An unusual CN stretching in Prussian Blue painted materials

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The present project deals with the study of the influence of the manufacturing process in the composition of the Prussian Blue (PB), a popular dark-blue pigment, widely used from ca. 1720 to the 1970's. PB, is a mixed valence compound and it can be obtained in two forms: insoluble (IPB) $Fe_4[Fe(CN)_6]_3 \cdot xH_2O$ or soluble (SPB) $KFe[Fe(CN)_6] \cdot yH_2O$. The presence of a CN^- group, bounded to both Fe(II) and Fe(III) ions, results in a well recognizable stretching band, □□(CN), in both infrared and Raman spectroscopy. This sharp absorption is commonly used as marker for the pigment identification [1] and, when shifted, it can be representative of alteration processes [2,3]. For instance, PB, identified in *Superficie lunare* (1969) by L. Turcato, shows an unusual □(CN) split in two components: one at ≈2085 cm^{-1}, characteristic of PB [4] while the other, at ≈2050 cm^{-1}, typical of ferrous ferrocyanide complexes. In general, literature data [2,3] report that these complexes can be representative of the PB photoreduction. On the contrary, in our case study, a thorough spectroscopic characterization (by means of *in-situ* Raman and ERFTIR and successively by □-ATR, and □-Raman) identified the presence in the pictorial layer of hydrate Fe(II) sulphate, rozenite, and an ammonium ferrous ferrocynide complex, typical of the indirect production methodology [5,6]. In order to understand if the presence a reaction intermediate, such as ammonium ferrous ferrocynide complex, could mislead the evaluation of alteration process, an experimentation on different mock-ups was projected. The mock-ups were prepared applying on different substrates both commercial PB paint tubes and laboratory formulations. Here the investigations on *Superifice Lunare* are briefly reported and the results of the starting materials characterization (by means of Infrared, Raman and Mössbauer spectroscopies) are presented and discussed. In the data discussion a special attention will regard the effect of the substrate on the □(CN) ERFTIR signal and the presence of manufacturing intermediate on the commercial formulations. Moreover, preliminary results on the effects of accelerate ageing will be presented.

References

[1] L. Samain, G. Silversmit, J Sanyova, B. Vekemans, H. Salomon, B. Gilbert, F. Grandjean, G. J. Long, R. P. Hermann, L. Vincze and D. Strivay, J. Anal. At. Spectrom., **26**, 930 (2011)
[2] L. Samain, B. Gilbert, F. Grandjean, G. J. Long, and D. Strivay, J. Anal. At. Spectrom., **28**, 4, 524, (2013).
[3] C. Gervais, M.A. Languille, S. Reguer, M. Gillet, S. Pelletier, C. Garnier, E.P. Vincenzi and L. Bertrand, J. Anal. At. Spectrom., **28**, 10, 1600 (2013).
[4] M. Zuena, S. Legnaioli, B. Campanella, V. Palleschi, P. Tomasin, M.K. Tufano, F. Modugno, J. La Nasa, L. Nodari, submitted to Microchem J, (2019)
[5] J. Kirby, National Gallery Technical Bulletin, **14**, 62 (1993).
[6] J. Kirby and D. Saunders, National Gallery Technical Bulletin, **25**, 73 (2004).