

Ultramarine blue from Asturian “hard” kaolins

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Abstract

Ultramarine blue made with Asturian refined hard kaolin from deposits associated with Armorican quartzite, is compared with the pigment made with China kaolin, both produced in the same synthesis conditions. Properties after a deep characterization (XRD, IRFT and Raman Spectroscopies, Light Reflectivity, Colorimetry and Micro-analysis) showed that the Asturian Teresa mine kaolin is good enough, once washed and classified, to produce a good blue pigment. The pigment is quite comparable in quality to the one produced with China kaolin. Moreover, it can be obtained from a cheap and abundant material which so far had only been used for calcined fire-clay raw materials, used in low alumina refractories and castables production.

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1. Introduction

The history of ultramarine blue goes back to Bible times, being still used widely today. The natural material with the typical colour is the mineral lazurite or lapis lazuli. The old trade of these stones from Afghanistan gives rise to the name of the powdered stone, used for paintings and ornament, ultramarine blue (UB in the following), because of the long trip from overseas of this appreciated material. This coloured mineral reached a high price due to its scarcity, and at the beginning of the 19th century UB was synthesised because of the big demand (Large, 1962).

China clay kaolin has been the traditional raw material for UB pigment synthetic production. On the other hand Asturian flint-clay (kaolin) has been used for many years in the production of refractory material, mainly when the alkaline and iron content allows reaching an appropriate value of refractoriness. The more selective needs of materials for steel refractory production made the Asturian kaolin business decrease quite a lot. This fact led to the stopping of most of the producers, because no one of them had installed a refinery, even though research made clear the commercial interest of refining Asturian hard kaolin deposits (Correa-Brizuela, 1995). The concentration studies and research opened up the possibility of the use of the kaolin produced, even not being plastic, for other purposes where the kaolin has much more value added. Some physical cleaning and the specific hydro-metallurgical treatment produce white kaolin, interesting for paper filler and ceramics (Correa-Brizuela, 1995).

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Table 1

Chemical composition of kaolins, wt.%

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	K ₂ O	Na ₂ O	L. on I.
Asturian	49	37	0.35	0.9	0.10	0.03	0.50	0.10	12.02
China	48.5	38	1.1	0.03	0.10	0.30	1.85	0.10	10.02

This paper deals with the use of Asturian kaolin for UB pigment synthesis in comparison with China clay kaolin from Devon.

Industrial procedure for UB fabrication was developed by J.B Guimet in Toulouse (France) and C. Gmelin in Germany 1828. F.A. Köttig improved the process for the Royal Porcelain Manufacturing (Mertens, 2004). Different UB formulations can be found in the bibliography (Prener and Ward, 1950; Hofmann and Herzenstiel, 1964; Hofmann et al., 1969; Schawarz and

Hofmann, 1970; Tarling et al., 1988; Gordillo et al., 1992; Cork, 1993; Gobeltz-Hauteceour et al., 2002) and Corck (1993) gave the following range composition: Na 6.3–10, Al 4.8–6, Si 6–7.2, O 24, S 1–4.5. Structurally UB pigment has an aluminosilicate framework (sodalite type) with Na⁺, S²⁻, S³⁻ and SO₄⁻ ions inside (Chivers and Drummond, 1973; Tarling and Barnes, 1988; Gobeltz et al., 1998; Reinen and Lindner, 1999; Arieli et al., 2004). S³⁻ polysulphur radical produces the strong blue colour as could be deduced

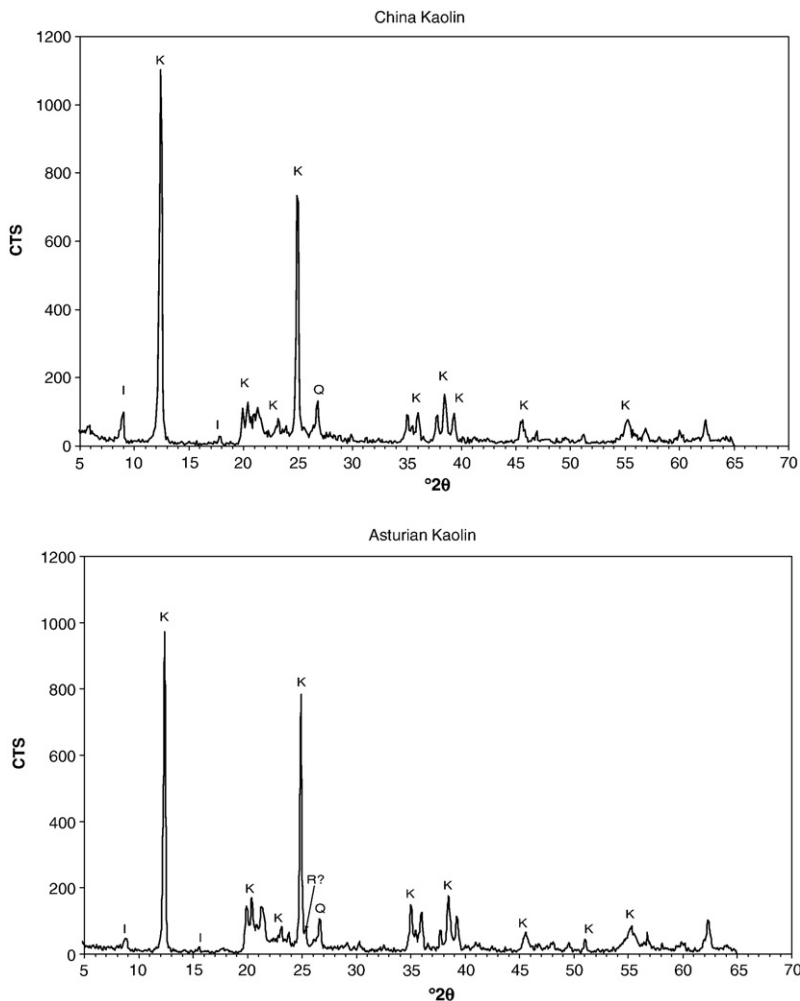


Fig. 1. XRD pattern of China and Asturian kaolins: I: Illite, K: kaolinite, P: pyrite, Q: quartz, A: anatase, G: graphite.

Table 2
Activation temperature determination by colour results

Sample	T (°C)	Light	L	a	b
China	700	N (natural)	34.5	18.5	-51.2
Asturian	750	N	37.5	15.0	-48.5
	700	N	38.5	14.0	-47.2
	680	N	35.5	18.5	-50.5
	650	N	37.5	17.3	-50.1

from most references that attribute to S^{3-} chromophore the blue colour of the UB (Wieckowski, 1970; Chivers and Drummond, 1973; Tarling and Barnes, 1988; Gobeltz-Hauteceur et al., 2002). For that, characterization of UB is done frequently determining the presence of this polyanion and quantifying it.

The structure and nature of UB has been studied by different methods: XRD, NMR, RE, IRS, ESR, EPR (Clark and Cobbold, 1978; Bell et al., 1997; Landman and de Wall, 2004; Arieli et al., 2004). Colour characterization is made by the determination of the colorimetric parameters and making visible reflectance studies (Gobeltz et al., 1998; Kowalisky, 1990).

Some of the best representations of the UB crystal structure are described in the papers by Tarling and Barnes (1988) and Gobeltz-Hauteceur et al. (2002), that include the S^{3-} chromophore and four Na^+ cations. This shows only three Na^+ cations and the S^{3-} chromophore polyion. A β -cage containing the ions, as well as the geometrics of S^{3-} , S^{2-} and $(Na_4S_3)^{3+}$, with the interatomic distances, are described by Arieli et al. (2004). Not all the β -cages are filled with S^{3-} , being possible the filled percentage determination.

Colorimetric studies of the pigment follows the indications defined by the Commission International d'Eclairage CIE (1976) as described in the works of Gobeltz and Kowalisky (Kowalisky, 1990; Gobeltz et al., 1998; Gobeltz-Hauteceur et al., 2002).

2. Experimentation

2.1. Raw materials preparation and characterization

The China clay kaolin was a commercial one from Dovey Basin, Devon England and was used as received from the

Table 3
Asturian and China ultramarine blue composition, wt.% (EDAX plus AA)

UB	Element							
	O	Na	Al	Si	S	K	Fe	Ti
Asturian	47.0	12.5	11.9	18.2	9.4	0.58	0.41	0.3
China	45.9	12.2	11.8	17.6	10.7	0.66	1.24	0.05

supplier. The Asturian kaolin from Teresa mine in Tineo, was crushed and trolled for disintegration. Fine material, less than 100 μm , was classified and concentrated by cycloning, producing silica and sulphide separation, and obtaining a fine product less than 45 μm size. Usually, graphite and iron minerals are eliminated by oxidation treatment using traditional sodium hypochlorite and sodium bisulphide oxidation, producing the whiter product used in the paper industry, but in our case material can be used directly after classification, because neither carbon nor sulphides are deleterious, moreover they are added for UB fabrication. Silica fines are also good for the pigment production, as some extra silica is needed over the compositional one from the clay.

The kaolins used were mineralogical and chemically characterized, showing that they have similar chemical composition (Table 1, Fig. 1). Table 1, shows the chemical composition of two kaolins: the English commercial China clay from Devon and the Asturian one. Theoretical Si/Al ratio in pure kaolin is 1.04; in practice China one used had 1.13 and the Asturian 1.17. Asturian kaolin has a bit less alumina and more silica and titanium oxide than China one, but has less potassium, iron and magnesium. Asturian kaolin, from Teresa mine is quite pure, with some signals of quartz, rutile/anatase and very small of pyrite illite and graphite. China kaolin has as minority minerals illite and orthoclase.

Quartz material was ground (<45 μm) sands, from Arija (Burgos) sand deposits used for glass making, having more than 98% SiO_2 .

Metallurgical pitch, the quality used for aluminium electrodes, from IQN was used as reducer material.

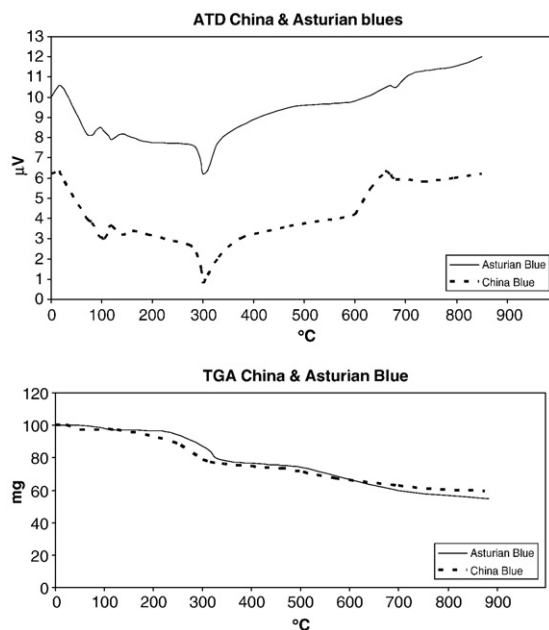


Fig. 2. Thermal analysis of the synthetic process of China and Asturian ultramarine blues.

Sodium carbonate was the Na supplier and pure sulphur as the chromophore generator, both industrial qualities from Probus P.Q.

2.2. Procedure of fabrication

The fabrication procedure was the same for both materials, except for the activation temperature that was 700 °C for China clay, value taken from bibliography (Landman and de Wall, 2004) and 680 °C for Asturian one as a result from some tentative colour quality determinations, (see Table 2).

Once the kaolin was calcined, mixtures were prepared following some practical experience of the authors and the indications from some references in the literature (Landman and de Wall, 2004), as follows: Calcined kaolin 35–37%, sodium carbonate 29–33%, sulphur 28%, ground quartz 5–10% and ground pitch 5–6%. Some additional silica, as quartz, was used to reach the required silica–alumina relationship for a good final product.

The mixture of the components was done in a rotary mixer, till full homogeneity. The mixture was charged in flat 50 cm³ ceramic container, introduced in a tube furnace and kept for 10–12 h at 750 °C. Afterwards, the sample was oxidized in the same furnace, by opening the ends at 550–600 °C for 3 h, having the precaution of not over oxidizing the material, using ceramic hole ends. In all the experiments, the 3–5 mm upper layer was discarded, grinding the rest in a ring mill till uniform colour (less than 45 µm). The powder was washed with water for sodium sulphate removal, and then dried at 110 °C for characterization.

3. Product characterization

Products were characterized by Atomic Absorption spectrometry (AAS) and Energy Dispersive Spectroscopy (EDS), colorimetric, IRFT and Raman spectroscopies, X-ray diffraction (XRD) and Thermal Analysis (DTA–TG).

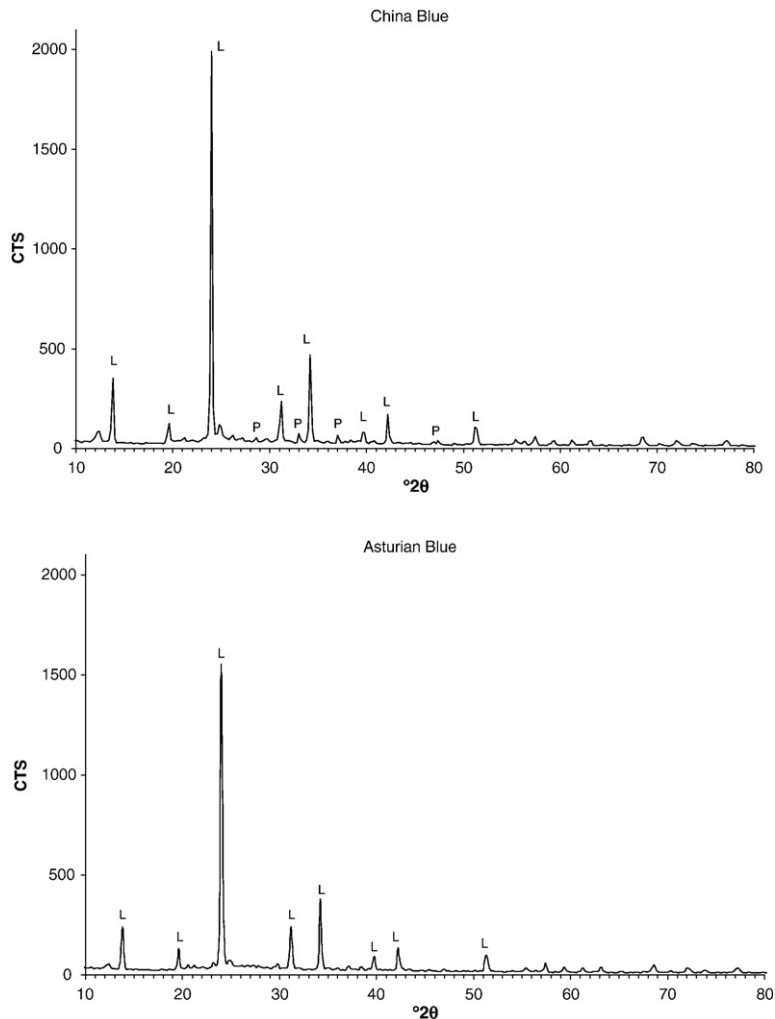


Fig. 3. XRD pattern of China and Asturian U.B (L: Lazurite, P: Pyrite).

Chemical composition analysis of UB materials was done in a Jeol JSM-6100 equipped with EDAX (averaging in 20 points in the powder sample) and by AAS using a Pye Unicam SP 9 equipment.

Thermal analysis was made using a Chio Balance model TRDA3-H, being the experimental conditions: Heating rate: 10 °C/min., DTA: 100 μV, air atmosphere, sample 100 mg, crucible of platinum.

Infrared spectra have been obtained with a Fourier Transformed I R 560 from Nicolet, through

a KBr source globar and DTGS piezoelectric detector. Spectra were obtained at 4 cm⁻¹ resolution, under vacuum, 64 pellet scans between 4000 and 400 cm⁻¹. 13 cm diameter and 120 mg pellet was prepared, using KBr matrix in a 1/100 sample/matrix relationship.

An H R 800 Jovin Yvon Horiba was used for Ramman spectroscopy, taking the green line of an argon laser (λ=514, 5 mm) as calibrating source, equipped with CCD camera. Power was 25 mW, excitation time

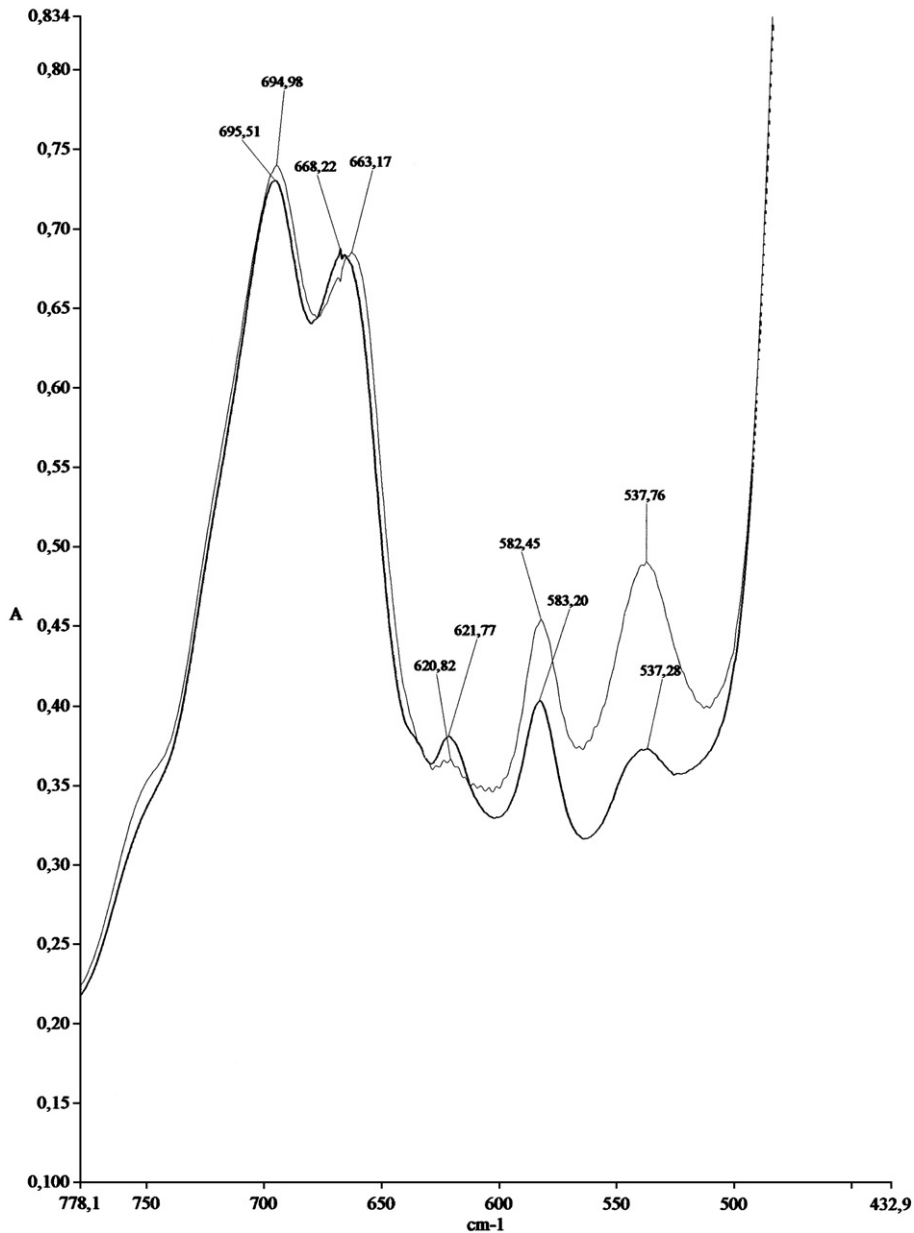


Fig. 4. Infrared spectra: Asturian Blue — China Blue - - - - -.

30 s, doing two spectra. Laser focalization was done on the powder sample with an Olympus M Plan optical microscope under 100× objective. Spectra were obtained between 200 and 1400 cm^{-1} .

XRD patterns were obtained in a PW 3040/60 Philips diffractometer, with $\text{Cu}_{\text{K}\alpha}$ cathode, graphite monochromator, 0.04 and 0.3 slits, 40 kV, 40 A, 0.02 $2\theta/\text{s}$, running 5–80°.

LENETA FORM 24-H-OPACITY cardboard was used for colour preparation. 10% pigment was homogeneously suspended in a polyurethane transparent resin, and then was extended with an Elcometer film 3520 Baker applicator on the form as a 250 μm layer. Datacolor Spectraflash SF 450 spectrophotometer was used for colorimetric and reflectance studies. L^* , a^* , b^* , C^* and h^* CIE parameters were determined with natural day, wolfram yellow lamp and fluorescent tube lights (D65, Y, F). Reflectance versus wavelength, measured between 350 and 700 nm, was obtained.

4. Results and discussion

Analytical elemental composition of the two synthesised blues is presented in Table 3. Some chemical differences are observed between both materials, but they will not have effect on the S^{3-} modification or stabilization (Booth et al., 2003), differentially affecting therefore the reddish shade in both products.

The sulphur analysed is the chromophore source internally inserted, because both UB products has been very well water washed. There is a higher content in the China clay blue, so there are some reasons for expecting slightly better quality in this one, but iron content is higher than the Asturian blue, which according to Landman and de Wall (2004) can affect the quality of the product.

Asturian blue is more consistent after fabrication, probably because of the clay fineness or sinterization effects by compositional or structural reasons. The grinding of this product increases the operation time, but no changes have been observed on the product colour.

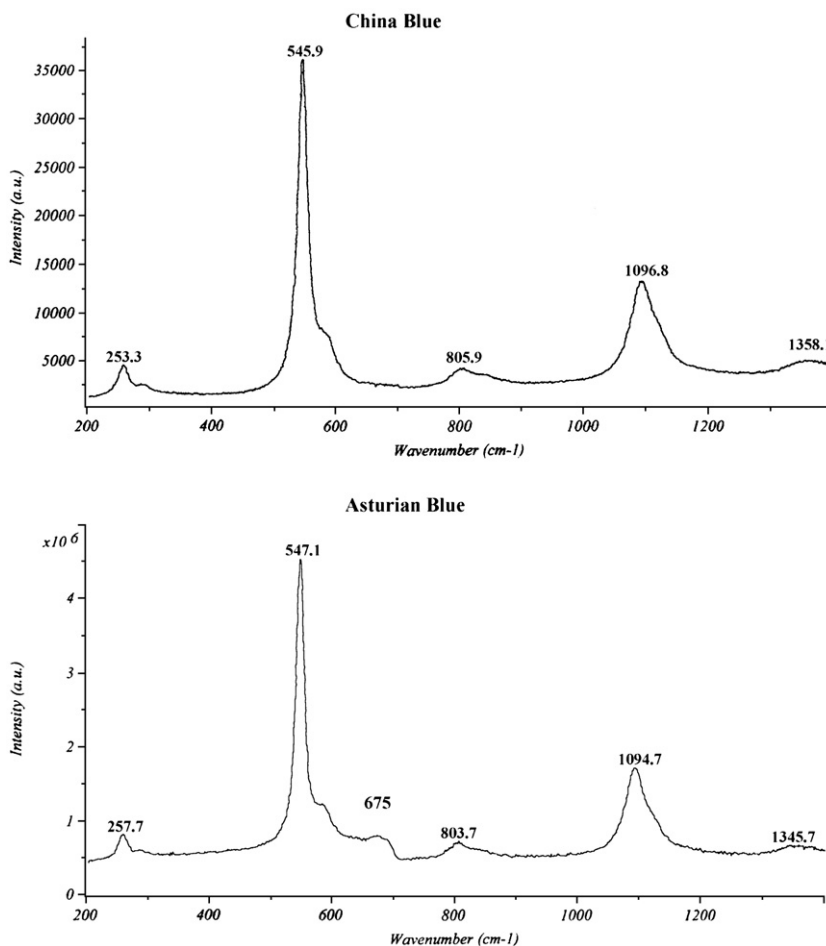


Fig. 5. Raman spectra of China and Asturian U.B.

DTA and TG analysis show that the two blues are similar (Fig. 2); in fact, only a higher stability of the kaolin is appreciated at dehydroxilation temperatures in the TGA and a slightly smaller exothermic is obtained with the Asturian blue between 600 and 750 °C, zone of blue synthesising, that could indicate some poorer or more difficult reactivity.

XRD studies, (Fig. 3), show a very high similitude between the Asturian and the China blues. The patterns correspond to Lazurite. Some pyrite is also detected in China blue.

Infrared spectra of the two pigments (Fig. 4) present typical sodalite bands, and correspond in both cases to ultramarine blue. Absorbance bands correspond to the

Table 4
Comparative Ramman signals of different samples spectra, including the Asturian and the China UB synthetized in this work, and its sulphur ions correspondence

U Red Clark	U Blue Clark	U Blue (M.)	U Blue f.a.	LazuriteBellClark	U Red	U Industrial	U. China	U Asturian	Assigned S ^{x-}
					216 w				
			256 w b			255 w b	255 w b		S ³⁻ bending
		259 w b		258 w				258 w b	S ³⁻ bending
			296 w sh			293 w sh			
352 w b									S4
410 w s					461 w				?
			546 st s			545 st s		546 st s	S ³⁻ sim.stretch
				548 st s				547 st s	S ³⁻ sim.stretch
		550 s							
547 w			566 m sh					565 m sh	ν_1 (S ³⁻) S ²⁻
						568 sh			
580 w sh		580 w sh						570 m sh	S ²⁻ ν (S ²⁻) ν (S ²⁻)
	586.5								
653.5 w-m					626 w				
674 m								675 w b	S4
		806 w b						804 w b	ν_1 ? S4
			813 w b					806	
				822 w					
					994 short				
1024 w b									S4
	1186								2 ν (S ²⁻)
1093 w b						1092 m b			2 ν_1 (S ³⁻) S ³⁻ overtone
				1096 m b				1095 m b	
		1097 m b						1097 m b	S ³⁻ overtone
			1099 m b						
1340 w b									S4
		1360 w b						1345 w b	S4
		1644 w b					1358 w b		S4
1650 w b									3 ν_1 (S ³⁻)
	1747								3 ν (S ²⁻)

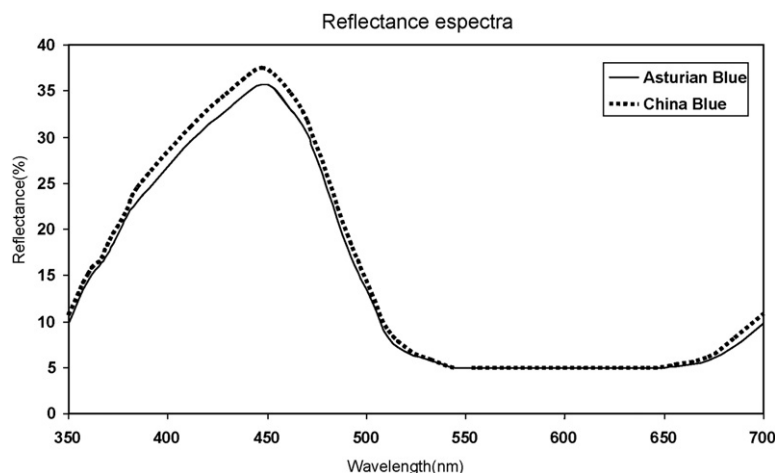


Fig. 6. Reflectance spectra of China and Asturian ultramarine blue.

chromophore S^{3-} . Some researchers (Clark and Cobbold, 1978) found strong bands at 582 and 547 cm^{-1} assigned to ν_3 and ν_1 frequencies from the S^{3-} ion. In Fig. 4 these bands are found around 582–583 and 537 cm^{-1} in both samples, the China and the Asturian blues, with very small differences. The ν_1 band is also found in the same wavenumber in the Ramman spectra 546–547 (Fig. 5) and it can mean that the mentioned ion is a nonlinear one. Regarding the peak intensity, in our case, ν_3 peaks are similar (582–583 cm^{-1}) in both blues, but ν_1 is stronger in the China blue, and is recorded at 538 cm^{-1} , similarly to other synthetic blues (Landman and de Wall, 2004) recorded at 542, not far from the referenced standard blue (547 cm^{-1}).

Ramman spectra of produced China and Asturian UB, (Fig. 5), are compared with different referenced and standard blues in Table 4, where the lines assigned are shown for a laser line of 514.5 nm. The two samples, China and Asturian Blues, have quite similar Ramman spectra. The only difference is the 675 broad band present in the Asturian Blue, a significant medium band from red ultramarine assigned to S4 (ν_1 ?) (Clark and Cobbold, 1978).

Colorimetric study and reflectance spectra show that both samples are very alike. Both samples have an absorbance peak (5% reflectance) at approximately 600 nm Fig. 6, which according to Arieli et al. (2004), reflects that both are typical blue colour. Absorption below 350 nm is due to sodalite framework. Also calcinations used for both pigments (550 °C) produced S^{3-} radicals and apparently no or very little S^{2-} , in accordance with Arieli et al. (2004), although this S^{2-} signal can be altered for the Al/Si relationship, higher in the samples produced, compared with those shown by Arieli et al. (2004) (Table 5).

Colorimetric parameters are presented in Table 6 with three different illuminations: natural day light, wolfram filament yellow and fluorescent. Comparison of the results are reflected in the differential (db,da) representation in Fig. 7, in which, taking as reference de China clay Blue (axial center), the Asturian pigment has small positive deviations towards red, yellow and hull sides of 0.42/18.94 (2.2%); 0.99/–50.24 (2%); 0.7/289.9 (0.26%). The lightness/darkness is slightly

Table 5

Al, Na, Fe and S^{3-} to Si ratios for a reference UB and the China and Asturian produced in this work

Molar ratios	Al/Si	Na/Si	S^{3-} /Si	Fe/Si
Areli Blue	0.64	0.76	0.11	<0.003
Asturian Blue	0.68	0.84	0.15	0.010
China Blue	0.70	0.84	0.18	0.035

Table 6

Colorimetric parameters for three different lights (natural, yellow, fluorescent) for China and Asturian UB

Sample	Light	<i>L</i>	<i>a</i>	<i>b</i>	<i>C</i>	<i>h</i>
China	N	34.47	18.52	–51.22	54.47	289.88
	Y	30.24	–0.33	–56.54	56.54	269.66
	F	30.76	15.00	–58.85	60.73	284.30
Asturian	N	33.74	18.94	–50.24	53.69	290.66
	Y	29.74	0.37	–55.14	55.14	270.38
	F	30.28	15.06	–57.45	59.39	284.69

smaller for the Asturian Blue $-0.73/33.47$ (-2.2%) and $-0.78/54.47$ (-1.4%). So, very little differences in colorimetric characterization are found between the Asturian and the China pigments. In fact, optical observation of the photo of both pigments can be checked when suspended in varnish, from where all the above parameters were obtained (Fig. 8).

5. Conclusion

Asturian refined kaolin from the huge Central hard formation, particularly from the Tineo-Salas Area (Teresa mine), is good enough for ultramarine blue fabrication, as it is China clay kaolin, raw material used normally for this purpose.

All the different analysis and characterization tests carried out in this work have effectively demonstrated the above affirmation, and a new and more interesting application can be done to a rich material that has been used in huge tonnages for fire-clay refractory and castables, now in strong regression in the traditional steel industry.

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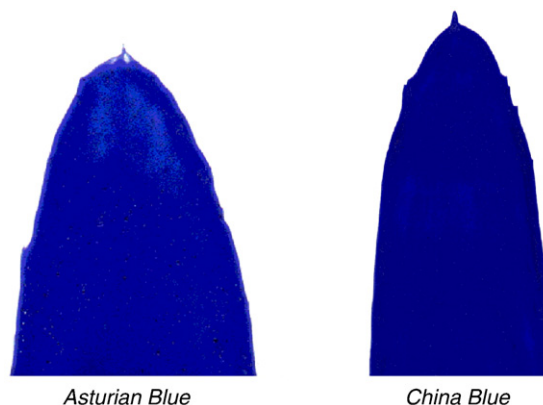


Fig. 8. China and Asturian U.B. colour aspect, suspended in transparent varnish.

tion help. And to D. Atanasio Lafuente for the Asturian clay mine samples supply.

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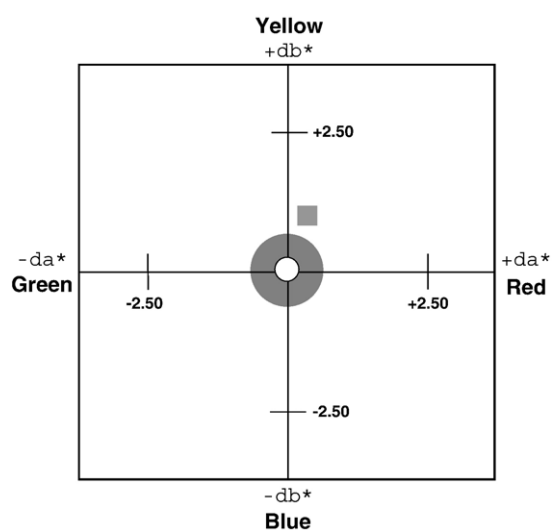


Fig. 7. Differential (db,da) representation of Asturian Blue taking China as reference. (Central references: China blue, small square in second quadrant: Asturian blue).

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