



Towards the Discrimination between Natural and Synthetic Pigments: The Case of Ultramarine

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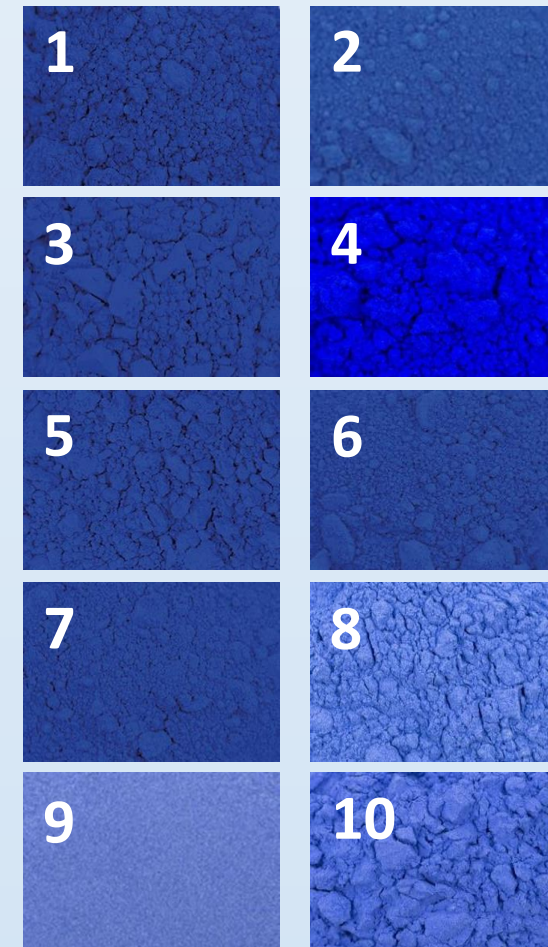


Introduction

Ultramarine has been for centuries one of the most highly prized pigments of all traditional artists' materials, due to its durability, excellent color, and its intrinsic value. For the production of Ultramarine, the rare semiprecious stone Lapis Lazuli is used. The production of a synthetic version by Guimet in 1828, which was obtained from the calcination of a mixture of metakaolin, sulfur, sodium carbonate, and a reducing agent, followed by an oxidation step, introduced an important change in artists' habits, in that a less expensive pigment was available for their palettes¹. The verification of the natural or synthetic origin of the pigment is particularly important in a project, e.g. in authentication cases.

Materials and Methods

| No | Pigment | Origin | Composition |
|----|----------------------------------|-----------------|--|
| 1 | Ultramarine Blue, very dark | 4500, Kremer | Synthetic mineral pigment |
| 2 | Ultramarine blue, light | 4508, Kremer | Synthetic mineral pigment |
| 3 | Ultramarine Blue, dark | 45010, Kremer | Synthetic mineral pigment |
| 4 | Ultramarine Blue, Belgian | 99750, Kremer | Synthetic mineral pigment (Historical stock) |
| 5 | Ultramarine Blue, reddish | 45020, Kremer | Synthetic mineral pigment |
| 6 | Ultramarine Blue, greenish light | 45040, Kremer | Synthetic mineral pigment |
| 7 | Ultramarine Blue, greenish extra | 45030, Kremer | Synthetic mineral pigment |
| 8 | Lapis Lazuli, good quality | 1052, Kremer | Natural ultramarine |
| 9 | Lapis Lazuli from Chile | 1056038, Kremer | Natural ultramarine |
| 10 | Lapis Lazuli, bright pure blue | 10550, Kremer | Natural ultramarine from South America |



- Fourier transform infrared (FTIR) spectroscopy:** Spectrum 1000 Perkin Elmer, mid-IR region (4000-400 cm⁻¹), transmittance mode, 32 scans, 4 cm⁻¹ resolution, 1% KBr pellets.
- X-ray Diffraction (XRD):** Rigaku Ultima, Bragg - Brentano, CuK α , 40 KV, 30 mA, range (2 θ): 5-90°, step size: 0.05°, count step: 2.0 s/step
- X-ray Photoelectron spectroscopy (XPS):** Kratos Analytical Axis UltraDLD (Shimadzu).
- SEM-EDS Microscopy:** JEOL JMS-840A with Oxford ISIS 300 detector, 20 kV accelerating voltage
- UV-Vis Spectrophotometry:** Lambda18 spectroscope (Perkin Elmer). X-ray Diffraction (XRD): Ultima Plus (Rigaku).

Results

FTIR

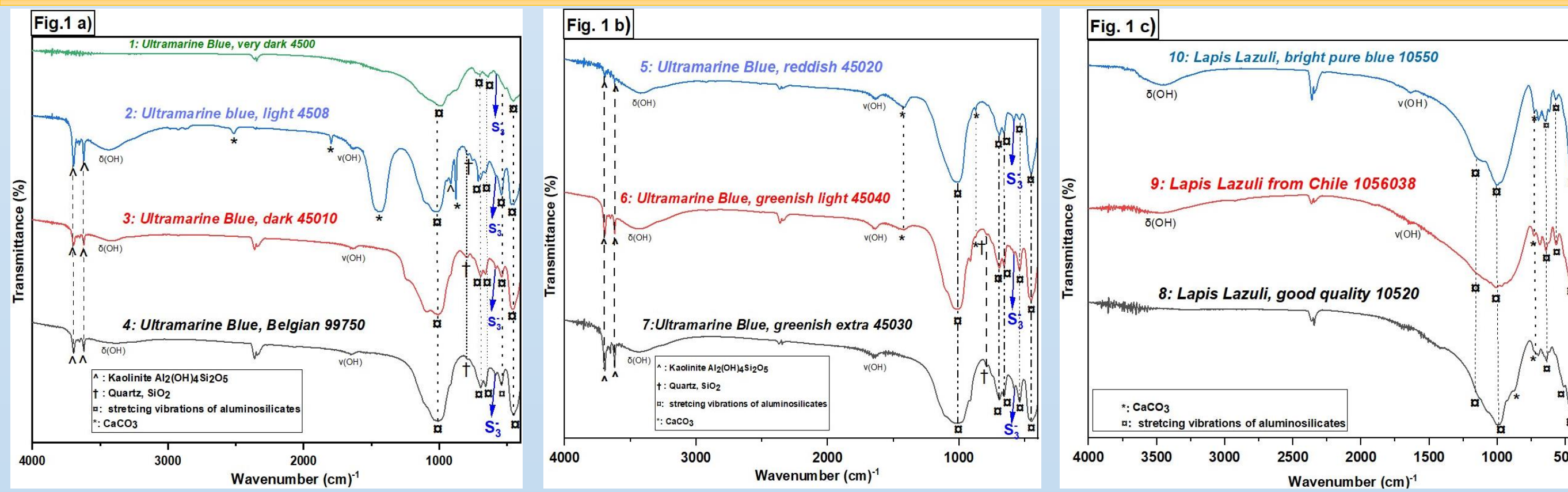


Fig. 1. The slight differences between the spectra of the natural and synthetic ultramarine are related to the presence of reagent residues, such as kaolinite in the synthetic pigment, whereas in the natural pigment calcite vibrations also occur. In general, all spectra are characterized by the fundamental vibrations of Al, and Si-O₄²⁻.

XRD

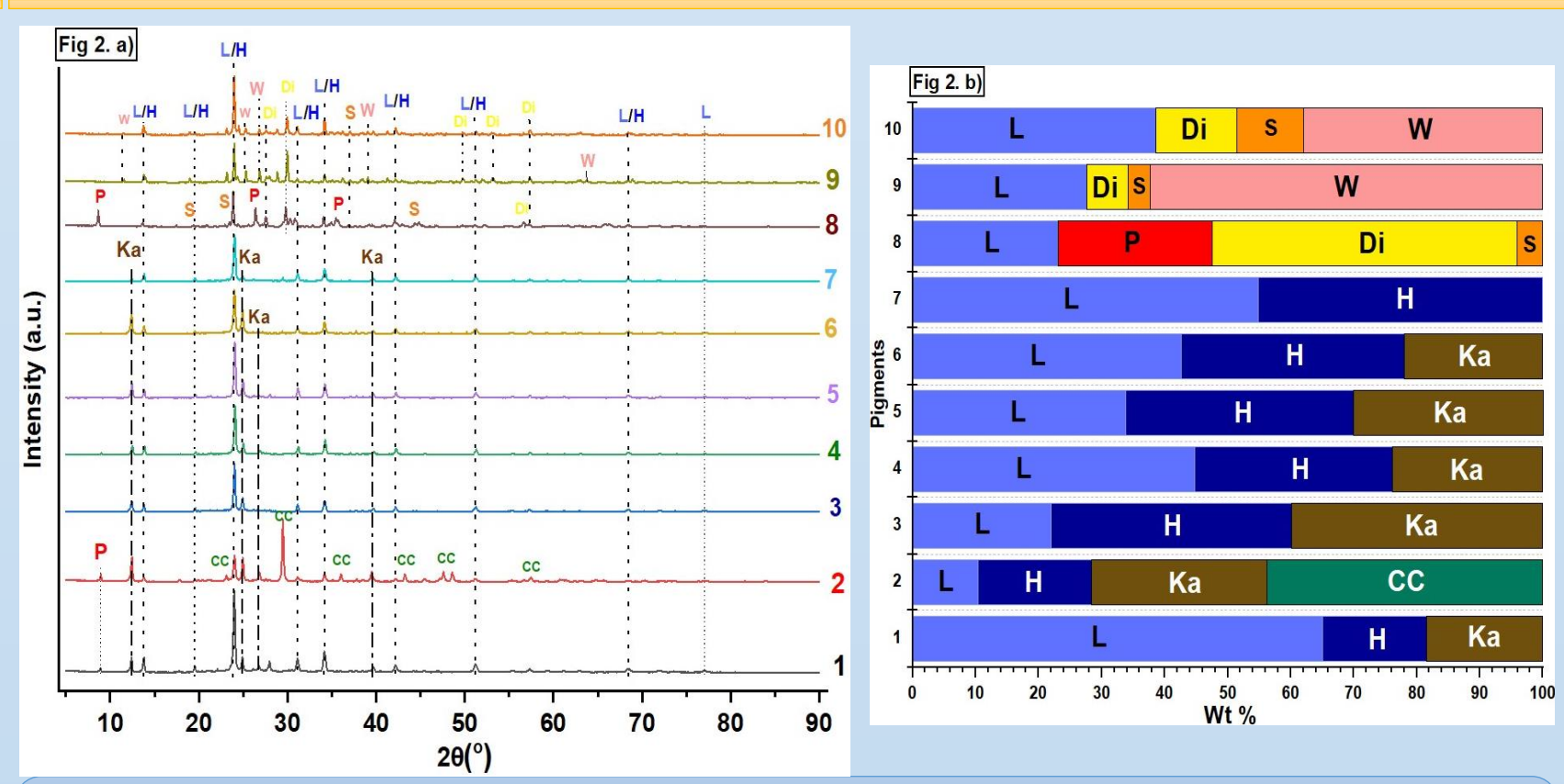


Fig. 2 a) X-Ray diffractograms of the pigments. 2 b) The percentages of the crystalline phases of the pigments. L: Lazurite, H: Haüyne, Ka: Kaolinite, CC: Calcite, Di: Diopside, P: Phlogopite, S: Sodalite, W: Wollastonite.

XPS

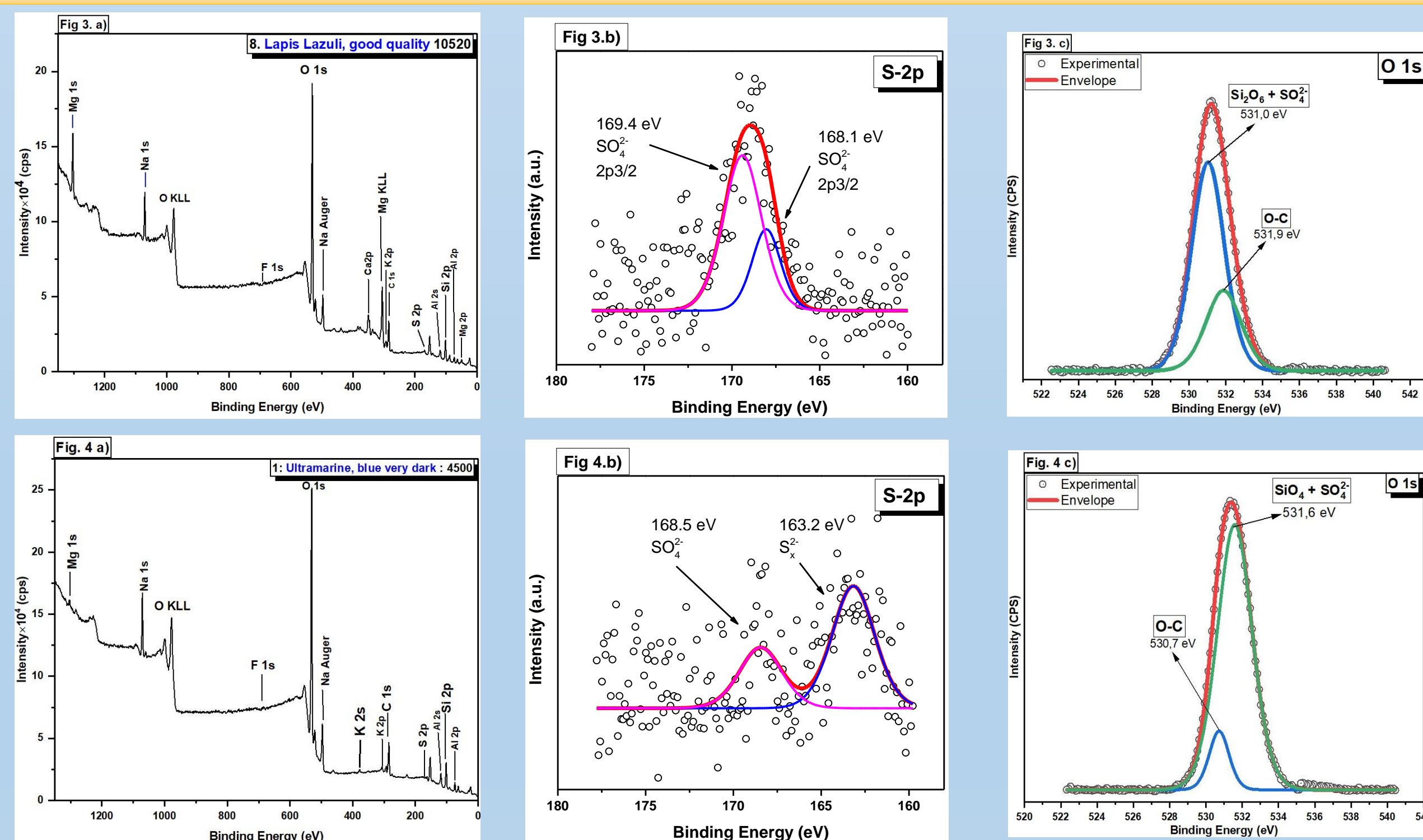
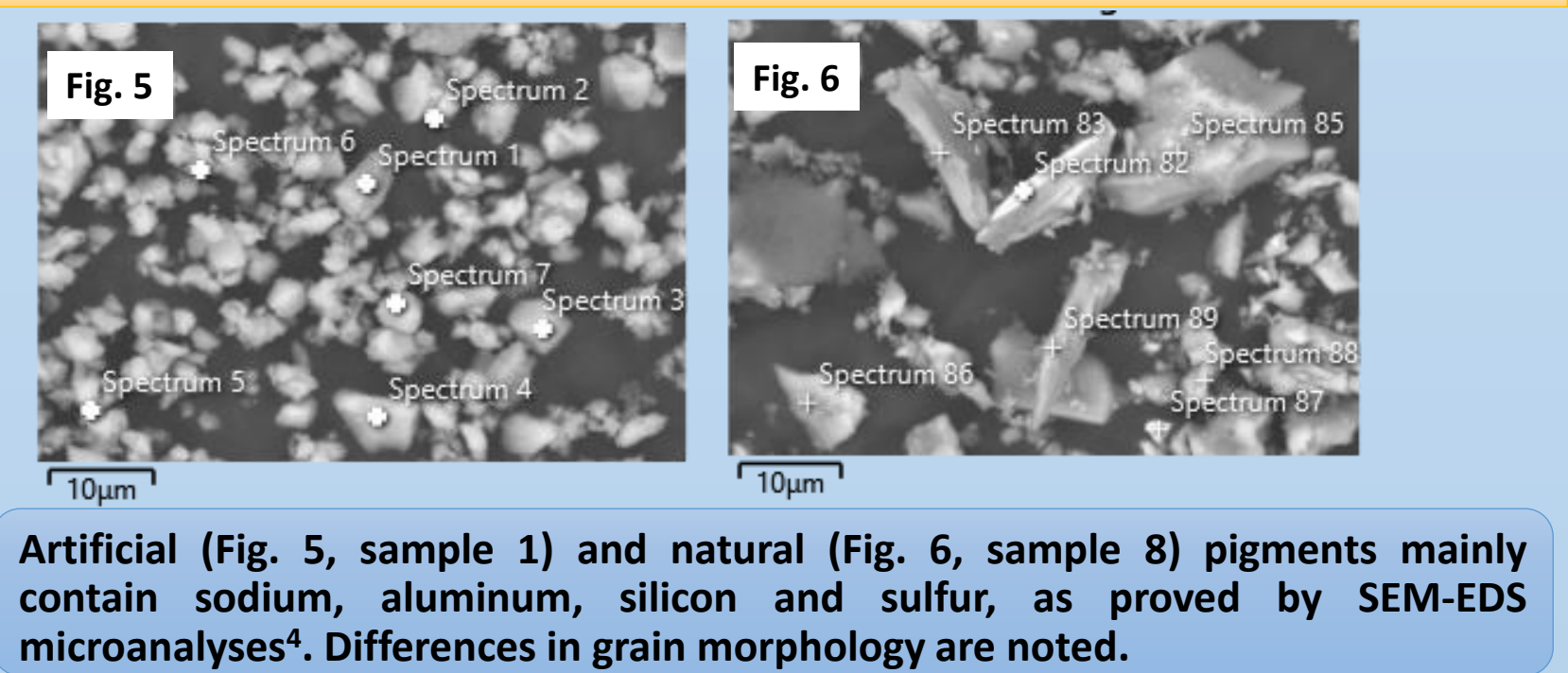
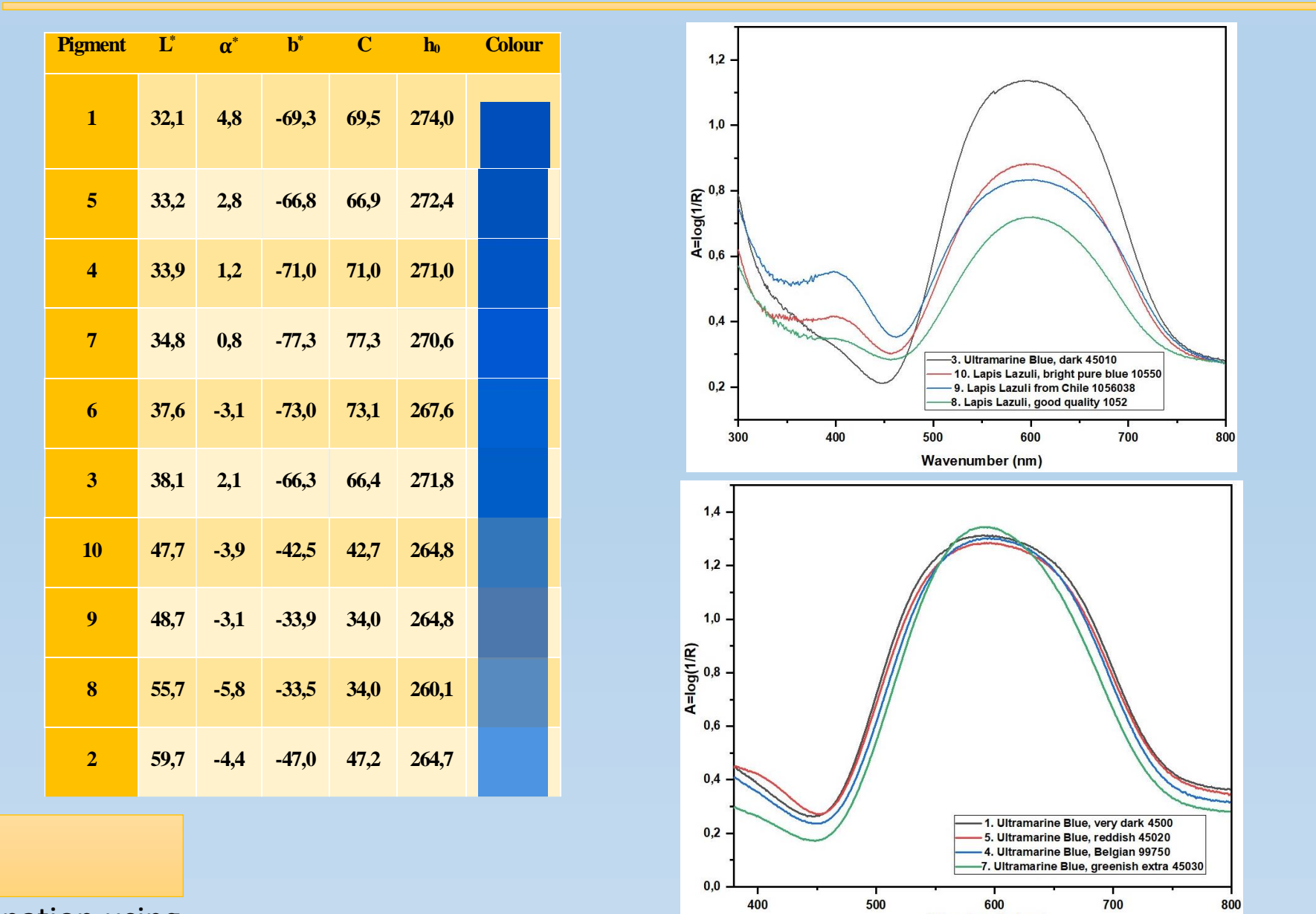


Fig. 3a), Fig. 4a) provide the identification and assignment of the binding energies of all the elements of a natural ultramarine (Sample 8) and an artificial one (Sample 1) on wide-scan XPS spectra. Fig. 3b), Fig. 4b) The atomic concentrations of sulfur species calculated from the areas of doublets S₂p_{3/2}-2p_{1/2}, S_x⁻ - polysulfide (x > 2) and SO₄²⁻ - sulfate. Fig. 3c), Fig. 4c) The spectrum of O 1s has been fitted with two peaks, Si₂O₆ (Diopside phase)-SO₄²⁻ in the natural pigment and SiO₄ (Haüyne and Lazurite phases) in the artificial one.⁵

SEM-EDS



UV-Vis



Conclusions

In this research work, ten samples of natural and synthetic ultramarine pigments were used to investigate the possibility of their discrimination using characterization methods. The differences between natural and synthetic ultramarine pigment are distinguished by the crystalline phases contained. Natural pigments show a greater variety of crystalline phases (Diopside, Phlogopite, Wollastonite, Sodalite) containing the elements mainly of e.g. Ca, Mg, F, while all samples show as main phases of lazurite and haüyne. This differentiation was shown through XRD with phase identification, through XPS from identification of the sulfur radical anions doublets with the appropriate assignment of compounds. Through SEM-EDS and UV-Vis characterization techniques, the percentages of elements in the samples and the absorbances corresponding to the blue colour were confirmed by colorimetric study for each sample, respectively.

References

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