Vitriol

An ingredient for Medieval and Renaissance medicines, acids and dyes.

Entry contents: 1) congealed blue vitriol, 2) "German vitriol," 3) starting materials (i.e., an example of the right sort of rock to use), and 4) this documentation.

What is Vitriol?

Vitriol is one of or a combination of three chemicals: copper, iron or zinc sulfate hydrate.[1] In period, vitriol was used in leather and fabric dyes, in several medicines, as a flux for assay and smelting , and as one of the base ingredients for making strong acids. Like its cousin alum, vitriol is one of the fundamental raw materials of the Middle Ages. This project involved making vitriol from scratch using period instructions.

Sources

There are three primary sources used for this project on vitriol, Pliny the Elder's *Natural History*, Biringuccio's *Pirotechnia*, and Agricola's *De Re Metallica*. Agricola and Biringuccio are available from Dover. The complete Pliny is available as a ten volume set from Harvard University Press. I would like to include Dioscorides in this list, but there is no English translation currently available which includes the essential Book V on minerals.[2] The only significant secondary sources are the Hoover and Hoover annotation of *De Re Metallica*, and the new Mineralogical Society of America volume on sulfates.

What the Sources Say About Vitriol (warning: 1.5 pages long)

Pliny is the logical starting place for most inquiries into medieval material science since he was frequently consulted in period. Both Biringuccio and Agricola quote him at length. Along with Dioscorides, Pliny gives one of the earliest known accounts of vitriol (Book XXXIV, section XXXII[3]), though his main interest was its use in medicine, particularly for the eyes. He thought that blue vitriol was the best, i.e., copper sulfate pentahydrate. He described that you could congeal blue vitriol crystals from evaporating certain spring waters or mine drainage waters (by implication) in a part of Spain and on the Island of Cyprus. Considering that copper sulfate saturated waters exist today in

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[1] Specifying whether the bound water is heptahydrate or pentahydrate is omitted in places for convenience sake.

[2] Contemporary with Pliny the Elder, the physician Dioscorides was known in both the Classical and Medieval periods for writing *De Materia Medica*. This book lists over 600 hundred plants and their medicinal usage in the classical world. What many people don't realize is that the *De Materia Medica* is not strictly an "herbal" since it also includes discussions on medicinal substances derived from animals and rocks. Dioscorides mentions blue vitriol specifically, in the context of it being used in medicines, used as the base ingredient of shoe blacking, and used as a poison. (Hoover and Hoover, pp. 572-574 and p. 607)

[3] The citations of Pliny used here follow the Classical Studies convention of citing book and section number, rather than following the Chicago/MLA convention of citing volume and page number.

southern Arizona near the Morenci copper district (pH = 2!)[4], I've always found this passage from Pliny both within the realm of possibility and also quite interesting.

Agricola divided vitriol into three types: white, green, and blue (i.e., zinc, iron and copper sulfate hydrate, respectively).[5] He discussed four different ways to make it, depending on what time of year it was and whether your starting material was acid mine drainage, sulfide-rich rock or sulfate-rich rich rock.[6] The first two methods are really just instructions for evaporating mine drainage waters, depending on the season, very much like Pliny's instructions. The third recipe is for making vitriol from sulfate-enriched rocks which have already partially or wholly oxidized *in situ* from the interaction of sulfides and acidic ground waters. The starting rocks are broken up and soaked, and the solutions are drawn off and allowed to evaporated, thus congealing vitriol crystals The fourth recipe involves dissolving iron sulfates in rock, plus oxidizing and then dissolving iron sulfides in the same rocks (which is aided by the sulfates already present, since these will lower pH significantly) to make sulfate-saturated solutions which were then evaporated.[7] In the fourth recipe only, Agricola mentions the addition of iron into the solution prior to evaporation.

Agricola's first two recipes should result in any of the three varieties of vitriol, or in a mix of two or more of the vitriols, depending on what's in solution in the mine drainage waters used. The fourth recipes should result in forming crystals of green vitriol, i.e., iron sulfate pentahydrate, since the insertion of metallic iron will force the precipitation of copper out of the solution.

Agricola did not give any specific instructions for making white vitriol. Hoover and Hoover speculate that the white vitriol Agricola described was naturally-formed goslarite (the mineral form of white vitriol, i.e.zinc sulfate heptahydrate), commonly found inside mines in the Goslar mining district in modern Germany. The last thing that needs mentioning is that Agricola's fourth recipe for making vitriol is almost a word for word a plagerism of Biringuccio's instructions in the *Pirotechnia*.[8]

Biringuccio confines himself to discussing green vitriol only, and ignores the blue and white varieties. This is something that I haven't quite figured out, since Biringuccio knew his Pliny and his Agricola very well. Biringuccio had read

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[4] Ed Melchiore, geologist, Morenci-Phelps Mine, seminar talk, Feb., 1994, Washington University., St. Louis, MO

[5] Agricola's De Re Fossilium, as quoted by Hoover and Hoover, pp. 572-574.

[6] Agricola, pp. 572-578.

[7] This method is essentially the same that's used today to do to manufacture iron sulfate hydrate and sulfuric acid.

[8] Biringuccio, *Pirotechnia,* pp. 95-98.

Agricola's *De Re Fossilium*, since he quotes from it in several places in the *Pirotechnia*. Regardless, he gives the correct instruction s for making green vitriol briefly in his section on the "semi-minerals," [9] which are the same instructions that Agricola lifted for *De Re Metallica*.

Instructions for Making Vitriol from Mine Drainage Waters

The Pliny/Agricola instructions are very simple. Sulfate-saturated spring or mine drainage waters are allowed to evaporate. Wires or strings with pebbles to weight them are lowered into the vitriolic solutions to act as surface area upon which the crystals of vitriol will coagulate and grow.

Instructions for Making Vitriol from Rocks

The Agricola/Biringuccio instructions on vitriol are as follows: take "vitriolous earth" and pyrite-bearing rocks and heap them for several months. Turn them occasionally. After they've been exposed to the elements long enough to make them easy to break apart (the result of *in situ* oxidation), dump the rocks in a pool or pit full of water and wash the clays off so that these settle to the bottom of the water. Skim the fluid to remove lighter solids in suspension off. Repeat the washing and skimming step. Once all the insoluble and suspended material is gone from the fluid, and the fluid is unclouded, put that fluid into a shallow pool or vat. If you want exclusively green vitriol, then insert wires or other metal pieces made of iron into the solution to help "purify" it.

We know from high-school chemistry that inserting iron into a solution will precipitate any dissolved copper out of the solution because of the relative positions that iron and copper have in the electromotive series. Once the copper has settled out and the solution has time to evaporate a bit, Agricola then transferred the fluid to smaller pans or basins, where it was finally allowed to congeal into crystals of green vitriol. Agricola's (and Biringuccio's) recipes should result in green vitriol exclusively due to the step that precipitates copper out of the solution. The only time that it would not work is if the solution was one of saturated copper sulfate to begin with, in which case the iron would have very little effect on the overall solution other than to dissolve the introduced iron.[10]

Making the Blue Vitriol

It was a cross between Pliny's instructions and Agricola's third recipe which I adhered to in making the blue vitriol, since I knew that my starting rock had abundant copper sulfate hydrate in it, but probably very little iron. My source of my rocks was the Majuba Hill Mine, in the middle of nowhere, 40 miles west of

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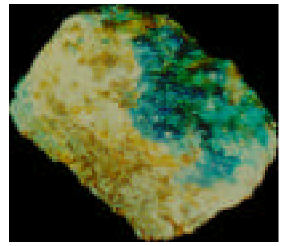
[9] Ibid.

[10] A saturated solution of copper sulfate is essentially a solution of copper ions in dilute sulfuric acid. Iron is soluble in most of the common inorganic acids, including sulfuric.

Winnemucca, NV. The photo immediately below is of a sample from this location. I collected a small bag of the clayey decomposed rhyolite mixed with native blue vitriol from this site (i.e., the mineral chalcanthite), and used one of these rocks to make my blue vitriol. The rock was crushed, soaked, and subsequently dissolved and dispersed into a beaker of water. The solution was skimmed and strained several times until a clear blue solution was achieved. Since the beaker I used for the final congealing step is much smaller than Pliny's or Agricola's vats, I did not bother to precipitate the vitriol onto strings or wires weighted with pebbles as described by Pliny.



Making the Green Vitriol??? (warning: 1.5 pages but with cool pictures)

There were small green crystals showing up in one of the batches of blue vitriol crystals and in the solids strained out of the initial solutions of crushed rock. This convinced me that there may be enough iron present in the clayey rhyolite+chalcanthite to make some green vitriol.

I made my first batch of green vitriol in 1997 using Agricola's first method, i.e. congealing the vitriol directly from iron sulfate saturated mine drainage simply by evaporating the water in the solution away. My starting material for that batch of vitriol was the iron sulfate saturated solution from the tank shown in photograph below. The congealed green vitriol made from this holding tank of acid mine drainage was then used to make the black leather dye described in recipe #173 from the 1548 Plictho of Gioanventura Rosetti.[11]

Agricola's first method of making vitriol takes vitriol-saturated waters that have collected underground and puts them in vats outside to settle and evaporate. The fluid in the above photos is not part of a vitriol making process, but it could have been in the middle ages. (The tank here is a holding tank for mine drainage at a superfund site; it is transferred, after the solids have settled out to a water treatment plant.) My colleagues and I were discussing sulfate chemistry on this particular sampling trip, and decided to see if we could get any copper to precipitate out of the iron-saturated mine drainage water. So Charlie stuck a vise-grip attached to a piece of PVC pipe into the tank of iron sulfate saturated water.

[11] This leather dye was entered by me in last year's Kingdom Arts and Sciences Championship.

We pulled the vise-grip out of the tank after about a half an hour and found we had a lovely copper-plated tool for Charlie[12] to explain to his boss at the US Geological Survey. I took a small sample of the water from this tank, and let it congeal into crystals of green vitriol, which I then used to make a period leather dye, using a recipe from the 1548 Plictho of Gioanventura Rosetti. There is no vitriol left from this batch – I used all of it to make my leather dye.

Obviously, this most recent attempt at making green vitriol would have to rely on the Agricola's fourth recipe described earlier in this documentation. For my first attempt at using the left over decantation products, I mixed and rehydrated the materials left over from making the blue vitriol. The new solution had a discernable tint of green, which left me thinking that I was on the right track. I then added a piece of iron to the solution as per Agricola's instructions, specifically one of my steel rock chisels. The next day I was horrified to discover that the solution had turned a brown ochre color. Upon removing the chisel, I discovered two things: 1) portions of the chisel exposed to the solution had been heavily oxidized (rust city!) and 2) where the chisel was not oxidized, a faint plating of copper was present. So while I was successful at precipitating copper out of the solution, I had also created an electrochemical battery with the chisel acting as a cathode. At this point, I decided to pull the chisel out of the solution (since the solution was now quite iron-saturated from the corrosion of the chisel), and to wait to see what would happen if the solution was allowed to congeal.

The initial ochre-colored decantations of the post-chisel solution ended up drying into a yuck-green plus ick-ochre colored, somewhat-botroidal crusty solid which is soluble. This substance is remarkably close to the description of Biringuccio's "German vitriol," i.e. a green and yellow streaked soluble solid.[13] This is the material that's in one of the two glass vials that accompany this documentation. It is important to the discussion immediately below to note that the "German vitriol" is almost completely soluble, with a small brown residual left over that disappears in a few days after letting the solution sit.

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[12] Charlie is the same person as C. N. Alpe rs, as per the Min. Soc. Am volume on sulfates – cf. the reference section below...

[13] Biringuccio, pp. 97-98.

I made a hand-separation of the "German vitriol" into more-green and more-yellow-ochre pile of coarsely crushed material. Using the mostly-green pile I made, decanted, and strained a few more iterations of solution. One of these iterations congealed into drusy crystals of pale green and white – and significantly, no more ochre or brown! Rehydration of those crystals produced a green sludge which was not soluble at all, plus a white flocc which would neither float nor sink in the solution. The green sludge was removed from the solution. The more sludge that was removed, the more flocc that would form – Le Chatier's principle of chemical reactions in action! The flocc was removed from the residual solution by straining through paper filters. Once the water drained from the filters, the residual material (formerly flocc) was the same pale green as the insoluble sludge. The strained residual solution was neither green nor brown, but clear! Obviously, neither the sludge nor the flocc behaved like green vitriol, since both are mostly insoluble. I count this as a significant failure. It is obvious that the addition of the highly-oxidized iron compounds from the corrosion of the chisel screwed up the chemistry of the vitriolic solution. I have no clear idea what I managed to make yet with my insoluble green solids (I don't have time to do any INAA analyses until maybe this summer). I also have not yet completely evaporated the fluid left over from this disaster to know if anything interesting will crystallize out of solution yet... (Ask me in a few more weeks – I may know by Uprising.)

Results

The blue vitriol turned out wonderfully. The attempt at making green vitriol fell flat on its face, probably due to the introduction of heavily oxidized iron into the solution via the chisel. The ick green-yuck brown crustiform material separated out of the initial green vitriol attempt matches Biringuccio's description of "German vitriol." There does not appear to be a description of the actual composition in any of the historic or modern literature of Biringuccio's German Vitriol. Since my look-alike substance is soluble, this leads me to think that I've managed to make an artificial "German vitriol." This then implies that German vitriol is nothing more than a mix of various iron sulfate hydrates, including iron sulfate pentahydrate, plus perhaps some iron oxyhydroxide hydrates (ie, limonites), all of which come in various colors of green, brown and yellow.

A Very Optional Epilogue on Using Vitriol

Both Dioscorides and Pliny equated blue vitriol with "shoemaker's black" - this should give you an idea just how long vitriol-based leather dyes have been around. Hoover and Hoover (p. 572-4, p. 607) state that Pliny and Dioscorides must have been mistaken, since copper sulfate hydrate does not provide the iron needed to turn the leather black.[14] Since Pliny's recipe and Agricola's first two

[14] The essential reaction to blacken leather is the reaction of the easily disassociated iron in the green vitriol with the tannic acid in the vegetable-tanned leather, to form iron tannate, which is black.

recipes omitted the step to add iron, Hoover and Hoover speculated that perhaps the blue vitriol of Pliny and Dioscorides had some iron in it, though not enough to shift the vitriol's color over to green. Modern experiments in the art and manuscript conservation field, however, show that copper in the place of iron will produce a brown to black color, depending on how much iron is mixed in with the copper,[15] where pure copper produces brown. As a test, I subjected some leather to a solution of blue vitriol based on some of the blue vitriol I made for this project. The scrap turned grey at first, but after exposure to sunlight (a requisite to cure all sulfate-based leather dyes), it achieved a deep brownish-black color when compared to the very black leather I dyed using my green vitriol-based dye. I interpreted this to mean (i.e., more black than brown) that there was probably some iron impurity in my blue vitriol.

Don't Do This In Your Kitchen!

Vitriols and the chemical solutions made during vitriol manufacture are mildly to highly acidic. All vitriols are poisons. The solutions made in the vitriol process contain mild to strong sulfuric acid. These can burn your skin, will eat your clothes and can blind you if splashed in your eyes. Vitriol is the starting ingredient for making all the strong acids known in period, and Agricola's 3rd recipe is the basis for the modern method of manufacturing sulfuric acid today. This stuff is dangerous if badly handled. If you want to play with making your own vitriol, whether you want to make period leather dyes or your own *aqua valens*, don't do this without taking the precautions of having running water easily available to wash eyes and skin, goggles to protect your eyes from splash, rubber or nitrile gloves for your hands, a well-ventilated work area, and no children or pets around who might get underfoot and cause an accident. If you can't locate and then get your eyes under your running water source WITH YOUR EYES SHUT, from anywhere is your work area, in under 10 seconds, then the running water source for your work area isn't good enough for you to play with vitriol. Be smart: be safe before you play with period alchemy.

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[15] Ad Stijnman, 2001, "Ink Corrosion Site: Recipe Source Research," The Netherlands Institute for Cultural Heritage, http://www.knaw.nl/ecpa/ink/html/source.html, accessed March 25, 2002.