

## CHAPTER 1 Making and tempering mosaic gold

*Se quisieres fazer o oro*



Figure 1 Main steps in the reproduction of the process of making mosaic gold.

'First of all take ten ounces of *Jupiter*, that is, tin, clear and pure, and take five ounces of *fugitive*, that is, quicksilver, and first melt the Jupiter and place the fugitive into a mortar. And the melted tin, place it in the mortar with the quicksilver. And mix with it five ounces of sulphur and 2 ounces of sal ammoniac, that is, anoxtar, and let this be well ground and sifted, and that which cannot be sifted, grind it again until it is all sifted, and then put it all together in a well-cleaned basin and then place it in a glass bottle. And cover it with pitch and good strong clay four or five times so that it can withstand the fire, and then put it in a pot full of ashes from the hearth and give it moderate heat until you see the fire becoming red, and then cover the mouth of the bottle with some clay and let [the pan] stand over the fire together with the bottle on a tripod. And from time to time uncover the mouth of the bottle, and when you see that it gives forth no smoke remove the pot along with the bottle from the fire and let [it] stand waiting one more day. And then break the bottle and take out an ingot of fine gold, and grind it very fine when you want to work with it, and temper it with gum-water, and do with it as you wish. And this gold is called *aurum musicum*.' [1,2].

### Reproduction

The first step consists on melting 0.5g of tin in an iron spoon beneath an oil lamp. At the same time, 0.25g of mercury, 0.25g of sulphur and 0.1g of ammonium chloride ( $\text{NH}_4\text{Cl}$ ) are placed in a mortar and well mixed with a pestle. Then, gradually, the mixture of mercury, sulphur and ammonium chloride is added to the melted tin (preferably still under heat) in order to ease the process of grinding (Attention: be cautious for the possible sulphur evaporation due

to high heat; if it starts reacting, take the spoon from the fire). After a short period, the amalgam turns into a black and homogeneous powder.

The black powder is then placed on a glass tube (Schlenk) and heated on a sand bath. The temperature is followed with a thermocouple, and kept between 270–370°C, for 4-5 hours.

The Schlenk tube is linked to a flask containing sulphur powder, to keep all the gases that are getting off during the heating procedure.

### Rationalisation / Chemical reactions

Butler and co-workers examined a Chinese recipe for the production of mosaic gold based on the reaction of tin with alum (ca 300 AD) [3] as well as the medieval European process in 'De Arte Illuminandi' (similar to the one in the 'Book on How to Make Colours'), which they describe as 'the oldest known European account is in an anonymous, untitled manuscript of the 14th century'). A complete mechanism for the formation of mosaic gold is discussed and the role of ammonium chloride disclosed.  $\text{NH}_4\text{Cl}$  is presented as the key ingredient that enables the transformation of  $\text{SnS}$  into  $\text{SnS}_2$ , i.e., the oxidation of tin (+2 to +4 state). This may be viewed as the critical step in the European process for mosaic gold, being the other to obtain it crystalline and glistening; indeed, tin (IV) sulphide, when crystalline (lamellar, flakes, pure hexagonal phase  $\text{SnS}_2$ ), looks very much like gold. The authors also conclude that the amalgam of tin and mercury is not necessary to produce tin (IV) sulphide, in agreement with previous published results [4-6], and also with our experiments. They also tested with other ammonium salts and concluded that 'the only salt that could bring about such reac-

tions is an ammonium salt of a strong acid', ruling out  $\text{NH}_4\text{NCS}$  or  $\text{KCl}$ , which was found to not produce any effect [3]. According to our experiments, the same results have been obtained regarding the use of thiourea (instead of  $\text{NH}_4\text{Cl}$ ), confirming the inefficiency of this compound in the production of mosaic gold from tin and sulphur.

In the medieval recipe, the two main ingredients, Sn and S, are brought into contact within a Hg-Sn amalgam to which sulphur and ammonium chloride are subsequently added and thoroughly mixed by grinding. The mixture is then gently heated (more details on the heating procedure are found below).

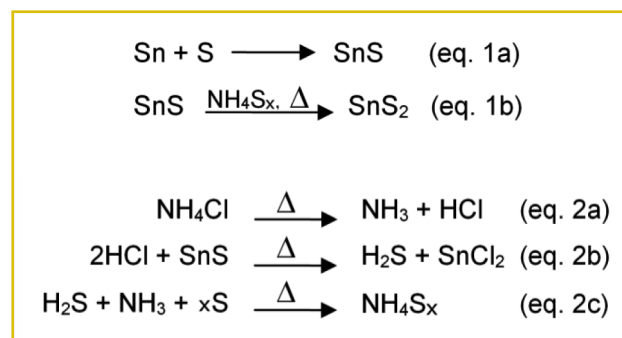


Figure 2 Reaction scheme for mosaic gold synthesis. [3]

As shown in Figure 2, the grinding will lead to the formation of  $\text{SnS}$ , and the heating to the decomposition of  $\text{NH}_4\text{Cl}$  into  $\text{NH}_3$  plus  $\text{HCl}$  (eq.2a). The latter will further react with  $\text{SnS}$ , producing  $\text{H}_2\text{S}$  plus  $\text{SnCl}_2$  (eq. 2b). Brought into contact,  $\text{H}_2\text{S}$ ,  $\text{NH}_3$  and S react, forming ammonium polysulphide ( $\text{NH}_4\text{S}_x$ ), which, finally, will promote the oxidation of  $\text{SnS}$  to  $\text{SnS}_2$ , mosaic gold (eq. 2c).

The authors do not discuss the evolution of  $\text{SnCl}_2$ , one of the products formed (eq. 2b); it is possible that it will act as a source of tin ions, but this must be further checked.

### Key aspects

**Reaction stoichiometry:** The amount of sulphur and tin given in the recipe is stoichiometric, as for each mole of tin, two moles of sulphur are being used. However, when reproducing the recipe, whenever the temperature was raised more than it should (leading to some loss of sulphur), more sulphur was introduced by grinding it with the reactional mixture.

**Ammonium chloride (salt ammoniac):**  $\text{NH}_4\text{Cl}$ , salt ammoniac, initiates the reaction between sulphur and tin, favouring the production of  $\text{SnS}_2$ , instead of  $\text{SnS}$ . On another hand, it reduces the loss of tin and sulfur

by sublimation. Moreover, the  $\text{NH}_3$  and  $\text{HCl}$  gases produced during the heating process seem to protect  $\text{SnS}_2$  [4].

**Temperature and time of reaction:** There are no specific instructions on this. According to Xiao and Zhang, the best reaction yield is in the range of temperature between 250–300°C and a reaction time of *circa* 10h [4].

**Cooling process:** It is important to allow sufficient time for a complete cooling of the mixture; during the cooling to room temperature, the orange yellow colour solid that is obtained during the heating will be transformed into the yellow glistening mosaic gold.

### Missing / Obscure indications

**Tin-mercury amalgam:** The amalgam used in the mosaic gold production almost certainly will increase the contact area between the reactants, an important parameter for improving the rate, and therefore the yield, of a solid state reaction. As it has already been stated, the presence of mercury is not necessary; however, our reproduction evidenced that the presence of mercury turned to be crucial on the grinding process: pure tin is extremely difficult to grind with sulfur and salt ammoniac, but when melted with mercury, the grinding is faster and easier.

### Comments

**heating temperature:** after a few minutes of heating the mixture it is possible to see the sublimation of sulphur. It is important to close the system at once. The temperature must be stable and controlled to allow the fusion of Sn with S (melting points 232°C and 113–119°C, respectively), and according to some authors it should be under 445°C, to avoid sulphur sublimation [4,6].

**modern synthesis:** It is necessary to refer that recent publications described the synthesis of  $\text{SnS}_2$  nanoplates, in a melt of tin dichloride and thiourea in air at 250–280°C for 0–5 h; the products obtained were phase pure hexagonal  $\text{SnS}_2$  nanoplates, of 20–70 nm thickness [5]. The working temperatures will decompose thiourea into ammonium isocyanate, which Butler *et al.* claim was ineffective in transforming  $\text{SnS}$  into  $\text{SnS}_2$ , when the reactants were tin and sulfur. The authors were also able to synthesize  $\text{SnS}_2$  'on heating the mixture of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  and excess S powders in air at 200–240°C or 0–10h' [5]. Products obtained were subsequently washed 'with carbon disulphide, deionized water and ethanol to remove the impurities (e.g., the residual S),





Figure 3 Examples of mosaic gold in Books of Hours. From left to right, Ms. 22, f.74 (PNM); IL. 15, f.66 (BNP); IL. 21, f.17 (BNP); with details on the bottom row.

dried in air at 80°C, and finally yellow  $\text{SnS}_2$  products were obtained'. They offer the following rationale for the efficiency of the novel process: 'the Sn source ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ) we use, it melts (that is,  $\text{SnCl}_2$  dissolves in its own crystal water) at temperature above 38°C; (...) the S powder (whose amount is in excess) also becomes molten and participates in the reaction just like a liquid, which certainly increases the interface and contact surface areas between the reactants, and so accelerates the reaction rate'. The same arguments may be applied to the reaction of tin dichloride and thiourea.

**Comparison with the process described in *De Arte Illuminandi*:** Whereas the *BHMC colours* approaches the stoichiometric proportion of Sn:S (1:2), *De Arte Illuminandi* applies Sn in excess (1:1). It seems that this is not the best way for the synthesis since tin is the most expensive reagent and easy to purify.

Most of the instructions are similar, except in the details of the addition of salt or the washing of the amalgam in *De Arte Illuminandi*. They also share identical descriptions on the use of a glass recipient, on the

application of clay, the use of ashes, and the recommendation to use gentle heat. The final product is obtained after breaking the glass recipient, which is described, has an 'ingot of fine gold'. Moreover, they also diverge in the indication of time for the heating. *De Arte Illuminandi* indicates 9h, whereas the *BHMC colours* does not specify any hour. But at the same time, the *BHMC colours* is more detailed in the description on the observation of different smoke colours during the procedure.

### Mosaic gold in Portuguese medieval illuminations

Mosaic gold has been found in the Galician-Portuguese medieval *Ajuda Songbook*, from the 13th-14th century [7]. We have also identified this pigment in French *Books of Hours* from the 15th century, combined with gold powder (ms. 22, PNM), with lead-tin yellow (ms. 24, PNM) [8], and also pure (IL. 21, BNP). Mosaic gold has been also detected pure in a Flemish *Book of Hours*, IL.15, BNP.

There have been other studies, reporting the use of mosaic gold in substitution of gold, in several Ital-

ian manuscripts dating from the end of the 13th-14th and 15th centuries [9,10] as well as in the German *Göttingen Model Book* from the 15th century [11].

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## Further reading

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## Appendix

### Mosaic gold characterisation: synthesised following 'The book on how to make colours'

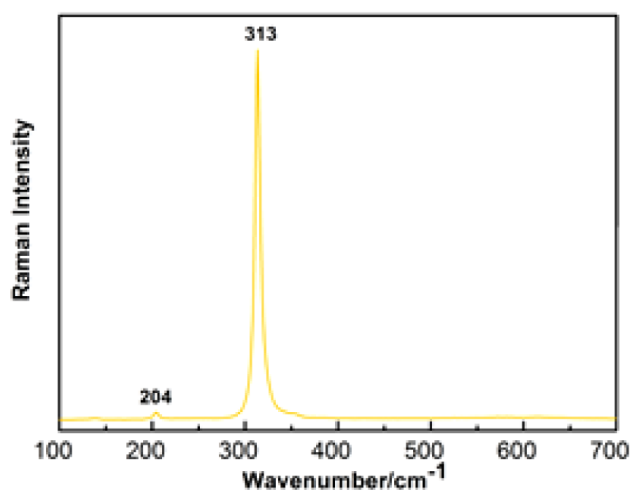


#### Colour

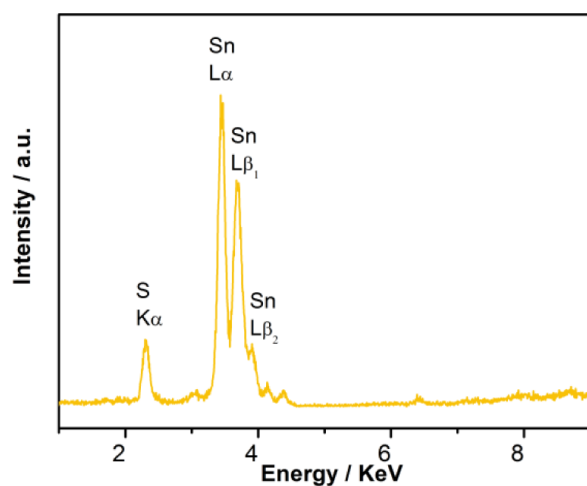
**Table 1** Colour coordinates, Lab\*, for mosaic gold paint reconstructions using two different binders (arabic gum and egg white) applied over filter paper and parchment.

Support	Binder	L	a*	b*
Filter paper	Egg white	60.12	13.54	34.39
	Arabic gum	62.77	13.18	32.01
Parchment	Egg white	59.66	14.59	38.87
	Arabic gum	58.04	14.61	38.41

#### Spectroscopic characterisation



Raman spectrum acquired with a Labram 300 Jobin Yvon spectrometer. Laser excitation, 632.8 nm; 100x objective ULWD; laser power 1.7mW (characteristic bands at 313 cm<sup>-1</sup> and weaker band at 204 cm<sup>-1</sup>).



EDXRF spectrum ArtTAX spectrometer of Intax GmbH, with a molybdenum (Mo) anode, Xflash detector refrigerated by the Peltier effect (Sidrift), with a mobile arm. Experimental parameters: 40 kV of voltage, 300 µA of intensity, for 200 s, under Helium gas flux.