P024S: Verdigris copper

### **Student Sheet**

In this practical I will be:

- Learning about how verdigris copper is produced, using key terms such as alloys,
  redox reactions, oxidation states, corroded and verdigris.
- Observing and analysing differences between the two groups of copper coins, when exposed to different experimental conditions.
- Identifying whether the changes seen are because of a chemical or physical change, using my scientific understanding to explain my prediction.

## Introduction:

Like nearly all other ancient Greek science-artists, you have seen and heard how corroded copper, and its alloys, are an interesting shade of green. Some artists have even started using this **verdigris copper** as the pigment in their paints. However, you have noticed that there are definite differences in colour between the paint pigments, despite being created from the same material.

You wonder if this is due to the conditions the copper alloys are exposed to. Like all good science-artists, you decide to investigate further...

### Wear eye protection.

# **Equipment:**

- 2 beakers (250 cm<sup>3</sup>)
- 100 cm<sup>3</sup> measuring cylinder
- Sodium chloride (24g 12g)
- Spatula
- Balance
- Weighing boat or galipot
- Stirring rod
- 1 M ethanoic acid or vinegar (100 cm<sup>3</sup>)
- 1 M citric acid (100 cm<sup>3</sup>)
- 6 new copper coins
- Paper towels
- Stopclock



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- Thermometer
- Pen

#### Method:

1. In a 250 cm<sup>3</sup> beaker, mix 100 cm<sup>3</sup> of ethanoic acid with 12 g sodium chloride. Stir until the sodium chloride dissolves.

Put 6 copper coins in the sodium chloride / ethanoic acid mixture.

- 2. Leave for around 10 minutes. Use the stopclock to time the process.
  - Why do you think the coins need to be left for a length of time?
  - Are there any visible signs of reaction e.g. colour change, heat from the reaction (you might need to use a thermometer) etc.?
- 3. Pour away the liquid, and then carefully tip the 6 coins onto a paper towel.
- 4. Take three of the coins, wash them in clean water and dry them.
- 5. Put these coins on another paper towel and mark them as A.
- 6. Take the paper towel with the other three coins on and mark this B.
- 7. Leave them for around 1–2 hours or left in a safe place for next lesson.
  - Why are the coins separated into two different groups?
  - Describe the appearance of the copper coins.
  - Is this a chemical or physical reaction?
  - Explain why you think that.

### Going further:

Instead of ethanoic acid try using citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid).

• Is the resulting colour change different with this acid?

#### Theory:

The vinegar mixture causes a chemical reaction between the copper and the air known as a **redox reaction**. This is what a reaction is called when atoms change their **oxidation** state.

A form of copper oxide had formed on the penny, and the copper oxide looks green.



Copper domes and copper covered roofs are often green in colour because chemicals in the air from the burning of fossil fuels react in different ways with the copper.

In the natural process there are formed a number of different verdigris such as:

- pale green nantokite, CuCl
- vitreous green atacamite, Cu<sub>2</sub>(OH)<sub>3</sub>Cl;
- pale green paratacamite, Cu<sub>2</sub>(OH)<sub>3</sub>Cl;
- pale bluish-green botallackite, Cu<sub>2</sub>(OH)<sub>3</sub>Cl;
- pale green clinoatacamite, Cu<sub>2</sub>(OH)<sub>3</sub>Cl;
- light green anarakite, (CuZn<sub>2</sub>)<sub>2</sub>(OH)<sub>3</sub>Cl.

In the mineral world the most common verdigris is nantokite (copper (I) chloride, CuCl) named after the mines in Chile where it was first identified.

2 Cu(s) + 
$$2H^+(aq) + Cl^-(aq) \rightarrow 2CuCl(s) + H_2(g)$$
  
Copper (I) chloride  
(nantokite)

In a wet environment the copper (I) chloride crust reacts with the water to produce copper(I) oxide (Cu<sub>2</sub>O) and hydrochloric acid. The hydrochloric acid produced will go on to react with more copper to produce additional nantokite.

$$2HCI(aq) + Cu(s) \rightarrow 2CuCI(s) + H_2(g)$$
  
hydrochloric acid + Copper  $\rightarrow$  copper (I) chloride + hydrogen  
(nantokite)

But if water and oxygen are both present in quantity then both copper(I) chloride (CuCl) and copper(I) oxide (Cu<sub>2</sub>O) will react to produce copper trihydroxychloride, which varies from emerald green to pale green to pale blue-green depending on the crystal structure.

The most common copper trihydroxychloride is atacamite named after the Atacama Desert in Chile. Its colour varies from blackish to emerald green.

Clinoatacamite is a copper trihydroxychloride that is pale green.

Botallackite is the least stable of the four copper trihydroxychloride structures and is pale bluish-green in colour. It was first found and identified in a mine in Cornwall, England and is a rare corrosion product on archaeological finds.



One other verdigris copper salt is the light green anarakite  $(CuZn_2)_2(OH)_3CI)$  named after the Anarak province in Iran. It contains zinc because many bronzes used in outdoor statues have been forged with some zinc.

The Greeks and Romans made verdigris by corroding copper. They mixed verdigris with oils to make green paints.

