ACS OMEGA
Article
Cite This: ACS Omega 2019, 4, 11424−11432
http://pubs.acs.org/journal/acsodf



# Color Source for the First Argentinian Flags

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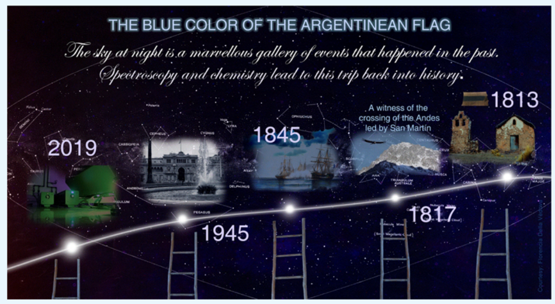
**ABSTRACT:** In this work, a historical controversy of more than 200 years is settled by the study of the oldest preserved Argentinian flag. The results of the present work reinforce the hypothesis of a number of historians who consider it to be the first flag that was originally hoisted on February 27, 1812, on the banks of the Paraná River. The work consists of a study of the original textile. Through chemical analysis and implementation of different types of analyses, techniques, and spectroscopies such as UV−vis, UV−vis diffuse reflectance spectroscopy, attenuated total reflectance Fourier transform infrared spectroscopy, scanning electron microscopy−energy-dispersive X-ray spectroscopy, and resonance Raman, the original characteristics of the flag of Macha were determined. The flag was colored with indigotin from Europe (from Isatis tinctoria) and made of silk; it is white, blue, and white in a horizontal arrangement. It was not treated with tin, and its blue color was subsequently adopted by the Central American Confederation and later by various states of Central America. According to related contemporaneous stories, its preservation was due to the watchfulness of the patriots.




## ■ INTRODUCTION

The oldest preserved Argentinian flag, which for many historians may be the first flag raised by its creator, Manuel José Joaquín del Corazón de Jesús Belgrano y González, on February 27, 1812, on the banks of the Paraná River, is preserved in the House of Freedom "Casa de la Libertad" in Sucre, Estado Plurinacional de Bolivia. The so-called Flag of Macha is in this unique location guarded by the remains of Doña Juana Azurduy de Padilla (Figure 1). This flag, the Flag of Macha, was found in the year 1883 in the vicinity of the town of Macha, in the church of Titiri by the village priest Martín Castro, and 2 years later, in 1885, his successor, the parish priest Primo Arrieta, transferred this insignia to the city of Sucre. A sister flag, called the Flag of Ayohuma, in reference to the battle of the same name in which the royalist army of Joaquín de la Pezuela defeated Belgrano's army, was also found in the same church under a painting of Santa Teresa. It is currently located in the National Historical Museum of Argentina. Both of these flags, carried by Belgrano, were preserved after the battles since they would have been delivered for protection by Colonel Cornelio Zelaya, a soldier who was under orders from Belgrano, to the parish priest of the Titiri church, Juan de Dios Aranívar. According to the historical records, there were signs that the result of the battle would not be favorable to Belgrano's army. In accordance with the testimonies of prominent soldiers of this period, a flag captured by enemy hands had a negative connotation in several dimensions that reached finally its exhibition in a European museum.[1] The environmental preservation of both banners was differentiated according to the different climatic conditions of the conservation sites, much more favorable to the city of Sucre.

Figure 1. Flag of Macha. House of Freedom, Casa de la Libertad, Sucre, Bolivia.

Our recent spectral-historical work linked the connection between the 1814 Governor of the Tucumán Province, General Bernabé Aráoz, with the creator of the Argentinian Flag, Manuel Belgrano.[2] It was in a small place of the department of Burruyacú, in La Encrucijada, where Bernabé Aráoz, who later ordered the construction of the blue and white ceremony flag of 1814 for the Temple of San Francisco in Tucumán, blue due to lapis lazuli pigment,[2] convinced Belgrano, who was on his way to Córdoba after the legendary Jujeño Exodus (Éxodo Jujeño), to challenge the commands of the central government of Buenos Aires and to face in Tucumán the once invincible Pío Tristán. On September 24, 1812, the so-called Battle of Tucumán took place, and after his

Received: May 15, 2019
Accepted: June 20, 2019
Published: July 1, 2019

victory, Manuel Belgrano pushed the royalist army by directing its troops in a northward direction toward the city of Salta.[3] The resonance of this achievement was notorious. The government of Buenos Aires, the First Triumvirate, resigned and, for instance, the flux of the oriental population was reversed. In October 1811, another exceptional event was recorded after the armistice was promulgated between the Buenos Aires government and the royalist Viceroy of Montevideo, Francisco de Elío. That was when the entire population of Montevideo accompanied their leader, José Gervasio de Artigas, to the province of Entre Ríos, currently Argentina, to the place of Ayuí. This event is known as the exodus of Montevideo or "la redota", a Río de la Plata word meaning defeat, "derrota". Some historians estimate that the number of people involved in that event may have reached 50 000.[4] The "redota" symbolized the unhappy feeling of the population toward the displacement of General Artigas, as ordered by the Government of Buenos Aires. This order originated his migration, but he was also accompanied by the entire population and his army.

On February 13, 1813, and days before the battle of Salta, all of the soldiers of the Army of the North swore allegiance to the flag on the banks of the Pasaje River, and from that moment on called the River Juramento (jurar is the Spanish verb swear and Juramento means oath), and so, one by one sealed his commitment to the flag with a kiss that today is again the center of our attention.

In relation to our previous work that covered several interesting questions to be continued, the current work focuses its objective on the determination of the dye that gave rise to this flag, which accompanied the beginning of the Argentine fatherland. There are dozens of publications, interviews, discussions, and conferences originated in the present subject that had as their central thesis the determination of the color of the Argentinian Flag, which, in historical terms, goes far beyond a mere discussion on coloration and goes back to issues already discussed by an eyewitness soldier of the Paso de los Andes of General San Martín in 1817, General Gerónimo Espejo.[1] This is how we propose in the present work: (i) the determination of the composition of the base fabric on which the ensign was made; (ii) a study of the presence or absence of Sn salts that contribute additional weight to silk or that could act as a preservative; (iii) revealing the original color of the insignia will be one of the fundamental questions to be addressed; (iv) the origin of either the dye or the pigment used for the preparation of the Belgrano flag will also be studied. The facts thus determined would provide information regarding the origin of the emblem, assuming the hypothesis that it may be the same flag raised for Belgrano the first time on the banks of the Paraná River on February 27, 1812. On the way to Alto Perú, Belgrano would have sworn allegiance to this flag on the Pasaje River, later known as the Juramento River; (v) in relation to the coloration, a correlation of the color of the pennant with that of the flags of the Central American countries will be mentioned, whose fights for independence were supported by the French-Argentine corsair Hipólito Bouchard in command of the frigate La Argentina, who under the orders of the government of the United Provinces of the Río de la Plata had a significant role in the contests for their Independence; and (vi) finally, another issue under debate is the contribution of this work to discuss some indication of the assertion of the "anguish" that being experienced would have caused the Argentine heroes to declare independence.[5]

With these objectives in mind, we used chemical methods, techniques, and those forms of spectroscopy that fall within this discipline whose name can be amalgamated in the spectral-historical topic, a remarkable tool to settle historical discussions with the central intervention of one of the branches of science, namely, spectroscopy.

## RESULTS AND DISCUSSION

To begin analyzing the questions raised, data and the analysis of a piece of a sample corresponding to Macha's flag are presented. For this, a piece of the flag, a crisp, smooth, plain interlaced fabric (Figure 2), was analyzed by attenuated total


**Figure 2.** Images taken during the scanning electron microscopy−energy-dispersive X-ray spectroscopy (SEM−EDX) experiment using the BSED mode with different amplifications of the colored region of the Flag of Macha.

reflectance Fourier transform infrared spectroscopy (ATR-FTIR) spectroscopy, as shown in Figure 3. Figure 2 shows an

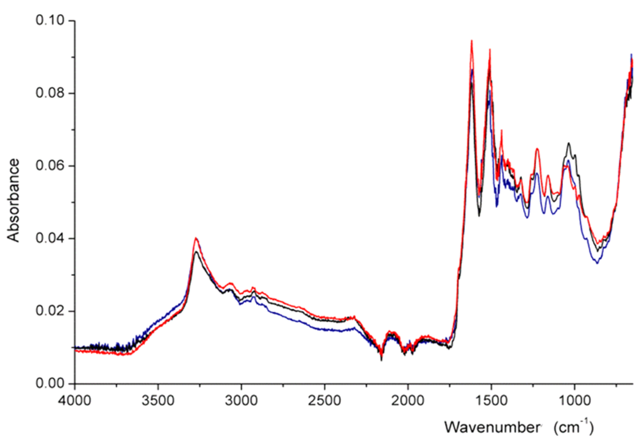



**Figure 3.** ATR-FTIR spectra of the colored region (blue trace), of the white region (black trace) of the Flag of Macha, and of a silk sample (red trace).

image of the colored part of the flag taken with different amplifications and measured experimentally with backscatter electron detector (BSED). According to Figure 2, the right-side part, the diameter of the fiber used reaches a value of approximately 12 $\mu$m in agreement with, for example, the expected value for Bombyx mori silk. It should be noted that the cross section of this particular silk is approximately triangular.[6]

As already mentioned, Figure 3 shows the results of the ATR-FTIR technique used to analyze the flag samples. The following measurements were made: (a) a piece of the colored Flag of Macha sample, (b) a piece of the white Flag of Macha sample, and (c) a piece of a silk sample. The same spectra are also reproduced with a piece of silk dyed with indigo in our laboratory and with the reported silk sample of the Aráoz flag.[2]



DOI: 10.1021/acsomega.9b01412
ACS Omega 2019, 4, 11424−11432

These spectra including both the colored and white regions of the Flag of Macha are conveniently compared with that of the original silk, evidencing a perfect agreement and reproducing the data published in the literature.[7]

Through the comparison of the ATR spectra, it is evident that the signals from the samples of the flag correspond to silk. The comparison of the respective spectra of the flag, colored and white, does not show any observable indications of differences attributable to the dye used to tint the central part of the flag. Moreover, silk has very intense absorptions in the same areas where indigo has the most prominent bands. This dye will be revealed as the cause of the coloration with future analysis. This result indicates a dye concentration lower than that detectable by the present method of analysis in the flag made more than 200 years ago. Only signals corresponding to fibroin are observed in the three spectra of Figure 3. This type of a polypeptide or protein presents in evolved organisms and is synthesized by combining up to 19 monomeric amino acids (−NH−CHR1−CO−) and one imino acid monomer (−NR1−CHR2−CO−), bonded through peptide bonds between the monomers. In evolved organisms, only the L-form of the amino acids is the one used, while in nonevolved bacteria or plants, the amino acid monomer D can be incorporated.[8]

Although there is evidence of photoevolution and phototendering processes (see below), the texture of the silk fiber of the flag under study is very well preserved, as demonstrated by the microscopic images taken with the SEM−EDX instrument with a BSED detector shown in Figure 2.

The SEM−EDX allows high-resolution images to be obtained that permit the study of the shape of an object and the elemental analysis of its surface. Figure 4 depicts the abundance of the chemical elements found in the white part (upper part of the figure) and colored part (lower) of the Flag of Macha as a function of the energy values (keV) for the transitions related to the K level of the given elements when external electrons, mostly of level L, reoccupy the vacant hole produced by the ionization of the respective K level. It is interesting to note that the ratios of C:N:O are approximately the same, within certain differences, for the two parts of the flag. This is an expected result since with this technique, the composition of the surface of the samples is basically observed. The differences can arise from the different compositions of the impurities, such as dust, deposited in each part of the surfaces analyzed. A joint evaluation of the results listed in Figure 4 with the chemical composition of fibroin and sericin also offers comparable results, moreover, taking into account the dust deposition on the flag evidenced for the presence of metals on the surface. Their weight (wt) % for C, N, and O are 47.6, 18.3, and 27.7 for fibroin and 46.5, 16.5, and 31.0 for sericin, respectively. Unlike the previously analyzed Aráoz flag, no presence of Sn has been found, which, in that case, could have been used as a salt, for example, to increase the weight of the silk or to protect that flag from deterioration.[2]

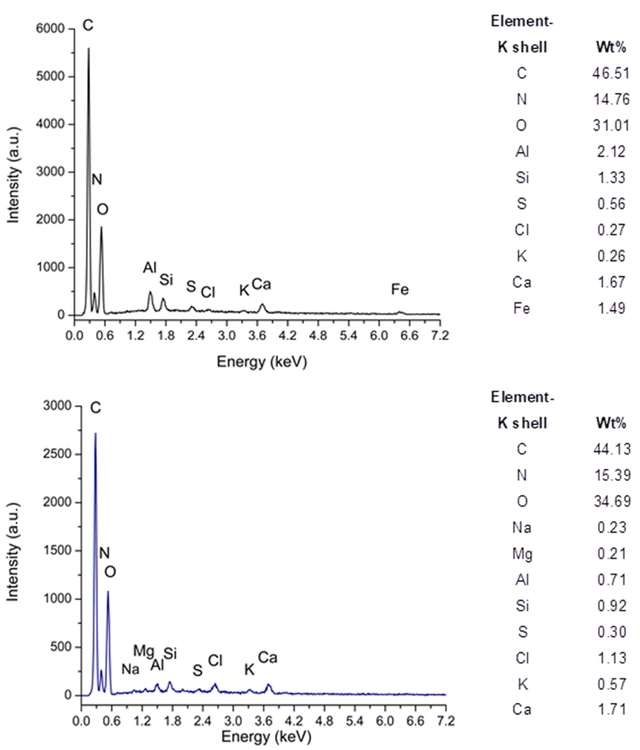



**Figure 4.** EDX spectra in keV of samples corresponding to the white (top) and colored (bottom) parts of the Flag of Macha. The elements and the corresponding abundances are tabulated on the right-hand side.

Other evidence confirming the composition of the sample as belonging to taffeta silk can be found through the microscopic images of enlarged areas of the Flag of Macha discriminated through different colorations presented in Figure 5 for the different elements as found in the EDX spectrum. While the elements C, N, and O present in the fibroin define the contour of the fibers, the other elements are homogeneously distributed and are due to the atmospheric dust. On the other hand, through this analysis, no evidence was found regarding the origin of the flag's coloration. As is plausible, the concentration of the dyes still existing in the colored part of the flag is below the detection limit of this technique.

To determine specifically the chemical species used to give coloration to the central strip of the Flag of Macha, additional forms of spectroscopy more sensitive than those already described were used. Figure 6 shows the UV−vis DRS spectra. With this information about the origin of the superficial absorption of the flag sample, indigo becomes a candidate employed as a tincture of the textile used to make the colored part of the Flag of Macha. The coincidence of the absorption maxima of the colored part of the Macha's flag with those of the commercial indigo is significant. Also, the difference in coloration between the current Macha's flag and the Aráoz flag is evident.[2]

The Flag of Macha, although well preserved, also suffered some temporary photoevolution given the specific climatic conditions of the area where it was stored. The photoevolution of silk by the absorption of the broad solar spectrum is linked to the presence of these amino acids among which tyrosine is considered the most important, given its abundance (greater than 4% wt), toward the formation of yellow chromophores generated by the bathochromic shift to red of the integrated absorption maximum, which for fresh silk is in the region of 280 nm. Tryptophan has a similar effect but its abundance in silk is less than 0.5%.[9] This process is the one that gives an intense yellow coloration to the piece of cloth of the white part of the flag under investigation and, for example, coloring the blue part of the flag in green color as in the case of the Aráoz flag recently studied, by the mixture of the blue and yellow colors.[2] It should be noted that the photoyellowing process is accompanied by phototendering, a process in which the



DOI: 10.1021/acsomega.9b01412
ACS Omega 2019, 4, 11424−11432

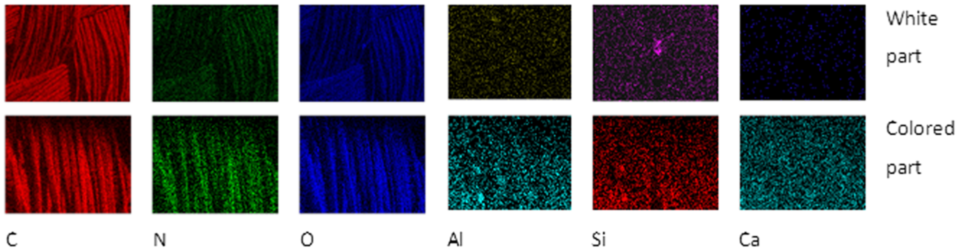



**Figure 5.** SEM−EDX microscopic images of the Flag of Macha flag according to the presence of the elements C, N, and O present in fibroin and other selected elements (Al, Si, and Ca). As already determined, the diameter of each fiber reaches a value of approximately 12 μm.

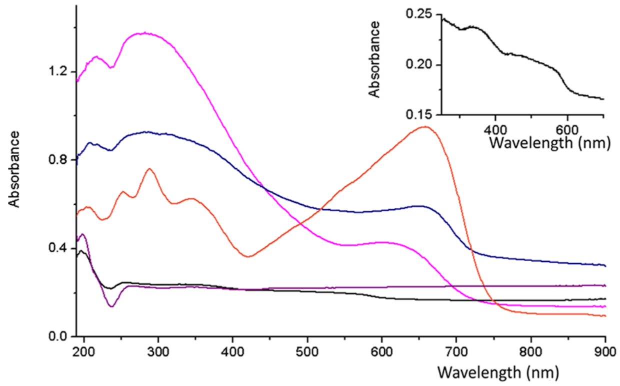


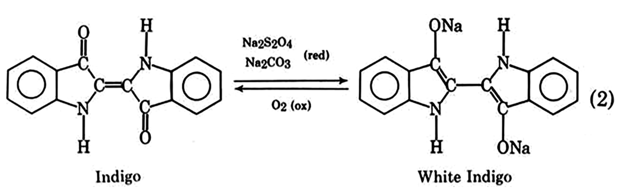

**Figure 6.** UV−vis diffuse reflectance spectrum of the colored part of the Flag of Macha (blue trace), of the colored sample of the Aráoz flag (magenta trace),[2] of pure indigo (orange trace), and of the white part of the Flag of Macha (black trace). This last spectrum is also enlarged in the upper part of the figure. The violet color line spectrum corresponds to a reference of Teflon between quartz windows.

phenomena spread from the surface to the interior of the silk by diffusion. Thus, the evaluation of the spectrum corresponding to the white part of the Macha flag clearly shows that the photoevolution process occurred, mainly through the red shift of the UV−vis band with a displacement of the original silk signal from 280 to greater than 300 nm (Figure 6, upper part).

Taking into account all of the evidence so far collected and to continue approaching the answer to one of the questions produced in this work, a colored fiber of the Flag of Macha was subjected to a typical reduction reaction for the hypothetical dye used. The observed changes can be interpreted through the equation explained in Scheme 1. The discolored leuco form is the one used to fix the reduced indigo species to the textile fiber.

Its coloration on the fiber is greenish yellow, and by later oxidation of the leuco form in the fiber by means of the oxygen of the air, the blue color of the diketo indigo form is reconstituted. This is practically conclusive evidence of the use of indigo as an agent for dyeing the Macha flag. With this confidence, the possibility of using a nondestructive and

### Scheme 1. Oxidation−Reduction Reactions between the Diketo and Leuco Forms of Indigo




sensitive technique such as Raman spectroscopy to confirm the previous analysis is raised. The bluish coloration of the flag is especially favorable for the use of the $Kr^+$ laser line, which has a wavelength of 647.1 nm and would enhance the signal of the dye through the resonance Raman effect. Figure 7 shows this

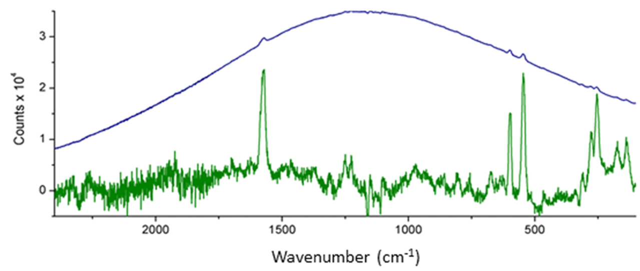
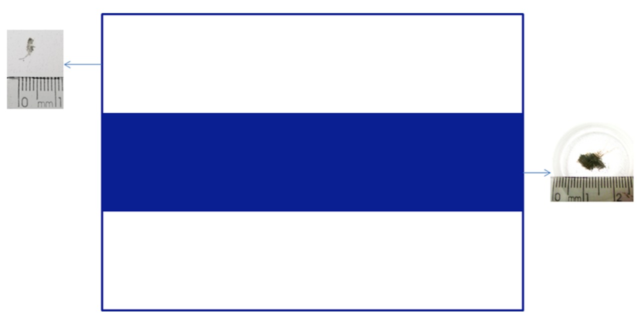



**Figure 7.** Resonance Raman spectrum of the colored part of the Flag of Macha. The color is due to the presence of indigo according to the observed bands. Excitation: 647.1 nm, 50 mW. Blue trace, spectrum without correction. Green trace, spectrum corrected by subtraction of the fluorescence found in the measurement by means of a polynomial function.

spectrum that undoubtedly agrees with that originated by indigo. The answer to the question of the original color of the banner is that the Flag of Macha was seen in 1813 with the colors white, blue, and white due to the dye indigo used in its coloration (Scheme 2).

Table 1 compares the Raman wavenumber values reported for synthetic indigo, extracted indigotin, and indirubin and those obtained in this work for the pigment giving coloration for the Flag of Macha. The origin of the indigo can also be traced through the spectroscopic data.

### Scheme 2. Flag of Macha[a]



[a]Red, green, blue combination of 9, 31, 146 (Isatis tinctoria); the size of the pavilion is 2.25 m × 1.60 m. The samples corresponding to the extreme and central strips of the Flag of Macha used for this work are also depicted in the diagram.



DOI: 10.1021/acsomega.9b01412
ACS Omega 2019, 4, 11424−11432

**Table 1. Comparison of Fourier Transform and Dispersive Raman Wavenumbers of Indigo, Indigotin, and Indirubin with the Dye Present in the Flag of Macha**

| synthetic indigo FT Raman[a,10] | FT Raman of natural indigo dyes from Isatis tinctoria and Indigofera tinctoria[b,10] | indirubin Raman[c,11] | indirubin Raman[d,12] | flag of Macha Raman[e] |
|---|---|---|---|---|
| 1700 m | 1703/1701 | 1700 | 1690 | |
| | | | 1651 | |
| 1622 m | 1621/1624 | 1636 | 1627 | |
| | | | 1607 | |
| 1581s | | 1578 | 1578 | 1586 |
| 1571vs | 1573/1573 | | | 1571 |
| 1481 m | 1482/1482 | | 1472 | |
| 1459 m | 1461/1460 | 1463 | 1453 | |
| | | 1402 | 1391 | |
| 1363s | 1363/1363 | 1355 | | 1368 |
| 1309s | 1311/1310 | | 1309 | 1310 |
| | | | 1281 | |
| 1247w | 1248/1247 | | 1265 | 1249 |
| 1224 m | 1225/1224 | | | 1226 |
| | | 1215 | 1204 | |
| | | | 1171 | |
| | | | 1144 | |
| | | | 1132 | |
| 1014 m | 1014/1014 | 1006 | 1013 | 1011 |
| | | | 997 | |
| | | | 952 | |
| | | | 885 | |
| | | | 865 | |
| 756w | 758/757 | | 792 | 759 |
| | | | 770 | |
| | | | 711 | |
| 674 m | 674/674 | | 669 | 674 |
| | | | 659 | |
| | | | 622 | |
| 598 | 598/598 | 585 | 575 | 598 |
| 544 | 545/544 | | 527;524[f] | 545 |
| | | | 486 | |
| | | | 462 | |
| | | | 393 | |
| | | | 373[g] | |
| | | | 358[g] | |
| | | | | 279 |
| | | | 259 | 255 |
| | | | 243 | |
| | | | 211 | |
| | | | 169 | 175 |
| | | | | 137 |

[a]vs: very strong, s: strong, m: medium, w: weak. [b]Indigotin from Isatis tinctoria and Indigofera tinctoria. [c]Raman spectrum measured with 514.5 nm. [d]Raman spectrum measured with 785 nm. [e]Raman spectrum measured with 647.1 nm. [f]Table and figure values, respectively. [g]Figure value.

The indigo of the early 19th century could have been extracted from different variants of plants, including those of the Indigofera, Isatis, Strobilanthes, and polygonum. The dyes originating from these plants can contain indigotin (indigo) and its structural isomer (indirubin). The published studies indicate that indirubin is found naturally in a greater proportion in the crops of South America and Asia. Indirubin originates only from indigo plants (Indigofera) and not from woad whose synonyms are Isatis tinctoria or glastum. Another reported result indicates that this fact may be due not only to the origin of the plants used for the extraction of the dye but also to the dying process that involves the obligatory stages of alkalization and reduction to solubilize the indigoid dye.[13] A work, which also reports the FT Raman spectra of the indigotin and indirubin substances, shows perceptible differences in the spectra of both species.[14] A mixture of indigotin and indirubin was also detected in Leeds collections, as well as in pre-Colombian Peruvian textiles.[15] Both the wavenumbers observed and the comparison of the spectral characteristics reported in the literature and mentioned in Table 1 indicate that the dye found in the flag of Macha is only indigotin. To perform a complementary spectroscopy study of the origin of the dye, the appropriate measurement conditions to record preresonance or resonance Raman spectra must be found. The maximum absorption of the UV−vis spectra reported for the indigotin species solubilized in dimethyl sulfoxide (DMSO) is 619 nm, while its structural isomer, the reddish indirubin species, has a hypsochromic effect and absorbs in the 550 nm region.[15] With this indication, it is expected that the detection of resonance Raman signals corresponding to the chromophore of the red substrate indirubin present in lower concentration will be favored by Raman measurements obtained with the green line of 514.5 nm of an $Ar^+$ laser. Due to its absorption and fluorescence, indigo is a problematic dye when explored with Raman spectroscopy. When the reported FT Raman intensities of the dye are compared with those obtained in our work with excitation at 647.1 nm, a close correlation is observed in the detection of the bands of greater intensity. However, relatively weak bands observed in the FT Raman spectrum are also observed in our case due to the resonance Raman effect despite the low concentration of the detected species. For example, in the FT Raman spectrum, the weak bands that appear at 1247 and 756 $cm^{-1}$ are attributed, among other contributions, to the CN stretching of the indigo molecule, which is part also of the chromophore of the molecule. When 647.1 nm radiation is used for excitation, these Raman bands are enhanced by several orders of magnitude. This is known as the resonance Raman effect, due to the process that originates them. It is a transition from the electronic fundamental state to the excited one, with the CN group being part of the indigo chromophore.

This spectrum did not show the presence of the vibrational signals corresponding to indirubin. To irrefutably confirm this conclusive result to establish the origin of the dye used to make the Flag of Macha, a small piece of the blue part of Macha's flag was used to dissolve its dye in d-DMSO for 20 days. Figure 8 shows the UV−vis spectrum of the solution of the extracted dye that can be identified as indigotin. A piece of the colored part of the flag of approximately 5 mm × 5 mm was contacted with 1 mL of d-DMSO (the DMSO cutoff is 268 nm). After 20 days of contact, the piece of the flag was separated from the d-DMSO solution and a UV−vis spectrum was measured (region 900−190 nm), evidencing a band with an absorbance of 0.02 at 620 nm. In addition, the presence of a shoulder at approximately 575 nm was observed. For the sake of comparison, a DMSO solution of synthetic indigo was also measured. The results reproduce the UV−vis spectrum of the Flag of Macha.

After extraction with the d-DMSO solvent, the flag fragment that still had some remnants of the blue color was reduced by means of dithionite in an alkaline aqueous medium. The reduced product was again dried and oxidized in the air. The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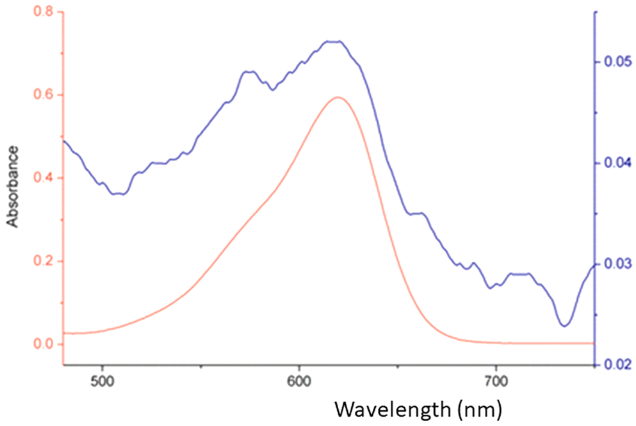


**Figure 8.** UV–vis spectrum (blue trace) of the solution obtained after a small piece of the Flag of Macha extracted for 20 days in 1 mL of d-DMSO and its comparison with the spectrum of an 8 ppm solution of indigo in DMSO (orange trace).

solid residues were dissolved in d-DMSO solution. The resulting spectrum is entirely similar to that found in Figure 8.

The bands that are clearly resolved in the spectrum of Figure 8 in the region of 617 and 572 nm compare perfectly with those obtained from commercial indigo dissolved in the same solvent d-DMSO. The entire extraction process was carried out in d-DMSO with the hope of being able to perform complementary NMR studies. However, the low concentration of extracted indigo (~0.4 mg/L) is far from sufficient to obtain NMR spectra given the relatively low sensitivity of this technique.

It is concluded that the origin of the only tincture found, the indigotin (without an appreciable amount of indirubin), does not come from the Andean zone of Peru (or from Asia) and that therefore the taffeta dyed with colorant from Europe probably had to enter through the port of Buenos Aires. This traceability would also coincide with the fact that the Flag of Macha (and that of Ayohuma) may have been the one that was originally raised for Belgrano for the first time on February 27, 1812, on the banks of the Paraná River and made by María Catalina Echevarría de Vidal.

Regarding the color of the Argentinian flag, the present conclusion agrees with the testimony of Gerónimo Espejo, a soldier who finally reached the rank of general and who witnessed the Paso de los Andes (the march of General San Martín to Chile through the Cordillera de los Andes).[1] He documented that during the year 1878 "was agitated by the press of this capital (Buenos Aires) a long controversy on the Argentinian flag". The author states that "the typical colors of the pavilion were, as they are, blue and white", mentioning the decree of 1813 of the National Assembly, the Congress of Tucumán in 1816, and the revalidation in Buenos Aires during the year 1818. This law under the number 62 of the Gazeta de Buenos Aires, dated 18 March, was promulgated in the following terms and adds that with the title War Department it has been sanctioned "That serving for all national flag the two colors blue and white in the way and form until now accustomed, be distinctive peculiar of the flag of war, a sun painted in the middle of it -It is copy- Irigoyen". Gerónimo Espejo also mentioned in his book that the Flag of the Paso de los Andes was blue and white as was the Flag of Macha, in agreement with the present work.

With these arguments, General Espejo also describes the blue color of the banner that sheltered the patriotic forces during the Paso de los Andes. The explanation of the vertical shape of the Paso de los Andes Flag is interesting because of its forcefulness. General Espejo argues with credibility that "The shops of a poor town as Mediterranean as Mendoza, poorly stocked with effects as one might imagine, unlike those of the coast of La Plata, had no silk goods in which to choose the necessary for the projected flag. However, fortunately they found themselves in a white twill and Turkish blue tent, from which the poles were bought, enough for two strips that joined perpendiculars, the white one in the part that is linked to the antler, and the blue one at the end".

He also comments that he does not know why the flag of three strips was not made "but we were inclined to believe that it was because there were no more strands of the blue genre, when, to a greater extent, the authorities of 1813 and 1816 had just designated the colors and not the form".

The amalgam of these results is linked to another singular fact for that time. According to the official website of the government of El Salvador, the blue and white colors of the Central American Federation Flag were suggested by Manuel José de Arce y Fagoaga, when the Central American militiamen was named El Salvador's chief of forces, opposing the annexation to Mexico during 1822.[16]

Thus, he expressed his gratitude to the Homeland of San Martín and Belgrano and to the libertarian crusade that came from the south of the continent centered in the French-Argentine corsair Hipólito Bouchard who at the command of the frigate "La Argentina" contributed to breaking the Royalist block in Centromérica.[17] According to the explanation of Felipe Pigna, it was Miguel Ángel de Marco who gave an account of the hypothesis of Julián Manrique according to which Hipólito Bouchard aspired to rescue Napoleón Bonaparte from his prison in Santa Elena.[18] When Bouchard discarded this idea, he continued with his trip to America. There, on November 24, 1818, under the command of the Frigates Chacabuco and La Argentina, he disembarked in Monterrey. Thus, for some days, the blue and white Argentinian flags waved in the city of Monterrey. On his way to the south to join the liberating army of General San Martín and with a final destination of Valparaiso, Bouchard was present in Acapulco and El Salvador. His action has been witnessed by the amalgam of blue banners of the countries of Central America (Scheme 3), all derived from the original banner that sheltered the United Provinces of Central America.

Throughout this whole spectral-historical study begun in the determination of the color of the Argentinian flag, we have, in several instances, traveled into the past. During the oath of another remarkable pavilion, the Flag of the Andes, Gerónimo Espejo states that San Martín pronounced the following words: "Soldiers: this is the first flag that has been raised in America: he beat it three times when the troops and the people responded with a Viva la Patria..." "...What a set of emotions the troops and the contest offered in those solemn moments" expressed Espejo in his story. As seen from this description, we cannot speak of anguish here either.

Recently, the debate on the color of the Argentine flag was further developed when the study of the color of the Aráoz flag of 1814 was presented. There, it was noted that it was Sarmiento, the president of Argentina (1868–1874), who introduced the light blue tone on the flag.[4] Fray Luis Cano was very incisive in his assertions referring to the attitude of the


DOI: 10.1021/acsomega.9b01412
ACS Omega 2019, 4, 11424–11432

**Scheme 3. Blue Amalgam of the Flags of Central America Influenced by the Argentinian Flag**


historian (and also the president of the Republic (1862–1868)) Bartolomé Mitre.[19] Although Mitre in his narrative about San Martín had Espejo as an eyewitness to the passage of the Andes, he dismissed his undoubted story, referring to the blue color of the flag of the army of San Martín.[20]

Belgrano, who was born rich and died very poor on June 20, 1820, indicated—in the regulation for the four schools of the North (Tarija, Jujuy, Tucumán, and Santiago del Estero) that he intended to build with his donation of the 40 000 gold pesos assigned to him by the Assembly of Year XIII (Asamblea del año 1813) in gratitude for his victories in the Battles of Tucumán and Salta—that the teacher will try with his/her conduct and in all his/her expressions and ways to inspire his/her students love of order; respect for religion; moderation and sweetness in treatment; feelings of honor; love of virtue and the sciences; disdain for vice; inclination to work; detachment from interest; contempt for everything related to abundance and luxury in eating, dressing, and other needs of life; and a national spirit, qualities that make them prefer public good and esteem more the American qualities rather than foreign—in relation to our entire continent.

The color of Belgrano's flag has been revealed in this work, along with the origin of the dye used to make it. Belgrano has forever left us his convictions, his love for the country, and his beliefs based on his actions and behavior. He also left us the uncertainty about his choice of blue color. He could have had only one reason or all of the hypothetical reasons at the same time. We believe that Belgrano had more than a single motive in the election of the blue color for the flag of divine origin.[2,21] Blue is the color of the mantle of the Virgin Mary, and Belgrano was a fervent Catholic. Blue is also adopted by many other religions as the color of their deities, and it is the color of the Bourbon dynasty; that is, it was blue and not light blue, meaning justice, obedience, loyalty, piety, and prudence, qualities always exalted by Belgrano.[22] Blue is also one the colors of the French flag, and it is the color of the sky. Toward the serene blue flies the injured eagle of the poet José Martí, and blue is the color of the legendary flower forget-me-not (No me olvides).[2]

In addition, the protagonists of history were vigilant and alert in the use of the flag. Their legacy was that the anguish was only to preserve their and our emblem. Gerónimo Espejo clearly expresses the reason and meaning for the alert and the need to not expose the flag to the adversary, like Macha's flag that was found in Titiri several decades after the battles that occurred there: "it was not strange to fear the din of the fighting, it was not strange that a pitched battle or partial action some of patriot soldiers would be defeated and lose their flag, honorary trophy that, taking it the adversary hands, would lead it proud to perpetuate its triumph in some of the cathedrals of the Spanish monarchy".[1]

## CONCLUSIONS

This article concludes that the Flag of Macha had a blue coloration originating from European indigo tincture. This work infers that in consequence, their textiles entered through the port of Buenos Aires. Therefore, it is also deduced that the Flag of Macha is probably the same one that was raised for the first time on the banks of the Paraná River in Rosario and that it was produced with silk that was not weighted with Sn. It is the emblem that the patriots defended and hid in 1813 in a secluded place at 4350 masl below a picture of Santa Teresa in the chapel of Titiri, Macha, Bolivia, Figure 9.

**Figure 9.** Titiri Chapel in Macha, Bolivia, at 4350 masl. There, under a painting of Santa Teresa, the flags of Macha and of Ayohuma were hidden between the years 1813 and 1885.

## EXPERIMENTAL SECTION

The samples of the flag were small pieces that were not used in the manual restoration work. They were made available by the Director of the House of Liberty of Sucre, Bolivia, Lic. Mario Linares Urioste, following the interest from the Ambassador of the Estado Plurinacional de Bolivia en Buenos Aires, Ing. Santos Javier Tito Véliz.

When the spectroscopic indications suggested the presence of indigo, a piece of the fiber of the colored part of the flag was reduced with $Na_2S_2O_4$ (Sigma-Aldrich) in an alkaline NaOH medium. Its subsequent oxidation in the air returns the species from its leuco to the diketo form of Scheme 1.

Samples were conveniently analyzed by nondestructive techniques using ultraviolet–visible spectroscopy (UV–vis), UV–vis diffuse reflectance spectroscopy (UV–vis DRS), attenuated total reflectance Fourier transform infrared spectroscopy (FTIR-ATR), scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM–EDX), and resonance Raman spectroscopy.

The UV–vis spectra were collected using a Shimadzu UV-2600 spectrometer. The choice of d-DMSO as a solvent for the dye extraction was related to the intention to carry out $^1$H- and $^{13}$C NMR spectra. A Bruker Avance Neo 500 instrument was employed for that purpose. However, the low concentration of


DOI: 10.1021/acsomega.9b01412
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the solution did not allow reliable NMR spectra to be obtained.

The UV–vis–DRS reflectance measurements were carried out by adding an integrating sphere attachment model ISR-2600 coated with $BaSO_4$ to the UV–vis equipment described above. For the purpose of comparison, the spectra of synthetic indigo (Sigma-Aldrich) diluted in $BaSO_4$, a silk textile dyed with indigo, and of the Flag of Macha sample were measured. These two last samples were placed between two glass slides. The slide located under the fabric portion (approximately a 10 mm × 10 mm dyed silk and a 5 mm × 5 mm flag sample) was conveniently conditioned with $BaSO_4$. The $BaSO_4$ was used as a reference in all measurements performed by reflectance. The range of the measurements was between 900 and 190 nm. When glass was used, the cutoff is in the region of 400 nm. These measurements were repeated using a quartz sample holder. However, the use of the quartz sample holder still did not allow the observation of the behavior of the dyes of the fabrics in the region lower than 400 nm due to the high absorption of the components of the textiles.

The FTIR spectra were taken on a Nexus Nicolet instrument equipped with an MCTB detector for the range of 4000–400 $cm^{-1}$. The solid synthetic indigo sample was measured in a KBr pellet with resolutions of 2 $cm^{-1}$ and 64 scans.

The textiles were also measured by reflection using the ATR-FTIR technique. For these determinations, an Agilent Cary 630 FTIR spectrometer was used. The spectral region was 4000–650 $cm^{-1}$ with resolutions of 2 $cm^{-1}$ and 64 scans.

The SEM was used to determine the morphology of the portions of the flag (white and colored) through the use of an SEM-FEI Quanta 200 instrument. Mappings of the samples were performed for elemental analysis through EDX spectroscopy. An acceleration voltage of 15 kV was used to collect the images, and a 20 kV voltage was used for the mappings. In these images, it will become clear whether an LFD image (secondary electrons, large-field detector) or backscatter electron detector (BSED) was used.

Raman spectra were recorded using a Horiba Jobin Yvon T64000 Raman spectrometer equipped with a confocal microscope. A liquid $N_2$-cooled back-thinned charge-coupled device detector was used. The samples were excited with light of different wavelengths provided by coherent Ar and Kr multiline lasers. An objective of 50× was used, and the sample experienced an energy of approximately 0.36 mW of a $Kr^+$ laser. The wavenumbers were calibrated with the 459 $cm^{-1}$ band of $CCl_4$.

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### Author Contributions

R.M.R. and C.O.D.V. conceived the project; A.L.P. and R.M.R. conducted the experiments; C.O.D.V. wrote the manuscript; and all authors discussed and commented on the results and the manuscript.

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

We would like to deeply thank the Embassy in Buenos Aires of the Plurinational State of Bolivia for its commitment and support and, especially, María Nélida Acuña Segovia. Without her attitude and assistance in support, it would not have been possible to travel to Bolivia with the certainty of obtaining the two little pieces of the Flag of Macha so well preserved in the Casa de la Libertad in Sucre. In the Casa de la Libertad, we are very grateful to its Director Lic. Mario Linares Urioste, its Researcher Lic. Roberto Salinas Izurza, with C. Lic. Roger E. Churata Villegas and Lourdes Quispe Vedia. The SEM–EDX measurements have been possible thanks to the unique work of Lic. María Alejandra Floridia Addato under the supervision of Dr Alberto Caneiro of Y-TEC-CONICET. We also thank Prof. Dr Gerardo Burton, the director of the UMYFOR (CONICET-FCEN-UBA), for his disinterested and valuable efforts to obtain NMR spectra; to Dr María Laura DellÁrciprete and Prof. Dr Mónica González (INIFTA-UNLP-CONICET) for their professional help in obtaining the ATR-FTIR spectra; and to Pablo Donadelli on behalf of all of those who in our research centre CEQUINOR (UNLP-CONICET and associated with CIC) collaborated to obtain the present results. We would like to thank the Facultad de Ciencias Exactas of the Universidad Nacional de La Plata and Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) for their financial support. ANPCYT is also gratefully acknowledged for the grants PICT 2014-2957 and PICT 2017-3230.

## DEDICATION

This work is dedicated to all libertarian women and men of our America, who despite having their shoes ruined and their shirts soiled were able to keep their minds bright and their ideas intact.

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DOI: 10.1021/acsomega.9b01412
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DOI: 10.1021/acsomega.9b01412
*ACS Omega* 2019, 4, 11424−11432