).*

The circled part (image on right, Figure 16) was analysed by EDX and a mapping performed on the same zone is reported in Figure 17. We can observe that titanium is not present on the bare part of the mica platelets. Tin is hardly visible everywhere.

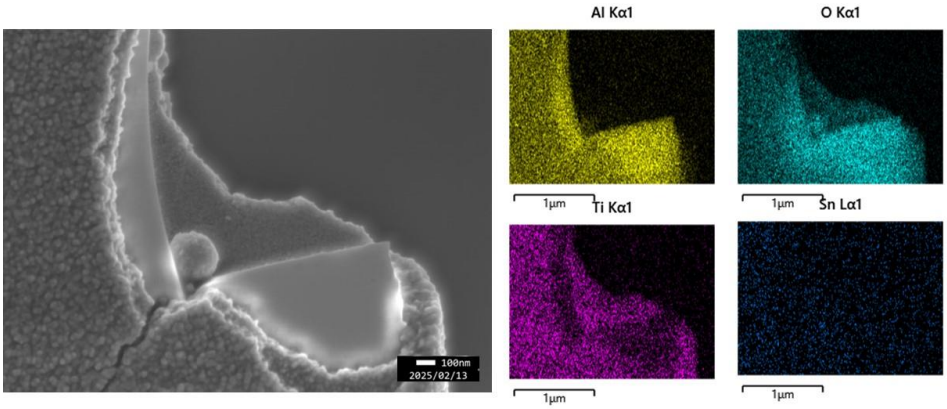


Figure 17 : *EDX mapping performed on the platelet imaged on the left (sample S5).*

3.1.6 Conclusions on S5

- The mica platelets are covered by TiO_2 nanoparticles.
- Agglomerates/aggregates of TiO_2 nanoparticles without mica are observed outside the platelets.
- The sizes (minimum Féret diameter) of TiO_2 particles within agglomerates/aggregates and platelets (29.5 nm ± 3.5 nm and 26.8 nm ± 3.5 nm respectively) are similar and are smaller than 100 nm. 100 % are considered as nanoparticles.
- The same TiO_2 nanoparticles are present on the platelets and in the agglomerates.
- Isolated agglomerates of TiO_2 nanoparticles with sizes smaller than 100 nm were observed.
- The presence of tin element is demonstrated but no pure tin oxide particles were observed. The form was not demonstrated. Tin oxide could be in the form of oxide layer (from literature).

3.2 SAMPLE S7 : SI SI LA PAILLETTE

A picture of the studied sample is shown in Figure 18.

Figure 18 : *Picture of the sample S7 reference SI SI LA PAILlETTE (indicated on label "Spray from a distance of 20 cm onto body and hair")*

The presence of titanium dioxide (CI 77891), iron oxide (CI 77491) and mica is indicated by the producer on the label.

3.2.1 Preparation of the sample

The sample preparation protocol is as follows:

- A sample fraction (11 mg) is mixed with 5 mL of MilliQ water.
- The resulting suspension is simply stirred manually to disperse the particles.

protocol for deposition on silicon substrate before analyzing by SEM and EDX.

- A droplet of the suspension is deposited on silicon wafer.
- The drop is left to dry naturally before observation.

Test report continued on next page

3.2.2 SEM measurements and EDX analyses performed on particle deposition.

Some examples of SEM images performed at magnification x1000 and x20 000 are shown on Figure 19.

The sample consists of typical platelet particles of mica pearlescent pigments (left, Figure 19). But agglomerates/aggregates made up of constituent particles having near-spherical shapes are also observed. Platelets and agglomerates have variable sizes.

Details on notions of constituent particles and agglomerates are given in the appendix to this report.

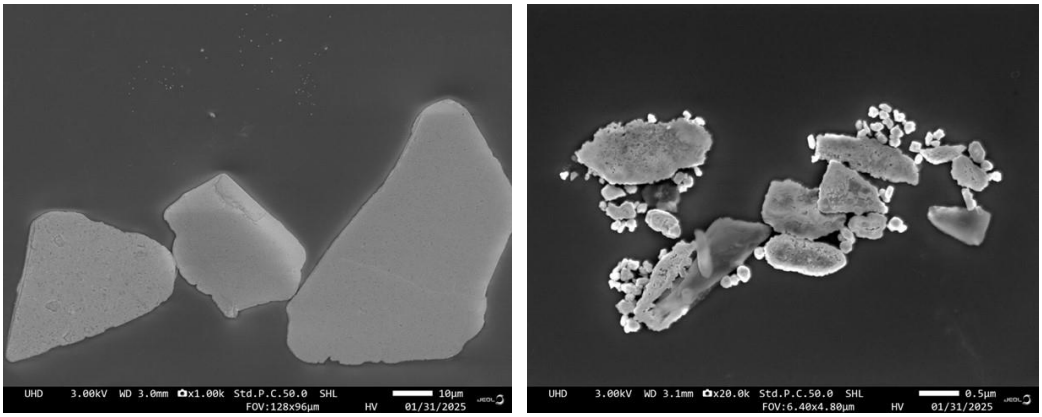


Figure 19 : *SEM image of the sample S7 reference SI SI LA PAILLETTE (Magnification: x1000 and x20 000).*

Analysis providing information on the constituent atoms of each particle was carried out on the platelets imaged in Figure 20 (left) using the EDX technique. This elementary analysis is performed on some areas of the sample prepared on a silicon substrate. Figure 20 (right) shows the EDX spectra of the population of particles constituting the agglomerates/aggregates and mica platelet imaged on the left.

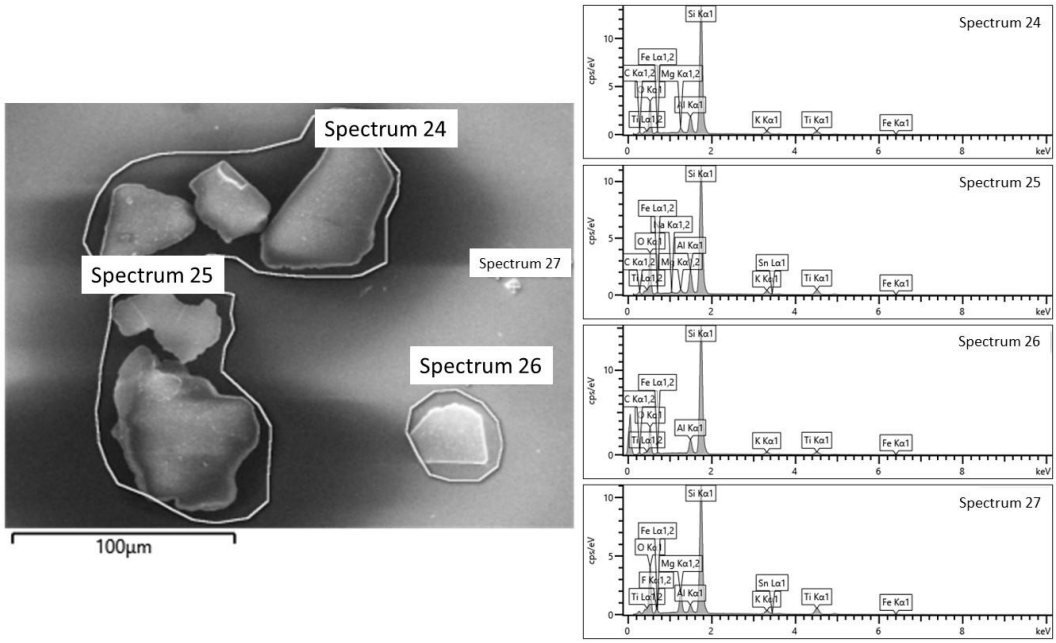


Figure 20 : SEM images of some platelets (left) and EDX spectra carried out on areas 24, 25 and 26, and on the point 27 *(sample S7)*.

In order to confirm the chemical composition of the agglomerates and platelets, X-ray mapping was carried out on the both particles. The results are shown in Figure 21. They show that elements oxygen, aluminium, titanium and tin are present in all parts of the platelet imaged on Figure 21 (left) and that the agglomerate mainly consists of oxygen and titanium.

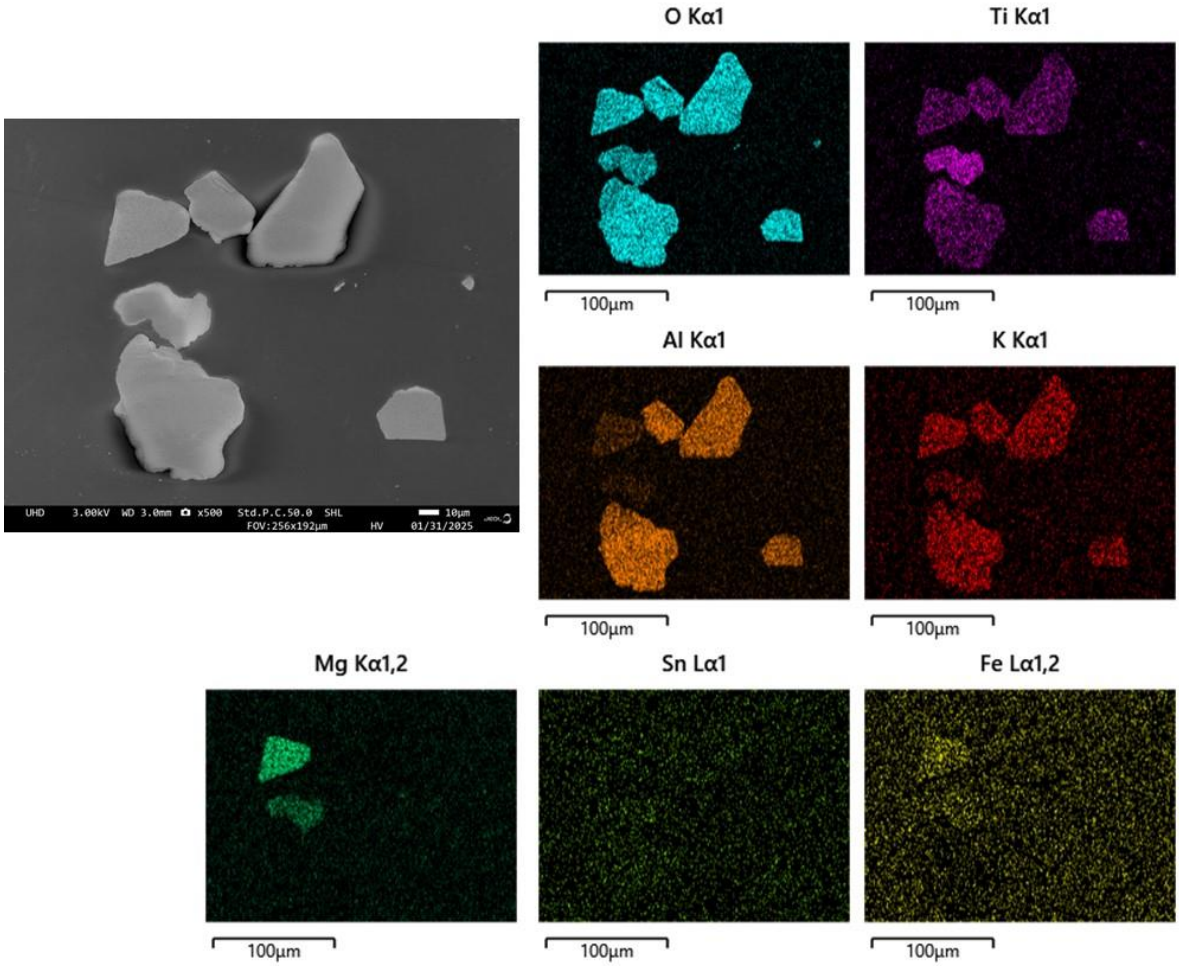


Figure 21 : *EDX mapping performed on the platelets imaged by SEM on the left with a magnification x 500 (sample S7).*

Table 6 : Information from EDX spectra and EDX mapping performed on S7, Figure 20.

	Peaks	Element	substance
Spectrum 24	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminium	Mica platelets (see reminder section 1.3)
	Mg Kα1,2	magnesium	Mica platelets (see reminder section 1.3)
	K Kα1	potassium	Mica platelets (see reminder section 1.3)
	Ti Kα1, Lα1,2	titanium	TiO_2 particles on mica platelet
	Fe Lα1,2; Kα1	iron	Iron oxide on mica platelet
	Si Kα1	silicon	Silicon substrate and/or mica platelets
	C Kα1,2	carbon	contamination especially linked to the scanning of the electron beam

Spectrum 25	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminium	Mica platelets (see reminder section 1.3)
	Mg Kα1,2	magnesium	Mica platelets (see reminder section 1.3)
	K Kα1	potassium	Mica platelets (see reminder section 1.3)
	Na Kα1,2	sodium	Mica platelets (see reminder section 1.3)
	Ti Kα1, Lα1,2	titanium	TiO_2 particles on mica platelet
	Fe Lα1,2; Kα1	iron	Iron oxide on mica platelet
	Sn Lα1,2	tin	Tin oxide on mica platelets
	Si Kα1	silicon	Silicon substrate and/or mica platelets
	C Kα1,2	carbon	contamination especially linked to the scanning of the electron beam
Spectrum 26	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminium	Mica platelets (see reminder section 1.3)
	K Kα1	potassium	Mica platelets (see reminder section 1.3)
	Ti Kα1, Lα1,2	titanium	TiO_2 particles on mica platelet
	Fe Lα1,2; Kα1	iron	Iron oxide on mica platelet
	Si Kα1	silicon	Silicon substrate and/or mica platelets
	C Kα1,2	carbon	contamination especially linked to the scanning of the electron beam
Spectrum 27	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminium	Mica platelets (see reminder section 1.3)
	Mg Kα1,2	magnesium	Mica platelets (see reminder section 1.3)
	K Kα1	potassium	Mica platelets (see reminder section 1.3)
	Ti Kα1, Lα1,2	titanium	TiO_2 particles on mica platelet
	Fe Lα1,2; Kα1	iron	Iron oxide on mica platelet
	Sn Lα1	tin	Tin oxide on mica platelet
	Si Kα1	silicon	Silicon substrate and/or mica platelets
	C Kα1,2	carbon	contamination especially linked to the scanning of the electron beam

The results combined with the results of the first elementary analysis indicates the presence of TiO_2 and iron oxide on the mica platelet. As mentioned in the reminder of section 1.3, mica sheets can contain Al, Mg, K and Na.

Test report continued on next page

A zone of the sample consisting of platelets and agglomerates/aggregates is imaged by SEM in Figure 22. We can show that isolated agglomerates/aggregates are made of TiO_2 particles and do not contain aluminum.

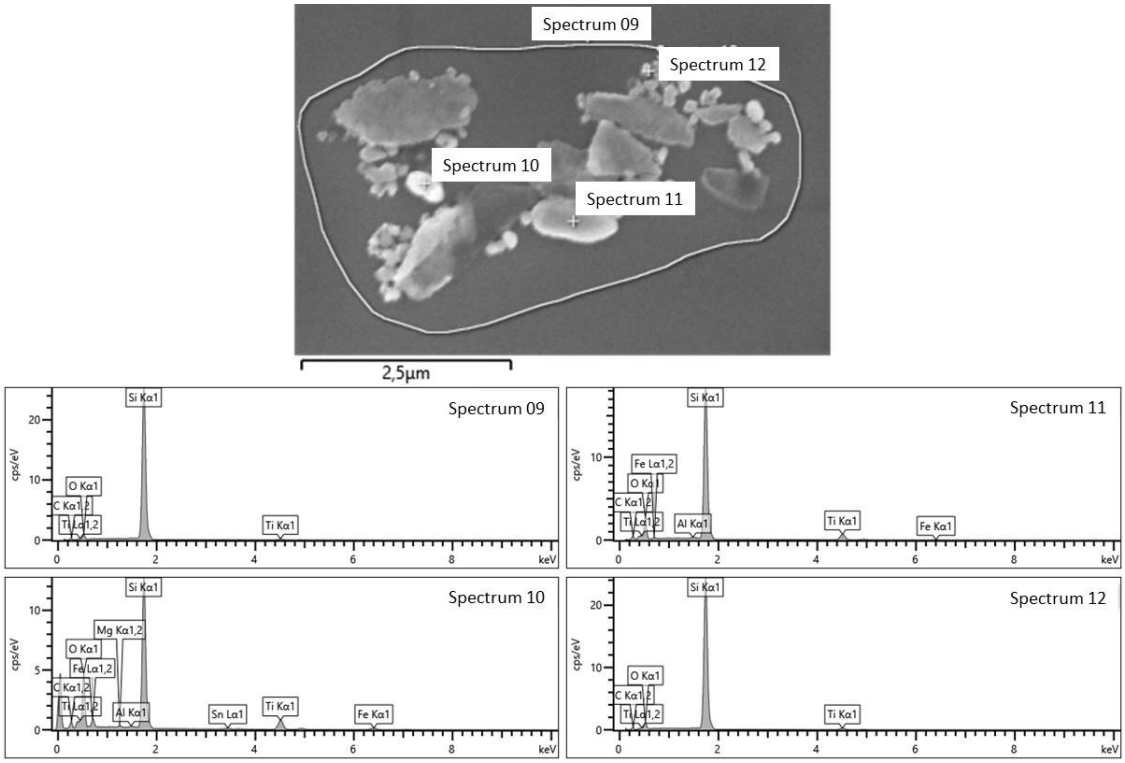


Figure 22 : *area analysed above and obtained spectra below. Spectrum 09 corresponds to a scanned area and spectra 10, 11 and 12 are single-point analysis (sample S7).*

Table 7 : Information from EDX spectra and EDX mapping performed on S7, Figure 22.

	Peaks	Element	substance
Spectrum 9	O Kα1	oxygen	oxides on mica platelets/agglomerates
	Ti Kα1, Lα1,2	titanium	TiO_2 particles on mica platelet/agglomerates
	Si Kα1	silicon	Silicon substrate and/or mica platelets
	C Kα1,2	carbon	contamination especially linked to the scanning of the electron beam
Spectrum 10	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminium	Mica platelets (see reminder section 1.3)
	Mg Kα1,2	magnesium	Mica platelets (see reminder section 1.3)
	Ti Kα1, Lα1,2	titanium	TiO_2 particles on mica platelet
	Fe Lα1,2; Kα1	iron	Iron oxide on mica platelet
	Sn Lα1,2	tin	Tin oxide on mica platelets
	Si Kα1	silicon	Silicon substrate and/or mica platelets
	C Kα1,2	carbon	contamination especially linked to the scanning of the electron beam

Spectrum 11	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminium	Mica platelets (see reminder section 1.3)
	Ti Kα1, Lα1,2	titanium	TiO_2 particles on mica platelet
	Fe Lα1,2; Kα1	iron	Iron oxide on mica platelet
	Si Kα1	silicon	Silicon substrate and/or mica platelets
	C Kα1,2	carbon	contamination especially linked to the scanning of the electron beam
Spectrum 12	O Kα1	oxygen	oxides within agglomerates/aggregates
	Ti Kα1, Lα1,2	titanium	TiO_2 particles within agglomerates/aggregates
	Si Kα1	silicon	Silicon substrate
	C Kα1,2	carbon	contamination especially linked to the scanning of the electron beam

The Figure 23, Figure 24, Figure 25, Figure 26 confirm that platelets are mainly composed of aluminum and the isolated agglomerates/aggregates consist of TiO_2 with a small amount of iron oxide. Tin element is sometime weakly detected. Aluminum is only detected on platelets (Figure 23). Mica is not present within agglomerates/aggregates imaged in Figure 24, Figure 25 and Figure 26.

Test report continued on next page

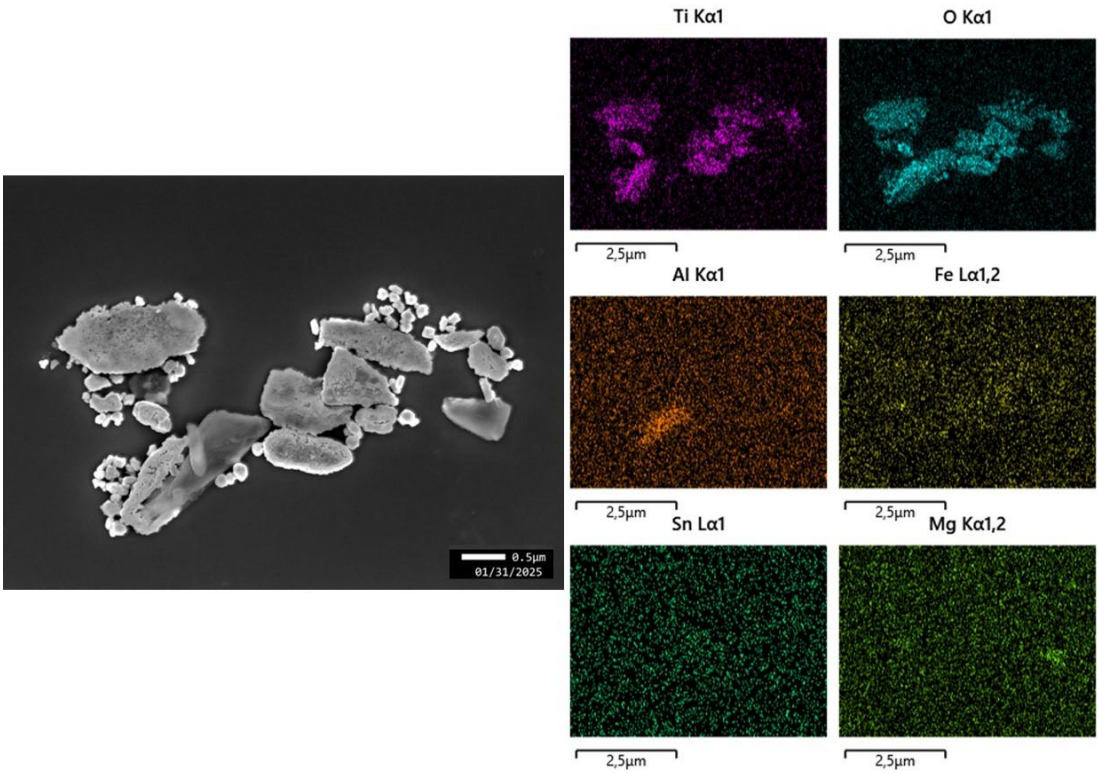


Figure 23 : *EDX mapping performed on the platelet and agglomerates imaged on the left (sample S7).*

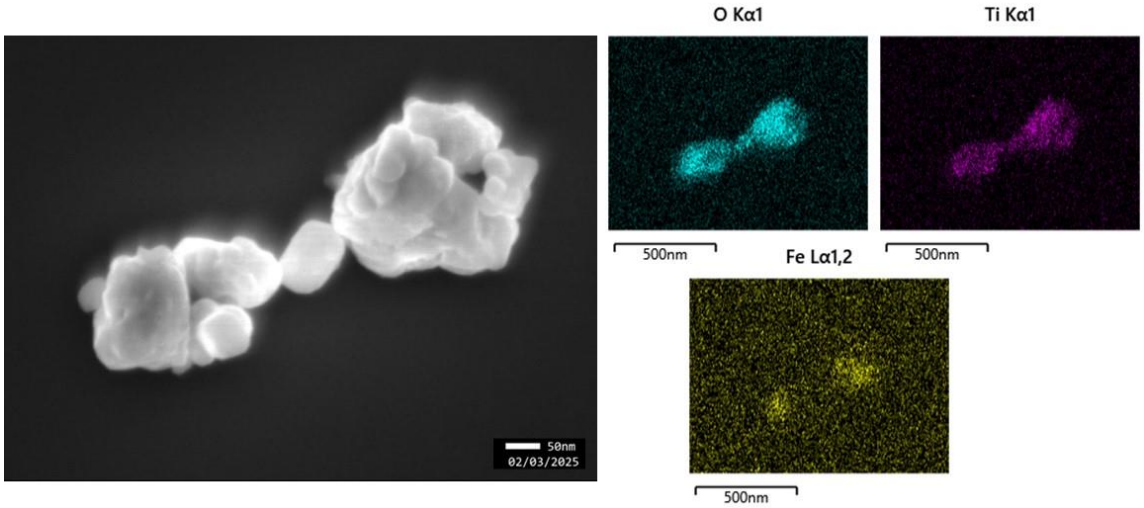


Figure 24 : *EDX mapping performed on the agglomerates imaged on the left (sample S7).*

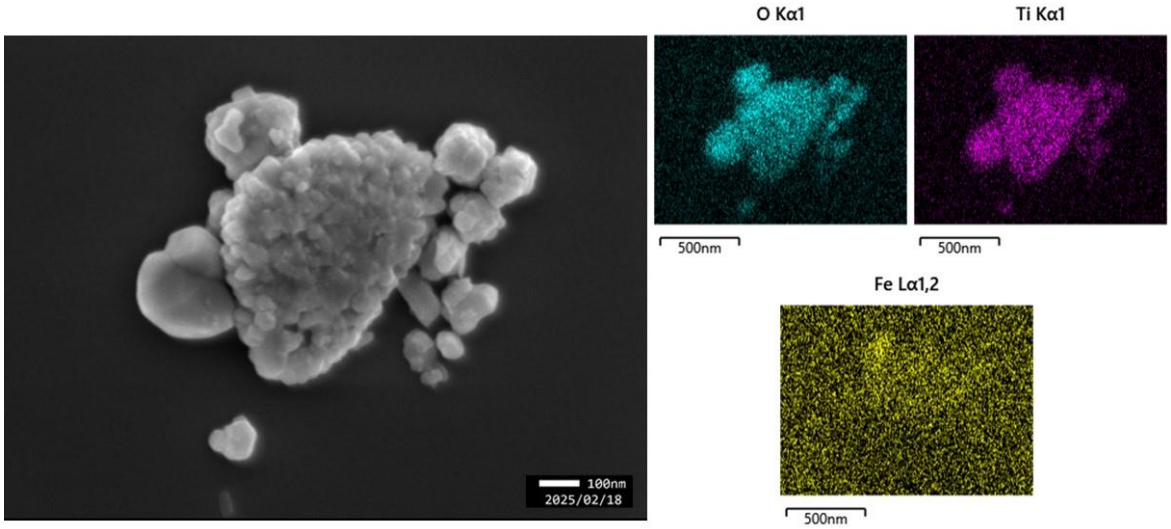


Figure 25 : *EDX mapping performed on the agglomerates imaged on the left (sample S7).*

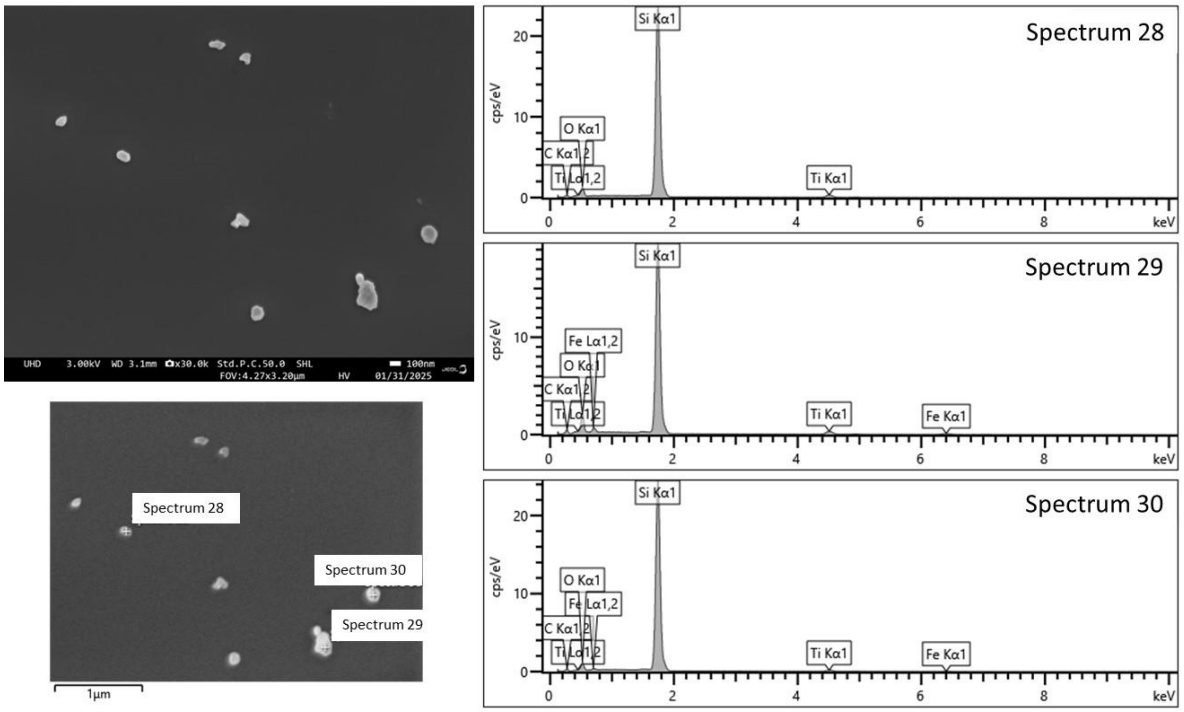


Figure 26 : *SEM of a few isolated particles (left) and single-point EDX spectra (28, 29 & 30, right) performed on three of them (sample S7).*

Test report continued on next page

Table 8 : Information from EDX spectra and EDX mapping performed on S7, Figure 26.

	Peaks	Element	substance
Spectrum 28	O Kα1	oxygen	oxides within agglomerates/aggregates
	Ti Kα1, Lα1,2	titanium	TiO_2 particles within agglomerates/aggregates
	Si Kα1	silicon	Silicon substrate and/or mica platelets
	C Kα1,2	carbon	contamination especially linked to the scanning of the electron beam
Spectrum 29	O Kα1	oxygen	oxides within agglomerates/aggregates
	Ti Kα1, Lα1,2	titanium	TiO_2 particles within agglomerates/aggregates
	Fe Lα1,2; Kα1	iron	Iron oxide within agglomerates/aggregates
	Si Kα1	silicon	Silicon substrate
	C Kα1,2	carbon	contamination especially linked to the scanning of the electron beam
Spectrum 30	O Kα1	oxygen	oxides within agglomerates/aggregates
	Ti Kα1, Lα1,2	titanium	TiO_2 particles within agglomerates/aggregates
	Fe Lα1,2; Kα1	iron	Iron oxide within agglomerates/aggregates
	Si Kα1	silicon	Silicon substrate
	C Kα1,2	carbon	contamination especially linked to the scanning of the electron beam

Test report continued on next page

3.2.3 Constituent particles size of the agglomerates and platelets

The sizes of the particles constituting the agglomerates and platelets were determined using the SEM image analysis. 300 particles were counted and measured to build each histogram of size distribution (Figure 27 and Figure 28). The results are reported in the Table 9.

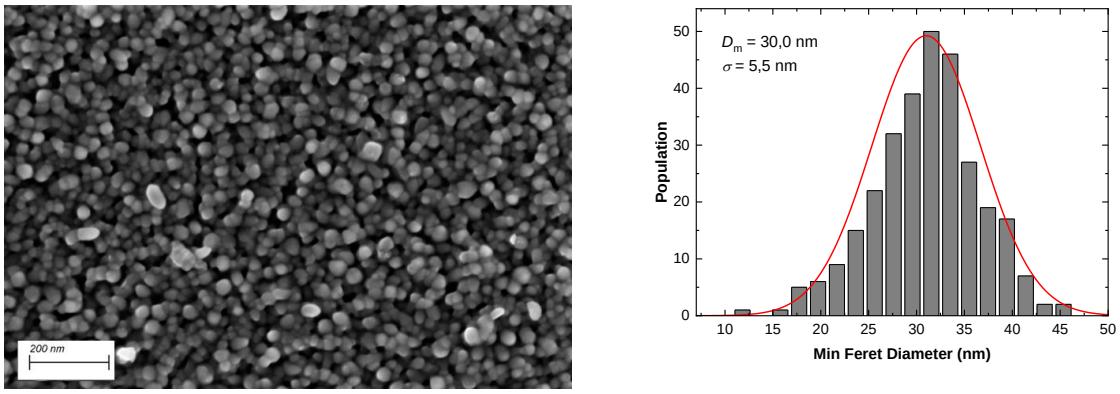


Figure 27 : *SEM image of mica surface (sample S7) with magnification x 80 000 (left) and size distribution histogram of the constituent particles (right).*

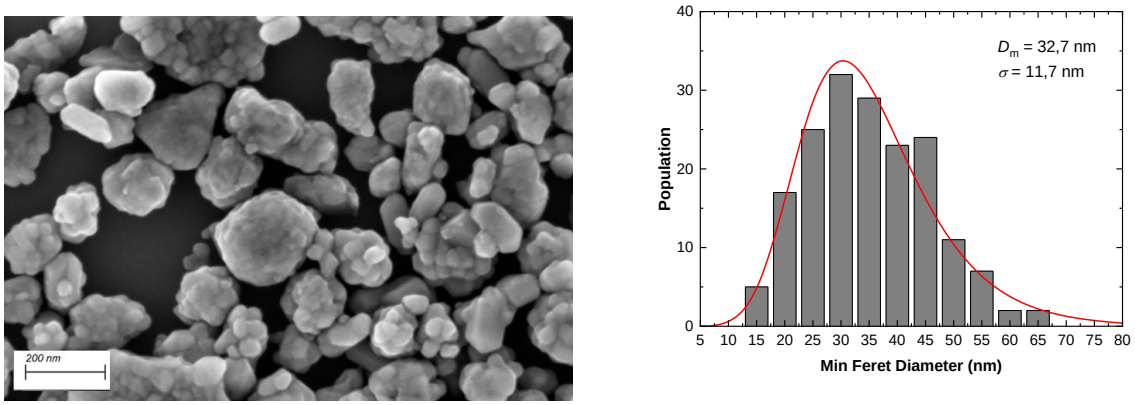


Figure 28 : *SEM image of agglomerate (sample S7) with magnification x 80 000 (left) and size distribution histogram of the constituent particles (right).*

Table 9 : *Results of constituent particle sizes obtained from the measurements carried out on agglomerates and platelets (sample S7).*

Objects	distribution	Mean Feret Diam. (nm)	Median (nm)	Mode (nm)	Polydispersity (nm)
Particle in agglomerate	Gaussian	29.7* ± 3.5	30.0	30.0	5.5
Particle in platelet	Lognormal	32.3* ± 3.6	30.8	27.3	11.7

*corrected value

The particles constituting the agglomerates and platelets are similar in size (Table 9) and in chemical composition (mainly TiO_2, see Figure 21 and Figure 23).

The median of particle size within agglomerates and platelets is smaller than 100 nm.

Consequently, 100 % of these particle populations are considered as nanoparticles.

3.2.4 Surface state of mica platelets

The surface state of some platelets were studied. Examples are given in Figure 29. The quality of the surface is quite poor and it is cracked in many places (Figure 29 and Figure 30). Agglomerates/aggregates of TiO_2 nanoparticles are observed at the surface. The presence of these agglomerates/aggregates seems to result from degradation of the upper layers of particles, as observed in Figure 30. The interaction between platelet surface and these agglomerates/aggregates could be weak and explains the presence of isolated agglomerates on the silicon substrate outside platelets.

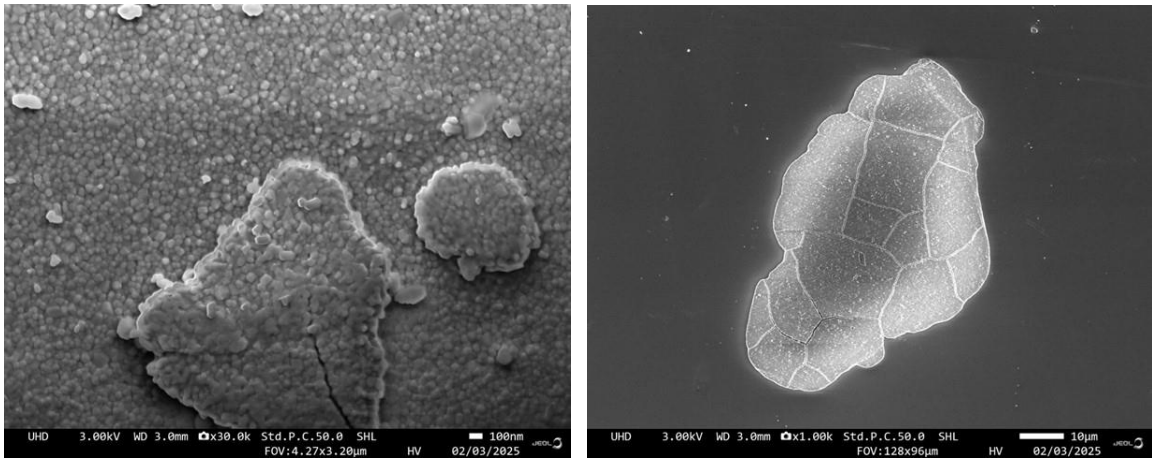


Figure 29 : *SEM images of the Surface state of a few platelets (sample S7).*

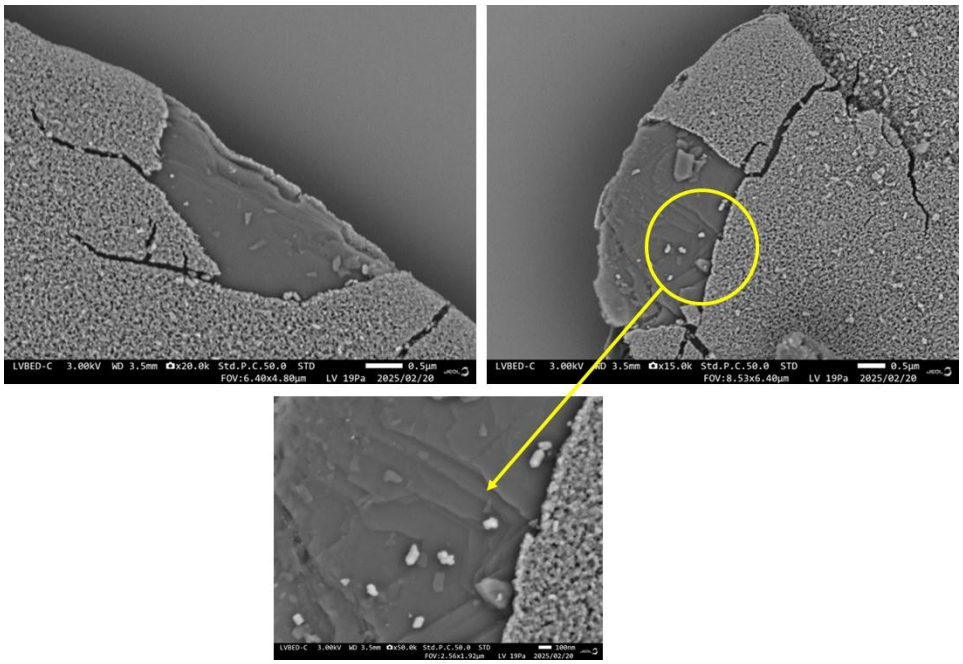


Figure 30 : *SEM images of very damaged surface state of platelets (sample S7).*

3.2.5 Surface state of mica platelets after sonication process

In a second stage, the suspension with mica platelets was sonicated with a gun before depositing on silicon substrate. SEM images of surface state are given in Figure 31 and Figure 32. This sonication step seems to further degrade the surface state.

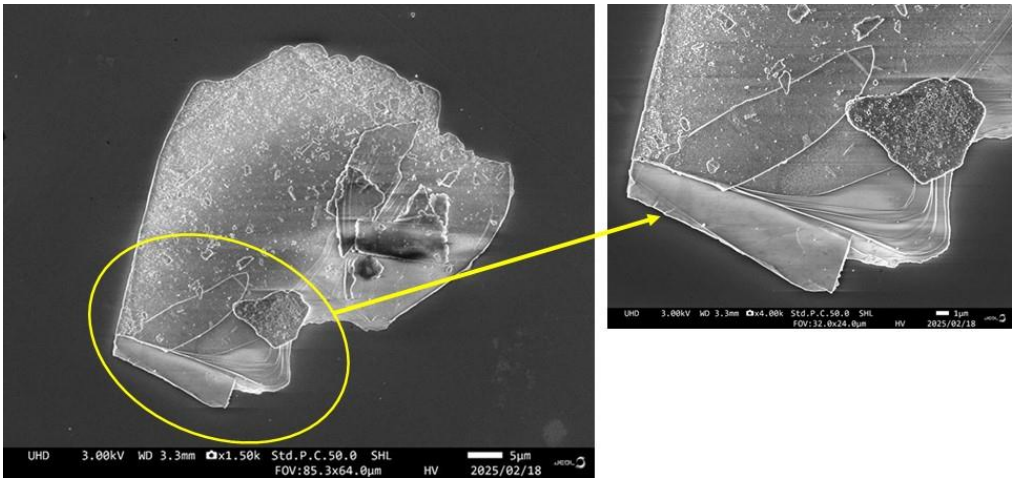


Figure 31 : *damaged surface of one platelet after sonication process (sample S7).*

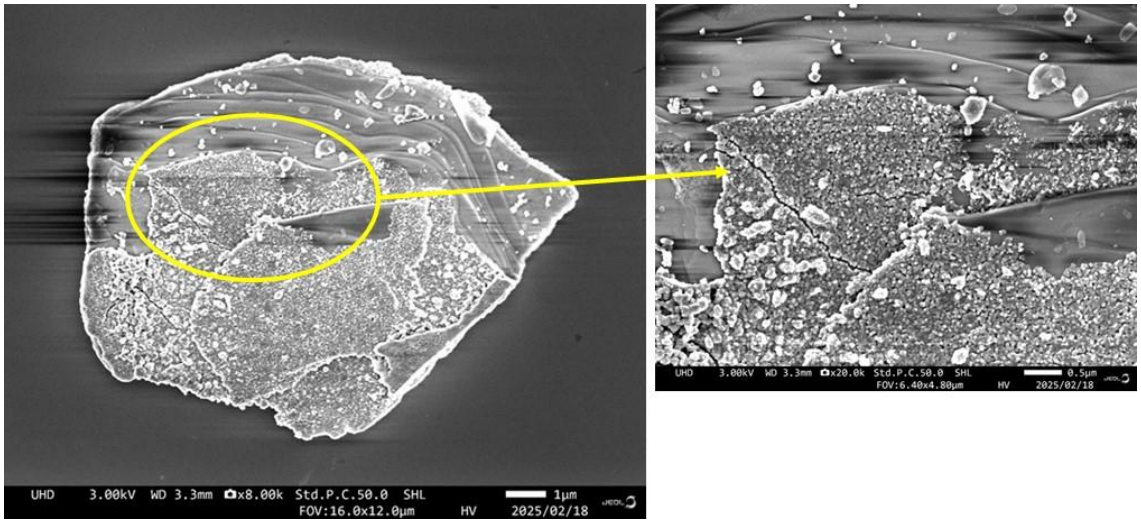


Figure 32 : *damaged surface of one platelet after sonication process (sample S7).*

Test report continued on next page

3.2.6 Conclusions on S7

- The mica platelets are covered by TiO_2 nanoparticles.
- Agglomerates/aggregates of TiO_2 nanoparticles without mica are observed outside the platelets
- The sizes (minimum Féret diameter) of TiO_2 particles within agglomerates/aggregates and platelets (29.7 nm ± 3.5 nm and 32.3 nm ± 3.6 nm respectively) are similar and are smaller than 100 nm. 100 % are considered as nanoparticles.
- The same TiO_2 nanoparticles are present on the platelets and in the agglomerates.
- Isolated agglomerates/aggregates of TiO_2 nanoparticles with sizes smaller than 100 nm were observed.
- The presence iron elements and sometime tin is demonstrated but no pure tin oxide or pure iron oxide particles were observed. The form was not demonstrated. Tin oxide or iron oxide could be in the form of oxide layer (from literature).

Test report continued on next page

3.3 SAMPLE S8 : MACOSMETOPERSO, MICA OR

A picture of the studied sample is shown in Figure 33

Figure 33 : *Picture of the sample S8 reference MaCosmetoPerso, Mica Or.*

The presence of titanium dioxide, di-iron trioxide (Fe_2O_3) and mica is indicated by the producer on the label.

3.3.1 Preparation of the sample

The sample preparation protocol is as follows:

- A sample fraction (11 mg) is mixed with 5 mL of MilliQ water.
- The resulting suspension is simply stirred manually to disperse the particles.

protocol for deposition on silicon substrate before analyzing by SEM and EDX.

- A droplet of the suspension is deposited on silicon wafer.
- The drop is left to dry naturally before observation.

Test report continued on next page

3.3.2 SEM measurements and EDX analyses performed on particle deposition.

Some examples of SEM images performed at magnification x200 and x2 500 are shown on Figure 34.

The sample consists of typical platelet particles of mica pearlescent pigments (Figure 34). But agglomerates/aggregates made up of constituent particles or isolated particles having near-spherical shapes are also observed (right image of Figure 34, left side). Platelets and agglomerates/aggregates have variable sizes.

Details on notions of constituent particles and agglomerates are given in the appendix to this report.

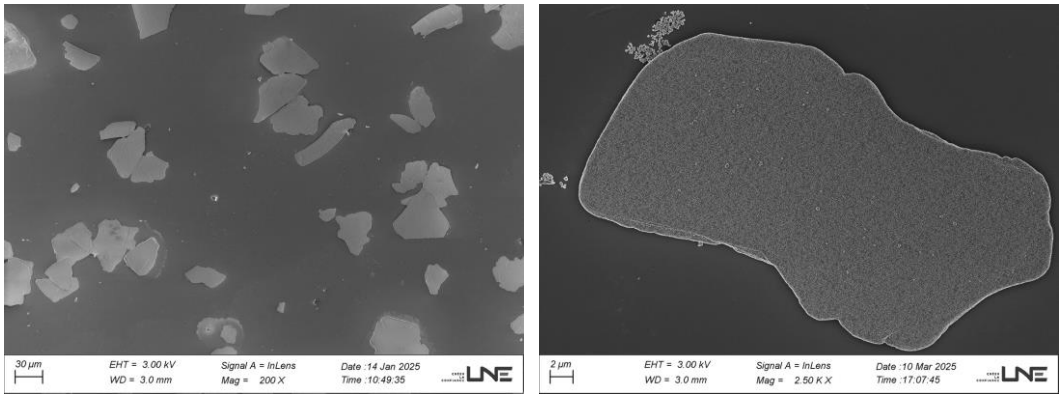


Figure 34 : *SEM image of the sample S8 reference MaCosmetoPerso, Mica Or (Magnification: x200 and x2 500).*

Analysis providing information on the constituent atoms of each mica platelet was carried out on the particles imaged in Figure 35 (left) using the EDX technique. This elementary analysis is performed on the sample prepared on a silicon substrate. Figure 35 (right) shows the EDX spectra performed on the areas 39 and 40 of the population of particles constituting the mica platelets imaged on the left.

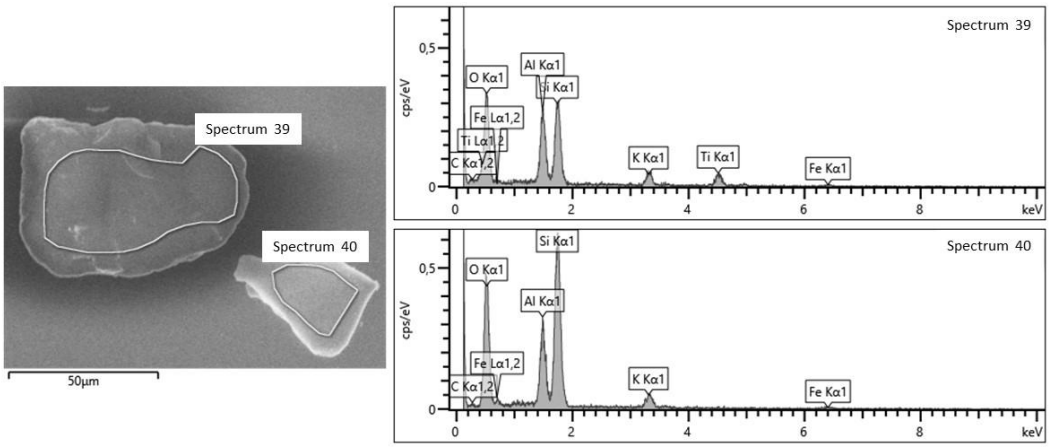


Figure 35 : SEM images of some platelets (left) and EDX spectra carried out on areas 39 and 40 (sample S8).

In order to confirm the chemical composition of platelets, X-ray mapping was carried out on the both particles. The results are shown in Figure 36. They show that elements oxygen, aluminum, titanium and potassium are mainly present in all parts of the platelet imaged on Figure 36 (left). Iron is hardly detected.

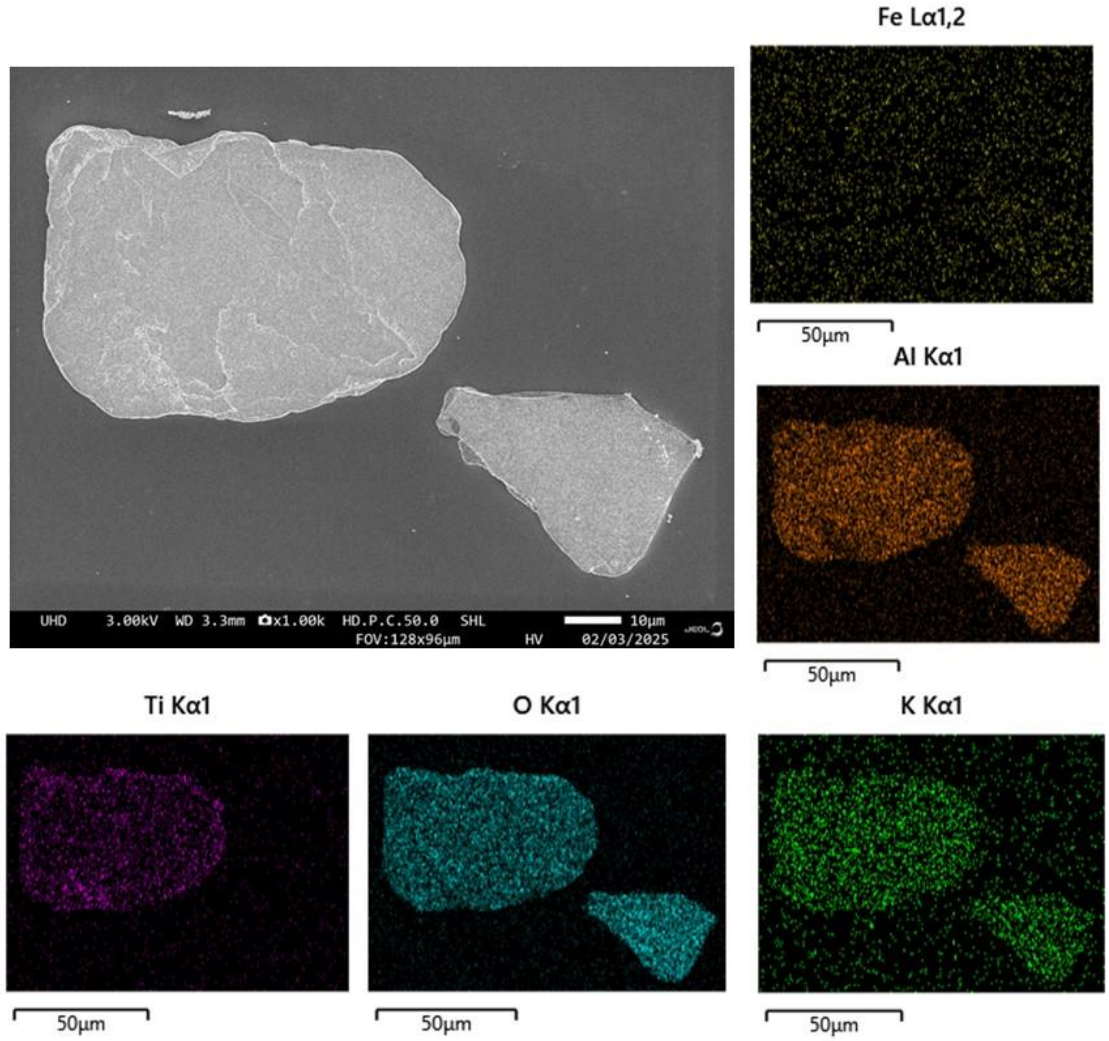


Figure 36 : *EDX mapping performed on the platelets imaged by SEM (magnification: x1,000) above (sample S8).*

Table 10 : Information from EDX spectra and EDX mapping performed on S8, Figure 35.

	Peaks	Element	substance
Spectrum 39	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminium	Mica platelets (see reminder section 1.3)
	K Kα1	potassium	Mica platelets (see reminder section 1.3)
	Ti Kα1, Lα1,2	titanium	TiO_2 particles on mica platelet
	Fe Lα1,2; Kα1	iron	Iron oxide on mica platelet
	Si Kα1	silicon	Silicon substrate and/or mica platelets
	C Kα1,2	carbon	contamination especially linked to the scanning of the electron beam

Spectrum 40	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminium	Mica platelets (see reminder section 1.3)
	K Kα1	potassium	Mica platelets (see reminder section 1.3)
	Fe Lα1,2; Kα1	iron	Iron oxide on mica platelet
	Si Kα1	silicon	Silicon substrate and/or mica platelets
	C Kα1,2	carbon	contamination especially linked to the scanning of the electron beam

The results EDX mapping combined with the elementary analysis performed on areas indicate the presence of TiO_2 and iron oxide on the mica platelet. As mentioned in the reminder of section 1.3, mica sheets can contain Al and K. The right platelet (area 40) does not contain TiO_2. It is a bare mica sheet with a small amount of iron oxide.

The results on the chemical composition of the platelets are confirmed by the Figure 37. A zoom of the constituent TiO_2 particles of platelets is inserted on the SEM image of the platelet (Figure 37).

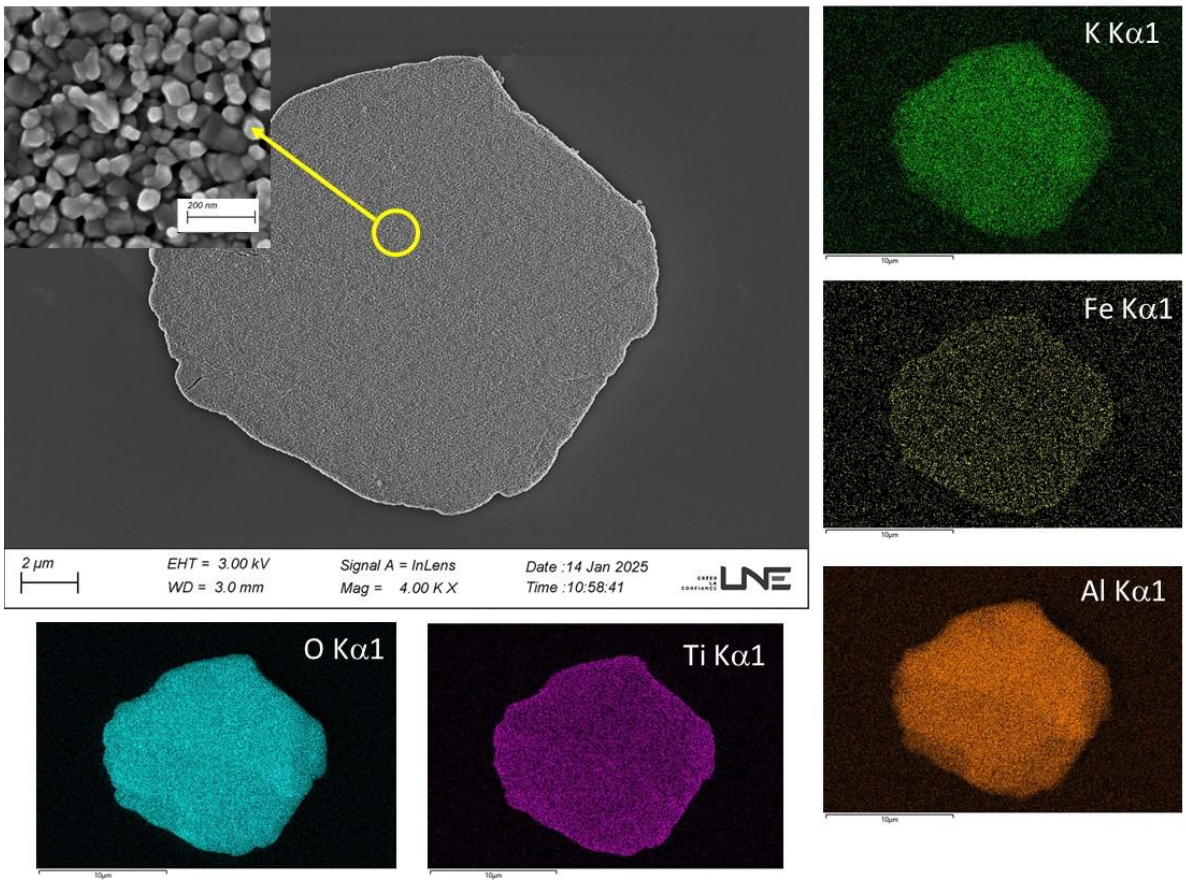


Figure 37 : *EDX mapping performed on the platelet imaged by SEM (above, x4,000) with a magnification x 4000 (sample S8).*

Some agglomerates/aggregates were imaged by SEM and analysed by EDX in Figure 38 and Figure 39.

Obtained results demonstrate that isolated agglomerates/aggregates consist of TiO_2 and Fe_2O_3 without being able to distinguish the both oxides. Iron is not visible on the spectra of small particles given in Figure 39.

The agglomerates do not contain mica. Aluminium is not present within agglomerates.

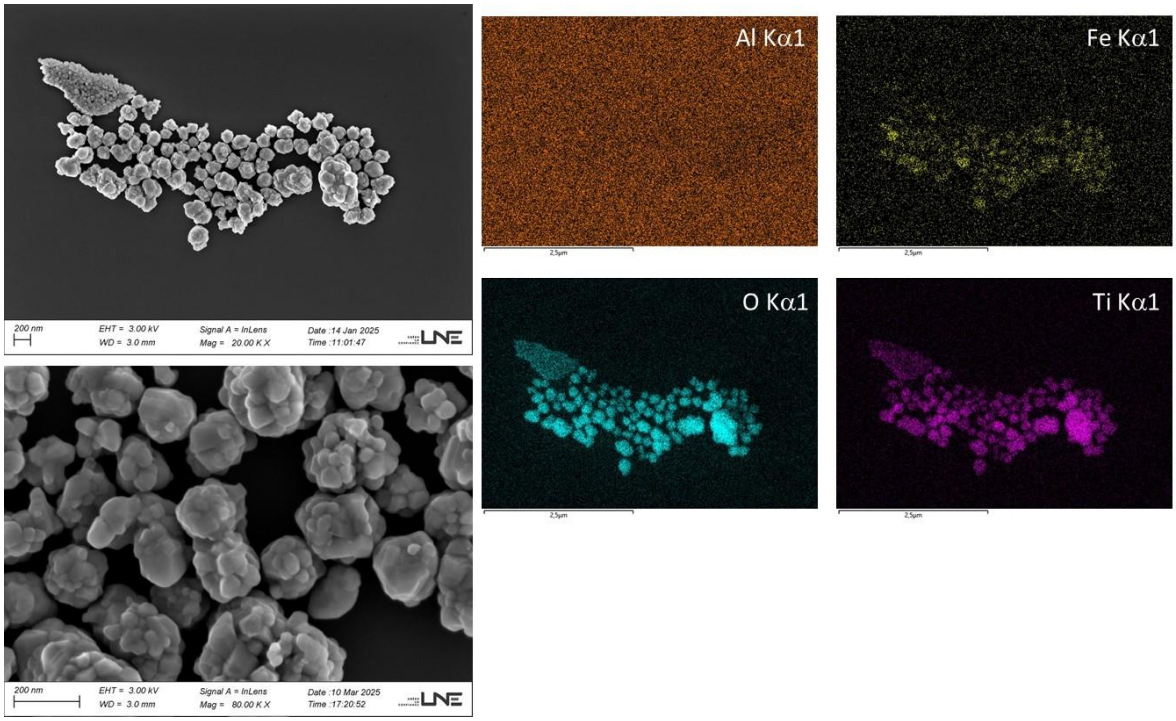


Figure 38 : *EDX mapping performed on agglomerates imaged by SEM (above) with two magnifications x 20 000 and 80 000 (sample S8).*

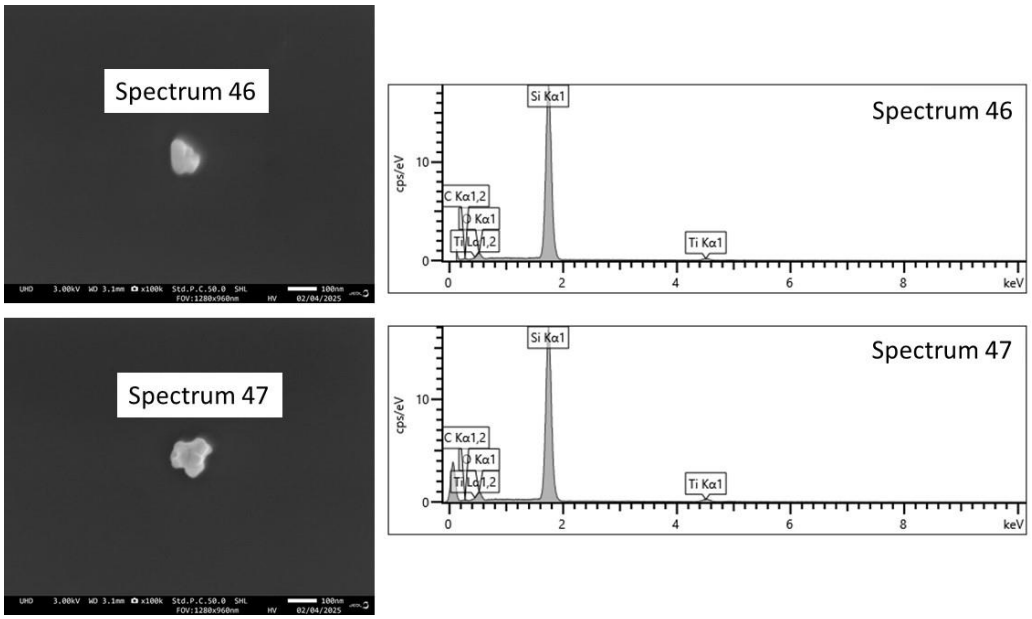


Figure 39 : SEM images of some *agglomerates*/aggregates (left) and EDX single-point spectra (46 and 47) carried out on particles (sample S8).

Table 11 : Information from EDX spectra and EDX mapping performed on S8, Figure 39.

	Peaks	Element	substance
Spectrum 46	O Kα1	oxygen	oxides within agglomerates
	Ti Kα1, Lα1,2	titanium	TiO_2 particles
	Si Kα1	silicon	Silicon substrate
	C Kα1,2	carbon	contamination especially linked to the scanning of the electron beam
Spectrum 47	O Kα1	oxygen	oxides within agglomerates
	Ti Kα1, Lα1,2	titanium	TiO_2 particles
	Si Kα1	silicon	Silicon substrate
	C Kα1,2	carbon	contamination especially linked to the scanning of the electron beam

3.3.3 Constituent particles size of the agglomerates and platelets

The sizes of the particles constituting the agglomerates and platelets were determined using the SEM image analysis. 300 particles were counted and measured to build each histogram of size distribution (Figure 40 and Figure 41). The results are reported in the Table 12.

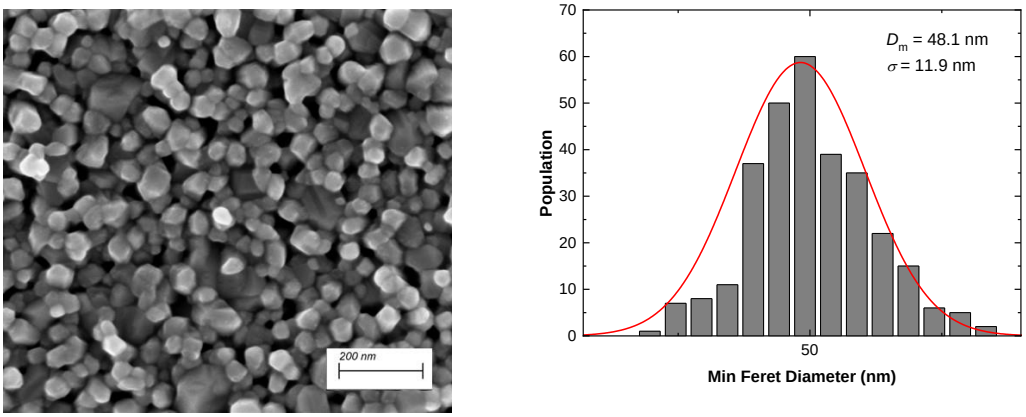


Figure 40 : *SEM image of mica surface (sample S8) with magnification x 80 000 (left) and size distribution histogram of the constituent particles (right).*

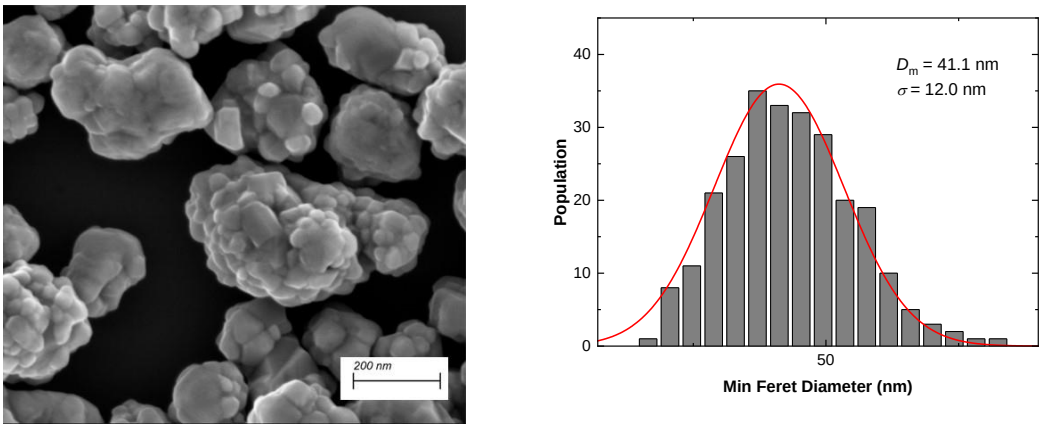


Figure 41 : *SEM image of agglomerate (sample S8) with magnification x 80 000 (left) and size distribution histogram of the constituent particles (right).*

Table 12 : *Results of constituent particle sizes obtained from the measurements carried out on agglomerates and platelets (sample S8).*

Objects	distribution	Mean Feret Diam. (nm)	Median (nm)	Mode (nm)	Polydispersity (nm)
Particle in agglomerate	Gaussian	47.6* ± 3.7	48.1	48.1	11.9
Particle in platelet	Gaussian	40.7* ± 3.7	41.1	41.1	12.0

*corrected value

The particles constituting the agglomerates and platelets are similar in size (Table 12) and in chemical composition (mainly TiO_2, see Figure 37and Figure 38).

The median of particle size within agglomerates and platelets is smaller than 100 nm.

Consequently, 100 % of these particle populations are considered as nanoparticles.

3.3.4 Surface state of mica platelets

The surface state of some platelets were studied. Examples are given in Figure 42. The quality of the surface is quite poor and it is cracked in many places. Agglomerates of TiO_2 nanoparticles are observed at the surface. The presence of these agglomerates seems to result from degradation of the upper layers of particles, as observed in Figure 42. The interaction between platelet surface and these agglomerates could be weak and explains the presence of isolated agglomerates on the silicon substrate outside platelets.

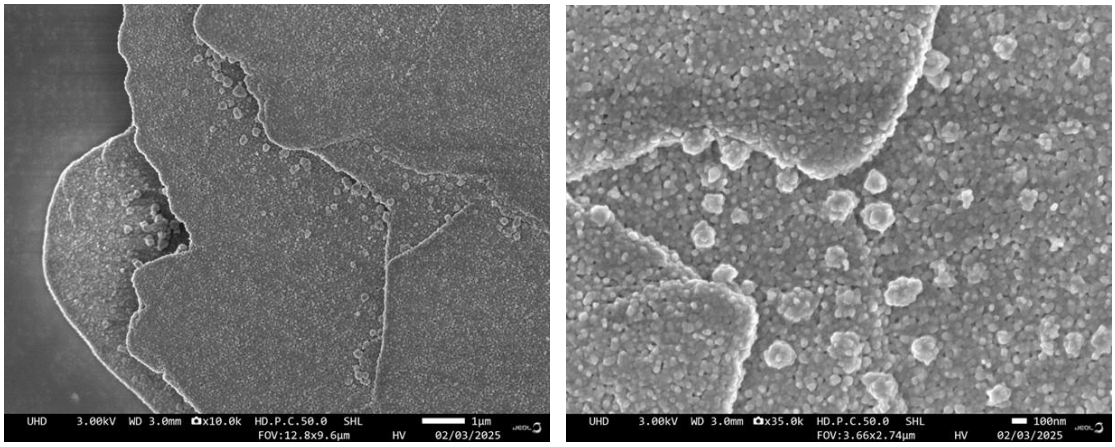


Figure 42 : *SEM images of the Surface state of a few platelets (sample S8).*

3.3.5 Conclusions on S8

- The mica platelets are covered by TiO_2 nanoparticles
- Agglomerates of TiO_2 nanoparticles without mica are observed outside the platelets
- The sizes (minimum Féret diameter) of TiO_2 particles within agglomerates and platelets (47.6 nm ± 3.7 nm and 40.7 nm ± 3.7 nm respectively) are similar and are smaller than 100 nm. 100 % are considered as nanoparticles.
- The same TiO_2 nanoparticles are present on the platelets and in the agglomerates.
- Isolated agglomerates of TiO_2 nanoparticles with sizes smaller than 100 nm were observed.
- The presence iron elements is demonstrated but no pure iron oxide particles were observed. The form was not demonstrated. Iron oxide could be in the form of oxide layer (from literature).

Test report continued on next page

4 STUDY ON THE PRESENCE OF NANOPARTICLES IN 7 COSMETIC PRODUCTS

4.1 SAMPLE S1 : NOCIBE, POUSSIERE D'ETOILES, LOT Q122

A picture of the studied sample is shown in Figure 43.

Figure 43 : *Picture of the sample S1 reference NOCIBE, POUSSIERE D'ETOILES, LOT Q122*

The presence of silica, titanium dioxide (CI77891), iron oxide (CI 77491), tin oxide and mica is indicated by the producer on the label.

4.1.1 Preparation of the sample

The sample preparation protocol is as follows:

- A sample fraction (12 mg) is mixed with 5 mL of MilliQ water.
- The obtained suspension is dispersed using a vortex device.

Analysis of nanoparticles (NPs) by electron microscopy (SEM) requires specific preparation of the samples to prevent excessive agglomeration of the NPs. To achieve this, LNE has developed an original protocol involving a spin-coater to deposit particles onto the substrate and improve their dispersion.

This protocol consists of two phases:

- Spreading a drop of suspension over a silicon substrate with a low rotation speed.
- Rapid drying of the drop at high rotation speed.

The particles deposited on the silicon substrate are then observed by SEM and analyzed by EDX.

Test report continued on next page

4.1.2 SEM measurements and EDX analyses performed on mica platelets.

Some examples of SEM images performed at magnification x1000 and x500 are shown in Figure 44.

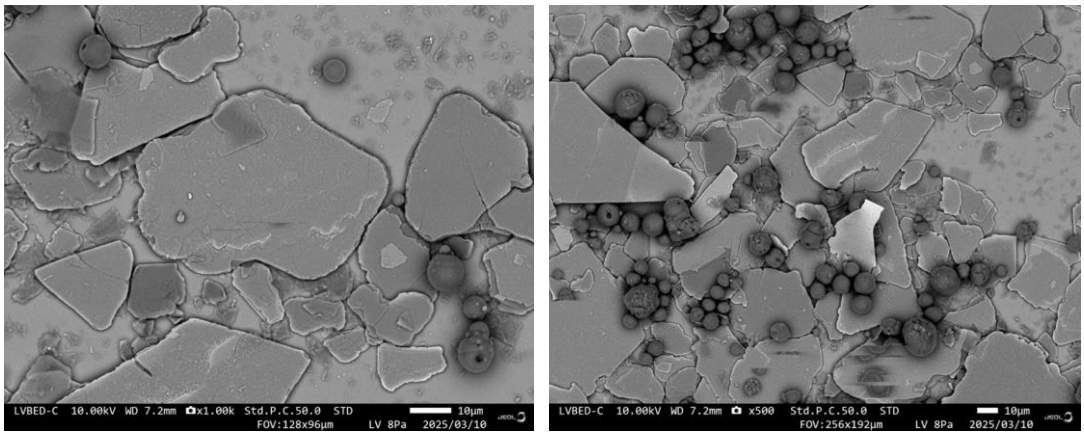


Figure 44 : *SEM image of the sample S1 (Magnification: x1000 and x500).*

The sample consists of typical platelet particles of mica pearlescent pigments. Some beads with a perfect spherical shape are also observed. Platelets and beads have variable sizes.

Platelets covered by particles are zoomed in Figure 45 and the thickness can be estimated. This thickness is ranged from 200 and 250 nm.

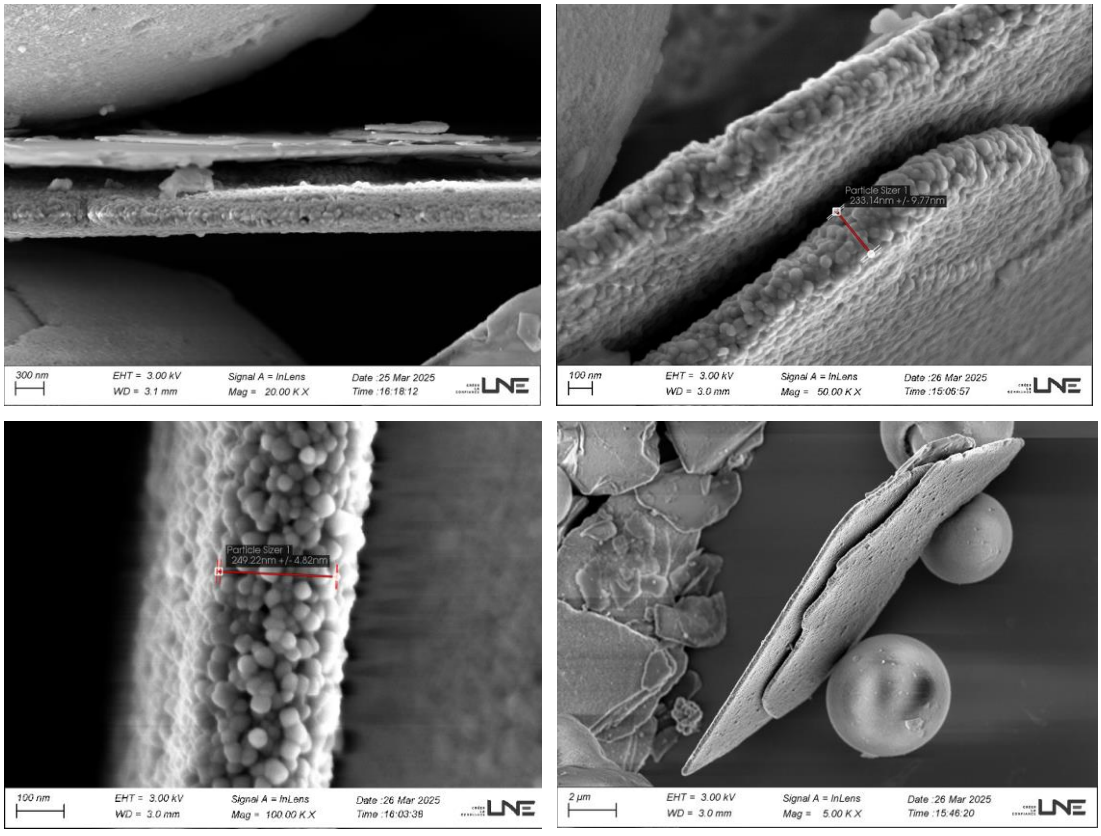


Figure 45 : *SEM images of platelets with different magnifications : x20 000, x50 000, x100 000 and x5 000.*

Analysis providing information on the constituent atoms was carried out on the platelets imaged in Figure 46 using the EDX technique. This elementary analysis is performed on the sample prepared on a silicon substrate.

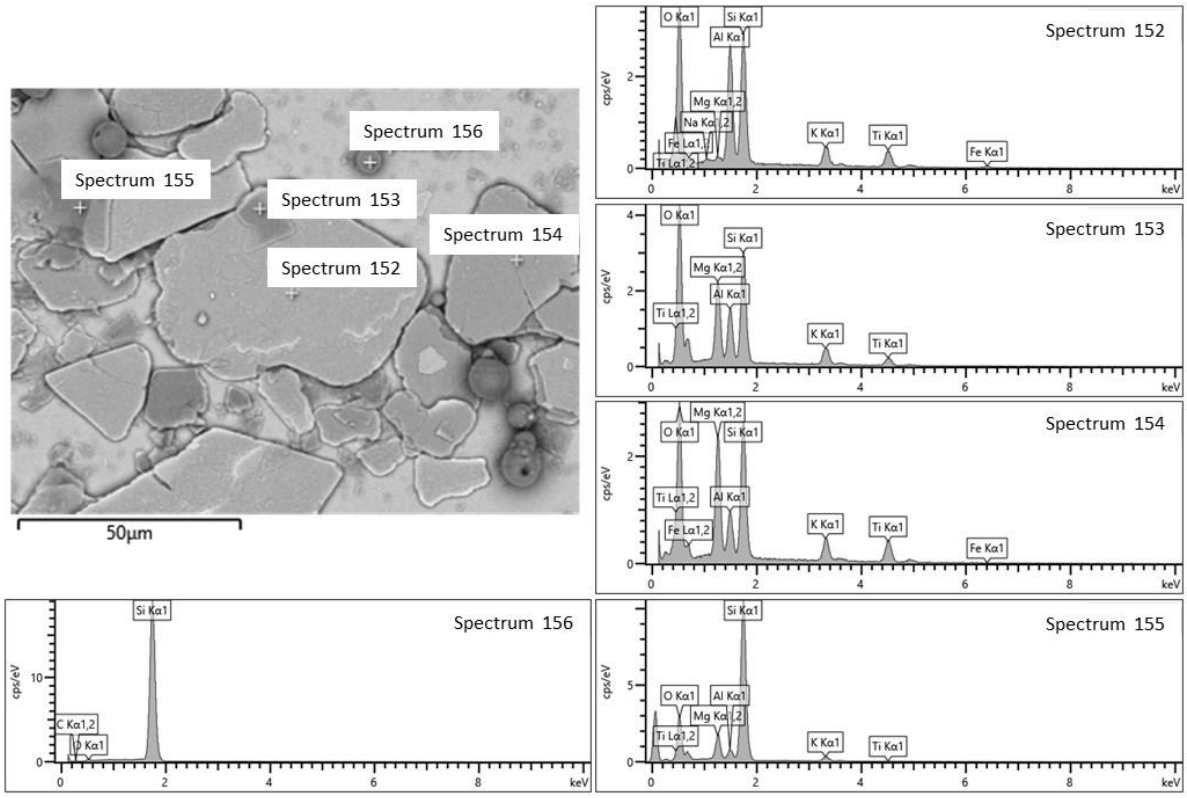


Figure 46 : *(on left, above) SEM image of platelet particles extracted from the sample S1 (magnification: x1 000). (on right) EDX spectra performed on the platelets.*

In order to confirm the chemical composition of the platelet, X-ray mapping was carried out. The results are shown in Figure 47. They show that elements oxygen, aluminum, potassium, titanium, iron and tin (hardly detected) are present in the imaged platelets. Sometimes, small amounts of magnesium and sodium are also detected. As mentioned in the reminder of section 1.3, mica sheets contain Al.

Test report continued on next page

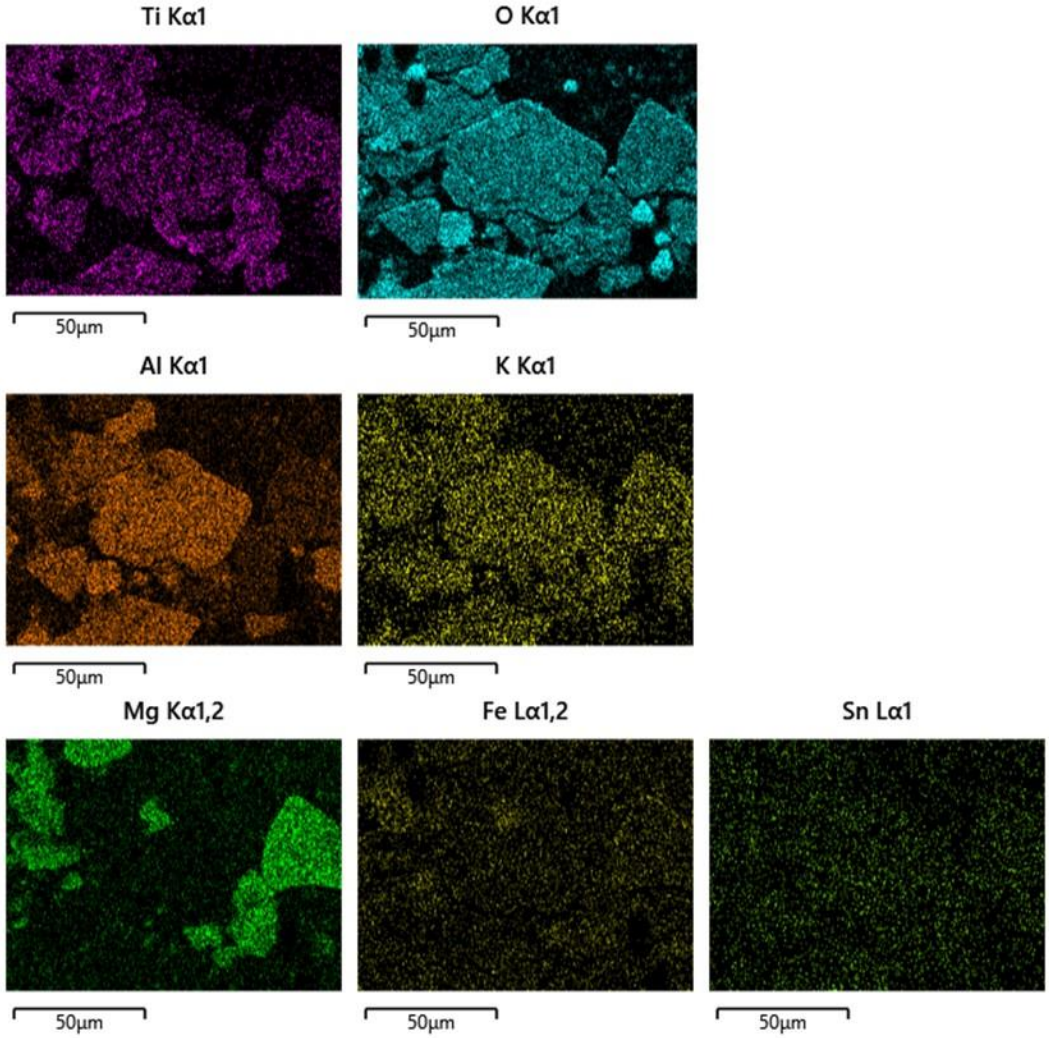


Figure 47 : *EDX mapping performed on the particle agglomerates (sample S1) of Figure 44(left).*

Test report continued on next page

Table 13 : Information from EDX spectra and EDX mapping performed on S1, Figure 46.

	Peaks	Element	substance
Spectrum 152	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminum	Mica platelets (see reminder section 1.3)
	K Kα1	potassium	Mica platelets (see reminder section 1.3)
	Na Kα1,2	sodium	Mica platelets (see reminder section 1.3)
	Mg Kα1,2	magnesium	Mica platelets (see reminder section 1.3)
	Ti Kα1, Lα1,2	titanium	TiO_2 particles
	Fe Kα1, Lα1,2		Iron oxide
	Si Kα1	silicon	Silicon substrate and/or mica platelets
Spectrum 153	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminum	Mica platelets (see reminder section 1.3)
	K Kα1	potassium	Mica platelets (see reminder section 1.3)
	Mg Kα1,2	magnesium	Mica platelets (see reminder section 1.3)
	Ti Kα1, Lα1,2	titanium	TiO_2 particles
	Si Kα1	silicon	Silicon substrate and/or mica platelets
Spectrum 154	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminum	Mica platelets (see reminder section 1.3)
	K Kα1	potassium	Mica platelets (see reminder section 1.3)
	Mg Kα1,2	magnesium	Mica platelets (see reminder section 1.3)
	Ti Kα1, Lα1,2	titanium	TiO_2 particles
	Fe Kα1, Lα1,2		Iron oxide
	Si Kα1	silicon	Silicon substrate and/or mica platelets
Spectrum 155	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminum	Mica platelets (see reminder section 1.3)
	K Kα1	potassium	Mica platelets (see reminder section 1.3)
	Mg Kα1,2	magnesium	Mica platelets (see reminder section 1.3)
	Ti Kα1, Lα1,2	titanium	TiO_2 particles
	Si Kα1	silicon	Silicon substrate and/or mica platelets
Spectrum 156	O Kα1	oxygen	oxides on spherical beads
	Si Kα1	silicon	Silicon on spherical beads/substrate
	C Kα1,2	carbon	contamination especially linked to the scanning of the electron beam

The results combining EDX mapping (Figure 48) and localized spectra (.

Table 14) indicates:

- **the presence of TiO_2, iron oxide and tin oxide (hardly detected) on the mica platelet. As mentioned in the reminder of section 1.3, mica sheets mainly contain aluminum (Al) and potassium (K).**
- **Beads with spherical shape are made of silicon.**

A SEM image of particles covering the mica platelet is given in Figure 48. Particles have a near-spherical shape.

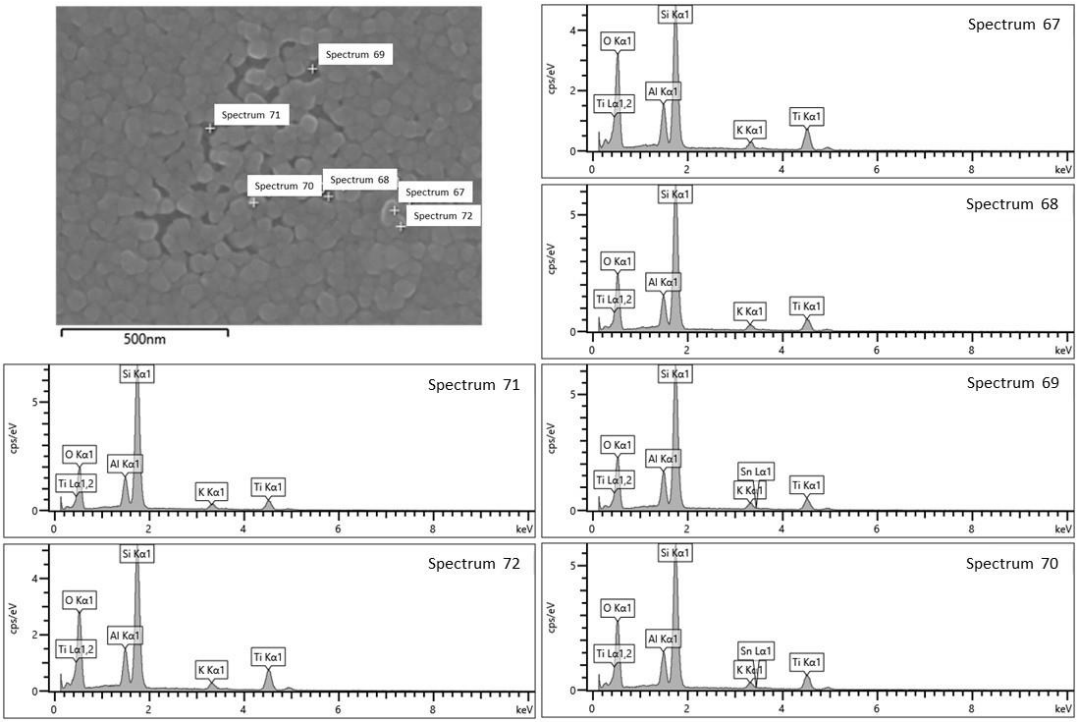


Figure 48 : *(on left, above) SEM image of platelet particles extracted from the sample S1 (magnification: x100 000). (around) single-point EDX spectra performed on the platelets.*

As shown on Figure 48 and .

Table 14, whatever the position of the single-point analysis, the spectra are all similar. Tin peaks is sometimes weakly visible.

Potassium and aluminium peaks come from mica sheets.

Particles covering the mica sheet is mainly made of TiO_2.

Table 14 : Information from EDX spectra and EDX mapping performed on S1, Figure 48.

	Peaks	Element	substance
Spectrum 67	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminum	Mica platelets (see reminder section 1.3)
	K Kα1	potassium	Mica platelets (see reminder section 1.3)

	Ti Kα1, Lα1,2	titanium	TiO_2 particles on mica platelet
	Si Kα1	silicon	Silicon substrate and/or mica platelets
Spectrum 68	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminum	Mica platelets (see reminder section 1.3)
	K Kα1	potassium	Mica platelets (see reminder section 1.3)
	Ti Kα1, Lα1,2	titanium	TiO_2 particles on mica platelet
	Si Kα1	silicon	Silicon substrate and/or mica platelets
Spectrum 69	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminum	Mica platelets (see reminder section 1.3)
	K Kα1	potassium	Mica platelets (see reminder section 1.3)
	Ti Kα1, Lα1,2	titanium	TiO_2 particles on mica platelet
	Sn Lα1,2; Kα1	tin	Tin oxide on mica platelet
	Si Kα1	silicon	Silicon substrate and/or mica platelets
Spectrum 70	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminum	Mica platelets (see reminder section 1.3)
	K Kα1	potassium	Mica platelets (see reminder section 1.3)
	Ti Kα1, Lα1,2	titanium	TiO_2 particles on mica platelet
	Sn Lα1,2; Kα1	tin	Tin oxide on mica platelet
	Si Kα1	silicon	Silicon substrate and/or mica platelets
Spectrum 71	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminum	Mica platelets (see reminder section 1.3)
	K Kα1	potassium	Mica platelets (see reminder section 1.3)
	Ti Kα1, Lα1,2	titanium	TiO_2 particles on mica platelet
	Si Kα1	silicon	Silicon substrate and/or mica platelets
Spectrum 72	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminum	Mica platelets (see reminder section 1.3)
	K Kα1	potassium	Mica platelets (see reminder section 1.3)
	Ti Kα1, Lα1,2	titanium	TiO_2 particles on mica platelet
	Si Kα1	silicon	Silicon substrate and/or mica platelets

Test report continued on next page

4.1.3 SEM measurements and EDX analyses performed on isolated particles.

Agglomerates/aggregates are also observed in the sample S1 deposited on silicon substrate. These agglomerates/aggregates have morphological properties different from platelets.

As shown in Figure 49, their size is smaller than platelet dimension (< 2 µm) and their shape is less flat.

An EDX spectrum performed on the agglomerates/aggregates imaged in Figure 49 (right) is given in Figure 50. Information about elemental analysis is reported in Table 15.

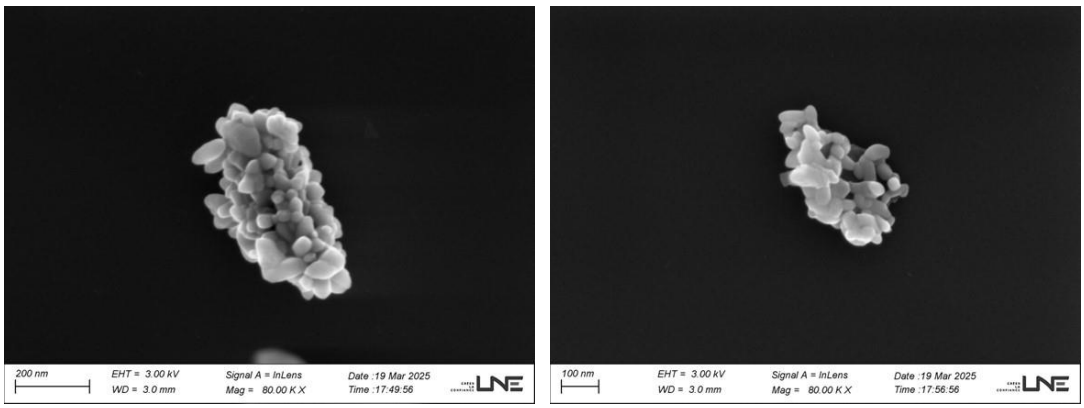


Figure 49 : *SEM images of some examples of agglomerates (sample S1) with a magnification x80 000.*

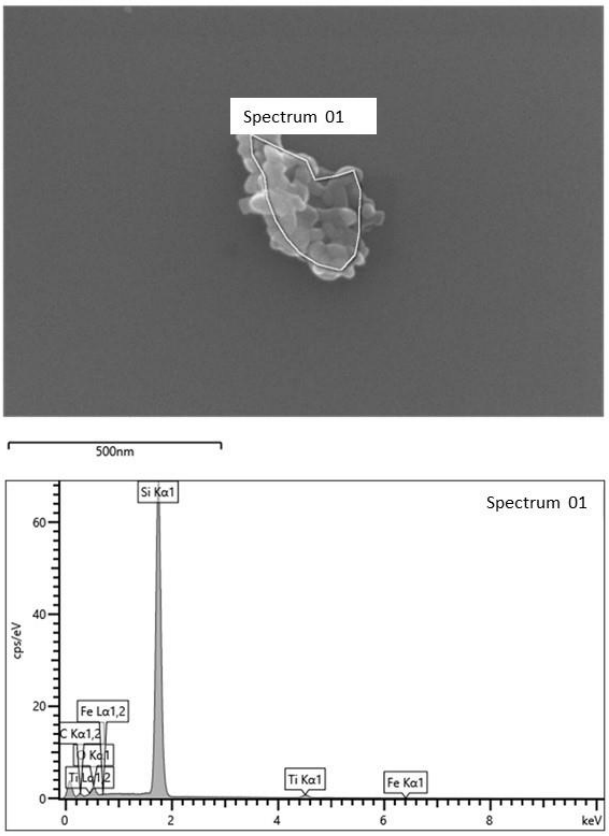


Figure 50 : *(above) SEM image of particle agglomerates extracted from the sample S1 (magnification: x80 000). (below) EDX spectrum performed on the particle agglomerates.*

Table 15 : Information from EDX spectra and EDX mapping performed on S1, Figure 50.

	Peaks	Element	substance
Spectrum 01	O Kα1	oxygen	oxides within agglomerates s
	Ti Kα1, Lα1,2	titanium	TiO_2 particles within agglomerates
	Fe Lα1,2; Kα1	iron	Iron oxide within agglomerates
	Si Kα1	silicon	Silicon substrate
	C Kα1,2	carbon	contamination especially linked to the scanning of the electron beam

The results show :

- **The constituent particles of these isolated agglomerates/aggregates are mainly composed of TiO_2.**
- **Iron element is localized on these agglomerates/aggregates but without being able to distinguish pure iron oxide particles.**
- **Agglomerates/aggregates do not contain mica because aluminium element is not observed on EDX mapping.**
- **TiO_2 agglomerates/aggregates are present outside mica platelets.**
- **Mean Féret diameters of the constituent particles within agglomerates are :**

  38.2 nm ± 6.1 nm (Figure 49, left)

  33.7 nm ± 4.4 nm (Figure 49, right)

  47.6 nm ± 4.5 nm (Figure 51)

Similar results were obtained with other agglomerates/aggregates as shown in Figure 51.

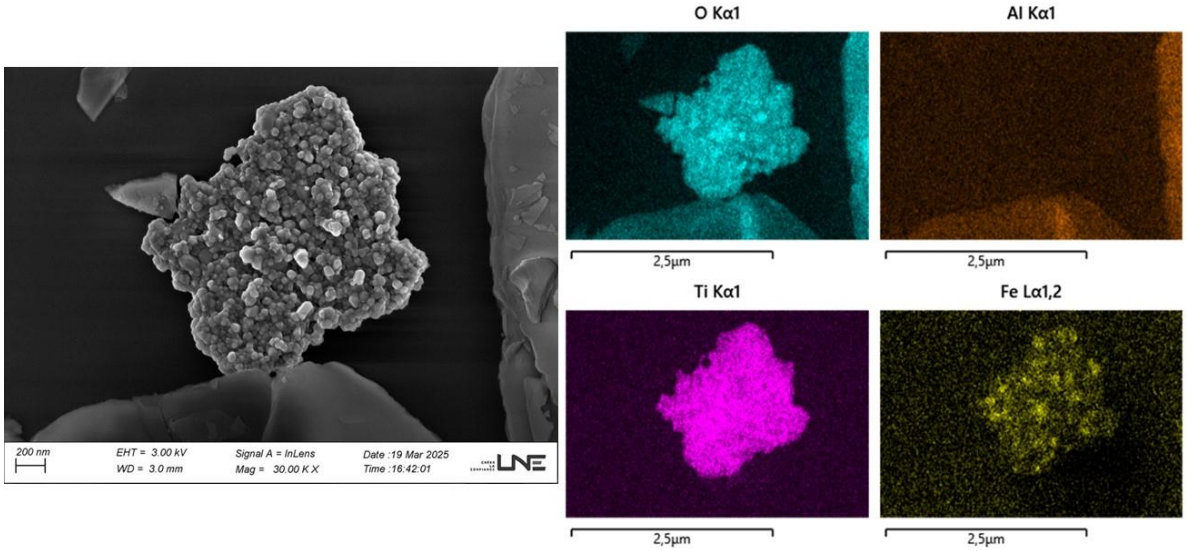


Figure 51 : *EDX mapping and of an isolated agglomerate imaged on the left side (sample S1).*

4.2 SAMPLE S2 : SEPHORA, 02 SPICY SUNSET, LOT 42780

A picture of the studied sample is shown in Figure 52.

Figure 52 : *Picture of the sample S2 reference SEPHORA, 02 SPICY SUNSET, LOT 42780*

The presence of silica, titanium dioxide (CI77891), iron oxide (CI 77491, CI 77492, CI 77499), tin oxide and mica is indicated by the producer on the label.

Some organic pigments are also included: Yellow 5 CI 19140 and Red 7 Lake CI 15850.

4.2.1 Preparation of the sample

The sample preparation protocol is as follows:

- A sample fraction (12 mg) is mixed with 5 mL of ethanol.
- The obtained suspension is dispersed using a vortex device.

Analysis of nanoparticles (NPs) by electron microscopy (SEM) requires specific preparation of the samples to prevent excessive agglomeration of the NPs. To achieve this, LNE has developed an original protocol involving a spin-coater to deposit particles onto the substrate and improve their dispersion.

This protocol consists of two phases:

- Spreading a drop of suspension over a silicon substrate with a low rotation speed.
- Rapid drying of the drop at high rotation speed.

The particles deposited on the silicon substrate are then observed by SEM and analyzed by EDX.

4.2.2 SEM measurements and EDX analyses performed on mica platelets.

Some examples of SEM images performed at magnification x500, x9,000 and x40,000 are shown in Figure 53.

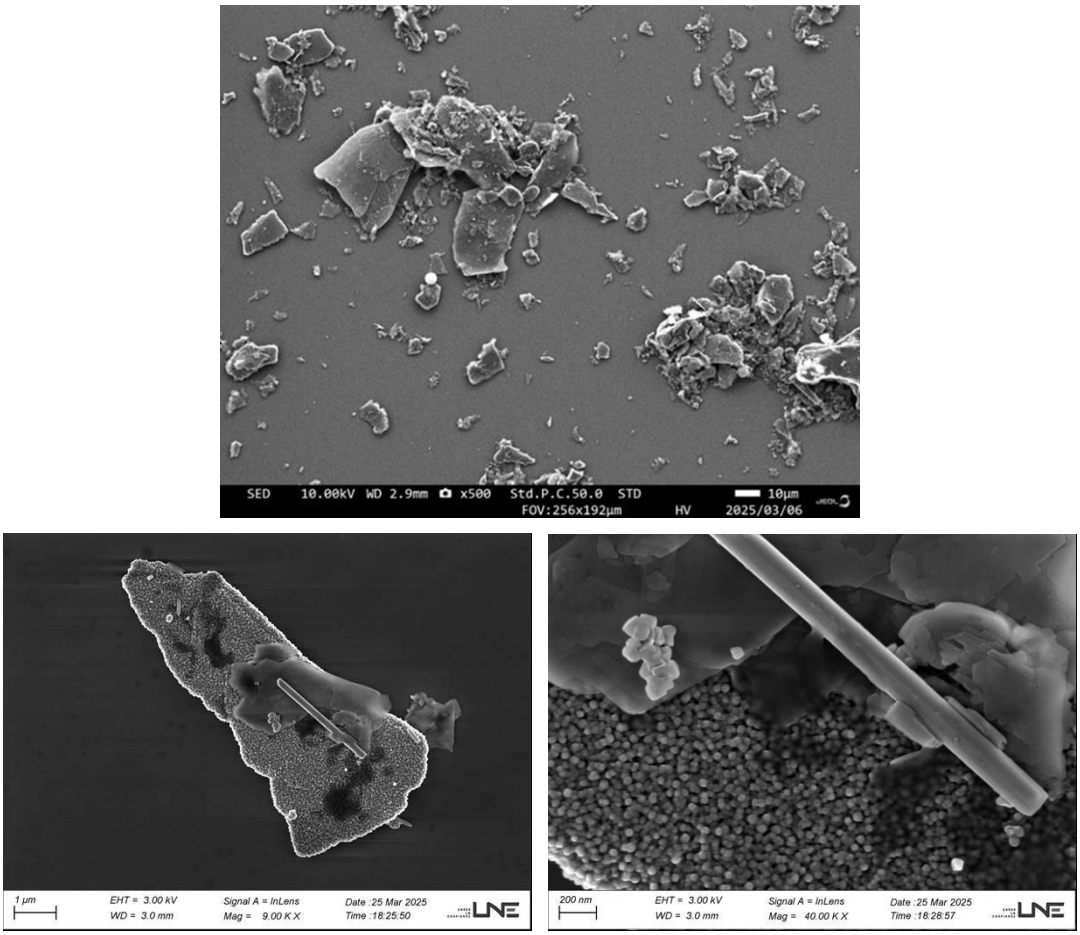


Figure 53 : *(above) SEM images of particles (platelets and agglomerates) extracted from sample S2, performed at magnification x10 000. (below) SEM image of a platelet with some rods and particles (x9,000) and a zoom (x40,000).*

The sample consists of typical platelet particles of mica pearlescent pigments. Some rods and particles with various shapes (near-spherical and cubic) are also observed. Platelets, rods and particles have variable sizes.

Analysis providing information on the constituent atoms was carried out on the platelets imaged in Figure 54 and Figure 55 using the EDX technique. This elementary analysis is performed on the sample prepared on a silicon substrate.

EDX analysis (Table 16) shows that elements oxygen, aluminum and potassium are present in the imaged platelets. As reminded in section 1.3, These chemical elements are constituents of mica. A layer of particles made of titanium covers the mica platelet.

Particles composed of iron are also present on the platelets. (spectrum 116, Figure 55).

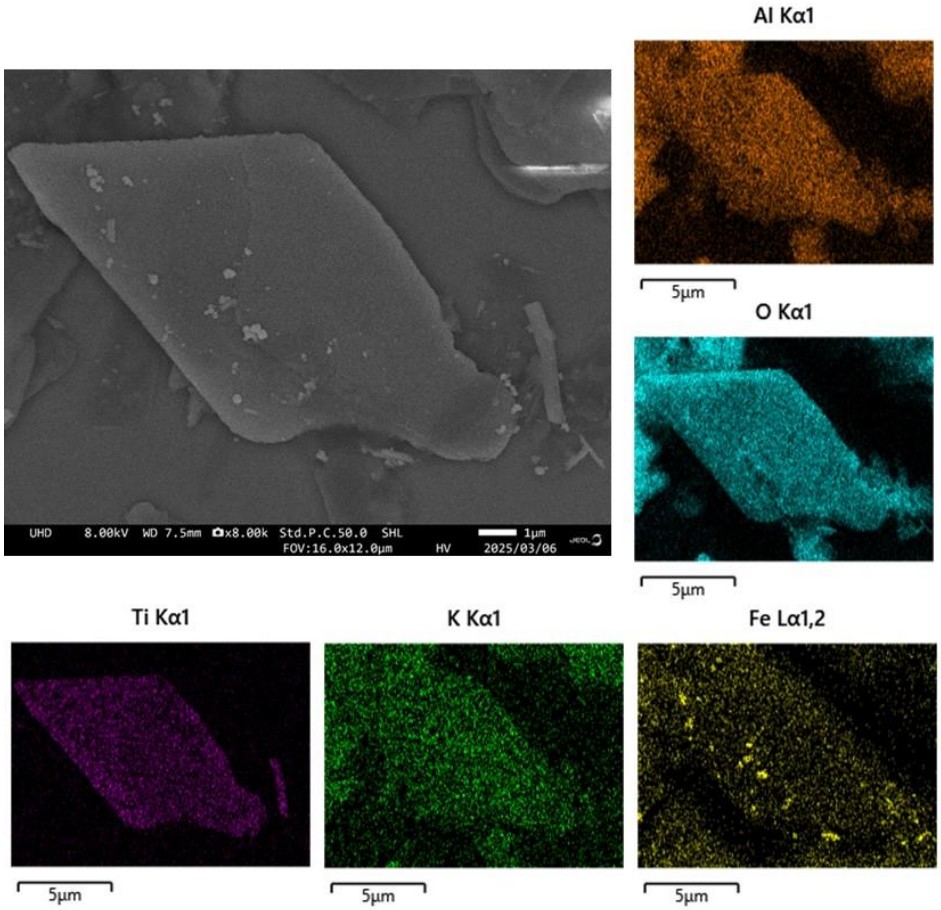


Figure 54 : *EDX mapping performed on the particle agglomerates imaged in picture above left (sample S2).*

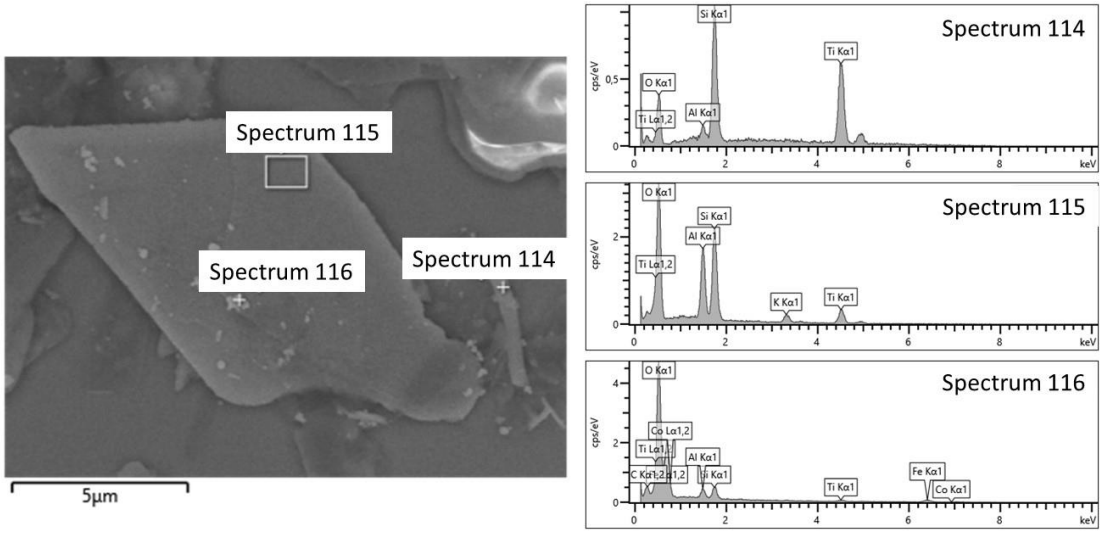


Figure 55 : *(on left) SEM image of one platelet with particles in surface extracted from the sample reference S2 (magnification: x8,000). (on right) EDX spectra performed on the area 115 and single-points 114 and 115.*

Table 16 : Information from EDX spectra and EDX mapping performed on S2, Figure 55.

	Peaks	Element	substance
Spectrum 114	O Kα1	oxygen	oxides on mica platelets and titanium
	Al Kα1	aluminium	Mica platelets (see reminder section 1.3)
	Ti Kα1, Lα1,2	titanium	TiO_2 rod
	Si Kα1	silicon	Silicon substrate and/or mica platelets
Spectrum 115	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminium	Mica platelets (see reminder section 1.3)
	K Kα1	potassium	Mica platelets (see reminder section 1.3)
	Ti Kα1, Lα1,2	titanium	TiO_2 particles on mica platelet
	Si Kα1	silicon	Silicon substrate and/or mica platelets
Spectrum 116	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminium	Mica platelets (see reminder section 1.3)
	Co Kα1, Lα1,2	cobalt	pollution
	Ti Kα1, Lα1,2	titanium	TiO_2 particles on mica platelet
	Fe Lα1,2; Kα1	iron	Iron oxide on mica platelet
	Si Kα1	silicon	Silicon substrate and/or mica platelets
	C Kα1,2	carbon	contamination especially linked to the scanning of the electron beam

Test report continued on next page

4.2.3 SEM measurements and EDX analyses performed on isolated particles.

Agglomerates/aggregates are also observed in the sample S2 deposited on silicon substrate. These agglomerates/aggregates have morphological properties different from platelets.

Rod-shaped particles are observed in Figure 56.

These rod-shaped particles are made of iron oxide as demonstrated by EDX mapping and EDX spectra given, respectively, in Figure 56 and Figure 57. Information about EDX spectra are given in Table 17.

This kind of acicular shape is typical of red iron oxide pigments (CI 77491) and yellow iron oxide pigments (CI 77492). These additives are present in the product S2, as mentioned in Table 1.

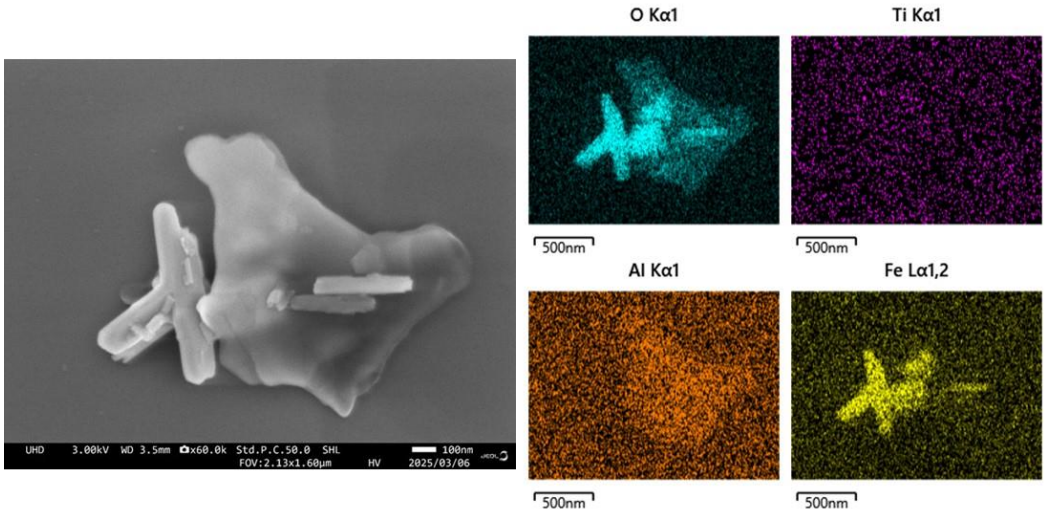


Figure 56 : *EDX mapping performed on the rod-shaped particles and agglomerates imaged on left side (sample S2).*

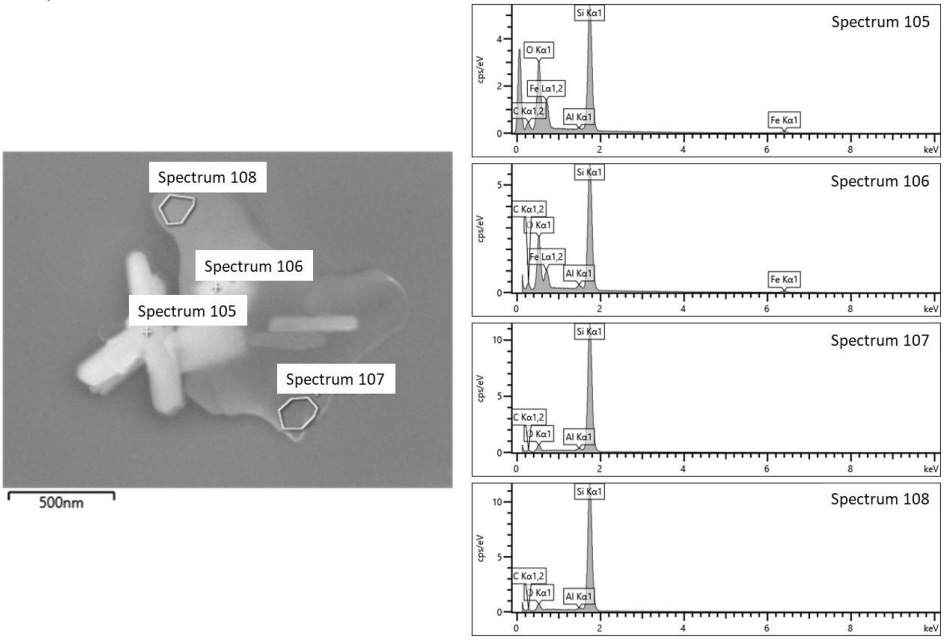


Figure 57 : *(on left) SEM image of rod-shaped particles and agglomerates extracted from the sample S2 (magnification: x3,000). (on right) EDX spectra performed on areas 107, 108 and single-points 105, 106.*

Table 17 : Information from EDX spectra and EDX mapping performed on S2, Figure 57.

	Peaks	Element	substance
Spectrum 105	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminium	Mica platelets (see reminder section 1.3)
	Fe Lα1,2; Kα1	iron	Iron oxide on mica platelet
	Si Kα1	silicon	Silicon substrate and/or mica platelets
	C Kα1,2	carbon	contamination especially linked to the scanning of the electron beam
Spectrum 106	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminium	Mica platelets (see reminder section 1.3)
	Fe Lα1,2; Kα1	iron	Iron oxide on mica platelet
	Si Kα1	silicon	Silicon substrate and/or mica platelets
	C Kα1,2	carbon	contamination especially linked to the scanning of the electron beam
Spectrum 107	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminium	Mica platelets (see reminder section 1.3)
	Si Kα1	silicon	Silicon substrate and/or mica platelets
	C Kα1,2	carbon	contamination especially linked to the scanning of the electron beam
Spectrum 108	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminium	Mica platelets (see reminder section 1.3)
	Si Kα1	silicon	Silicon substrate and/or mica platelets
	C Kα1,2	carbon	contamination especially linked to the scanning of the electron beam

Test report continued on next page

Some SEM images of rod-shaped particles within agglomerates/aggregates are given in Figure 58.

Regarding the measurements performed on the particles of Figure 58, the Féret diameter corresponding to cross-sectional diameter of rods is ranged from 25 nm to 150 nm.

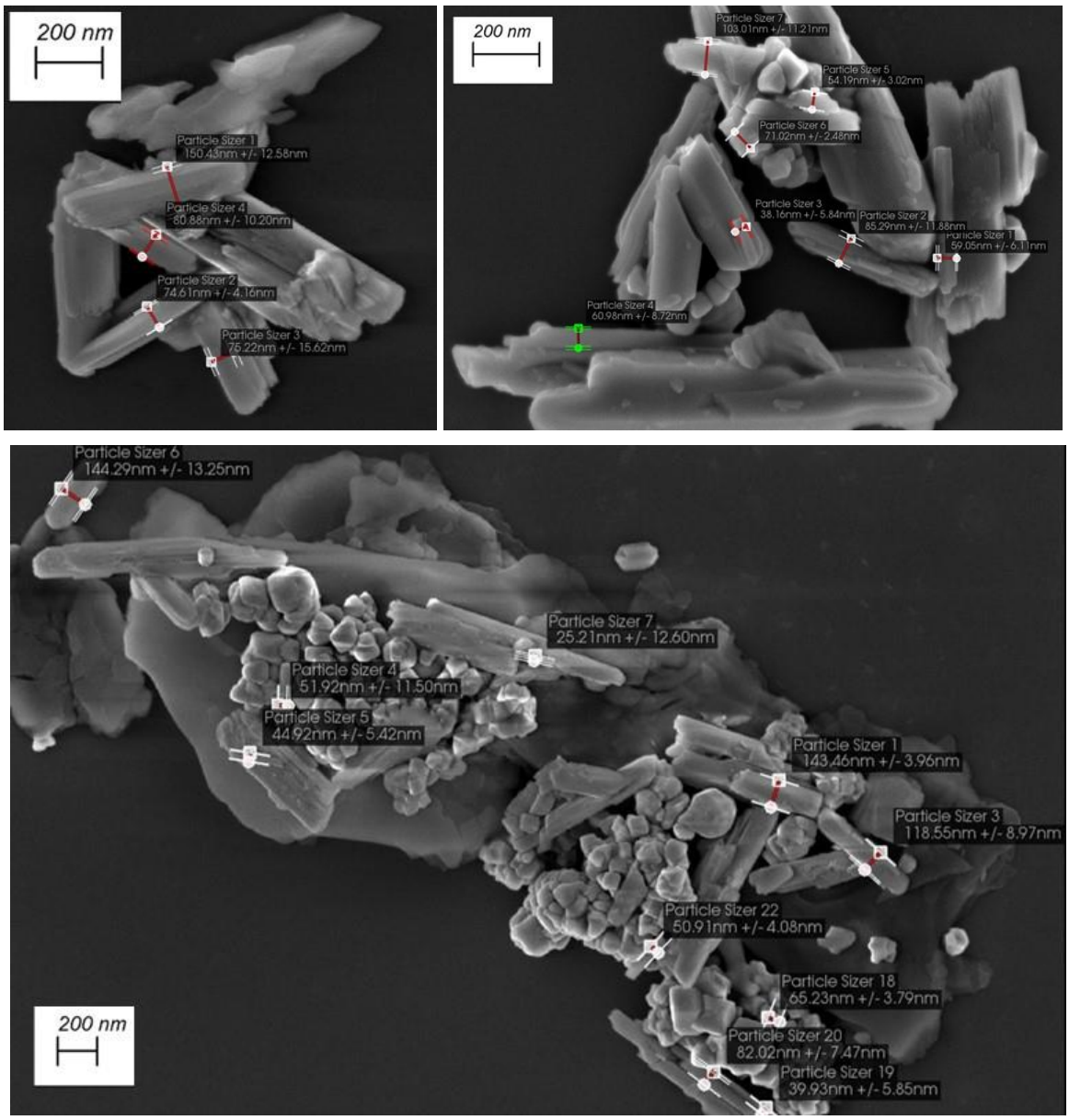


Figure 58 : SEM images (magnification: x30,000, left above; x40,000, right above; x20,000 below) of several examples of agglomerates of particles with various shapes (elongated, spherical, cubic) extracted from sample S2 and deposited on silicon substrate. The Féret Minimum Diameter was determined for some particles.

Near-spherical and cubic-shaped particles are observed in Figure 59 and Figure 60.

These shapes are typical of red iron oxide pigments (CI 77491) and black iron oxide pigments (CI 77499). These additives are present in the product S2, as mentioned in Table 1.

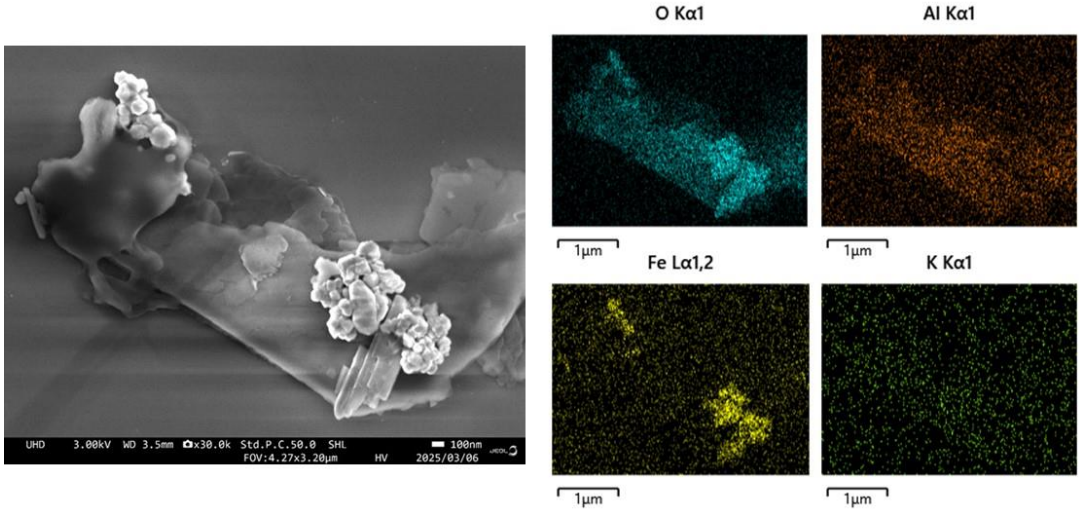


Figure 59 : *EDX mapping performed on the particle agglomerates extracted from sample S2 and imaged on the left side.*

The minimum Féret diameters of iron oxide near-spherical and cubic-shaped particles were measured and the mean has been found to be 92.2 nm ± 10.2 nm.

Regarding Figure 60, The same measurements were performed and the minimum Féret diameters are 98.7 nm ± 19.4 nm for left agglomerates and 63.0 nm ± 9.0 nm for right one.

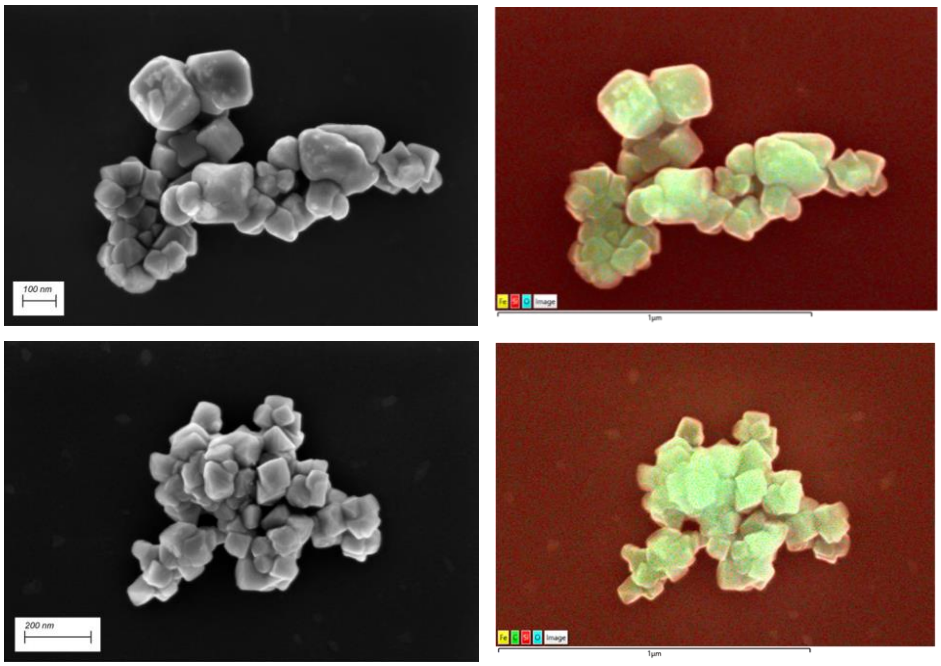


Figure 60 : SEM images (magnification: x80,000) of several examples of agglomerates of cubic particles extracted from sample S2 and deposited on silicon substrate.

4.3 SAMPLE S3 : AROMA ZONE, NACRE MINERALE LOT 03052

A picture of the studied sample is shown in Figure 61.

Figure 61 : *Picture of the sample S3 reference 03052 from AROMA ZONE, NACRE MINERALE LOT 22COLO0008/8*

The presence of titanium dioxide (CI77891), iron oxide (CI 77491) and mica is indicated by the producer on the label.

4.3.1 Preparation of the sample

The sample preparation protocol is as follows:

- A sample fraction (12 mg) is mixed with 5 mL of ethanol.
- The obtained suspension is dispersed using a vortex device.

Analysis of nanoparticles (NPs) by electron microscopy (SEM) requires specific preparation of the samples to prevent excessive agglomeration of the NPs. To achieve this, LNE has developed an original protocol involving a spin-coater to deposit particles onto the substrate and improve their dispersion.

This protocol consists of two phases:

- Spreading a drop of suspension over a silicon substrate with a low rotation speed.
- Rapid drying of the drop at high rotation speed.

The particles deposited on the silicon substrate are then observed by SEM and analyzed by EDX.

Test report continued on next page

4.3.2 SEM measurements and EDX analyses performed on sample 3.

Some examples of SEM images performed at magnification x30,000 and x50,000 are shown in Figure 62.

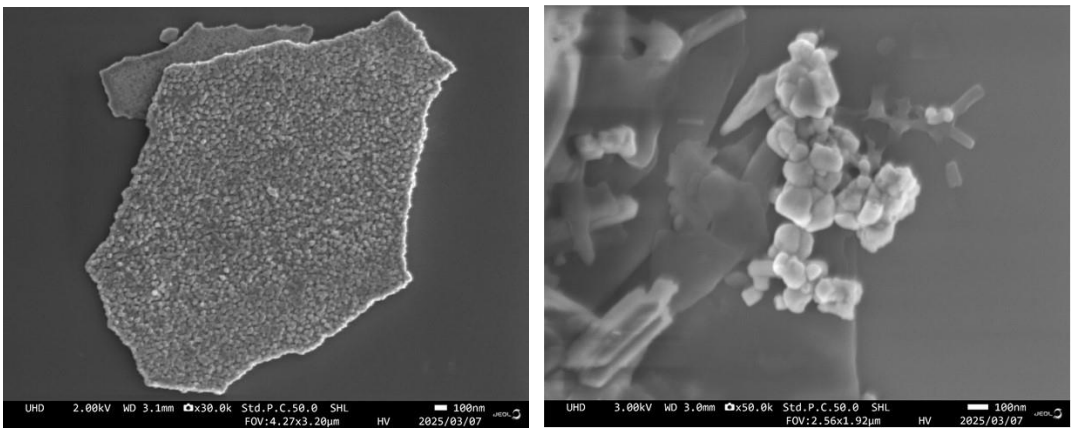


Figure 62 : *SEM images of platelets (left, magnification: x30,000), cubic, spherical and elongated particles (right, x50,000) extracted from the sample reference S3.*

The sample consists of typical platelet particles of mica pearlescent pigments. Some rods and particles with various shapes (near-spherical and cubic) are also observed. Platelets, rods and particles have variable sizes.

Analysis providing information on the constituent atoms was carried out on the platelets imaged in Figure 63 and Figure 64 using the EDX technique. This elementary analysis is performed on the sample prepared on a silicon substrate.

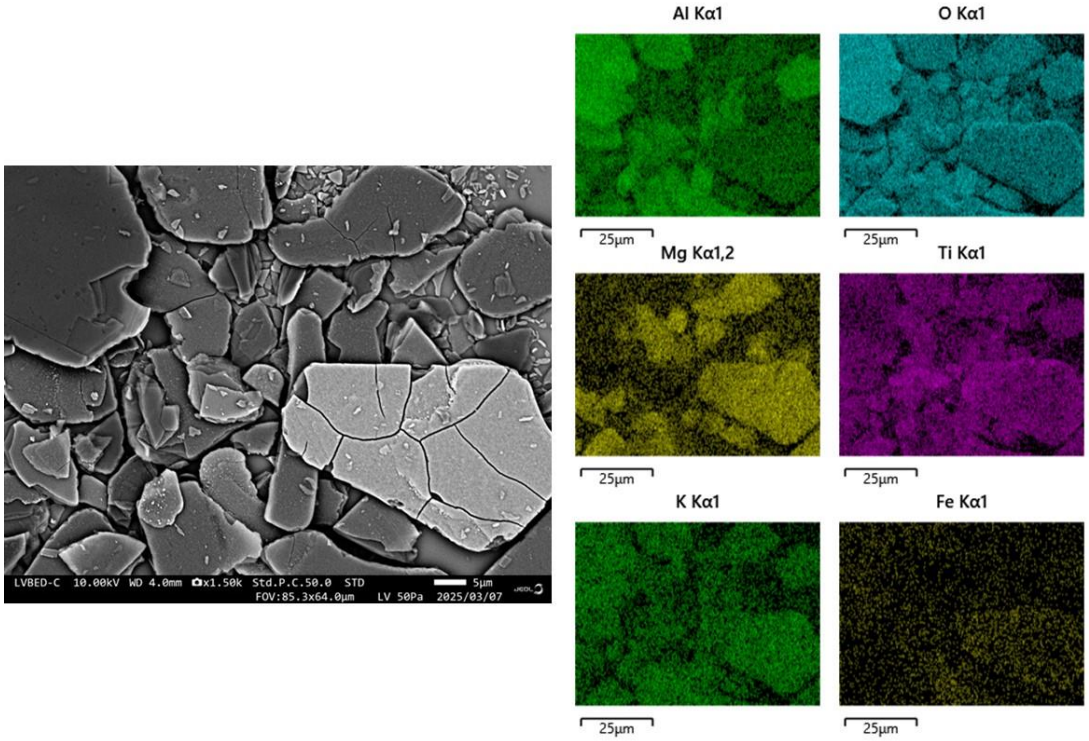


Figure 63 : *EDX mapping performed on the platelets imaged by SEM on the left side (sample S3).*

EDX analysis (Table 18) shows that elements oxygen, aluminum, potassium, magnesium and sodium are present in the imaged platelets. As reminded in section 1.3, These chemical elements are constituents of mica. A layer of particles made of titanium covers the mica platelet. Iron and tin elements are also present within the platelets. However, no pure particle of iron or tin oxides have been identified.

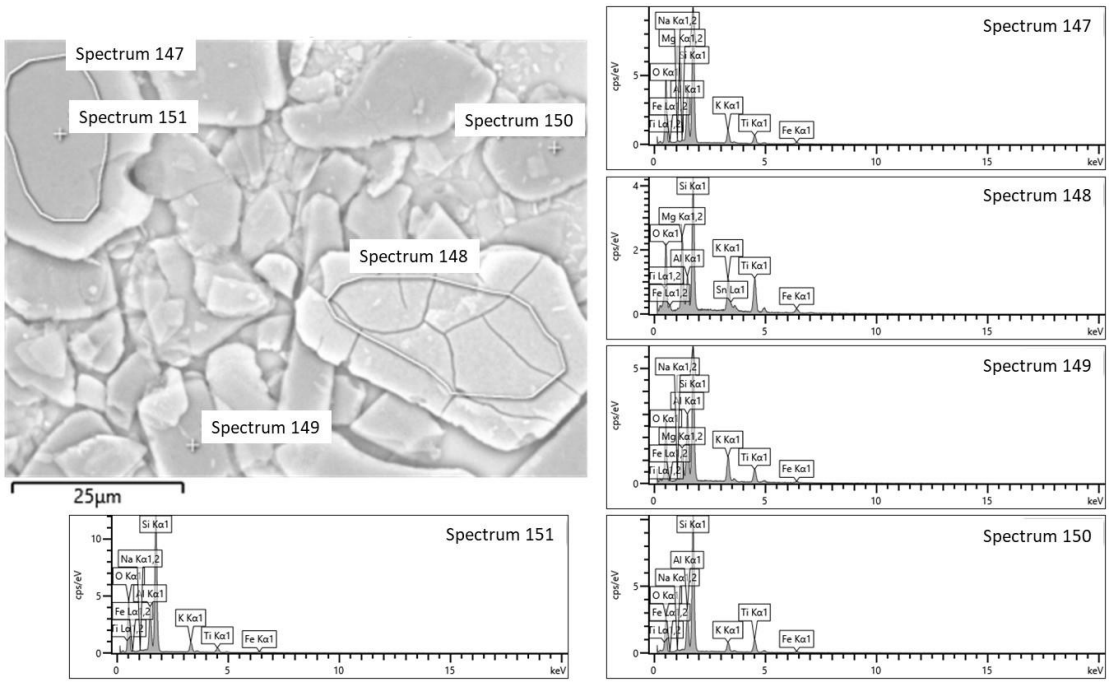


Figure 64 : *areas (147, 148) and single-point (149, 151) analyses on the left image and obtained spectra on the right (sample S3).*

Table 18 : Information from EDX spectra and EDX mapping performed on S3, Figure 64.

	Peaks	Element	substance
Spectrum 147	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminium	Mica platelets (see reminder section 1.3)
	Mg Kα1,2	magnesium	Mica platelets (see reminder section 1.3)
	K Kα1	potassium	Mica platelets (see reminder section 1.3)
	Na Kα1,2	sodium	Mica platelets (see reminder section 1.3)
	Ti Kα1, Lα1,2	titanium	TiO_2 particles on mica platelet
	Fe Lα1,2; Kα1	iron	Iron oxide on mica platelet
	Si Kα1	silicon	Silicon substrate and/or mica platelets
Spectrum 148	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminium	Mica platelets (see reminder section 1.3)
	Mg Kα1,2	magnesium	Mica platelets (see reminder section 1.3)
	K Kα1	potassium	Mica platelets (see reminder section 1.3)
	Ti Kα1, Lα1,2	titanium	TiO_2 particles on mica platelet
	Fe Lα1,2; Kα1	iron	Iron oxide on mica platelet
	Sn Lα1,2	tin	Tin oxide on mica platelets
	Si Kα1	silicon	Silicon substrate and/or mica platelets

Spectrum 149	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminium	Mica platelets (see reminder section 1.3)
	K Kα1	potassium	Mica platelets (see reminder section 1.3)
	Mg Kα1,2	magnesium	Mica platelets (see reminder section 1.3)
	Na Kα1,2	sodium	Mica platelets (see reminder section 1.3)
	Ti Kα1, Lα1,2	titanium	TiO_2 particles on mica platelet
	Fe Lα1,2; Kα1	iron	Iron oxide on mica platelet
	Si Kα1	silicon	Silicon substrate and/or mica platelets
Spectrum 150	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminium	Mica platelets (see reminder section 1.3)
	K Kα1	potassium	Mica platelets (see reminder section 1.3)
	Na Kα1,2	sodium	Mica platelets (see reminder section 1.3)
	Ti Kα1, Lα1,2	titanium	TiO_2 particles on mica platelet
	Fe Lα1,2; Kα1	iron	Iron oxide on mica platelet
	Si Kα1	silicon	Silicon substrate and/or mica platelets
Spectrum 151	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminium	Mica platelets (see reminder section 1.3)
	K Kα1	potassium	Mica platelets (see reminder section 1.3)
	Na Kα1,2	sodium	Mica platelets (see reminder section 1.3)
	Ti Kα1, Lα1,2	titanium	TiO_2 particles on mica platelet
	Fe Lα1,2; Kα1	iron	Iron oxide on mica platelet
	Si Kα1	silicon	Silicon substrate and/or mica platelets

Test report continued on next page

Two platelets were imaged by SEM and analyzed by EDX in Figure 65.

The first one is mainly composed of titanium and the iron element is only present in the second one without detection of aluminum. Regarding the second platelet, we assume that the mica layer has peeled off and the sandwiched layer between TiO_2 particles and mica sheet is accessible to be analyzed. As a result, the iron oxide layer would be localized between the mica sheet and TiO_2 particle upper layer.

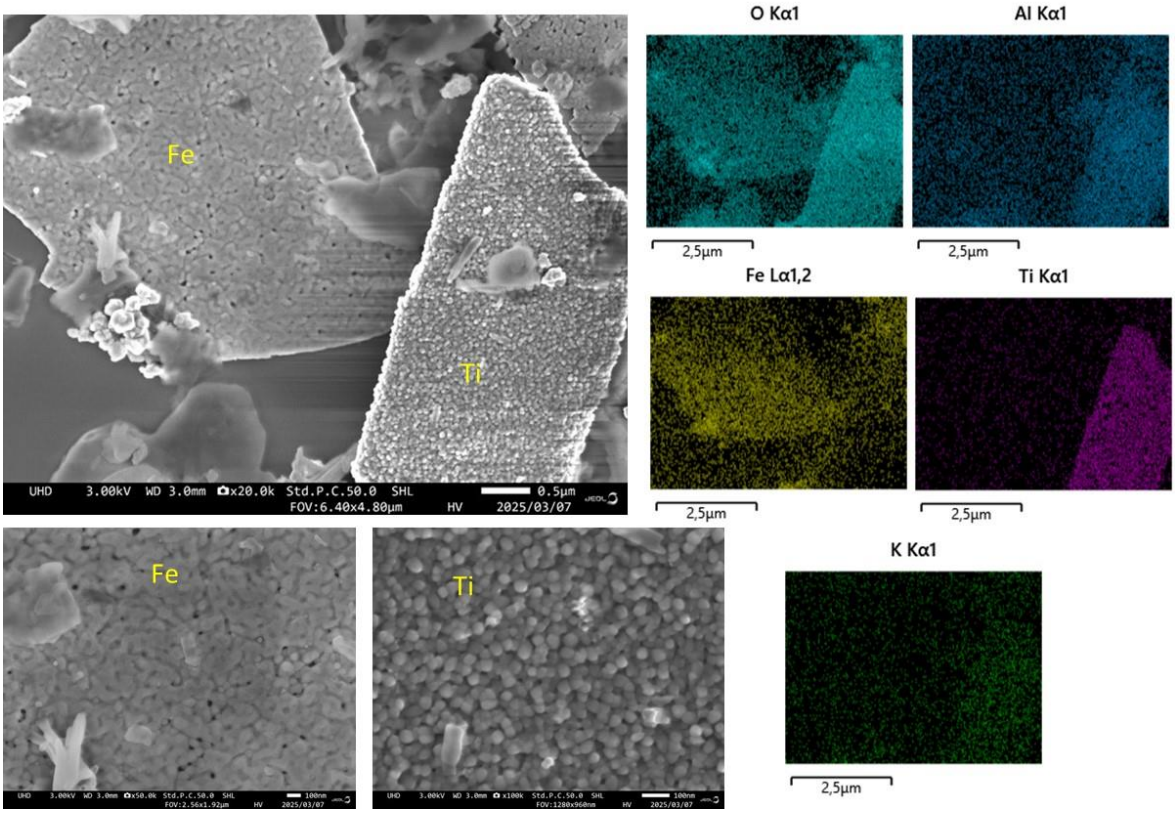


Figure 65 : *EDX mapping performed on the platelets and particle agglomerates (sample S3) imaged on the left side. (left below, x20,000) the two platelets imaged above and composed respectively of iron and titanium are zoomed (magnification x50,000 and x100,000).*

Test report continued on next page

4.3.3 SEM measurements and EDX analyses performed on isolated particles.

Agglomerates/aggregates are also observed in the sample S3 deposited on silicon substrate, for instance in Figure 66. These agglomerates/aggregates have morphological properties different from platelets.

These agglomerates/aggregates consist of near-spherical particles and do not contain mica.

The constituent particles of these agglomerates/aggregates are mainly made of titanium oxide as demonstrated by EDX mapping in Figure 66. Iron and tin elements are also present within these agglomerates/aggregates.

The constituent particles of the agglomerate/aggregate imaged in Figure 66 have minimum Féret diameter of 39.7 nm ± 4.9 nm.

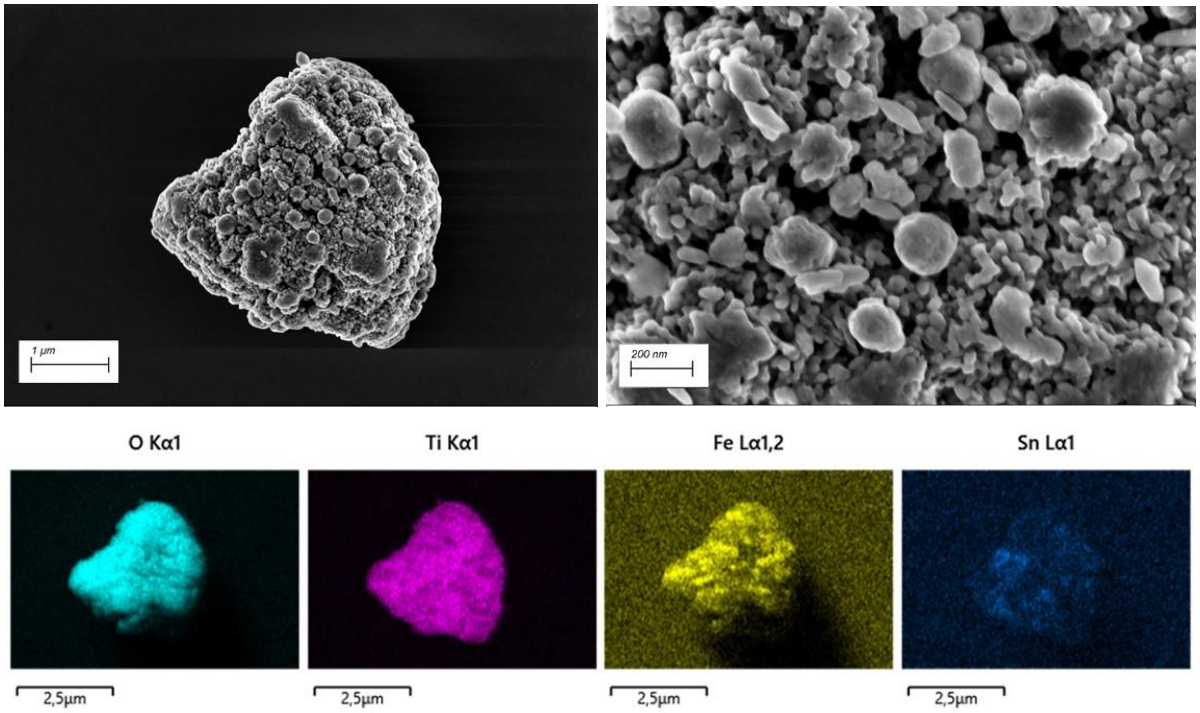


Figure 66 : *(above) SEM image of an isolated particle agglomerate/aggregate (magnification x15,000) with a zoom (left, x60,000). (below) EDX mapping performed on this agglomerate/aggregate (sample S3).*

Test report continued on next page

Other examples of isolated TiO_2 particles and agglomerates/aggregates are given in Figure 67.

The minimum Féret diameter is lower than 100 nm for some of them. For instance, the TiO_2 particles within yellow circles (Figure 67) have minimum Féret diameters of 69.6 nm and 65.8 nm, respectively.

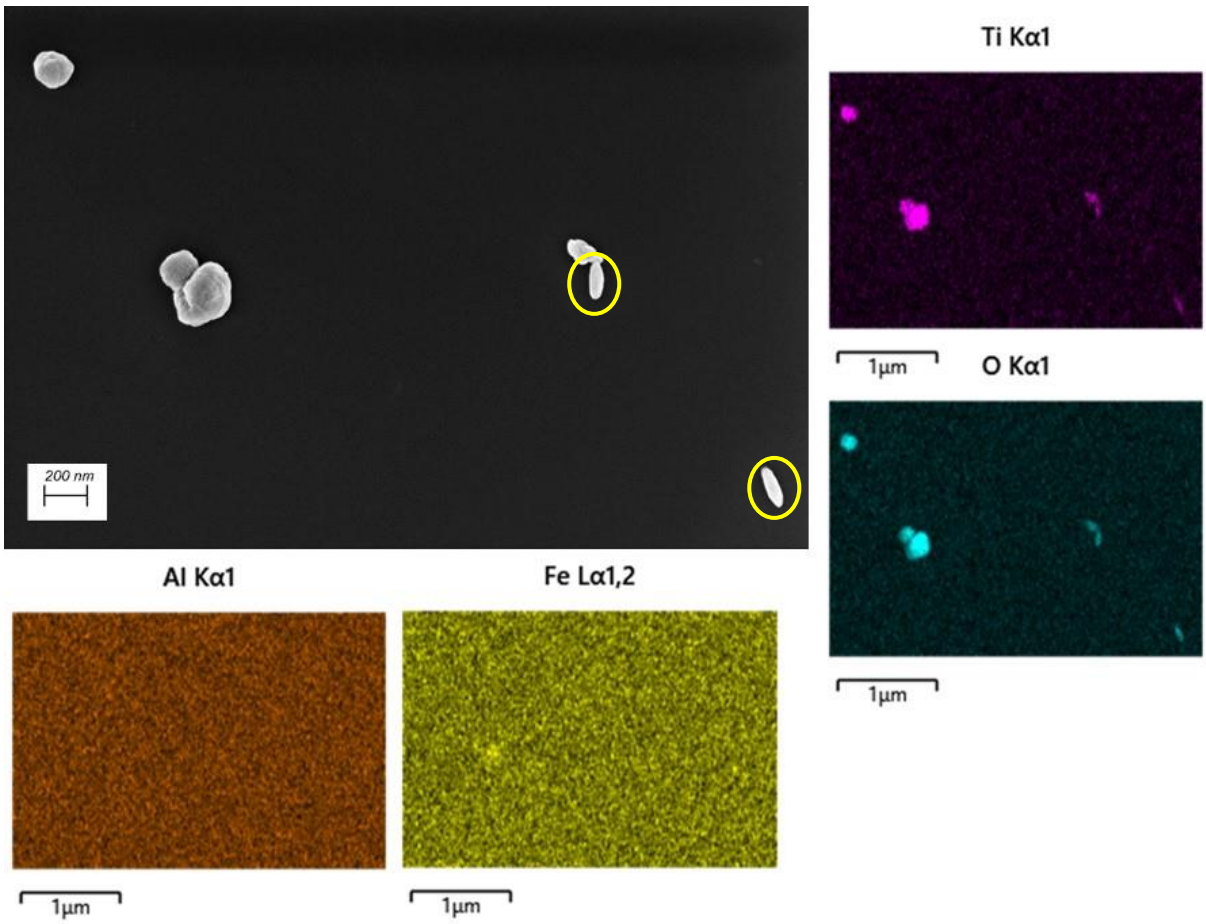


Figure 67 : *EDX mapping performed on isolated particles (sample S3) imaged by SEM (left above, x30,000).*

Test report continued on next page

Two platelets were imaged by SEM in Figure 68.

The first wafer is mainly composed of titanium, while the second is made of iron oxide.

Note the presence of fluorine, which may be one of the components of mica, as mentioned in section 1.3.

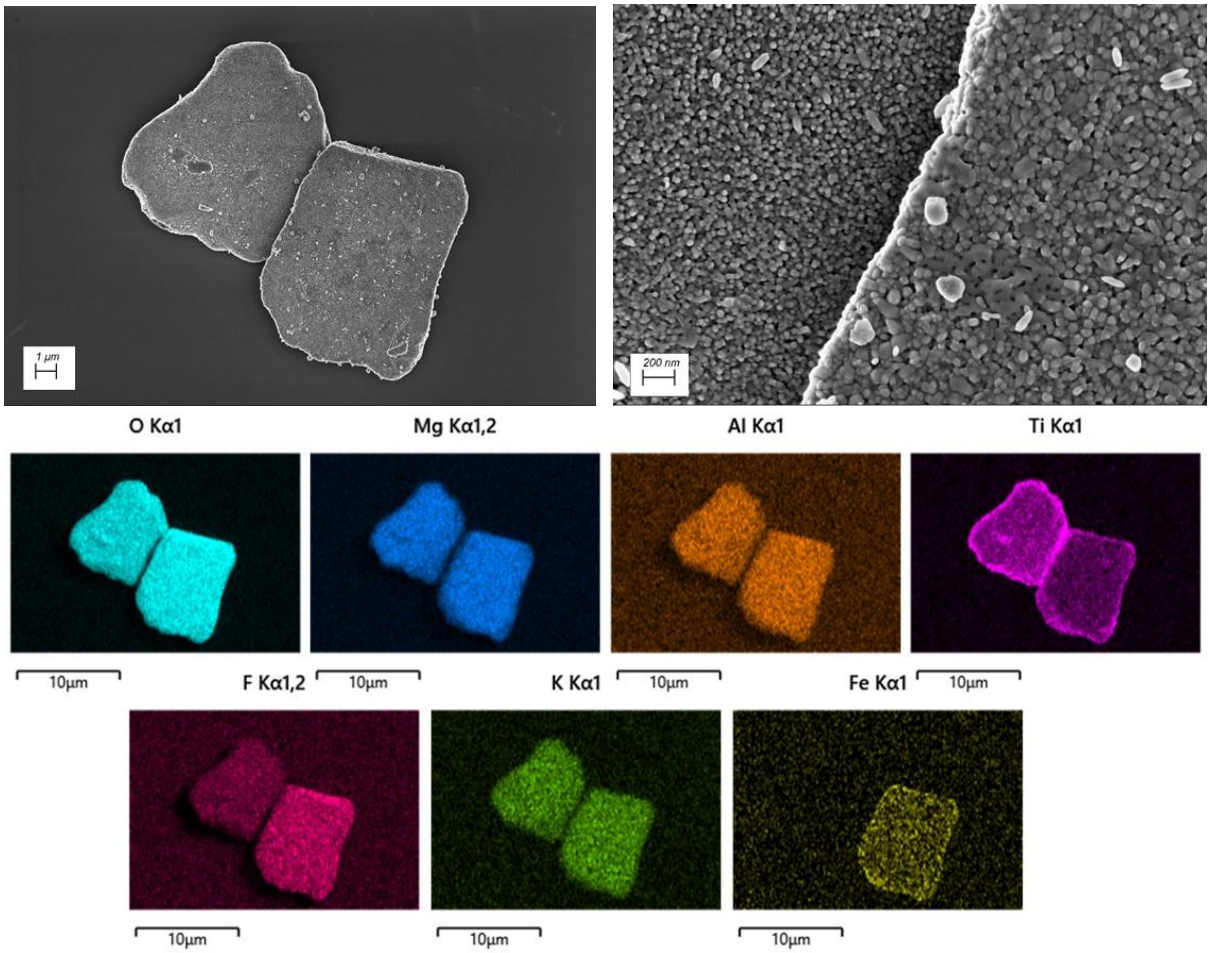


Figure 68 : *(above) SEM image of two platelets (magnification x3,000, sample S3) with a zoom (left above, x30,000). (below) EDX mapping performed on this two platelets (x3,000).*

Test report continued on next page

4.4 SAMPLE S4 : RENE FURTERER, OKARA BLOND

A picture of the studied sample is shown in Figure 69.

Figure 69: *Picture of the sample S4 reference RENE FURTERER, OKARA BLOND*

The presence of titanium dioxide (CI77891), iron oxide (CI 77491) and mica is indicated by the producer on the label.

4.4.1 Preparation of the sample

The sample preparation protocol needing a washing step is as follows:

- This product is a spray. So, 4 mL are sprayed in a 20 mL vial and centrifuged during 20 minutes at 15,000 rpm.
- Then, the supernatant is removed.
- The supernatant is mixed with 5 mL of ethanol before ultrasonication bath.
- The washing process described above is repeated 5 times.

The washed suspension is then deposited on a silicon substrate.

Analysis of nanoparticles (NPs) by electron microscopy (SEM) requires specific preparation of the samples to prevent excessive agglomeration of the NPs. To achieve this, LNE has developed an original protocol involving a spin-coater to deposit particles onto the substrate and improve their dispersion.

This protocol consists of two phases:

- Spreading a drop of suspension over a silicon substrate with a low rotation speed.
- Rapid drying of the drop at high rotation speed.

The particles deposited on the silicon substrate are then observed by SEM and analyzed by EDX.

4.4.2 SEM measurements and EDX analyses performed on mica platelets.

In Figure 70, a SEM image performed at magnification x1,000 on platelets of sample S4.

EDX mapping given in Figure 70 shows that platelets are made of aluminum and potassium. As reminded in section 1.3, These chemical elements are constituents of mica. A layer of particles made of titanium covers the mica platelet. Iron element is also present within the platelets.

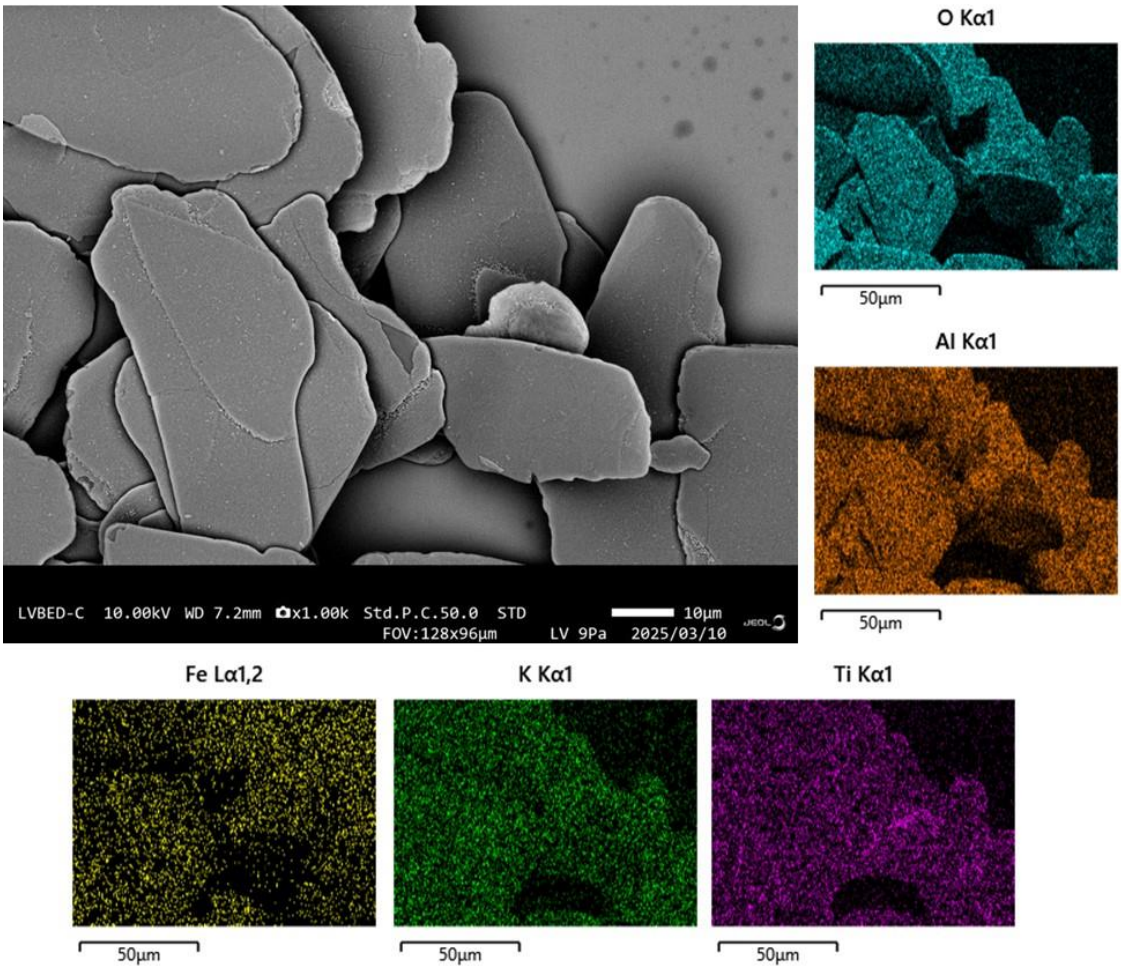


Figure 70 : *(left above) SEM image of the sample S4 reference RENE FURTERER, OKARA BLOND (Magnification: x1000). (right and below) EDX mapping performed on the platelets.*

Test report continued on next page

Some SEM images showing the surface state of platelets are reported in Figure 71. Agglomerates/aggregates are present on the surface and seem to be weakly bonded to the platelets.

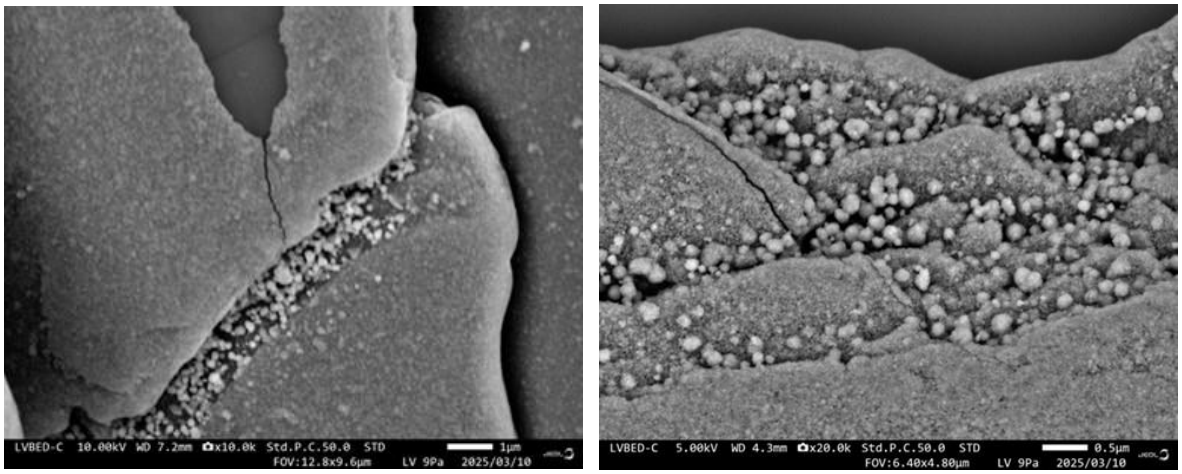


Figure 71 : *Some examples of SEM images of particle agglomerates/aggregates on the surface of the platelets (sample S4).*

These agglomerates/aggregates on the surface are mainly made of titanium, as observed in EDX mapping of the Figure 72.

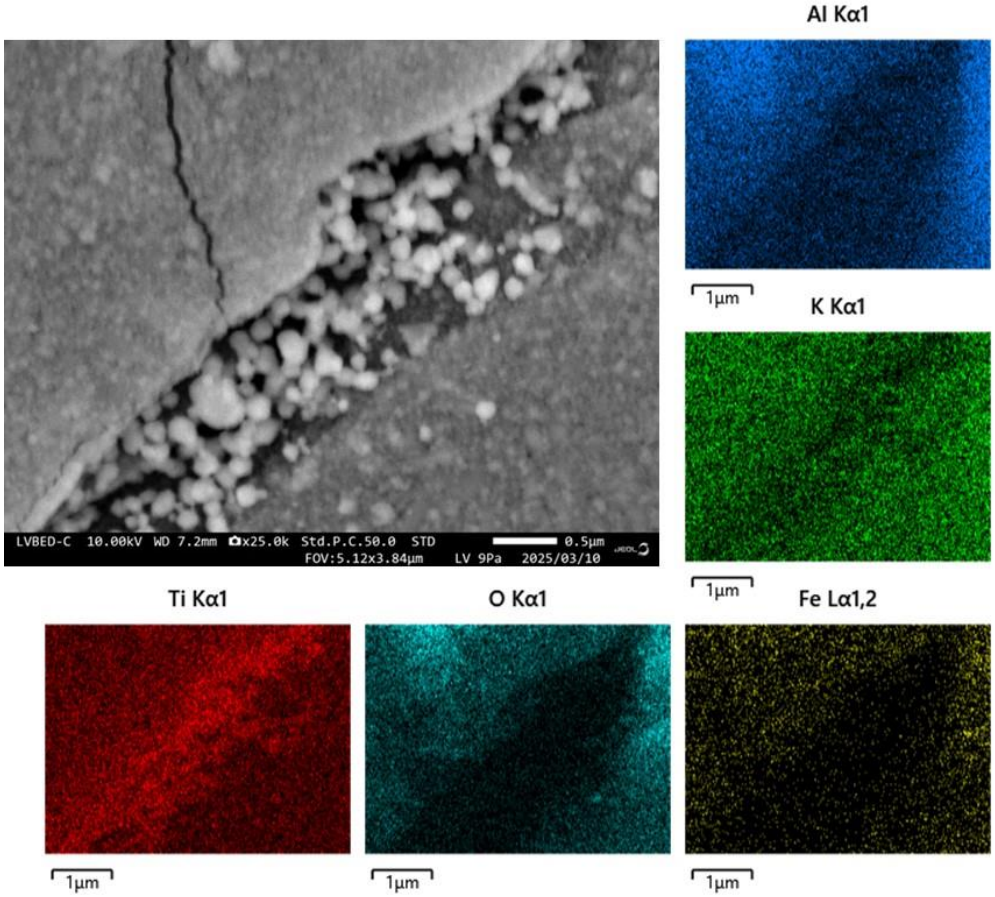


Figure 72 : *(left above) zoomed part of the image given in Figure 71 (x 25,000). (right and below) EDX mapping performed on this area (sample S4).*

4.4.3 SEM measurements and EDX analyses performed on isolated particles.

Figure 73 and Figure 74 report SEM images of platelets consisting of titanium oxide without mica (aluminum is not detected), as demonstrated by EDX mapping. Iron element is weakly detected on these TiO_2 platelets. According figure to scale, the TiO_2 particles have sizes smaller than 100 nm.

After measuring the minimum Féret diameter of particles consisting of the platelet imaged in Figure 73, the mean size has been found to be 32.9 nm ± 4.6 nm.

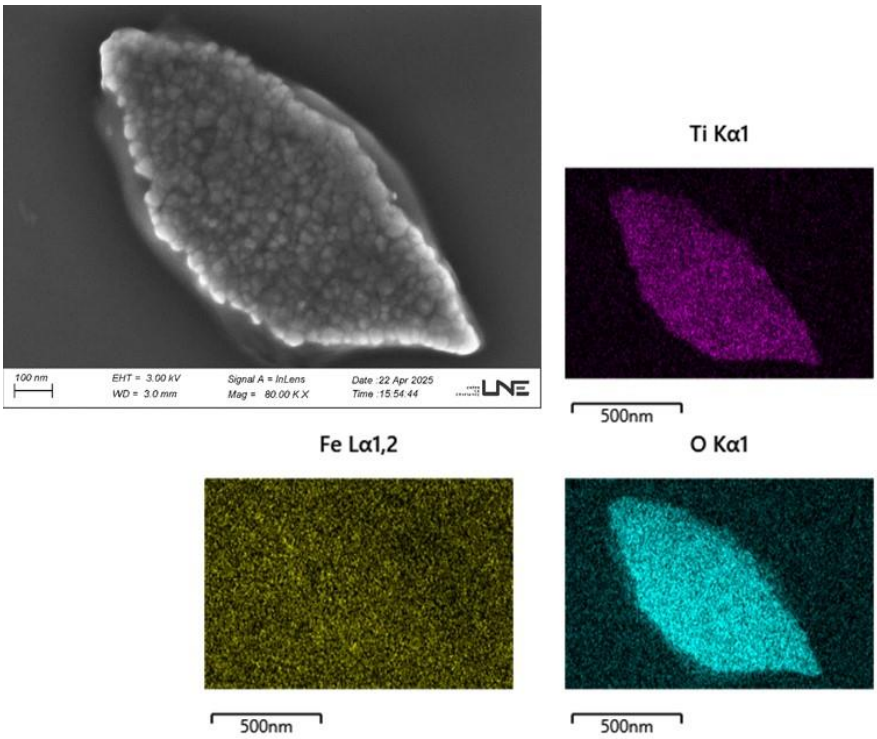


Figure 73 : *EDX mapping performed on a particle agglomerate/aggregate (sample S4) imaged on the left side (x80,000).*

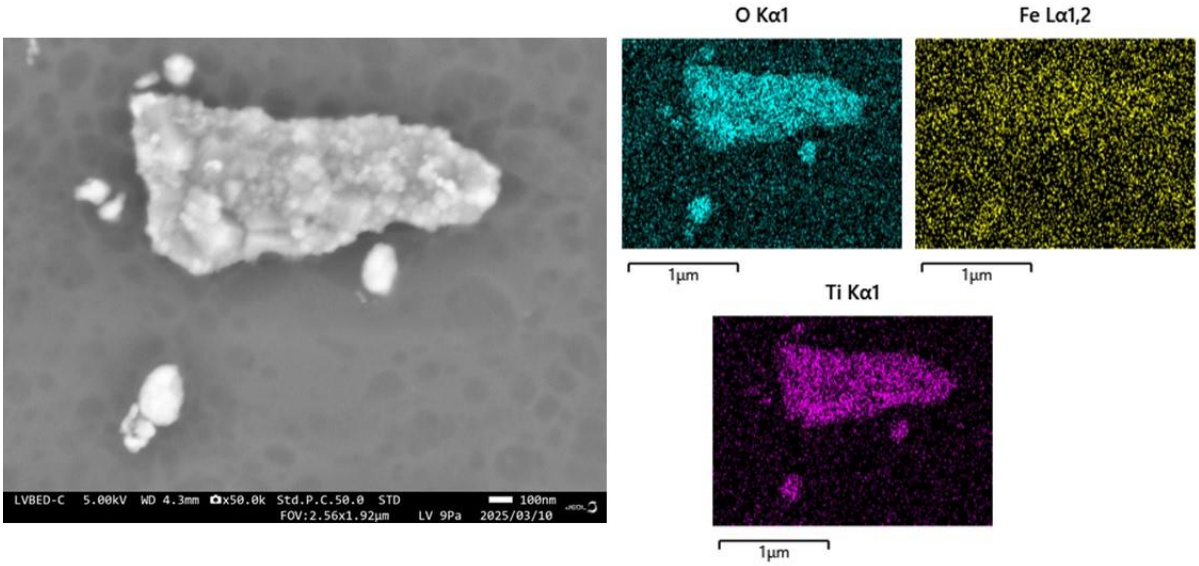


Figure 74 : *EDX mapping performed on the particle agglomerate/aggregate (sample S4) imaged by SEM on the left side (x50,000).*

Some isolated agglomerates/aggregates are imaged in Figure 75, Figure 76 and Figure 77.

All these agglomerates/aggregates are composed of TiO_2 with sometimes detected iron element (Figure 75).

Most of the constituent particles within agglomerates/aggregates are smaller than 100 nm.

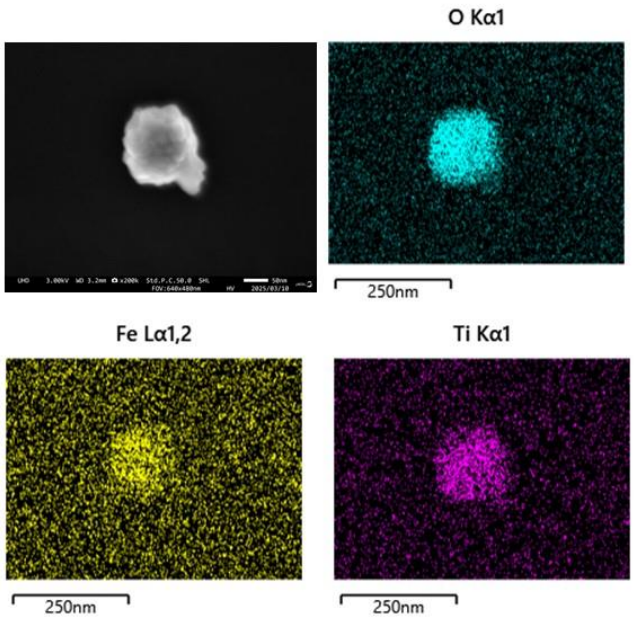


Figure 75 : *EDX mapping performed on the particle agglomerate/aggregate (sample S4)imaged by SEM on the left side (x200,000).*

The TiO_2 constituent particles of the agglomerate/aggregate imaged in Figure 76 have a mean minimum Féret diameter of 31.1 nm ± 5.1 nm.

The size of the constituent particles of the agglomerate/aggregate imaged in Figure 77 is ranged from 91 nm to 117 nm.

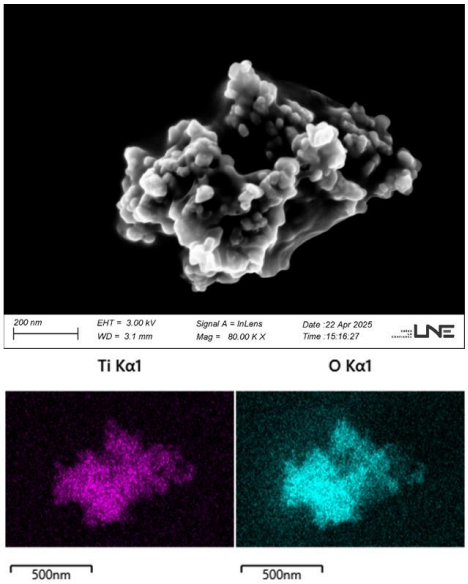


Figure 76 : *EDX mapping performed on an agglomerate/aggregate (sample S4) imaged above (x80,000).*

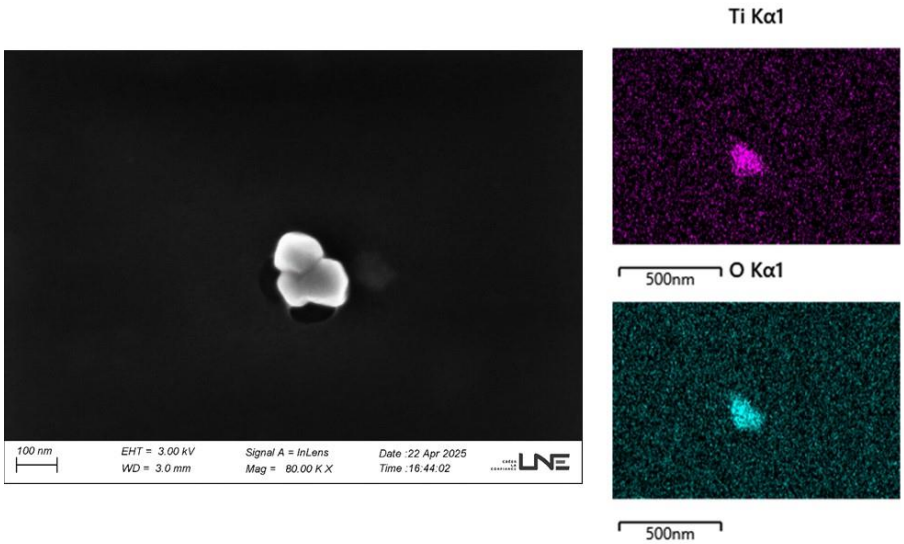


Figure 77 : *EDX mapping performed on an agglomerate/aggregate (sample S4) imaged on the left side (x80,000).*

Test report continued on next page

4.5 SAMPLE S6 : ADOPT WONDERFUL INTENSE

A picture of the studied sample is shown in Figure 78.

Figure 78: *Picture of the sample S6 reference ADOPT WONDERFUL INTENSE*

The presence of titanium dioxide (CI77891), iron oxide (CI 77491) and mica is indicated by the producer on the label.

4.5.1 Preparation of the sample

The sample preparation protocol needing a washing step is as follows:

- This product is a spray. So, 4 mL are sprayed in a 20 mL vial and centrifuged during 20 minutes at 15,000 rpm.
- Then, the supernatant is removed.
- The supernatant is mixed with 5 mL of ethanol before ultrasonication bath.
- The washing process described above is repeated 5 times.

The washed suspension is then deposited on a silicon substrate.

Analysis of nanoparticles (NPs) by electron microscopy (SEM) requires specific preparation of the samples to prevent excessive agglomeration of the NPs. To achieve this, LNE has developed an original protocol involving a spin-coater to deposit particles onto the substrate and improve their dispersion.

This protocol consists of two phases:

- Spreading a drop of suspension over a silicon substrate with a low rotation speed.
- Rapid drying of the drop at high rotation speed.

The particles deposited on the silicon substrate are then observed by SEM and analyzed by EDX.

Test report continued on next page

4.5.2 SEM measurements and EDX analyses performed on mica platelets.

Some examples of platelets imaged by SEM at magnification x300 are given in Figure 79.

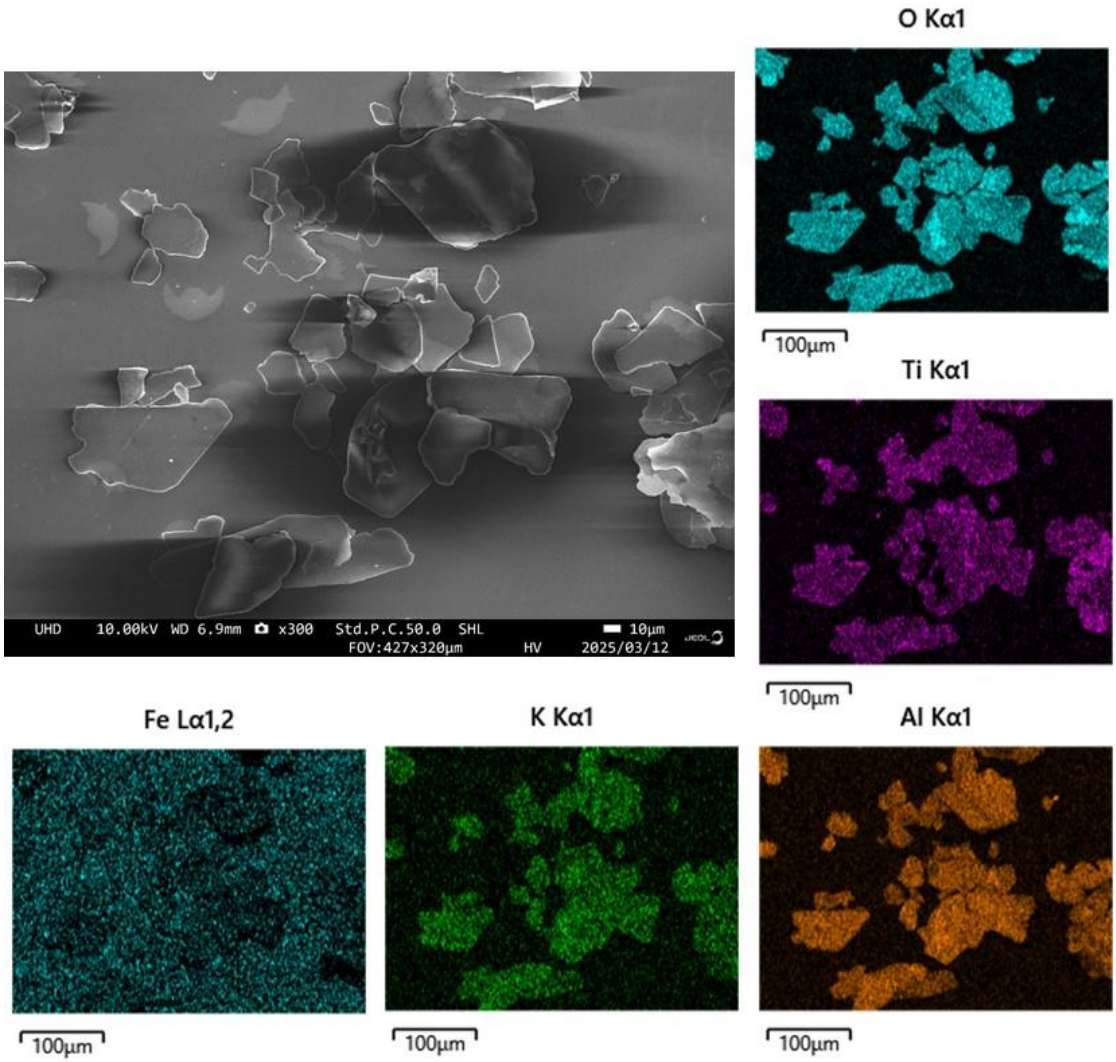


Figure 79 : *(left above) some platelets of the sample S6 imaged by SEM. (right and below) EDX mapping performed on these platelets.*

EDX mapping (Figure 79) shows that elements oxygen, aluminum and potassium are present in the imaged platelets. As reminded in section 1.3, These chemical elements are constituents of mica. A layer of particles made of titanium covers the mica platelet.

Particles composed of iron are also present on the platelets.

Test report continued on next page

Some examples of surface state of platelets are given in Figure 80 and Figure 81.

The surface state shows cracks and fissures. Some particle agglomerates/aggregates seem to form at the platelet surface. The TiO_2 nanoparticles (size < 100 nm, as seen in the scale of Figure 81) in the top layer disappear in favor of the formation of agglomerates.

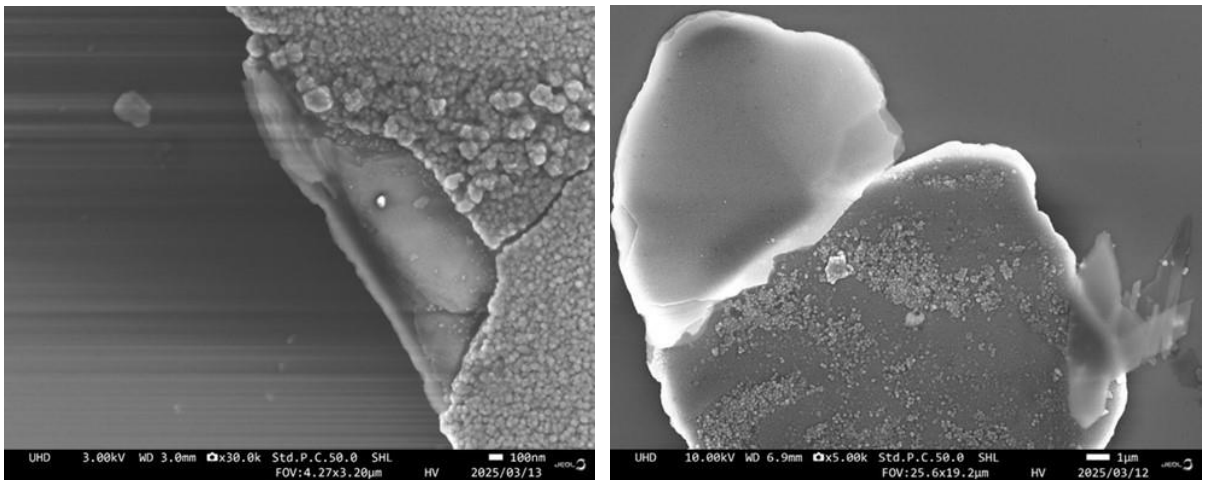


Figure 80 : Some examples of the platelets surface state performed on the sample S6 (image magnification: x30,000, left, and x5,000, right)

The TiO_2 particles covering the platelet surface imaged in Figure 81 have a mean minimum Féret diameter of 33.8 nm ± 3.8 nm.

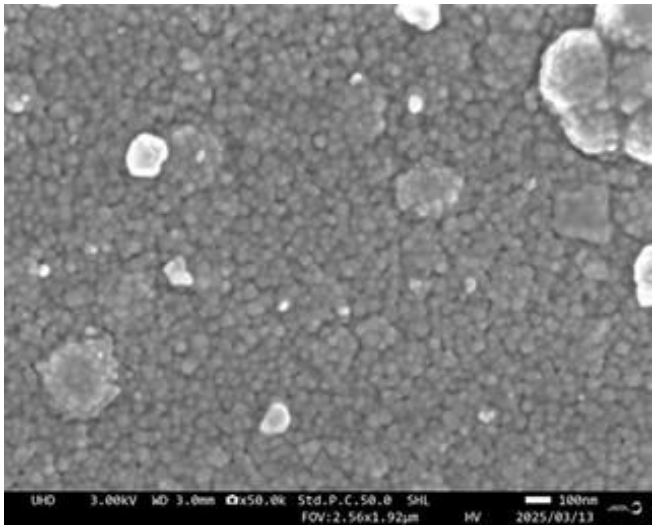


Figure 81 : *SEM image (sample S6) of the surface state of a platelet (x50,000).*

Test report continued on next page

4.5.3 SEM measurements and EDX analyses performed on isolated particles.

The platelet imaged in Figure 82 only consists of TiO_2 particles without mica (aluminum is not detected) as demonstrated by EDX mapping.

The layer of TiO_2 particles has probably peeled off the mica sheet.

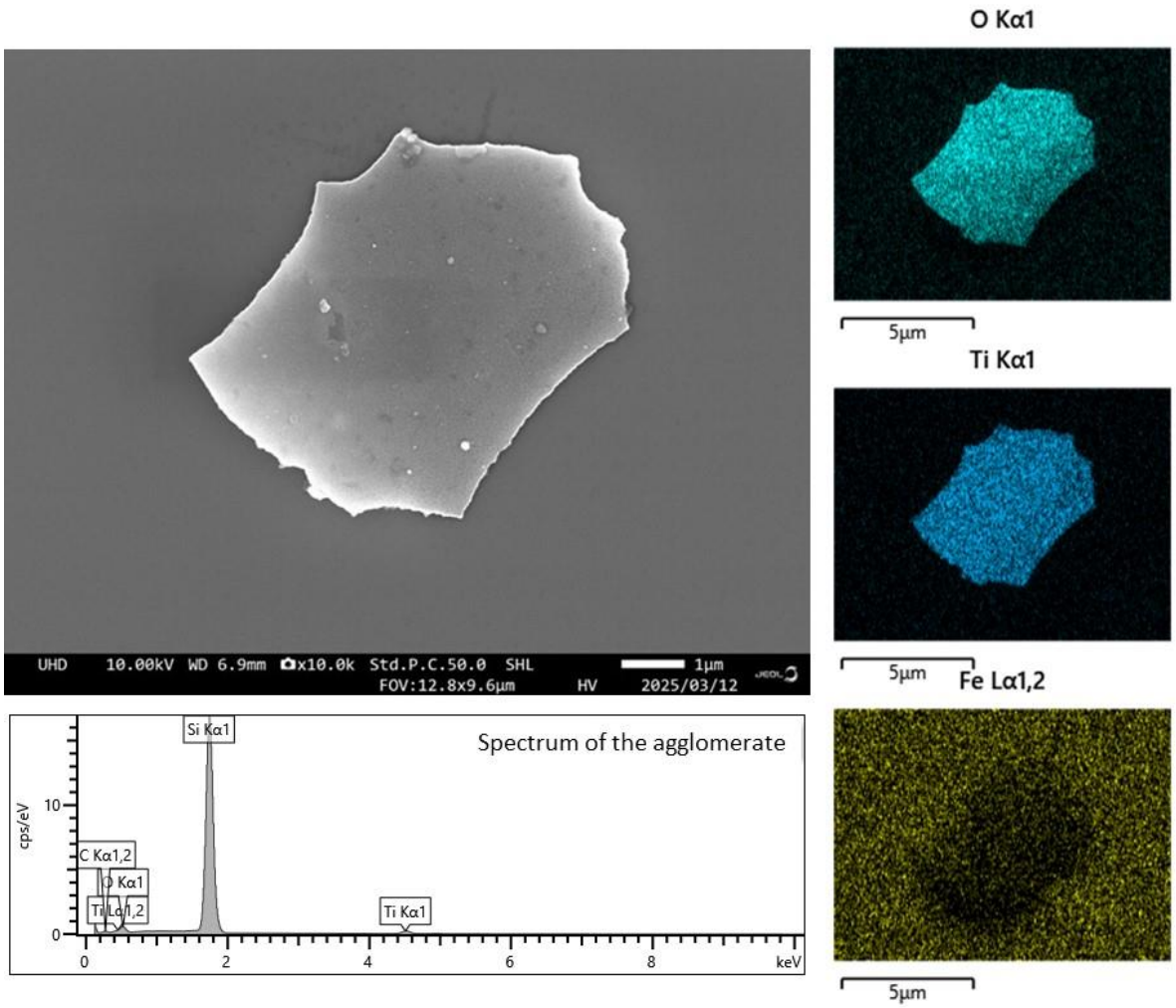


Figure 82 : *EDX mapping performed on the agglomerate/aggregate (sample S6) imaged above side (x10,000). (below) the spectrum carried out on the whole agglomerate/aggregate.*

Table 19 : Information from EDX spectra and EDX mapping performed on S6, Figure 82.

	Peaks	Element	substance
Spectrum of the agglomerate	O Kα1	oxygen	oxides within particle layer
	Ti Kα1, Lα1,2	titanium	particle layer
	Si Kα1	silicon	Silicon substrate
	C Kα1,2	carbon	contamination especially linked to the scanning of the electron beam

Some isolated particle agglomerates/aggregates are imaged by SEM in Figure 83 and Figure 84.

The mean minimum Féret diameter of the particles consisting of the agglomerate/aggregate imaged in Figure 83 is 29.8 nm ± 6.1 nm.

The mean minimum Féret diameter of the particles consisting of the agglomerate/aggregate imaged in Figure 84 is 33.3 nm ± 7.1 nm.

The size of these nanoparticles is very close to the size of particles covering the platelets (Figure 81).

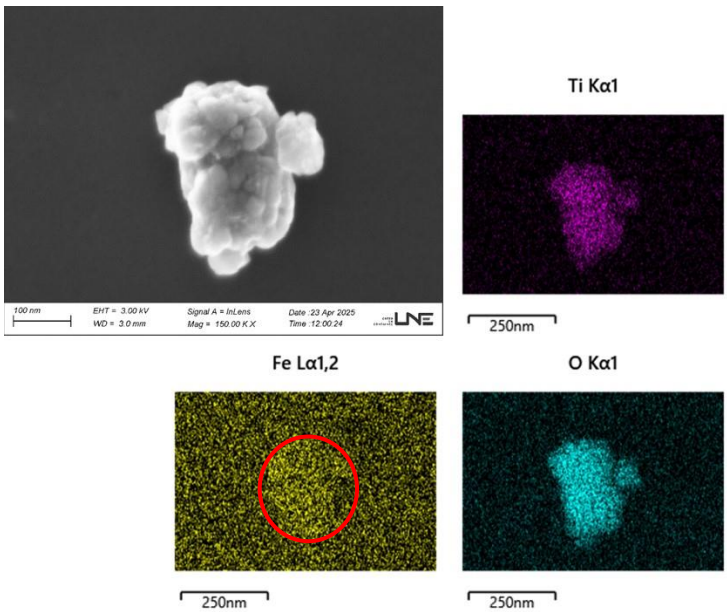


Figure 83 : *EDX mapping performed on a particle agglomerate/aggregate (sample S6) imaged on the left above (x150,000).*

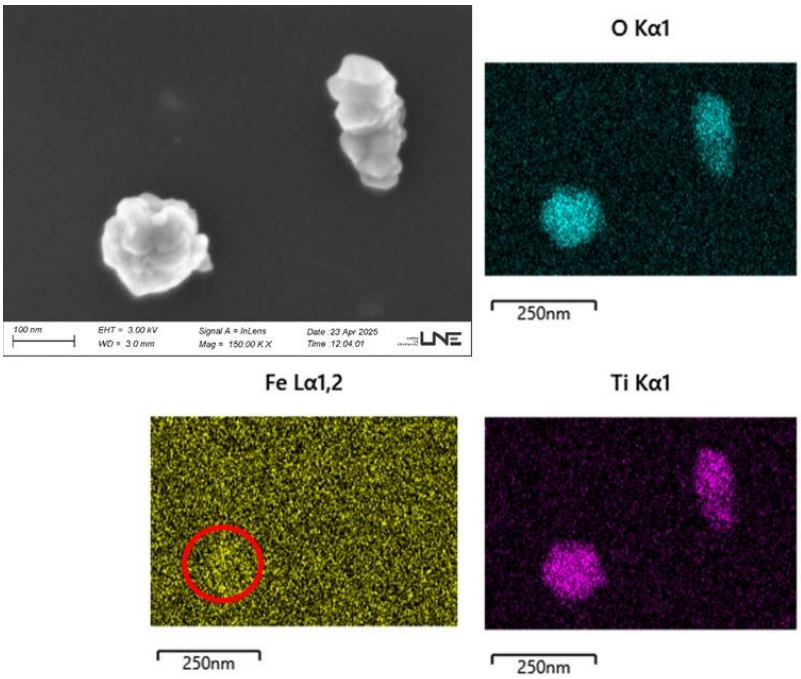


Figure 84 : *EDX mapping performed on particle agglomerates/aggregates (sample S6) imaged on the left above (x150,000).*

4.6 SAMPLE S9 : SLA SUN BAY TERRE DE SOLEIL

A picture of the studied sample is shown in Figure 85.

Figure 85 : *Picture of the sample S9 reference SLA SUN BAY TERRE DE SOLEIL*

The presence of titanium dioxide (CI77891), iron oxide (CI 77491, CI 77492, CI 77499) and mica is indicated by the producer on the label.

Some organic pigments are also included in the product : Yellow 6 Lake CI 15985, Ultramarines CI 77007.

4.6.1 Preparation of the sample

The sample preparation protocol needing a washing step is as follows:

- A sample fraction (12 mg) is mixed with 5 mL of MilliQ water.
- The obtained suspension is dispersed using a vortex device.
- The supernatant is mixed with 5 mL of ethanol before ultrasonication bath.
- The washing process described above is repeated 5 times.

The washed suspension is then deposited on a silicon substrate.

Analysis of nanoparticles (NPs) by electron microscopy (SEM) requires specific preparation of the samples to prevent excessive agglomeration of the NPs. To achieve this, LNE has developed an original protocol involving a spin-coater to deposit particles onto the substrate and improve their dispersion.

This protocol consists of two phases:

- Spreading a drop of suspension over a silicon substrate with a low rotation speed.
- Rapid drying of the drop at high rotation speed.

The particles deposited on the silicon substrate are then observed by SEM and analyzed by EDX.

Test report continued on next page

4.6.2 SEM measurements and EDX analyses performed on mica platelets and isolated particles.

Some examples of SEM images performed at magnification x500, x2,000 and x15,000 are shown in Figure 86.

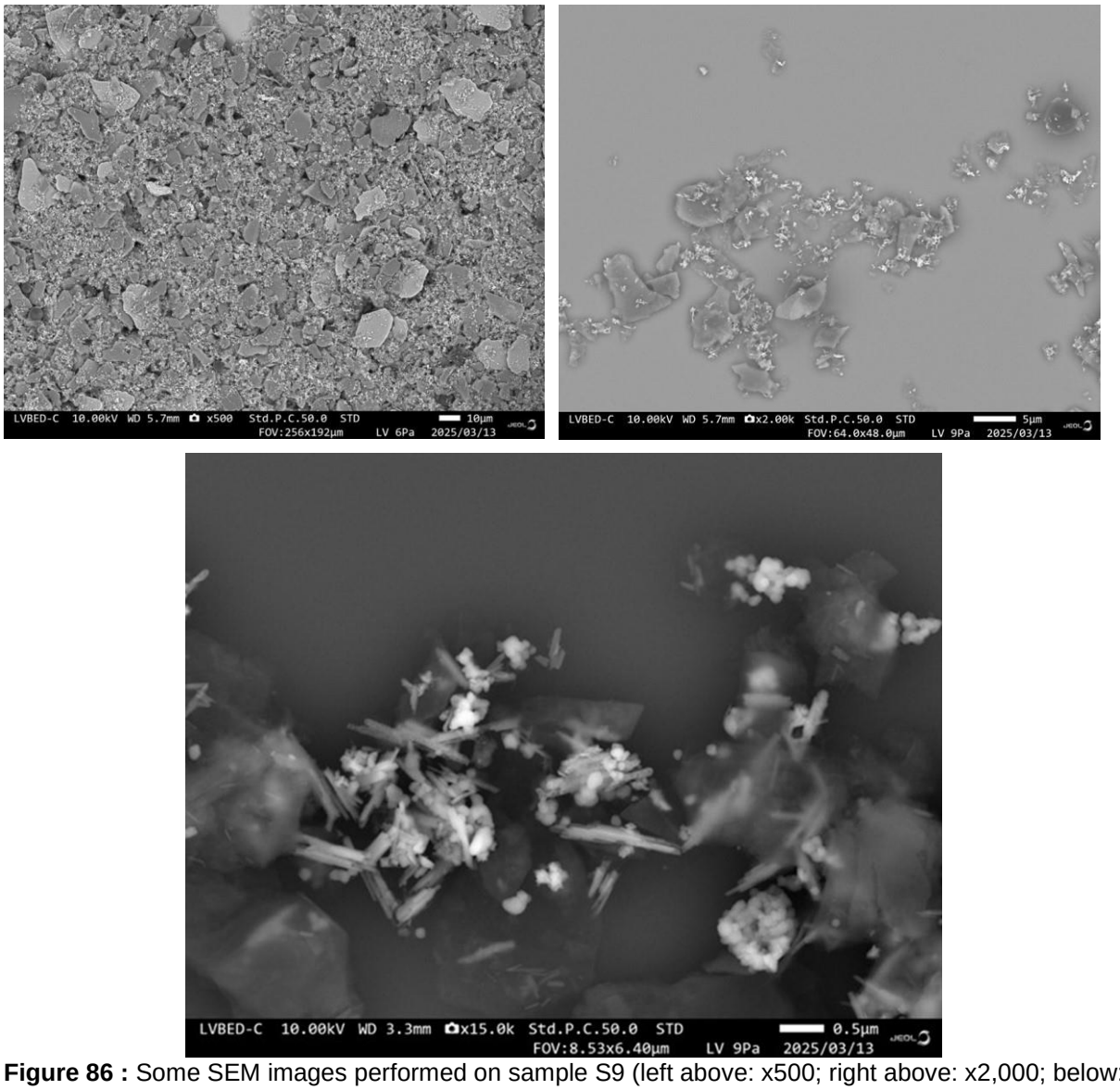


Figure 86 : Some SEM images performed on sample S9 (left above: x500; right above: x2,000; below: x15,000).

The sample consists of typical platelet particles of mica pearlescent pigments. Some rods and particles with various shapes (near-spherical and cubic) are also observed. Platelets, rods and particles have variable sizes.

Analysis providing information on the constituent atoms was carried out on the platelets and various shape particle imaged in Figure 87 using the EDX technique. This elementary analysis is performed on the sample prepared on a silicon substrate.

EDX mapping shows that elements oxygen, aluminum and magnesium are present in the imaged platelets. As reminded in section 1.3, These chemical elements are constituents of mica. A layer of particles made of titanium covers the mica platelet.

The acicular, near-spherical and cubic-shaped particles are made of iron oxide as demonstrated by single-point EDX spectra given in Figure 88. Information about EDX spectra are given in Table 20, spectrum 225.

These acicular, near-spherical and cubic shapes are typical of red iron oxide pigments (CI 77491), yellow iron oxide pigments (CI 77492) and black iron oxide pigments (CI 77499). These additives are present in the product S9, as mentioned in Table 1.

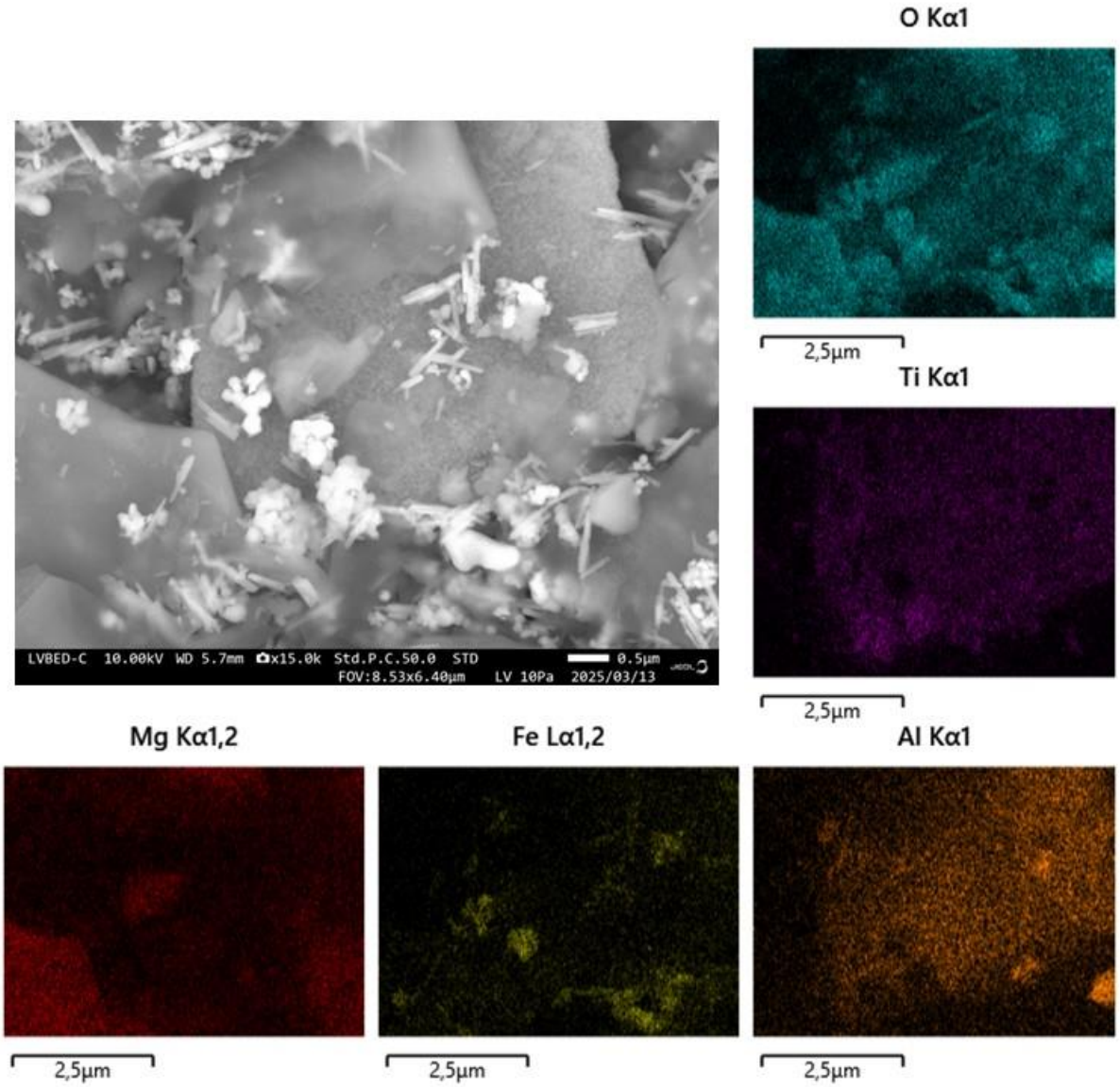


Figure 87 : *EDX mapping performed on the platelets and particles (sample S9) imaged on the left side (x15,000).*

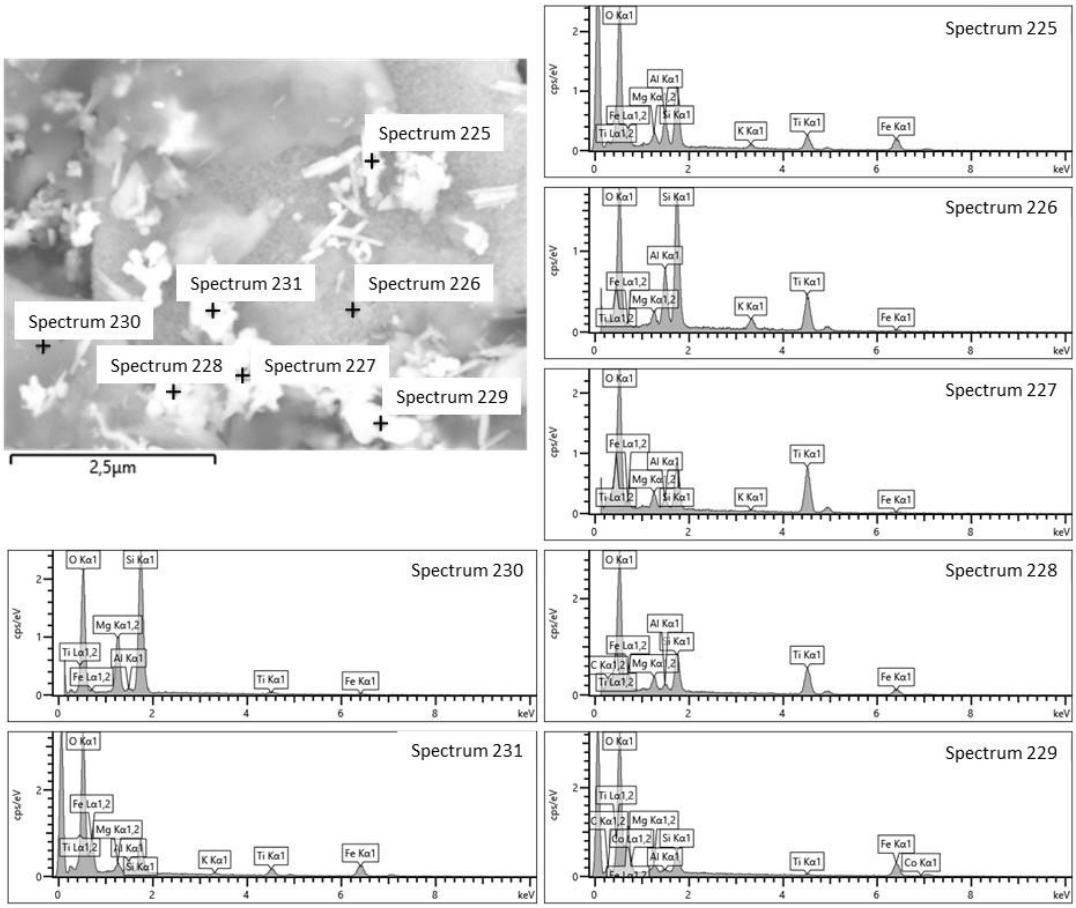


Figure 88 : Single-point spectra performed at different locations of the image given in Figure 87.

Table 20 : Information from EDX spectra and EDX mapping performed on S9, Figure 88.

	Peaks	Element	substance
Spectrum 225	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminium	Mica platelets (see reminder section 1.3)
	Mg Kα1,2	magnesium	Mica platelets (see reminder section 1.3)
	K Kα1	potassium	Mica platelets (see reminder section 1.3)
	Ti Kα1, Lα1,2	titanium	TiO_2 particles on mica platelet
	Fe Lα1,2; Kα1	iron	Iron oxide on mica platelet
	Si Kα1	silicon	Silicon substrate and/or mica platelets
Spectrum 226	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminium	Mica platelets (see reminder section 1.3)
	Mg Kα1,2	magnesium	Mica platelets (see reminder section 1.3)
	K Kα1	potassium	Mica platelets (see reminder section 1.3)
	Ti Kα1, Lα1,2	titanium	TiO_2 particles on mica platelet
	Fe Lα1,2; Kα1	iron	Iron oxide on mica platelet
	Si Kα1	silicon	Silicon substrate and/or mica platelets

Spectrum 227	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminium	Mica platelets (see reminder section 1.3)
	Mg Kα1,2	magnesium	Mica platelets (see reminder section 1.3)
	K Kα1	potassium	Mica platelets (see reminder section 1.3)
	Ti Kα1, Lα1,2	titanium	TiO_2 particles on mica platelet
	Fe Lα1,2; Kα1	iron	Iron oxide on mica platelet
	Si Kα1	silicon	Silicon substrate and/or mica platelets
Spectrum 228	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminium	Mica platelets (see reminder section 1.3)
	Mg Kα1,2	magnesium	Mica platelets (see reminder section 1.3)
	Ti Kα1, Lα1,2	titanium	TiO_2 particles on mica platelet
	Fe Lα1,2; Kα1	iron	Iron oxide on mica platelet
	Si Kα1	silicon	Silicon substrate and/or mica platelets
	C Kα1,2	carbon	contamination especially linked to the scanning of the electron beam
Spectrum 229	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminium	Mica platelets (see reminder section 1.3)
	Mg Kα1,2	magnesium	Mica platelets (see reminder section 1.3)
	Ti Kα1, Lα1,2	titanium	TiO_2 particles on mica platelet
	Co Kα1, Lα1,2	cobalt	pollution
	Fe Lα1,2; Kα1	iron	Iron oxide on mica platelet
	Si Kα1	silicon	Silicon substrate and/or mica platelets
	C Kα1,2	carbon	contamination especially linked to the scanning of the electron beam
Spectrum 230	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminium	Mica platelets (see reminder section 1.3)
	Mg Kα1,2	magnesium	Mica platelets (see reminder section 1.3)
	Ti Kα1, Lα1,2	titanium	TiO_2 particles on mica platelet
	Fe Lα1,2; Kα1	iron	Iron oxide on mica platelet
	Si Kα1	silicon	Silicon substrate and/or mica platelets
Spectrum 231	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminium	Mica platelets (see reminder section 1.3)
	Mg Kα1,2	magnesium	Mica platelets (see reminder section 1.3)
	Ti Kα1, Lα1,2	titanium	TiO_2 particles on mica platelet
	Fe Lα1,2; Kα1	iron	Iron oxide on mica platelet
	Si Kα1	silicon	Silicon substrate and/or mica platelets

Some agglomerates/aggregates of particles with various shapes are imaged in Figure 89. The EDX mapping reported on the right side shows merged information about the localisation of Ti and Fe elements. This figure demonstrates that these agglomerates/aggregates consist of a mixing of titanium oxide and iron oxide particles.

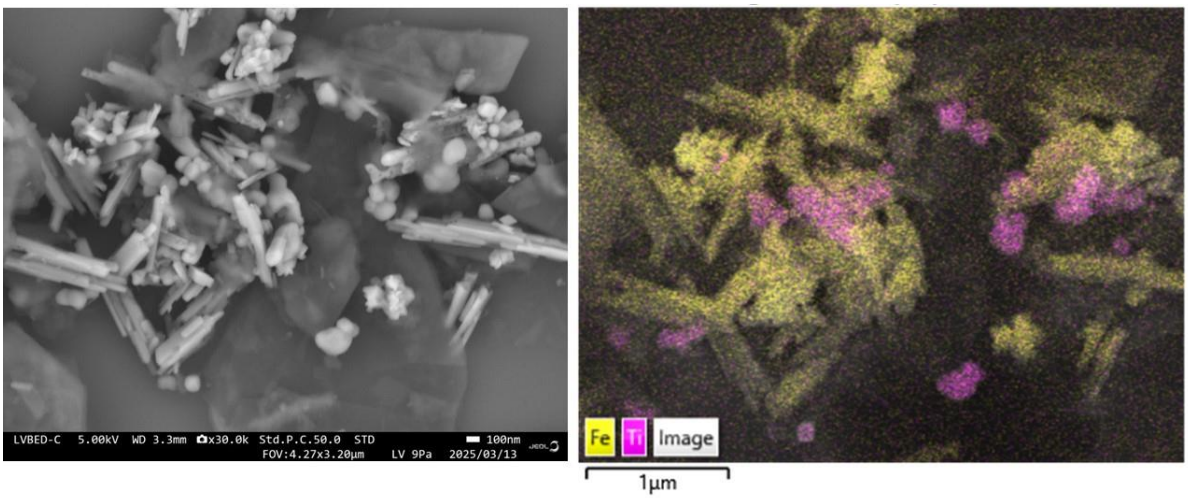


Figure 89 : *EDX mapping with merged information performed on the various shape particles (sample S9) imaged on the left side (x30,000).*

An isolated agglomerate/aggregate of near-spherical particles is imaged by SEM in Figure 90. The merged EDX information regarding Fe and Ti elements shows that this agglomerate/aggregate is a mixing of titanium oxide and iron oxide particles.

The mean size of these constituent particles is 103.5 nm ± 17.1 nm with 53% of nanoparticles.

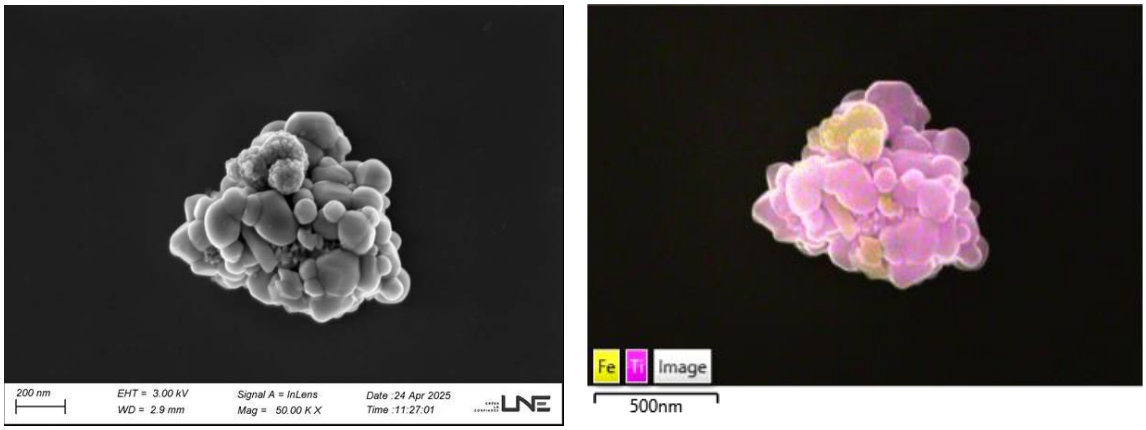


Figure 90 : *EDX mapping with merged information performed on the various shape particles (sample S9) imaged on the left side (x50,000).*

Test report continued on next page

Other examples of agglomerates/aggregates of near-spherical particles or rods are given in Figure 91.

The minimum Féret diameter of some rods have been measured on the right side of Figure 91. This minimum Féret diameter corresponds to cross-section diameter of the acicular shape.

The minimum Féret diameters are ranged from 26 nm to 91 nm.

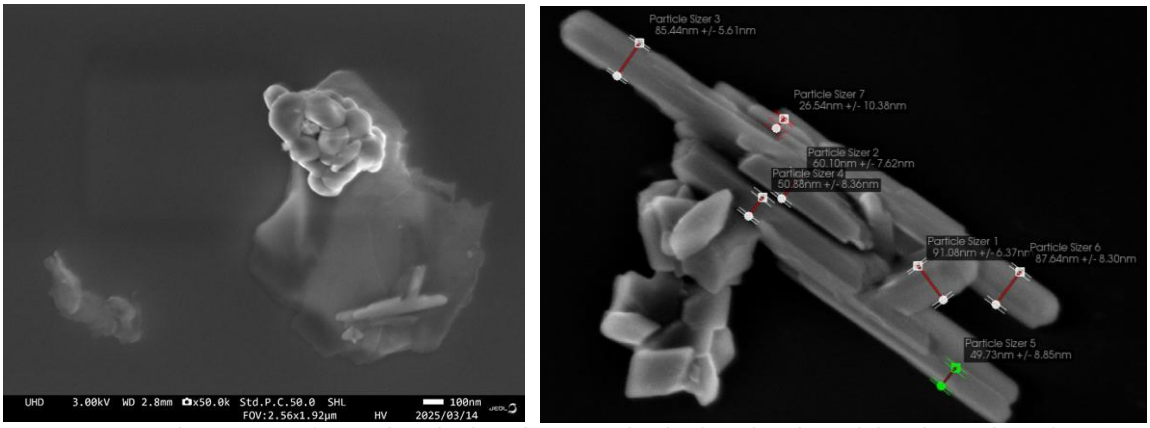


Figure 91 : SEM images performed on isolated near-spherical and rod particles (sample S9)**.**

The SEM image of an agglomerate/aggregate consisting of iron oxide particles with various shapes and near-spherical TiO_2 particles is given in Figure 92.

The cubic-shaped iron oxide particles (probably CI 77491 and CI 77499) have a mean minimum Féret diameter of 153.3 nm ± 30.3 nm.

The near-spherical TiO_2 particles have a mean minimum Féret diameter of 98.5 nm ± 24.0 nm.

The rods (acicular particles) have a mean minimum Féret diameter of 57.8 nm ± 13.0 nm.

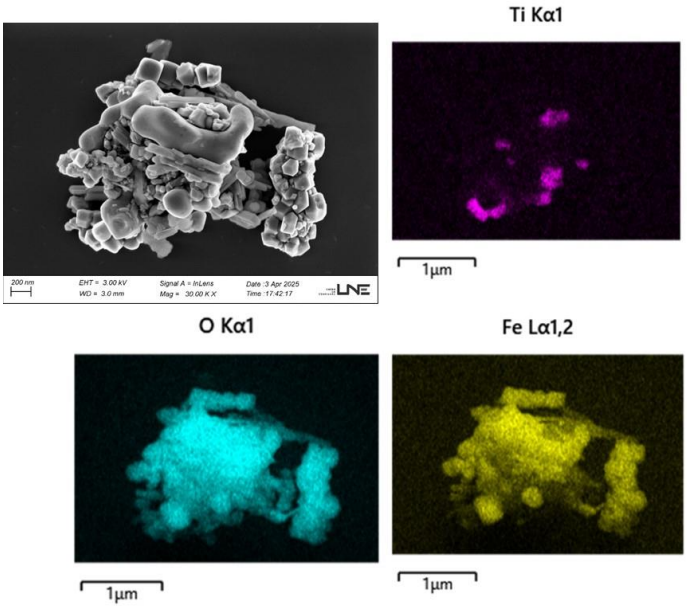


Figure 92 : *EDX mapping performed on an agglomerate/aggregate of near-spherical, cubic and rod particles (sample S9) imaged on left above (x30,000).*

4.7 SAMPLE S10 : LE PETIT MARSEILLAIS

A picture of the studied sample is shown in Figure 93.

Figure 93 : *Picture of the sample S10 reference LE PETIT MARSEILLAIS*

The presence of silica, titanium dioxide (CI77891) and mica is indicated by the producer on the label.

Some organic pigment are also included in the product: Yellow 5 (CI 19140) and Yellow 6 Lake (CI 15985).

4.7.1 Preparation of the sample

The sample preparation protocol needing a washing step is as follows:

- A sample fraction (81 mg) is mixed with 5 mL of MilliQ water.
- The obtained suspension is dispersed using a vortex device (1 second).
- The suspension is centrifuged (10 minutes at 10,000 rpm).
- The supernatant is then recovered and mixed with 5 mL of MilliQ water.
- The washing process described above is repeated 5 times.

The washed suspension is then deposited on a silicon substrate.

Analysis of nanoparticles (NPs) by electron microscopy (SEM) requires specific preparation of the samples to prevent excessive agglomeration of the NPs. To achieve this, LNE has developed an original protocol involving a spin-coater to deposit particles onto the substrate and improve their dispersion.

This protocol consists of two phases:

- Spreading a drop of suspension over a silicon substrate with a low rotation speed.
- Rapid drying of the drop at high rotation speed.

The particles deposited on the silicon substrate are then observed by SEM and analyzed by EDX.

4.7.2 SEM measurements and EDX analyses performed on mica platelets.

Examples of SEM images of S10 platelet performed at magnification x5,000 and x80,000 are shown in Figure 94.

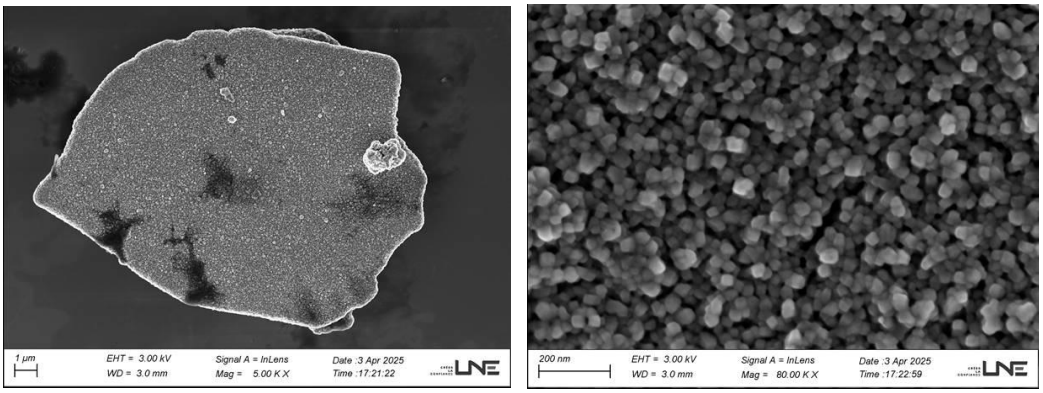


Figure 94 : SEM image of a platelet extracted from S10 (x5,000) with a zoomed part on the right side (x80,000).

The sample consists of typical platelet particles of mica pearlescent pigments. Platelets have variable sizes.

Chemical analysis providing information on the constituent atoms was carried out on the platelets imaged in Figure 95 using the EDX technique. This elementary analysis is performed on the sample prepared on a silicon substrate.

EDX mapping and spectra (Table 21) show that elements oxygen, aluminum and potassium are present in the imaged platelets. As reminded in section 1.3, These chemical elements are constituents of mica. A layer of particles made of titanium covers the mica platelet.

The TiO_2 particles on the mica surface (Figure 94, right) have a size of 34.5 nm ± 3.8 nm.

Test report continued on next page

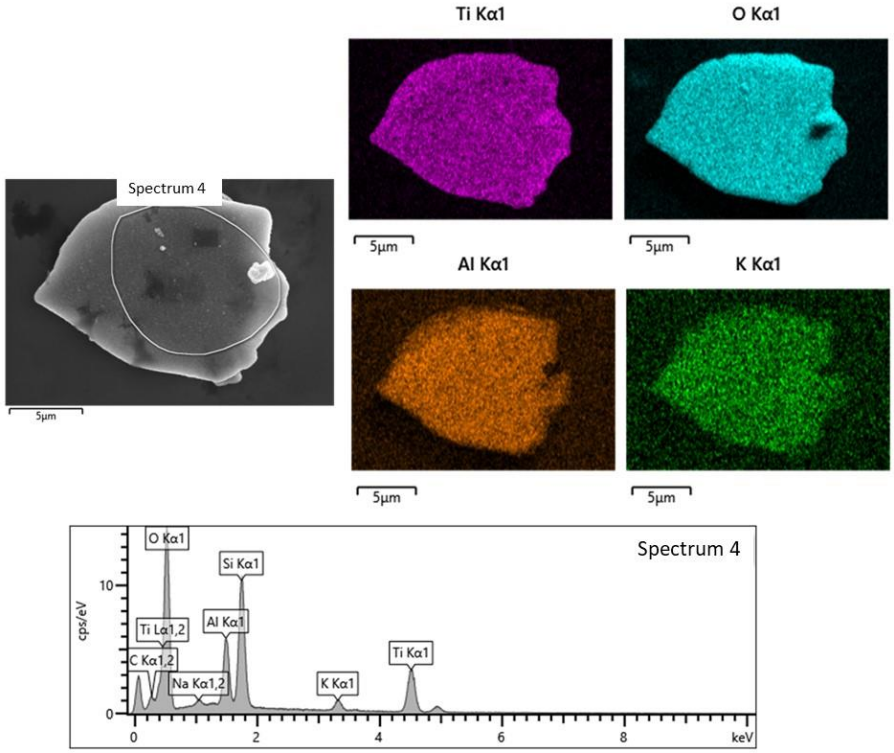


Figure 95 : *EDX mapping performed on the platelet (sample S10) imaged in* Figure 94*. (below) the spectrum carried out by scanning the area n°4 of the agglomerate/aggregate.*

Table 21 : Information from EDX spectra and EDX mapping performed on S10, Figure 95.

	Peaks	Element	substance
Spectrum 04	O Kα1	oxygen	oxides on mica platelets
	Al Kα1	aluminium	Mica platelets (see reminder section 1.3)
	Na Kα1,2	sodium	Mica platelets (see reminder section 1.3)
	K Kα1	potassium	Mica platelets (see reminder section 1.3)
	Ti Kα1, Lα1,2	titanium	TiO_2 particles on mica platelet
	Si Kα1	silicon	Silicon substrate and/or mica platelets
	C Kα1,2	carbon	contamination especially linked to the scanning of the electron beam

Test report continued on next page

Some examples of surface state of platelets (sample S10) are given in Figure 96.

The surface state shows cracks and fissures. At some areas, the mica layer is bare. Some particle agglomerates/aggregates seem to form at the platelet surface.

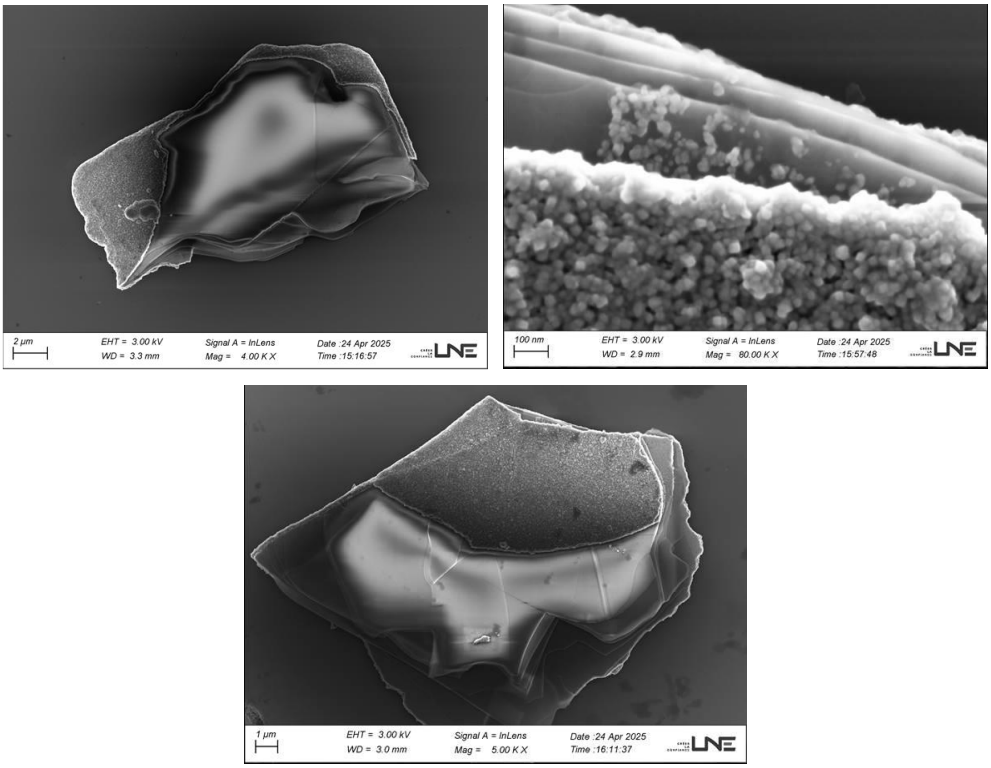


Figure 96 : Some examples of the platelets surface state performed on the sample S10 at various magnifications (left above: x4,000; right above: x80,000; below: x5,000).

Test report continued on next page

4.7.3 SEM measurements and EDX analyses performed on isolated particles.

An agglomerate/aggregate imaged by SEM is given in Figure 97.

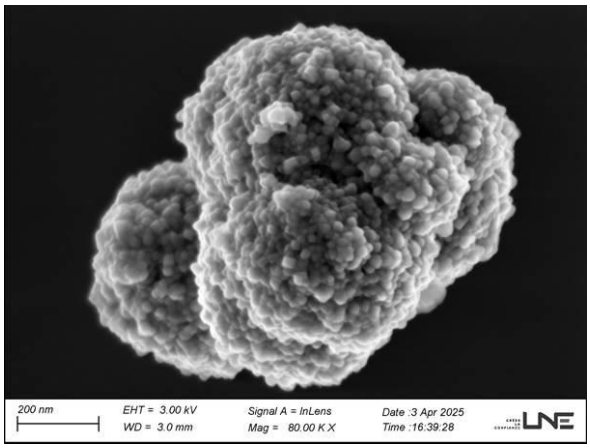


Figure 97 : Example of an isolated agglomerate/aggregate imaged by SEM (x80,000).

EDX mapping and spectrum performed on this agglomerate/aggregate are reported in Figure 98. Information about EDX spectrum n°1 is given in Table 22.

The agglomerate/aggregate consists of TiO_2 particles.

The mean size of constituent particles within agglomerate/aggregate is 25.5 nm ± 3.7 nm.

This size is quite similar to the size of consistent particles covering the mica platelets measured in Figure 94.

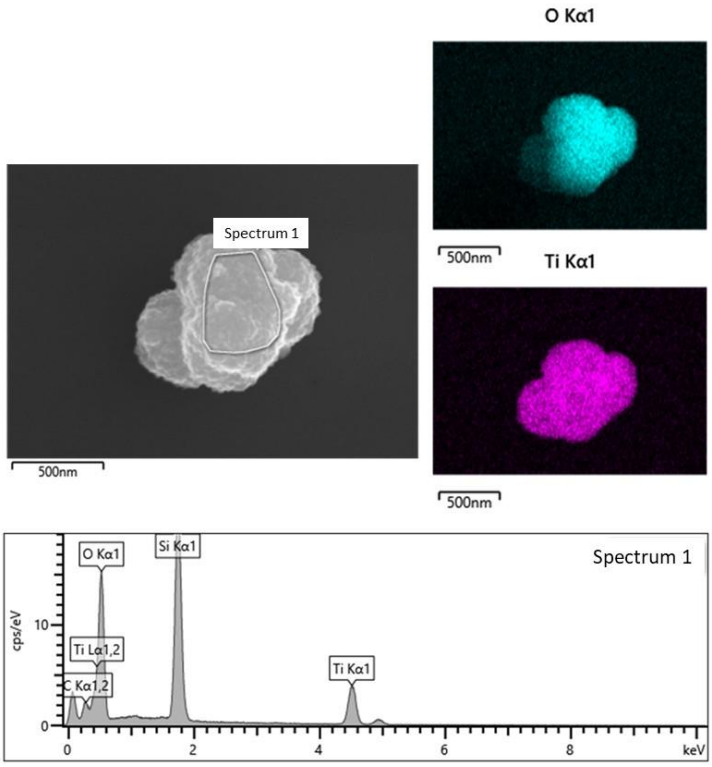


Figure 98 : *EDX mapping performed on the agglomerate/aggregate (sample S10) imaged in* Figure 97*. (below) the spectrum carried out by scanning the area n°1 of the agglomerate/aggregate.*

Table 22 : Information from EDX spectra and EDX mapping performed on S10, Figure 98.

	Peaks	Element	substance
Spectrum 04	O Kα1	oxygen	oxides within agglomerate/aggregate
	Ti Kα1, Lα1,2	titanium	TiO_2 particles within agglomerate/aggregate
	Si Kα1	silicon	Silicon substrate
	C Kα1,2	carbon	contamination especially linked to the scanning of the electron beam

An example of the surface state of platelets is given in Figure 99.

The surface state shows cracks and fissures. Some particle agglomerates/aggregates seem to form at the platelet surface.

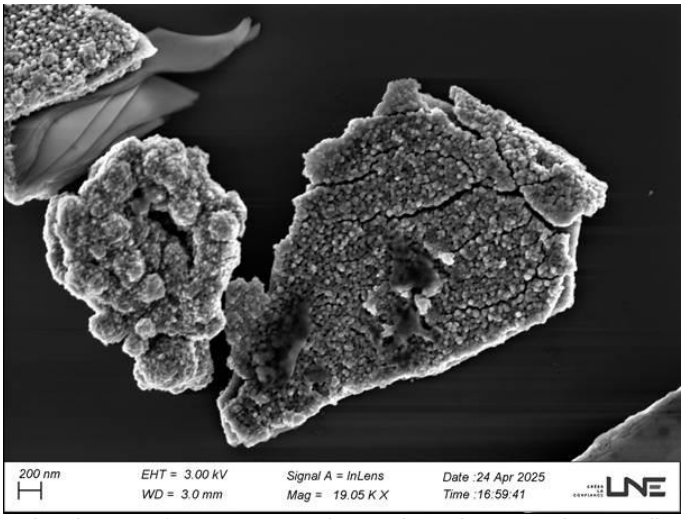


Figure 99 : Example of the platelets surface state performed on the sample S10 (image magnification: x19,050).

Test report continued on next page

4. CONCLUSIONS

Table 23 : *information about analysed samples.*

n°	Reference	Description	LNE analysis								UVSQ analysis
			Contains mica	Presence of TiO_2 agg./agg.	TiO_2 particle size	Presence of Fe oxide agg./agg	Iron oxide particle size	% nanoparticles	Cracks/fissures observation	bare platelet part observation	TiO_2 coating
S1	NOCIBE, poussières d'étoiles, lot Q122	Glitter powder	yes	yes	From ~30 nm to 50 nm in aggl/aggr	-	-	-	-	-	-
S2	SEPHORA, 02 SPICY SUNSET, lot 42780	Bronzing powder	yes	yes	-	yes	From~25 nm to 150 nm in aggl/aggr	-	-	-	-
S3	AROMA ZONE, nacre minérale ref: 03052	Golden powder	yes	yes	From ~40 nm to 70 nm in aggl/aggr	-	-	-	yes	-	-
S4	René Furterer, OKARA blond	Brightening spray for hair	yes	yes	-	-	-	-	yes	-	-
S5	L.A. Girl Shimmer spray gold réf GFS918	Finishing spray for face & body	yes	yes	~30 nm in platelets ~30 nm in aggl/aggr	-	-	100 %	yes	yes	
S6	Adopt Wonderful Intense	Glittery eau de parfum	yes	yes	From ~30 nm to 50 nm in aggl/aggr	-	-	-	-	-	-
S7	SI SI la paillette	Glitter powder (hair & body)	yes	yes	~30 nm in platelets ~30 nm in aggl/aggr	-	-	100%	yes	yes	Probably no
S8	MaCosmetoPerso, MICA OR	Pigment for homemade cosmetics	yes	yes	~50 nm in platelets ~40 nm in aggl/aggr	-	-	100%	yes	yes	Probably no
S9	SLA SUN BAY Terre de soleil	bronzing powder	yes	yes	~ 100 nm in aggl/aggr	yes	From ~60 nm to 150 nm in aggl/aggr	-	-	-	-
S10	Le Petit Marseillais	Pearly moisturizing milk	yes	yes	~25 nm in aggl/aggr	-	-	-	yes	yes	-

- All studied cosmetics (from S1 to S10) contain mica-based pearlescent pigments.
- Several types of mica were analyzed with different chemical compositions:

  S5 = (Al); S1, S3, S7 = (Al, Mg, K, Na); S9 = (Al, Mg, K); S2, S4, S6, S8 = (Al, K); S10 = (Al, Na, K). The presence of silicon in the mica composition has not been demonstrated, as the particles are deposited on a silicon substrate.
- The mica platelets are coated with TiO_2 particles. Chemical composition is confirmed by XPS results given in Appendix 2. The mean Féret diameter of this particle is ranged from 30 nm to 50 nm. 100% of the constituent particles of TiO_2 coating are smaller than 100 nm.
- The presence of TiO_2 particle coatings (silicate or aluminate) is unlikely in view of the XPS results. Indeed, the Si-2p and Al-2p spectra are very noisy, indicating that silicon and aluminum are beneath the layer of TiO_2 particles. Moreover, Titanium instability over time is demonstrated, which would be incompatible with a protective layer around the TiO_2 particles. See study reported in Appendix 2.
- The presence of tin element is demonstrated in the platelet coating of the samples S1, S2, S3, S5 and S7 but no pure tin oxide particles were observed. The tin oxide form was not demonstrated.
- The presence of iron element is demonstrated in the platelet coating of the samples S1, S2, S3, S4, S6, S7, S8 and S9 but no pure iron oxide particles were observed. EDX and XPS techniques were not capable of distinguishing between the existence of discrete iron oxide layers or a mixed TiO_2/ iron layer as a coating.
- In samples S1, S3, S4, S5, S6, S7, S8 and S10, outside platelets, isolated agglomerates/aggregates containing TiO_2 nanoparticles without mica were clearly identified.
- Many platelets show cracks and fissures in the TiO_2 layer (S3, S4, S5, S7, S8 and S10). The samples S5, S7, S8 and S10 exhibit bare part of mica.
- The presence of talc identified in sample S9 can also explain the presence of the elements Mg and Si.
- Regarding samples S2 and S9, the agglomerates/aggregates composed of nanoparticles mainly consist of iron oxide/hydroxide particles coming from additives CI 77491, CI 77492 and CI 77499.

Trappes, 08 july 2025

Test manager

Nicolas FELTIN

Appendix 1

Demonstration of the "nano" character of a particle-state substance - General elements of understanding

The term "nanomaterial" can mean substances that are natural (volcanic ash, etc.), anthropogenic (transport, etc.) or intentionally manufactured on this scale to take advantage of:

- either new properties which appear specifically in this size range,
- or increased surface to volume ratio and an associated increased reactivity as the particle size tends to decrease.

These two specific characteristics of nanomaterials are directly responsible for the interest focussed today on these substances by all industrial sectors (*health, energy, food, construction, etc.).* Within the food sector or cosmetic product sector, nanomaterials are used as additives in the products themselves (E551 = amorphous silica, E171= titanium dioxide TiO_2, etc.) or for packaging materials (nanoclay, nanoAg), etc. in order to improve various properties. Some of them, such as E551, have even been used for decades as anti-caking agents in powder products.

Several studies, however, have shown that nanomaterials, and notably nanoparticles, have a toxicity which is clearly different from macroscopic materials of the same composition, which means that studies are required on risk assessments linked to these new materials. The fact that nanomaterials are defined by a large number of parameters, as reported in document ISO TS 13014 (*size, size distribution, shape, agglomeration/aggregation state, etc.),* does not however enable general rules to be currently applied as to their performance and possible toxicity. This reflects the importance of having exhaustive characterisation data and positions nanometrology as the basis for better control of manufacturing processes, improvement of quality systems and risk assessments linked to these new materials.

The specific characteristics of nanomaterials have therefore been taken into consideration in European regulatory texts (*Cosmetic regulation No. 1223/2009), INCO Regulation No. 1169/2011, Biocide Regulation No. 528/2012, etc*.) or French regulatory texts (*Decree No. 2012-232 and Order of 6 August 2012*). Among the various requirements associated with these texts, companies are notably required to **attach to the ingredient concerned the wording [nano] on the product label in order to inform the consumer.** This means there is a requirement to be able to **determine in a reliable way the nano character of the targeted particle-state substances**.

Various **definitions of nanomaterials currently co-exist** in Europe with certain particularities, such as:

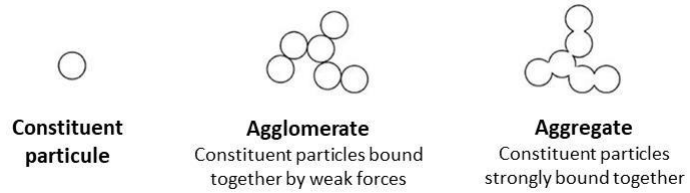
- intentionally-manufactured, with a size of less than 100 nm OR greater than 100 nm BUT with specific nanoscale properties, in the Novel Food Regulation No. 2283/2;
- intentionally manufactured + insolubility and size less than 100 nm, in Cosmetic Regulation No. 1223/2009.

To harmonise what is meant by nanomaterials and avoid a situation where a substance has to be considered as nano in one sector and not in another, the European Commission proposed a Recommendation on the Definition in 2011, revised in June 2022 (2022/C 229/01):

" 'Nanomaterial' means a ***natural, incidental or manufactured material*** *consisting of* ***solid particles that are present, either on their own or as identifiable constituent particles in aggregates or agglomerates, and where 50 % or more of these particles in the number-based size distribution fulfil at least one of the following conditions:***
(a) ***one or more external dimensions of the particle are in the size range 1 nm to 100 nm****;*
(b) ***the particle has an elongated shape, such as a rod, fibre or tube, where two external dimensions are smaller than 1 nm and the other dimension is larger than 100 nm****;*
(c) ***the particle has a plate-like shape, where one external dimension is smaller than 1 nm and the other dimensions are larger than 100 nm****.*

In the determination of the particle number-based size distribution, particles with at least two orthogonal external dimensions larger than 100 µm need not be considered.

However, a material with a specific surface area by volume of < 6 m2/cm3 shall not be considered a nanomaterial. "



The demonstration of the nano character within the meaning of the Recommendation on the Definition 2022/C 229/01 therefore requires **a determination of the particle size distribution of the population of constituent particles (free or constituting agglomerates or aggregates present) and to extract from them the median diameter corresponding to the 50% threshold.** The JRC document « Guidance on the implementation of the Commission Recommendation 2022/C 229/01 on the definition of nanomaterial » reviews concepts and terms used in the Recommendation (https://publications.jrc.ec.europa.eu/repository/handle/JRC132102).

Numerous techniques enable the size distribution of a sample to be characterised (*DLS, A4F-MALS, sp-ICPMS, CLS, SMPS, NTA, SEM, TEM, AFM*, etc.), but to date, none of them is perfect. Completely different results may thus be obtained depending on the technique used as the associated measurand will not necessarily be the same, as was demonstrated by an inter-laboratory comparison organised within the scope of the Club nanoMetrologie (www.club- nanometrologie.fr). Each one has its own specific limitations (*low accessible size limit, confusion between nanoparticle agglomerates/aggregates and larger constituent particles, etc.*) and many of them cannot therefore be used in an initial screening step (*DLS, CLS, sp-ICPMS, etc*.). It is therefore **recommended to combine results obtained via several of these analytical techniques in order to ensure that the information retrieved is reliable.**

In order to access **quantitative and reliable data**, it is **necessary to use** SEM (*Scanning Electron Microscopy*) or TEM (*Transmission Electron Microscopy*) **microscopy techniques**. A high degree of expertise in sample preparation and interpretation of the images obtained is however necessary in order to extract high quality results. These conclusions are notably those given by the flagship project by the European Commission on this subject (NanoDefine project, www.nanodefine.eu) and the NANOMET project (www.nanomet.fr) financed in France by the DGE. The LNE participates in these two research projects and has thus developed reference methodologies over recent years in order to ensure that the various key steps in the measurement process are reliable:

- sample preparation,
- instrument calibration,
- data acquisition protocol,
- data processing and measurement uncertainty evaluation.

The application of ultrasound and adjustment of the pH during the sample preparation phase enable agglomerates present to be broken down and thus enables the constituent particle size to be characterised more reliably.

Note

LNE implements its cutting-edge instrumentation and reference protocols developed during this research work as the French National Metrology Laboratory in order to determine the "*nano*" character of particle-state substances and to provide reliable results.

Its expertise focusses on measurements and metrology and under no circumstances on toxicity issues potentially associated with these substances.

Appendix 2

Report concerning the determination of the chemical composition of the samples S7 and S8 by XPS (X-ray Photolectron Spectroscopy), performed by Institut Lavoisier de Versailles (ILV).