

The Preparation and Verification of Malachite

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With modifications by David A. Katz, Pima Community College, Tucson, AZ 85709

Malachite, a mineral of copper, is one of the most beautiful minerals known. In the natural state, this relatively soft mineral usually shows various tints of green, varying from a dark, rich green to bright Kelly green. Since earliest civilizations, it has been carved into art forms or semiprecious jewelry, or ground into a fine powder for use as an artist's pigment (1). Today, tourists to Elat, a city on the Gulf of Akaba, can purchase "stones of Elat" which are malachite-bearing rocks. King Solomon's mines, mentioned in the Bible, are believed to have been located there.

Malachite is found in dry or semiarid regions, usually near the surface, and is a good indicator of deeper copper deposits. Chemically, it is a combination of copper(II) carbonate and copper(II) hydroxide, $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$.

In the history of chemistry, malachite has been important, too. In the early 1800's, a controversy existed about the nature of compounds and mixtures. At that time, Claude Louis Berthollet (1748-1822) was publishing his findings about the varied composition of compounds. A book (2) on the history of that period states "Unfortunately Berthollet drew incorrect conclusions from some of his [own] experiments, holding that the composition of certain compounds may vary within small limits." During this same period, another chemist, Louis Joseph Proust (1754-1826) had already completed chemical analysis on samples of malachite obtained from various natural sources. His findings showed without doubt that the composition of malachite was the same (2), regardless of its source: "[Berthollet's incorrect conclusions were] quickly noted by Proust, who, in a series of researches continued until about 1808, established the law of definite proportions ... thus ending the famous controversy between the two men" and, also, ending the confusion about what is a mixture and what is a compound.



But still, another chemist of the same period, Jeremias Benjamin Richter (1762-1807) was working on the same topics and was much aware of the controversy about mixtures and compounds and its resolution. Impact of the resolution on his own work (2) is reflected in his writing: ". . . the science of measuring the quantitative proportions . . . of the masses in which chemical elements stand in regard to each other [in a compound]." Beginning students of chemistry might be interested to know that Richter coined the term, stoichiometry.

Malachite and the beautiful blue azurite are two of the most common ores of copper. Today it is indeed sad to note that as we, in this highly industrialized society, use up the Earth's supply of copper, malachite and azurite becomes more and more scarce. If this continues, one day soon samples of malachite and azurite might be found only in museums.

By following the experiment described here, you can make malachite by combining the ingredients, as nature did, perhaps millions of years ago. But unlike nature, which required

probably millions of years, you can complete the process during a single laboratory period.

Safety Precautions

Goggles must be worn in the laboratory at all times.

Copper(II) nitrate solutions can be irritating to the eyes. Ingestion of solutions can cause vomiting and diarrhea with severe abdominal pain.

Ammonia, although dilute in the experiment, has a strong odor and is irritating to the mucus membranes. If the odor of ammonia is irritating to you, work with the ammonia under a hood.

Nitric acid, although dilute in this experiment, is corrosive to the skin. In the event of skin contact, wash the affected area with water. Yellow stains on the skin may occur.

Hydrochloric acid, although dilute in this experiment, is corrosive to the skin. In the event of skin contact, wash the affected area with water.

Disposal

Dispose of all materials in the proper containers in the laboratory.

Materials Needed

0.5 M copper(II) nitrate, $\text{Cu}(\text{NO}_3)_2$. (Prepared by dissolving 120.8 grams $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ per liter of solution)

1.0 M ammonia, NH_3 . (Prepared by dilution of 67.5 mL concentrated ammonia to one liter.)

carbonic acid solution, concentrated. Available as club soda, sodium free, at supermarkets

1.0 M nitric acid, HNO_3 . (Prepared by the dilution of 62.5 mL concentrated nitric acid to one liter of solution.)

1.0 M hydrochloric acid, HCl . (Prepared by the dilution of 83.3 mL concentrated hydrochloric acid to one liter of solution.)

beakers, 250 mL, 400 mL and 600 mL

graduated cylinder, 50 or 100 mL

test tubes, 18 x 150 mm

stirring rod

Bunsen burner

Procedure

Place 25 mL of 0.5M solution of copper(II) nitrate, $(\text{Cu}(\text{NO}_3)_2$, in a 400-mL beaker.

Measure 40 mL of 1.0M solution of ammonia, NH_3 in a 50 or 100 mL graduated cylinder.

Add the ammonia to the copper nitrate solution slowly with stirring. A light blue precipitate, $\text{Cu}(\text{OH})_2$, will form initially, and will redissolve with the addition of more ammonia solution.

When all the ammonia is added, the solution should be a deep blue color with *no* precipitate present. This deep blue color results from formation of the complex, $\text{Cu}(\text{NH}_3)_4^{2+}$. If any precipitate is present, add additional ammonia solution 1 mL at a time, with stirring, until all the precipitate is dissolved.

Measure 150 mL of concentrated carbonic acid solution, H_2CO_3 into a 250 mL beaker. *Slowly* add the carbonic acid to the deep blue solution in the beaker. (Carbonic acid solution in the form of Club Soda can be purchased in local supermarkets, and is the source of CO_3^{2-} in this experiment.)

Stir the mixture well, then pour the mixture into several large test tubes and place them in a 600-mL beaker of boiling water which will serve as a constant temperature bath. Heat the water bath and test tubes to boiling, 100°C, and continue heating for 20 minutes. Check the temperature regularly and regulate the hot plate, or Bunsen-burner flame, to maintain a temperature as close to 100°C as possible. At lower temperatures the heating time must be increased.

At the end of the heating time, allow the sample to cool for a few minutes outside the water bath.

Filter the malachite mixture through a funnel lined with filter paper. If the filter paper becomes clogged, remove it from the funnel and save it on a watch glass. Add a new piece of filter paper to the funnel and continue filtering the malachite solution.

After filtering, remove the filter paper containing the precipitate, place on a watch glass, and allow to dry thoroughly. The total sample should be left to dry overnight or until the next laboratory class.

You may have difficulty cleaning the green residue from the test tubes used for heating the samples. This residue is easily removed by rinsing the test tube with a 1.0M solution of nitric acid, HNO_3 , before washing them with soap and water.

Next laboratory class. Determine the mass of the malachite you made.

Mass of malachite obtained _____ g

Verification Tests

Properties (3) of pure crystalline malachite: monoclinic crystals; specific gravity(density), 3.9 to 4.03; color, bright green; luster, vitreous, silky; streak, green; pH, 7; soluble in acid; decomposed when heated.

Now the question is, do you really have malachite? Collect samples of the precipitate from several members of your class and determine the specific gravity (or density) of the combined sample. To determine the specific gravity, first weigh your dry sample and record the mass. Place 7.0 to 8.0 mL of water in a 10-mL graduated cylinder. (If your yield of malachite is large, add it to 10.0 mL of water in a 25 mL graduated cylinder.) Record the volume of the water. Add the weighed malachite sample to the water in the graduated cylinder. It may be necessary to tap the graduated cylinder with your finger to remove any air bubbles. Read the volume of the malachite and water. Determine the change in volume. Divide the weight of the dry sample in grams by the milliliters of volume change of the water observed in the cylinder and compare your

results with those given above. Save the malachite sample for further tests.

Volume of water used _____ mL

Mass of the malachite sample _____ g

Volume of the malachite sample _____ mL

Density of the malachite sample _____ g/mL

Next, carefully wash a sample of the malachite with several small portions of distilled water. Then pour 25 mL of distilled or deionized water into a clean mortar and add the washed malachite. After about five minutes, check the pH of the water with pH paper. Next gently grind the precipitate in the water for about two minutes, and re-check the pH of the water. Compare your results with those given above.

pH of water after 5 minutes _____

pH of water after grinding the malachite _____

Look at the formula of malachite, given earlier in this experiment. Predict what will happen if you add some hydrochloric acid, HCl, onto a dry sample of malachite. Try the procedure by adding a few drops of 1.0 M hydrochloric acid, HCl, onto a dry sample of the precipitate. Does it agree with your predictions? Does your prediction and observation agree with the expected behavior of a compound containing the CO_3^{2-} ion with an acid?

Borrow a sample of the real mineral, malachite, or study a color photo of a multitinted layered specimen. What causes the color to vary from light tints of green to darker tints of green?

Take a small sample of the malachite and heat it very gently in an evaporating dish using a Bunsen burner. Observe what happens to the color. Speculate about what might cause some of layers to be darker green in color. Now continue to heat the sample strongly. Predict the chemical formula for the resulting decomposition product.

References

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