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# A Two-Message Sign

Can one sign have two invisible messages? In this activity one reagent reveals a hidden message and the second reagent erases the first message and develops a new one.

## Activity Guidelines

This activity is most effective as a demonstration.

## Time

Getting Ready: 15-30 minutes
Doing the Activity: 5 minutes

## Materials

- 25 mL of phenolphthalein indicator solution
- 25 mL of thymolphthalein indicator solution
- 20 mL of vinegar
- 50 mL of 0.1 M sodium hydroxide {NaOH} solution
- 50 mL of 5% potassium thiocyanate {KSCN}
- 50 mL of 5% potassium hexacyanoferrate(II) solution (also named potassium ferrocyanide) {$K_4Fe(CN)_6$}
- 50 mL 1% acidified iron(III) chloride {$FeCl_3$} solution
- sheets of chromatography paper or white construction paper, paper towels, or coffee filters
- two household spray bottles
- three water-color-type paint brushes or cotton-tipped applicators
- masking tape to hang the painted sign

## Safety and Disposal

Wear goggles during both the preparation of the solutions and presentation of this demonstration.

Dust, pellets, and concentrated solutions of sodium hydroxide {NaOH} are very caustic. They can cause severe chemical burns

and destroy cell membranes. Contact with the skin and eyes must be prevented. Should contact occur, rinse the affected area with water for 15 minutes. If the contact involves the eyes, medical attention should be sought while the rinsing is occurring.

Concentrated solutions of hydrochloric acid are very corrosive. They can cause severe chemical burns. The vapor is extremely irritating to the skin, eyes, and respiratory system. Should contact occur, rinse the affected area with water for 15 minutes. If the contact involves the eyes, medical attention should be sought while the rinsing is occurring.

When diluting acids, ALWAYS ADD ACID TO WATER, not the reverse. The heat given off in the dissolving process can cause splattering if the procedure is not carried out in the correct sequence.

Potassium hexacyanoferrate (II) MUST NOT be mixed with hot or concentrated acids. This may cause hydrogen cyanide, an extremely toxic gas, to be produced. Solutions of hydrogen cyanide and the gas itself can be absorbed through the skin and are a fast acting poisons. Cyanide compounds should not be stored or transported with acids. Anyone exposed to hydrogen cyanide should be removed from the contaminated area immediately. Medical attention should be sought immediately. Mouth-to-mouth resuscitation should NOT be used. The Silvester method of resuscitation should be applied if the person is not breathing.

Unused solutions can be saved for further use. Solutions can be saved in the spray bottle for future use only if the sprayers are removed and rinsed with water. Otherwise, the sprayers become clogged with dried salt, and they are difficult to clean once this happens. Alternatively, the solutions used in this activity can be diluted with water and flushed down the drain.

## Getting Ready

**Prepare Paper (optional):**
Spray the paper with water and allow it to dry. This causes the paper to wrinkle slightly so that the "painted" areas will be less visible.

**Prepare Solutions:**

1. Purchase indicator solutions from a chemical supply company or prepare the solutions as follows:

- To prepare phenolphthalein indicator solution:
  - ❑ dissolve 0.05 g of phenolphthalein powder in 50 mL of ethyl alcohol and dilute the resulting solution to 100 mL with water;
    or
  - ❑ crush an Ex-Lax® tablet (do not use chocolate flavored as the brown color may detract from the pink phenolphthalein color) and cover with about 10-20 mL of rubbing alcohol. The alcohol solution will contain dissolved phenolphthalein. The filler from the tablet will remain undissolved. You can filter the mixture to remove the filler and collect the phenolphthalein solution.

- To prepare thymolphthalein indicator solution: dissolve 0.04 g of thymolphthalein in 50 mL of ethyl alcohol and dilute the resulting solution to 100 mL with water.

If the indicator solutions are colored, add dilute acid (e. g., vinegar) drop by drop, while stirring, until the color just disappears.

2. Prepare the 0.1 M sodium hydroxide solution by dissolving 0.2 g sodium hydroxide in 50 mL distilled water (or one-quarter teaspoon of lye in one-half cup of water). Place this sodium hydroxide solution into a spray bottle.

3. Prepare the 5% potassium thiocyanate solution {KSCN}. by dissolving 2.5 g of potassium thiocyanate in 50 mL of distilled water.

4. Prepare the 5% potassium hexacyanoferrate (II) solution {$K_4Fe(CN)_6$} by dissolving 2.9 g of potassium hexacyano-ferrate (II) trihydrate, $K_4Fe(CN)_6 \cdot 3\,H_2O$ (s), in 50 mL of distilled water.

See Safety and Disposal for handling and disposal of these solutions.

5. Prepare the 1% acidified iron (III) chloride solution {$FeCl_3$} by dissolving 0.8 g of iron(III) chloride hexahydrate, $FeCl_3 \cdot 6\,H_2O$ in 50 mL of 0.1 M hydrochloric acid {HCl}.) (To prepare 0.1 M hydrochloric acid, add about 10 drops of concentrated hydrochloric acid to 50 mL of water.) Place this acidified iron(III) chloride solution into the second spray bottle.

ALWAYS ADD THE ACID TO THE WATER to avoid splattering.

**Prepare the messages:**

Place a pencil mark on top of the sheet of paper (so you know which way to position the paper when it is dry). Paint your messages on the paper. Use the appropriate solution to achieve the results described below:

First Message: (developed with the sodium hydroxide solution)

- ❑ phenolphthalein solution gives pink writing when sprayed with the sodium hydroxide solution.

- ❑ thymolphthalein solution gives blue writing when sprayed with the sodium hydroxide solution.

Second Message: (developed with acidic iron(III) chloride)

- using potassium thiocyanate solution gives blood red writing when sprayed with acidic iron(III) chloride.
- using potassium hexacyanoferrate(II) (potassium ferrocyanide) solution gives blue writing when sprayed with acidic iron(III) chloride solution.

The acidic iron(III) chloride, used to develop the second message, causes the first message to disappear.

To prevent smearing and running together of the messages allow one message to dry before painting the second message on top of it.

Do not leave the sprayer assemblies in these solutions for extended periods of time as the sprayer nozzle will clog. When not in use, remove the sprayer and store the bottle covered with a stopper or a lid. Rinse each sprayer thoroughly with water before storing.

## Doing the Activity

1. Hang the paper on the wall, an easel, or a piece of string stretched between two ring stands or other supports.

2. Develop the phenolphthalein and/or thymolphthalein message first by spraying with the 0.1 M sodium hydroxide solution. (If both were painted, both will develop simultaneously.)

3. To erase the first message and develop the second message painted with potassium thiocyanate and/or potassium hexacyanoferrate(II), spray with the acidic iron(III) chloride solution.

When spraying, moisten just enough to develop the message; excessive spraying can cause smearing and running.

## Explanation

Phenolphthalein is an acid-base indicator. It is colorless in solutions below pH 8 where its colorless acid form predominates, and it is pink in basic solutions above pH 10 where its colored base form predominates. Thymolphthalein is also an acid-base indicator. It is colorless in solutions below pH 9 where its acid form predominates, and it is deep blue in basic solutions above pH 11 where its colored base form predominates.

When sprayed with the sodium hydroxide solution, the basic color predominates. When the acidic solution of iron(III) chloride is sprayed on the colored phenolphthalein or thymolphthalein indicators, they change back to their colorless acid forms and the message disappears.

The second set of colors results from iron(III) complexation reactions. The thiocyanate ion {$SCN^-$} in the potassium thiocyanate message reacts with the iron(III) ion {$Fe^{3+}$} in the acidified iron(III) chloride solution of the spray, resulting in a blood red color (this is a sensitive test for iron):

$$Fe^{3+}\ (aq) + SCN^-\ (aq) \longrightarrow FeSCN^{2+}\ (aq)$$

The hexacyanoferrate(II) ion {$Fe(CN)_6^{4-}$} from the potassium hexacyanoferrate solution reacts with the iron(III) ion {$Fe^{3+}$} in the acidified iron(III) chloride solution of the spray, resulting in a dark blue precipitate, Prussian blue. The reaction is as follows:

$$K^+\ (aq) + Fe^{3+}\ (aq) + Fe(CN)_6^{4-}\ (aq) + H_2O(l) \longrightarrow KFe\,[Fe(CN)_6]\cdot H_2O\ (s)$$

## Curriculum Integration

Some suggested uses of this activity include units on acid-base indicators, formation of iron(III) complexes, or evidence of a chemical reaction. It can also be used as an attention-getter.

## Reference

Shakhashiri, B. Z. *Chemical Demonstrations;* University of Wisconsin Press: Madison, WI, 1983; Vol. 1. pp 338-343.