Making Archaeological Ink

Summary
Historically, tannins, compounds found in tea, were used for making ink by mixing them with iron salts, such as iron(II) sulfate to form complex, water-soluble blue-black compounds. On standing, the complex becomes darker and insoluble, producing a permanent ink, called iron gall ink.¹ This ink has been used to write historic documents such as the Declaration of Independence. We will make this ink using wine tannin and iron(II) sulfate.

Materials
1. Wine tannin, 2 tablespoons per working group (Wine tannin can be purchased online; it usually comes in 1-lb packages.)
2. Iron(II) sulfate heptahydrate (1 tablespoon per working group) (available in garden shops or online)
3. Cornstarch (from retail food stores)
4. Plastic cups (or other suitable container – 2 per working group); plastic spoons
5. Paintbrush, or dip pen such as used for calligraphy, and paper

Safety Suggestions
- Safety Goggles Required
- Protective clothing suggested
- Do not eat or drink any of the materials used in this activity
- Thoroughly wash hands after this activity
- Use only disposable containers
- Clean up quickly and thoroughly; product is indelible

Procedure
1. Place 2 tablespoons of wine tannin in a disposable cup.
2. Add an equal amount of water and stir, preferably with a plastic spoon
3. Observe the color of the mixture; record your observation
4. Add 1 tablespoon of iron(II) sulfate heptahydrate and stir thoroughly
5. Observe the color immediately, and observe again after five minutes; record both observations.
6. If the mixture is too viscous, add a little water. If it is too thin, add a little cornstarch.
7. Using a paintbrush or dip pen, practice your calligraphy on a sheet of paper
8. Thin or thicken the ink as needed to produce satisfactory letters or images
9. Clean up quickly. Place your ink in a container provided by your workshop leader.
10. Wash your hands thoroughly.

Where's the chemistry?
Tannins contain compounds called polyphenols that chemically react with iron in solution to produce black products. A word equation for this reaction is

tannin + iron(II) → iron gall ink

More specifically, the tannin contains a compound called gallic acid which reacts thus:

gallic acid + iron(II)(aq) → gallatoiron(II) which oxidizes to bis(gallato)diiron(III) (iron gall ink)²

The reaction in structural formulas is:
What did you see?
Step A: Wine tannin mixed with water
Step B: Wine tannin mixed with water and iron(II) sulfate heptahydrate (after 5 minutes)
Step C. Writing produced with the iron gall ink.
Step C

References

Photographs by Mary Virginia Orna; structural formulas by Seth C. Rasmussen
Activity developed by
Patricia Smith, Colorado Education Partners, Pella, IA
Seth Rasmussen, North Dakota State University, Fargo, ND
Mary Virginia Orna, Chemistry Professor, The College of New Rochelle, ret., New Rochelle, NY
Contact: maryvirginiaorna@gmail.com