AUTOMATED ID OF
ULTRAMARINE BLUE PIGMENT
WITH RAMAN SPECTROSCOPY

Abstract

This application note documents the use of a TSI ChemLogix EZRaman-I instrument and our new software offering, SpectraGryph, to the identification of ultramarine blue, a historically important pigment.

Motivation

Lapis lazuli has been in demand for millennia and used for both jewelry and pigments. The material itself is a complex rock whose composition is dominated by the mineral lazurite $(Na,Ca)_8(AlSiO_4)_6(SO_4,S,Cl)_2$ which is the source of the brilliant blue coloration. Inclusions of other various materials are sometimes present, including pyrite, calcite, diopside, fosterite and wollastonite. The blue color of lazurite is attributed to sulfur polyanion radicals trapped in sodalite cage structures. Variations in color may be related to the ratios between sulfur species. The S_3^- radical seems responsible for the blue coloration; S_2^- and S_4^- radicals can shift the color toward yellow and red.[1]

Lapis lazuli has been used as a pigment since the 7th C. CE, and was so prized that it was generally reserved for the most important figures in ecclesiastical art (The Virgin Mary's cloak, for example, as is shown in Figure 1). In the 13th century, a number of processes were developed to intensify the hue of the pigment after grinding the raw lapis. These processes have been documented in a variety of places, perhaps most clearly in Cennini's *Il Libro dell'Arte*. This book describes the lengthy extraction process including the grinding and the blending with pine rosin, gum mastic and beeswax to produce a doughy mixture. This mixture was then further processed by kneading and exposure to a solution of ash. These steps are shown in Figure 2, from Ganio et al[1].

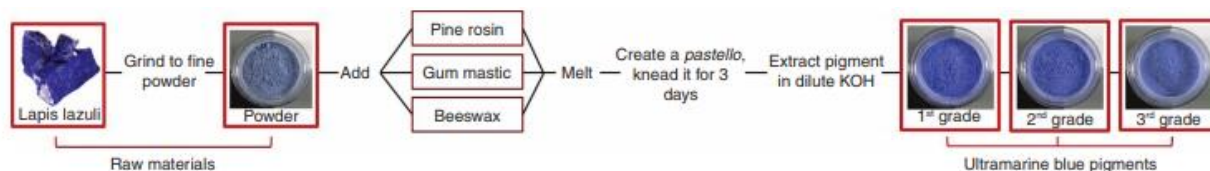**Figure 1. Sassoferrato's The Virgin in Prayer - 1640-50, featuring lapis lazuli pigments.**

Figure 2. Pictorial representation of ultramarine production.[1]

Lapis was at this time mined almost exclusively in Afghanistan and imported to Europe through Venice, its rarity leading to its cost (Vermeer has been accused of going deeply into debt because of his use of this pigment). Because of the demand and the cost, the French government's Societé d'Encouragement offered a reward of six thousand francs to anyone who could develop a synthetic substitute for ultramarine. Two men, Jean-Baptiste Guimet, a French chemist, and Christian Gmelin, a German professor from the University of Tübingen, came forward. The selection was difficult because of the lack of a publication: Gmelin stated he had arrived at a solution a year earlier but had waited to publish his results. Guimet countered by declaring that he had conceived his formula two years prior but—like Gmelin—had opted not to publicize his findings. The committee eventually awarded the prize in 1828 to Guimet, and the artificial blue became known as "French ultramarine."[2]

Synthetic ultramarine has an approximate formula $Na_{6-10}Al_6Si_6O_{24}S_{2-4}$ which can vary with the manufacturing conditions, namely with the purity and the different proportion of the ingredients.[1]

Gmelin eventually published his process first, stating that silica, alumina and soda are the main components of ultramarine and attributed the blue color to sulfur.

Raman spectroscopy can easily be used to distinguish ultramarine from other blue pigments, such as smalt, indigo and Mayan, Cerulean and Egyptian blue. It has also been documented to be useful in distinguishing natural from synthetic ultramarine, although this is more challenging and a multivariate analysis was required to aid the differentiation.[3,4]

Samples

Pigment powders of both types of ultramarine are commercially available. The TSI samples were obtained from an anonymous artist.

Measurements and Results

A TSI ChemLogix EZRaman-I with 532 nm excitation was used to analyze various blue pigments. The conditions varied by material, but were done in general with low laser power and long acquisition times to avoid the accidental heat processing of the pigments.

The raw spectra of most of these pigments contain a substantial amount of fluorescence. The automated background function of RamanReader was used to flatten the backgrounds of these spectra, permitting the use of SpectraGryph+ and two publically available pigment Raman spectral libraries to identify them.

The raw and background corrected spectra of powdered lazurite is shown in Figure 3. The background correction function is a basic process found in TSI RamanReader software and is easily applied with a single click. The result of the background correction was saved in .spc format and then imported into SpectraGryph, a new spectral processing program now available with the TSI ChemLogix hardware.
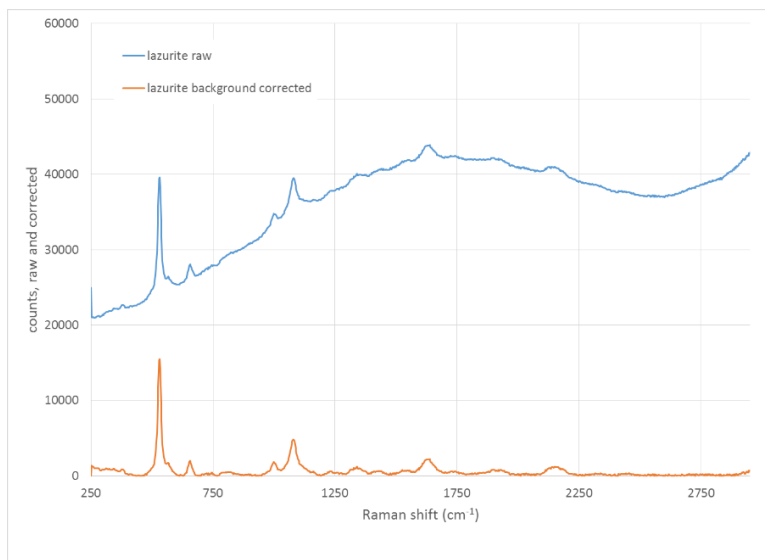
Available with SpectraGryph are a series of free libraries translated into the appropriate format to permit comparison of unknown materials with the existing

Figure 3. Raw and corrected lapis lazuli spectra.

databases. The databases used for this work were "Raman Spectroscopic Library of Natural and Synthetic Pigments," University College, London, UK[6] and the Cultural Heritage Science Open Source Pigment Checker Raman Library[7].

Figure 4 shows the ID match screen of SpectraGryph, the corrected spectrum of lazurite powder and the five best matches from the University College library.
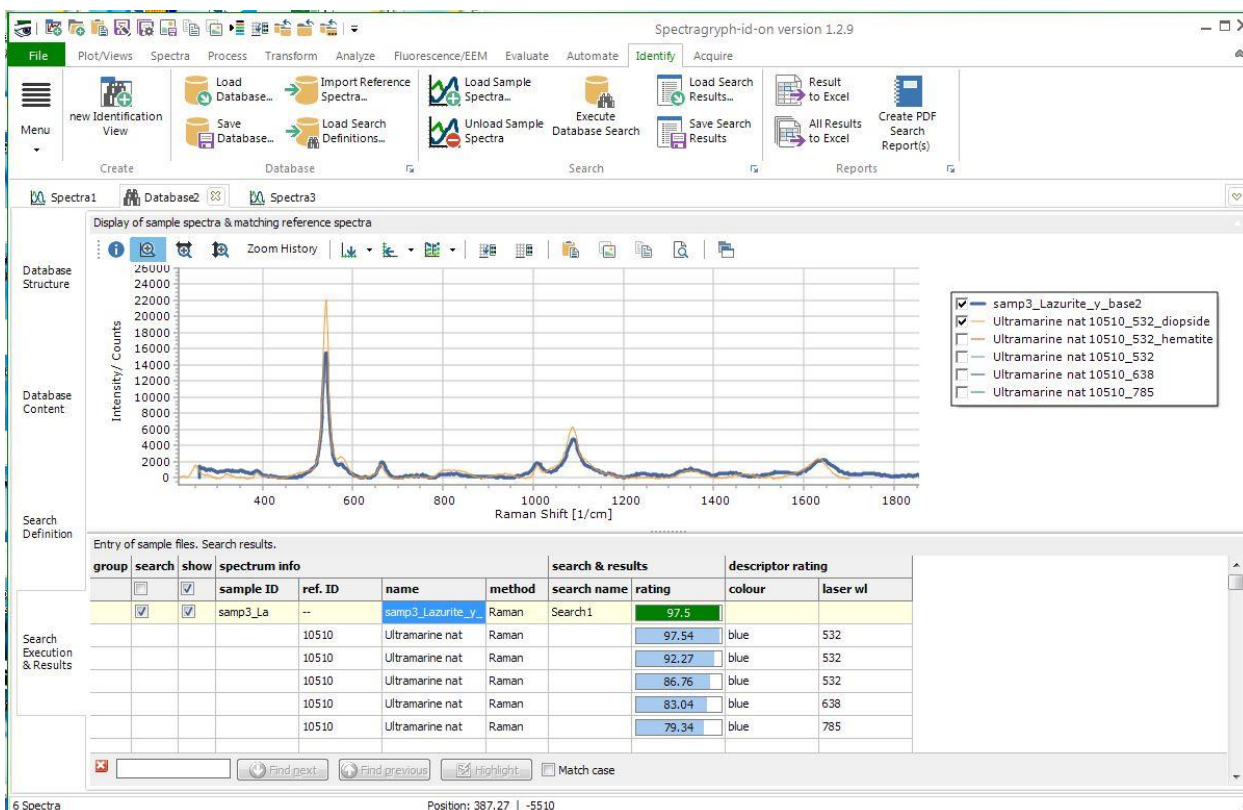

Figure 4. Powdered lazurite spectrum and the SpectraGryph five best matches to it.

The principal features in the match are the S_3^- sulfur band at 541 cm^{-1} and a weaker band at 582 cm^{-1} (S_2^- symmetric stretching mode) as shown in Figure 5.[8]

Figure 6 demonstrates the ease of differentiating other blue pigments using Raman spectroscopy once any fluorescence has been removed. Shown in the Figure are members of the University College London library.

Summary

This application note documents the combined use of a TSI ChemLogix EZRaman I instrument, the RamanReader background correction and our new software product, SpectraGryph, to identify ultramarine blue, and by extension demonstrate the ease of identifying other blue pigments of cultural importance.
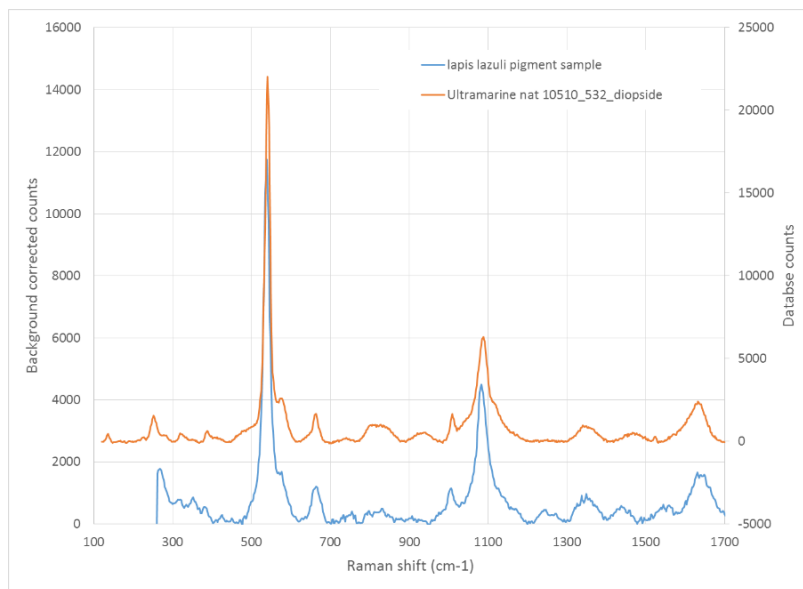
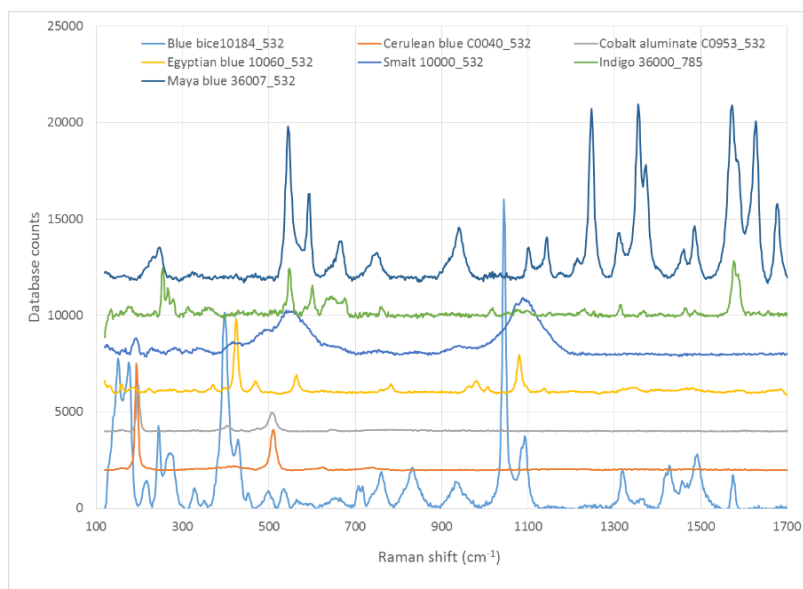**Figure 5. Background corrected spectrum and database match of natural ultramarine.**

Figure 6. Raman spectra of a variety of blue pigments.[7]

References

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