



Perspectives - Summer School 2014

Chemistry

Molecular Beauty: Visible and Invisible

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Perspectives - OUMC Summer School 2014

'Molecular Beauty: Visible and Invisible' Chemistry Module Tutorial Sheet

The Blackening of Vermilion

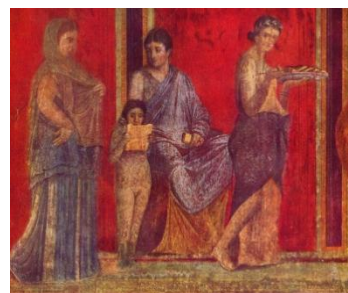


"Vermilion, cinnabar, mercury sulfide, HgS. Four names for pretty much the same thing – chemically, at least. It's not only one of the oldest, brightest, most widely used and best-loved red pigments, but possibly one of the first compounds to be made synthetically."

- Neil Withers in Chemistry World

The use of the pigment vermilion stems back to very ancient human history. Because of its bright red colouration, vermilion was an all-time favourite paint which saw usage in various genres of art and craft, from Pompeii murals to European portraits and even to Chinese lacquerware in the Far East.

Since the 4th century BC, Chinese alchemists have already discovered the way to synthesize vermilion by heating its constituent elements in a pot. Vermilion synthesis was widely regarded as an "alchemist's dream", for it involved the union of a "liquid metal" (elemental mercury, Hg) and bright yellow powder (elemental "crown" sulfur, S₈) strongly heated in a pot to eventually form a striking red solid. Vermilion had such a beautiful red hue that it was even thought of as a precursor to the magical "philosopher's stone" which is said to be able to transform other substances into gold (we know today that that is obviously not true).



"Red tikka powder" by McKay Savage from Chennai, India - India - Colours of India - 019 - Red tikka powder. Licensed under Creative Commons Attribution 2.0 via Wikimedia Commons - http://commons.wikimedia.org/wiki/File:Red_tikka_powder.jpg#mediaviewer/File:Red_tikka_powder.jpg

"Lacquerware-roundbox-w-children". Licensed under Creative Commons Attribution-Share Alike 2.0 via Wikimedia Commons - <http://commons.wikimedia.org/wiki/File:Lacquerware-roundbox-w-children.jpg#mediaviewer/File:Lacquerware-roundbox-w-children.jpg>

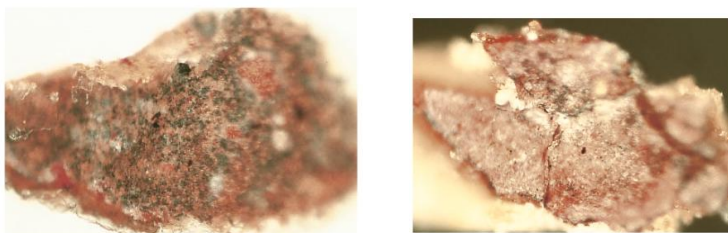
"Villa Mystery fresco" by Unknown - Ancient Goths. Licensed under Public domain via Wikimedia Commons - http://commons.wikimedia.org/wiki/File:Villa_Mystery_fresco.jpg#mediaviewer/File:Villa_Mystery_fresco.jpg

"Masaccio, pala colonna, santi girolamo e giovanni battista" by Masaccio - book: John T. Spike, Masaccio, Rizzoli libri illustrati, Milano 2002. Licensed under Public domain via Wikimedia Commons - http://commons.wikimedia.org/wiki/File:Masaccio_pala_colonna_santi_girolamo_e_giovanni_battista.jpg#mediaviewer/File:Masaccio_pala_colonna_santi_girolamo_e_giovanni_battista.jpg

For all its artistic glory, however, vermilion suffers from the inevitable fate of eventual discolouration. Examine the pictures shown below:

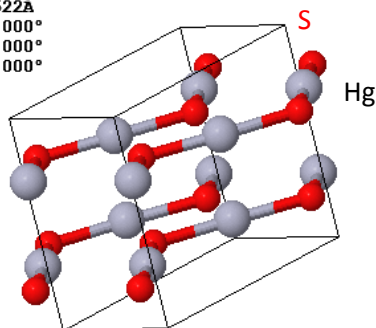


The area enclosed by the two blue circles very clearly show signs of graying/blackening of the vermilion pigment used to paint the picture. A finer observation of the discoloured patches would show that they are actually made of thin layers of fine-grained black and white particles.



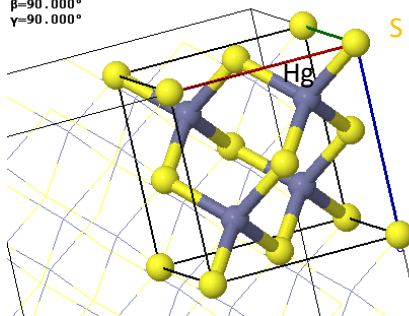
It was originally thought that the blackening involved a change in the crystal structure of the vermilion pigment from cinnabar form to meta-cinnabar form due to long-term exposure to ambient (atmospheric and lighting) conditions:

HM: P n m a
a=6.613Å
b=5.521Å
c=3.522Å
 $\alpha=90.000^\circ$
 $\beta=90.000^\circ$
 $\gamma=90.000^\circ$



cinnabar

HM: F-43m
a=5.434Å
b=5.434Å
c=5.434Å
 $\alpha=90.000^\circ$
 $\beta=90.000^\circ$
 $\gamma=90.000^\circ$



meta-cinnabar

(Image source: ChemTube3D. Please visit <http://www.chemtube3d.com/solidstate/SSHgO.htm> and http://www.chemtube3d.com/solidstate/_blende%28final%29.htm if you wish to manipulate the 3D models of these structures.)

A simple Google image search will show you the stark difference in colour between the striking red cinnabar and the dull grey meta-cinnabar. From this, it is actually shown that the same chemical compound can exhibit very different colourations depending on its molecular structure and the arrangement of its constituent atoms. **How would you describe the co-ordination geometries ("shape" of atomic arrangement) of cinnabar and meta-cinnabar respectively? Which of these arrangements do you think allow for a closer packing between the atoms?** (Hint: In HgS, Hg exists as the positively-charged Hg^{2+} ion whereas S exists as the negatively-charged S^{2-} ion)

We also know that ionic solids like HgS have colour because visible light can be absorbed by their electrons. When the electrons absorb a certain colour of light (photons), the compound will appear as the colour which is complementary to the photon absorbed (refer to the colour wheel). **What colour of light does cinnabar absorb? Also, what colour of light do you think meta-cinnabar absorbs?**

Blue light is of higher frequency and hence have a higher energy content, whereas red light is of lower frequency and hence a lower energy content. An electron in a compound will only absorb light that corresponds to its "excitation energy", which has a fixed value for each atomic arrangement. **Previously, you were asked about the closeness of packing between the atoms in the structure, and now we shall stretch the concept a little bit more -- how do you think the closeness of atomic (ionic) packing affects the "excitation energy" of the electrons and hence the colour of the compound?**

Eventually, proponents of the idea that cinnabar reacts with atmospheric compounds to transform into meta-cinnabar was proven wrong when sophisticated analytical techniques such as EDX Spectroscopy as well as Raman Spectroscopy was used to show that the black/grey grains which formed on the surface of the paint actually contains a variety of mercury-chloride compounds, which means that the HgS must have reacted with a source of chlorine present in the air.

Sub-topic: Spectroscopy

Before we explore the reactions between HgS and chlorine, however, let's look briefly at the instruments which modern-day chemists use to analyze chemical compounds. In the paragraph above you would have noticed the word spectroscopy - in simple terms, spectroscopy basically involves the firing of some electromagnetic waves (we shall from here on refer to EM-waves generically as *light*) at a compound and analyzing the waves that pass through or are reflected by the compound. Conventionally, spectroscopic techniques are named based on the frequency of light it involves - for example, the technique involving UV and visible light is named UV-Vis Spectroscopy, and the technique involving infrared light is named IR Spectroscopy. Raman Spectroscopy involves a phenomenon known as Raman Scattering, which occurs when photons (particles of light) "collide" with chemical bonds in a compound and are scattered inelastically, whereas EDX is short for Energy Dispersive X-ray Spectroscopy. Raman Spectroscopy is an advanced spectroscopic technique and will not be covered in this short course, but we shall briefly look at the basic principles of X-ray spectroscopy later on.

All modern chemistry courses inevitably will begin their spectroscopic education with basic techniques such as UV-Vis and IR Spectroscopy. Easy-to-digest information on these techniques are readily available online, and my favourite sources for pre-university/secondary school students are:

<http://www.chemtube3d.com/Organic%20Structures%20and%20Bonding.html>
<http://www.chemguide.co.uk/analysis/menu.html#top>

Please read up about IR and UV-Vis spectroscopy from the two websites listed above (do not worry if you cannot understand the mathematics or the graphs - a conceptual, descriptive understanding is more important for students at your academic level), and see if you can get a rough idea of how to answer the following questions:

1. What happens to molecules/chemical compounds when one shines IR or UV-Vis light on them? How does knowing this allow us to make use of light to identify molecules from one another?
2. Can you identify the limitations of IR and UV-Vis spectroscopy and hence why we need more advanced techniques for complete molecular identification?

We may now briefly discuss X-ray Spectroscopy. Easily understandable sources on this topic are difficult to obtain online, however you may try looking at

http://chemwiki.ucdavis.edu/Physical_Chemistry/Spectroscopy/X-ray_Spectroscopy/XAS%3a_Theory
http://instructor.physics.lsa.umich.edu/adv-labs/X-Ray_Spectroscopy/x_ray_spectroscopy_v2.pdf

for a brief overview. Even these two sources are quite math-heavy so it is entirely okay to not understand a thing from them.

The chemistry of vermilion blackening

The hypothesis that the blackening of the paintings was caused by atmospheric chlorine is supported by the fact that the National Gallery and Pompeian paintings only started to blacken between the mid- to late- twentieth century when air pollution was at its most heavy and chlorine was released into the environment from the combustion of coal.

Spectroscopic analysis of the blackened/whitened samples show that there are a mixture of compounds containing Hg, S and Cl that was formed on vermilion paintings. One of the most prominent compounds (Compound A) was shown to be made up of 81.7% Hg, 8.7% S and 9.6% Cl by mass. **Deduce the molecular formula of Compound A, knowing that one molecule of the compound contains 3 Hg atoms.**

We know that HgS reacts with Cl₂ in a redox reaction to form the Compound A. **Devise a chemical equation for this reaction, and identify which is the reduced species and which is the oxidized species.**

Compound A is one of the molecular species contributing to the black colouration found on degraded vermilion. Upon exposure to light, Compound A further degrades into two Hg containing compounds, one of

which is HgS and the other being Compound B, and elemental sulfur S. Devise a chemical equation for this reaction, and identify which is the reduced species and which is the oxidized species.

Compound B contributes to the white colouration on the vermilion. Compound B disproportionates into elemental Hg and Compound C. Write out the chemical equation for this reaction.

Why do you think Compound C was identified on Pompeian wall paintings but not the paintings kept in the National Gallery? (The cinnabar paint used in both cases are identical)

After going through the equations for these chemical reactions, are you able to identify why vermilion is a toxic pigment and as a result has been replaced by safer pigments?

End of Tutorial

Further reading

<http://en.wikipedia.org/wiki/Vermilion>

<http://en.wikipedia.org/wiki/Cinnabar>

<http://www.rsc.org/chemistryworld/2014/06/vermilion-cinnabar-mercury-sulfide-podcast>

<http://www.rsc.org/chemistryworld/2014/06/colour-chemistry>

<http://www.nationalgallery.org.uk/the-blackening-of-vermilion-an-analytical-study-of-the-process-in-paintings>

<https://docs.google.com/file/d/0B7GmyDM3E1rKaGIzYzBP1J0UjA/edit>

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