PURPLE OF CASSIUS: NANO GOLD OR COLLOIDAL GOLD?

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The purple pigment that is used in colouring molten glass and porcelain known as Purple of Cassius discovered in the 17th century was found by Richard Zsigmondy in 1897 to consist of nano gold with stannic oxide. The preparation of this material involves gold being dissolved in aqua regia, then reacted with a solution of tin(II) chloride. The tin(II) chloride reduces the dissolved gold to elemental gold supported on tin dioxide to give a purple precipitate which is thermally stable and is used as a pigment to give purple colour to glass and porcelain.

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INTRODUCTION

In the 1650's Andreas Cassius a chemist in Hamburg, Germany discovered a purple pigment that can be used in colouring glass and porcelain (Figure 1). It was prepared by adding a solution of stannous chloride to a dilute gold chloride solution. The precipitate was known as Purple of Cassius and was applied in the most famous glass and porcelain factories of Europe in Meissen in Saxony and in Sèvre in France.

Figure 1. Museum pieces of glass coloured with Purple of Cassius

That compounds of gold could impart a red colour to glass had been known for many centuries. Egyptian manuscripts from the Greco-Roman era make reference to it. The great metallurgist Georgius Agricola (1494-1555) knew of it, as did Paracelsus von Hohenheim (1493-1541), in the first half of the sixteenth century, while Benvenuto Cellini (1500-1571) at about the same time refers to a transparent red enamel discovered by an alchemist who was also a goldsmith. Andreas Libavius (*ca.* 1540-1616) the German alchemist who wrote the first text-book of chemistry, *Alchemia,* in 1597 knew also about the purple pigment.

In 1650 few years before Cassius publication Johann Rudolph Glauber (1604-1670) described the purple color of a gold pigment. Another distinguished contemporary alchemist Johann Kunckel (1630-1703) (Figure 2) who was well familiar with the glass technology of his time and in 1678 and was given charge of a glass factory at Potsdam in Germany.

Figure 2. Johann Kunckel (1630-1703)

He produced many products of ruby glass between 1679 and 1689. He published his *Ars Vitraria Experimentalis, oder Vollkommene Glasmacherkunst.* This work remained a standard treatise on glass technology for many years, and it is here that are found references to the production of ruby glass by the use of the purple precipitate described later by Cassius.

ANDREAS CASSIUS

There were two Andreas Cassius: the father (1605-1673) and the son (1645- *ca* 1700). It is quite possible that the elder did devise a process for making the purple precipitate and it was his son who wrote *De Auro* (Figure 3) in which he described the procedure but in the book he made no mention of his father. The full title reads: "Thoughts Concerning That Last and Most Perfect Work of Nature and Chief of Metals, Gold, Its Wonderful Properties, Generation, Affections, Effects and Fitness for the Operations of Art; Illustrated by Experiments".

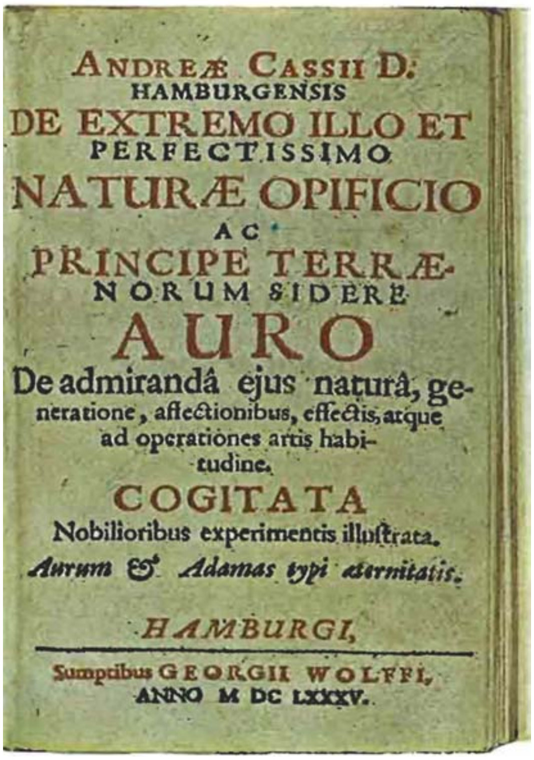
ANDREÆ CASSII D.
HAMBURGENSIS
DE EXTREMO ILLO ET
PERFECTISSIMO
NATURÆ OPIFICIO
AC
PRINCIPE TERRÆ-
NORUM SIDERE
AURO
De admirandâ ejus naturâ, generatione, affectionibus, effectis, atque ad operationes artis habitudine,
COGITATA
Nobilioribus experimentis illustrata.
Aurum & Adamas typi æternitatis.
HAMBURGI,
Sumptibus GEORGII WOLFFI,
ANNO M DC LXXXV.

Figure 3. *De Auro* by Andreas Cassius in 1685

LATER WORK

Swedish chemists

The Swedish chemist Carl Wilhelm Scheele (1742-1786) observed that when MnO_2 is dissolved in hydrochloric acid a red color is formed which when diluted precipitates the black MnO_2. The Swedish chemist Jöns Jakob Berzelius (1779-1848) described the yellow colour obtained by passing hydrogen sulfide into arsenious acid. He mentioned that the coloured solution should probably be regarded as a suspension of arsenic sulfide because it settled out. Other examples like the formation of colloidal sulfur when H_2S reacts with SO_2, etc.

Faraday

Michael Faraday (1791-1867) (Figure 4) spent much time in the mid 1850s investigating the properties of light and matter. He made several hundred gold slides and examined them by shining light through them. To make the gold leaf thin enough to be transparent, however, Faraday had to use chemical means rather than mechanical: commercial gold leaf was made by hammering the metal into very thin sheets but this was too thick for his purposes. Part of this process involved washing the films of gold, which Faraday noticed produced a faint ruby coloured fluid.

Figure 4. Michael Faraday (1791-1867)

Figure 5. Thomas Graham(1805-1869)

He shined a beam of light through the liquids and observed a cone was well defined in the fluid by the illuminated particles.

He realized that this cone effect was made because the fluid contained suspended gold particles that were too small to see with the scientific apparatus of the time but which scattered the light. He noted the light scattering properties from suspended small gold particles. It is because of this discovery that Faraday is seen as one of the first researchers into nano science and nano technology.

Graham

Thomas Graham (1805-1869) (Figure 5), Professor of chemistry at University College in London, realized in 1861 that some solutions were different: when the suspended materialdid not precipitate and could not pass through parchment filters. With diffusion rates much slower than normal, Graham suggested these peculiar solutions must consist of larger particles, inventing the terms 'sol' and 'colloid' to describe them. Colloid comes from Greek *Κόλλα* means glue.

Tyndall

British scientist John Tyndall (1820-1893) (Figure 6) described in 1869 light scattering by particles in a colloidal solution. Figure 7 shows light beam passing through a normal solution [right] and then passing through a colloidal solution where scattering is observed.

Figure 6. John Tyndall(1820-1893)

Zsigmondy

The nature and constitution of Purple of Cassius presented scientists with a problem which, throughout the whole of the nineteenth century, was attacked by some of the most distinguished chemists of the time. The formation of the purple precipitate was used to test for trace amounts of gold in solution. Richard Zsigmondy (1865-1929) (Figure 8) a Hungarian chemist in the Austrian Empire also prepared red colloidal gold solutions by the reduction of gold chloride with formaldehyde in a weakly alkaline solution.

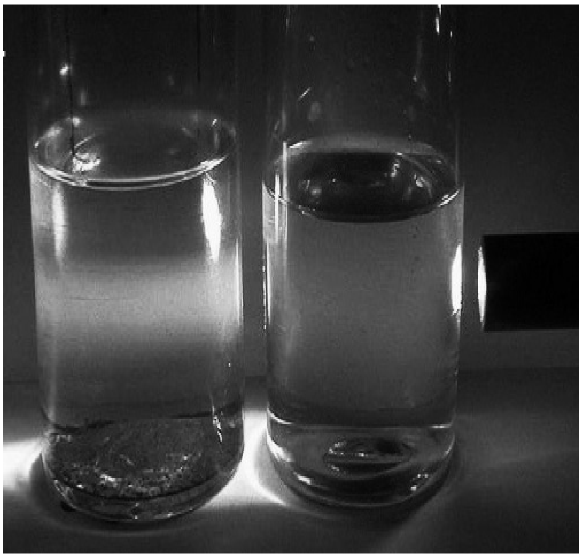

Figure 7. Tyndall effect: scattered light in the colloidal solution to the left

In his own words it was a clear solution like red wine. In dialysis experiments, however, they behaved like colloidal solutions, i.e., gold particles did not pass through the parchment membrane. Blue colloidal gold could also be obtained from dilute gold chloride solution by reduction with hydrazine or hydroxylamine.

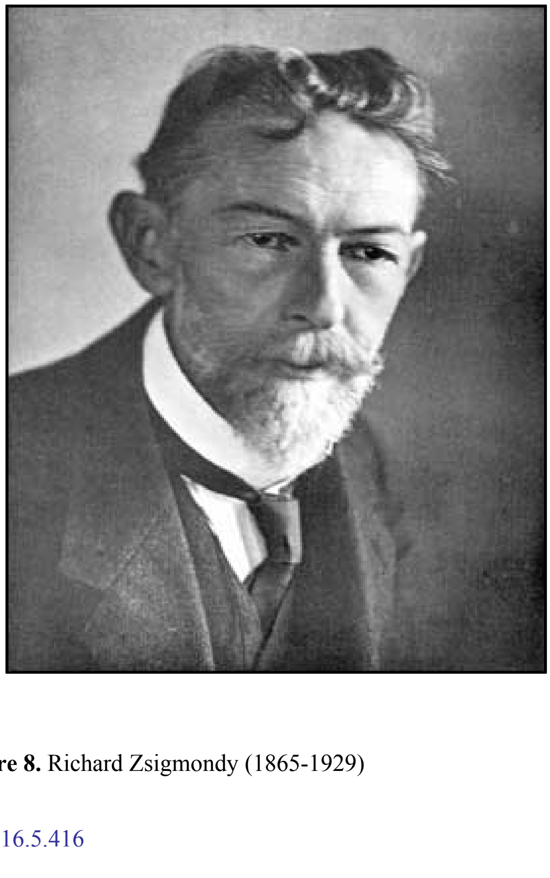

Figure 8. Richard Zsigmondy (1865-1929)

It was Zsigmondy, who had spent some years studying gold colours and had joined the Schott Glassworks in Jena in 1897, developed the ultramicroscope (Figure 9) for the examination of colloids. He showed that the *Purple of Cassius* consisted of very finely divided gold with stannic oxide and that a mixture is capable of behaving like a chemical compound. For this investigation, he was awarded the Nobel Prize in Chemistry in 1925.

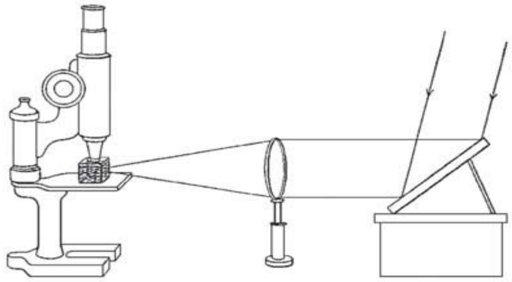

Figure 9. The ultramicroscope: illuminating colloidal particles from the side scatters light, making them visible

The reaction taking place is an oxidation-reduction process:

$$Au^{3+} + 3e^{-} \rightarrow Au$$

$$Sn^{2+} \rightarrow Sn^{4+} + 2e^{-}$$

and the overall reaction is

$$2Au^{3+} + 3Sn^{2+} \rightarrow 2Au + 3Sn^{4+}$$

In addition to the precipitation of ultra fine gold particles, the hydrolysis and the precipitation of stannic oxide in the reaction mixture

$$Sn^{4+} + 2H_2O \rightarrow SnO_2 + 4H^{+}$$

is essential for stabilizing the colloidal gold. The purple precipitate is then used in colouring porcelain or glass.

CONCLUSIONS

Colloidal solutions are heterogeneous in nature and are closely related to nano chemistry. They consist of particles between 40 and 900 nanometers in a liquid too small to be visible to the naked eye or through conventional microscopes. On the other hand nano particles are between 1 and 100 nm in size and may be in colloidal suspension or in the solid state. They are smaller than the wavelength of visible light which is 400 - 700 nm (Figure 10).

Materials change as their size approaches the nano scale mainly due to their large surface area. They often possess unexpected optical properties. Gold colloidal solution appears deep-red to blue in solution depending on their size (Figure 11).

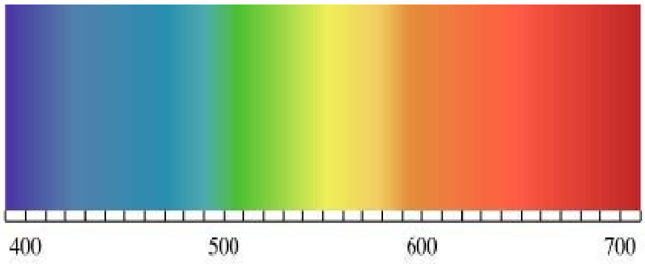

Figure 10. Wave length of visible light

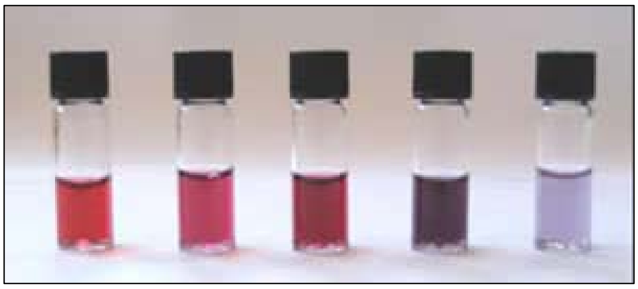

Figure 11. Effect of particle size on nanogold**.** Particle size increasesfrom left to right [https://en.wikipedia.org/wiki/Colloidal_gold]

Purple of Cassius are nano gold particles supported on colloidal tin oxide and is capable of coloring glass and porcelain deep red in color although gold is yellow in color.

Recently, gold nano particles are utilized in organic photo voltaics, sensory probes, therapeutic agents, drug delivery in biological and medical applications, electronic conductors, and catalysis.

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