Electronic Supplementary Information

Characterization and Utilization of Prussian Blue and its Pigments

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The two original eighteenth-century recipes that were used as far as possible in the preparation of the "ancient" samples studied in our work are given below. The R. Dossie recipe was originally published in English, whereas the M. Le Pileur d'Apligny recipe was published in French and it is followed by a translation into English.

Dossie, 1758 [from R. Dossie, *The Handmaid for the Arts*, Nourse, J., London, 78-80 (1758).]

"The Prussian blue may be prepared in perfection by the following process. Take of blood any quantity; and evaporate it to perfect dryness. Of this dry blood, powdered, take six pounds, and of the best pearl-ashes two pounds: mix them well together in a glass or stone mortar; and then put the mixt matter into large crucibles or earthen-pots; and calcine it in the furnace described, p.22; the top of the crucible or pot being covered with a tile, or other such convenient thing, but no luted. The calcination should be continued, so long as any flame appears to issue from the matter; or rather till it become very slender and blue; for if the fire be very strong, a small flame would arise for a very long time. When the matter has been sufficiently calcined, take the vessels which contain it out of the fire; and, as quickly as possible, throw it into two or three gallons of water; and, as it soaks there, break it with a wooden spatula, that no lumps may remain. Put it then in a proper tin-vessel, and boil it for the space of three quarters of an hour or more; and filter it while hot through paper in the tin cullenders described, p.27; and pass some water through the filter when it is run dry, to wash out the remainder of the lixivium of the blood and pearl-ashes; the earth remaining in the filter may be then thrown away. In the mean time, dissolve of clean alum four pounds, and of green vitriol or copperas two pounds, in three gallons of water. Add this solution gradually to the filtered lixivium, so long as any effervescence appear to arise on the mixture; but, when no ebullition or ferment follows the admixture, cease to put in more. Let the mixture then stand at rest, and a green powder will be precipitated: from which, when it has thoroughly subsided, the clear part of the fluid must be poured off, and fresh water put in its place, and stirred well about with the green powder: and, after a proper time of settling, poured off like the first. Take then of spirit of salt double the weight of the green vitriol which was contained in the quantity of solution of vitriol and alum added to the lixivium, which will soon turn the green matter to a blue colour; and, after some time, add a proper quantity of water, and wash the colour in the same manner, as has been

directed for lake; and when properly washed, proceed in the same manner to dry it in lumps of convenient size."

Le Pileur d'Apligny, 1779 [from M. Le Pileur d'Apligny, *Traité des couleurs matérielles et de la manière de colorer relativement aux différents arts et métiers*, Saugrain and Lamy, Paris, France, 36-38 (1779).]

« Le bleu de Prusse est une couleur animale, qui a néanmoins le fer pour base. Voici la manière de faire cette couleur. On prend une livre de potasse bien sèche, qu'on mêle à autant de sang de bœuf desséché et pulvérisé : on met ce mélange dans un creuset, et on le fait calciner doucement. Il faut avoir attention que le creuset ne soit plein qu'aux deux tiers, afin que la matière qui se gonfle ne se répande pas. Dans les commencemens [*sic*], il s'élève beaucoup de fumée et de flamme; lorsque la flamme cesse, on augmente le feu, pour faire rougir la matière et pour qu'en cet état elle ne laisse plus paroître qu'une flamme légère et bleuâtre. On ôte alors le creuset du feu, et on le laisse refroidir. On ramasse avec une cuiller de fer la pâte rouge qu'il contient, et on jette dans six pintes d'eau bouillante: on filtre la lessive qui en provient, et l'on repasse de l'eau chaude sur le marc, pour achever de le dessaler, et ensuite on réunit les lessives, qu'on fait réduire sur le feu, si l'on veut donner plus d'activité. D'un autre côté, on fait dissoudre ensemble dans une suffisante quantité d'eau chaude six onces de vitriol de Mars et huit onces d'alun de roche et l'on verse dans cette dissolution la lessive susdite chaude. Après une vive effervescence, il se précipite une fécule verdâtre : on remue le mélange et on le verse sur une toile serrée ; la liqueur passe au travers et le précipité reste sur le linge : on l'enlève avec une cuiller, pour le mettre dans une terrine de grès, l'on verse par dessus huit onces d'acide marin, qui lui fait prendre aussitôt une belle couleur bleue ; mais ce précipité reste toujours chargé d'une colle tenace qui lui ôte sa vivacité : on l'en débarrasse par des lotions répétées. L'usage a appris que l'eau de puits, ou toute eau dure avait pour cela plus d'efficacité que l'eau de rivière. Ce lavage exige de la patience ; car il faut trois à quatre semaines, en changeant d'eau ce bleu deux fois par jour : au bout de ce temps, on le passe au travers d'un linge serré ; on le laisse égoutter, et on en forme des gâteaux ou tablettes, qu'on fait sécher à l'ombre et à l'abri de la poussière. »

Le Pileur d'Apligny, 1779. A literal translation from French into English of the above preparation follows.

Prussian blue is an animal color, that has nevertheless iron as a base. Here is the way to prepare this color. One takes one pound (1 livre = 489.5 g) of very dry potassium carbonate or hydroxide (The French is not clear, "potasse" is a mineral mixture of potassium carbonate and potassium chloride.) and mixes it with one pound of dry powdered cattle blood. One places this mixture in a crucible and calcines slowly the content. One must be careful that the crucible must only be two-thirds full so that the material that swells does not overflow. At the beginning, much smoke and flames come out; when the flames stop, one increases the temperature to redden the material and only a light blue flame appears. One removes the crucible from the heat source and let it cool down. One scoops with an iron spoon the red paste contained in the crucible and throws it in six pints (1 pint = 952.146 mL) of boiling water: one filters the brew that is formed and one washes the

grounds with hot water to remove all salts and then one remixes the brews that one reduces on the fire if one wishes more activity. Separately, one dissolves together in enough hot water six ounces (1 ounce = 30.594 g) of iron(II) sulfate, $FeSO_4$, (vitriol de Mars) and eight ounces of alum (alum = $KAl(SO_4)_2 \cdot 12\ H_2O$) and one pours in this solution the above hot brew. After strong bubbling, a green powder precipitates, one stirs this mixture and filters it on a fine-mesh cloth; the liquor goes through and the precipitate remains on the cloth: one removes it with a spoon to put it in a pottery jar, one pours on top eight ounces of hydrochloric acid, that gives the precipitate a beautiful blue color; but this precipitate still remains loaded with a strong glue that removes its vivacity: one removes the glue by repeated washings. Experience has taught that well water, or any hard water, was more efficient than river water. This washing requires patience; because it takes three to four weeks, changing the water of this blue powder twice a day: after this time, one filters it through a fine-mesh cloth; one lets the water drip and forms cakes or tablets, that one dries in the shade and sheltered from dust.

Table S1. Mössbauer Spectral Parameters of the Iron(III) in Prussian Blue Compounds[a]

Approximate Composition	δ^{III}, mm/s[b]	$\Delta E_Q{}^{III}a$, mm/s	$A^{III}a$, %[c]	$\Delta E_Q{}^{III}b$, mm/s	$A^{III}b$, %[c]	$\Delta E_Q{}^{III}c$, mm/s	$A^{III}c$, %[c]	$A^{III}total$, %
$K_{1.9}[Fe^{III}_4Fe^{II}_3(CN)_{18}]\cdot\{1.9\ OH + 7\ H_2O\}$, **1**[d]	0.406(1)	0.000	19.8(8)	0.21(2)	21.3(8)	0.61(2)	7.3(7)	48.4(2.0)
$Fe^{III}_4Fe^{II}_3(CN)_{18}\cdot 11.2\ H_2O$, **2**[d]	0.410(2)	0.000	15.1(9)	0.29(1)	25.0(8)	0.63(2)	9.7(9)	49.8(9)
$KFe^{III}[Fe^{II}(CN)_6]\cdot x\ H_2O$, **3**	0.4018(15)	0.000	29.0(1)	0.237(3)	14.1(1)	0.672(8)	6.1(1)	49.2(3)
$NH_4Fe^{III}[Fe^{II}(CN)_6]\cdot x\ H_2O$, **4**	0.4412(8)	0.000	13.0(1)	0.268(3)	16.3(1)	0.637(3)	19.1(1)	48.4(1)
$KFe^{III}[Fe^{II}(CN)_6]\cdot x\ H_2O$, **5**	0.413(1)	0.000	16.3(1)	0.261(1)	14.6(1)	0.596(1)	17.1(1)	48.0(1)
$NH_4Fe^{III}[Fe^{II}(CN)_6]\cdot x\ H_2O$, **6**	0.399(2)	0.000	5.0(5)	0.514(4)	35.0(5)	0.89(1)	10.0(5)	50.0(5)
$Fe_4^{III}[Fe^{II}(CN)_6]_3\cdot x\ H_2O$, **7**	0.399(4)	0.000	7.5(5)	0.532(8)	35.5(8)	1.07(3)	10.0(8)	53.0(8)
$KFe^{III}[Fe^{II}(CN)_6]\cdot x\ H_2O$, **8**	0.406(4)	0.000	16.1(4)	0.46(1)	26.8(6)	0.86(3)	7.7(8)	50.6(6)
$Fe_4^{III}[Fe^{II}(CN)_6]_3\cdot x\ H_2O$, **9**	0.396(1)	0.000	4.0(2)	0.548(3)	33.7(3)	1.037(8)	12.5(3)	50.2(8)
$KFe^{III}[Fe^{II}(CN)_6]\cdot x\ H_2O$, **10**	0.416(2)	0.000	12.3(2)	0.351(6)	18.0(2)	0.619(6)	17.8(2)	48.1(2)
Ancient Prussian blue, **11**[f]	0.42(1)	0.000	5(3)	0.31(5)	25(2)	0.65(3)	22(3)	52(3)
Ancient Prussian blue, **14**[f]	0.412(3)	0.000	21.5(8)	0.40(1)	24.5(8)	1.01(3)	8.5(6)	54.5(2)

[a]Statistical fitting uncertainties are shown; more realistic experimental uncertainties are ±0.005 mm/s for the isomer shifts, δ, and ±0.01 mm/s for the quadrupole splittings, ΔE_Q, and linewidths, Γ, and ±1 % for the relative spectral absorption areas. [b]The isomer shift, δ, is referred to α-iron powder at 295 K. [c]A^{III} is the percent area of the iron(III) component. [d]The compositions as determined from Rietveld refinement of the powder x-ray diffraction patterns; the applicable compositional uncertainties are given in Table 2. [f]The preparation and approximate composition of these "ancient" Prussian blue samples are given in reference 10.