Chemical Flags: Red, White, Blue, and Beyond

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Abstract: Dramatic color-changing displays, where a reagent is added to clear solutions to produce brightly colored patterns, are described for use on an overhead projector or document camera. Based on the classic "Red, White, and Blue" demonstration, where ammonia is added to beakers containing phenolphthalein, lead(II) acetate, and copper(II) nitrate, we have adapted this as a projection display using 96-well plates and automatic pipettes. The two-dimensional nature of the 96-well plates enables the production of interesting patterns, such as flags, words, logos, etc. The color-changing reagent can be added as a liquid from a wash bottle, as an aerosol from a spray bottle, as a gas from a concentrated solution, or most conveniently as a solid, which needs to be sieved to an appropriate size. The best display is made by adding solid NH_4SCN to solutions of Fe^{3+}(red), Ag^{+}(white), and Co^{2+} in alcohol (blue).

Introduction

Color-changing demonstrations utilizing the colors red, white, and blue have been in use for a number of years [1–9]. One of these classic demonstrations involves placing small quantities of solutions of phenolphthalein, lead(II) ions, and copper(II) ions in separate beakers [3]. The copper solution initially appears very pale blue, the other two solutions appear colorless. When aqueous ammonia solution is added to the three solutions the colors change: The phenolphthalein solution turns pink-red as this acid–base indicator comes into contact with the basic ammonia solution, the lead solution forms a white precipitate, lead(II) hydroxide, and the copper solution turns dark blue with formation of tetraamminecopper(II) complex. Many variations on this demonstration, using various reagents, assorted demonstration geometries, and even different colors have been studied.

This paper introduces a variation involving color-changing solutions distributed throughout a multi-well plate, Figure 1. When the solutions in the well plate are activated with the proper reagent, the relatively colorless solutions change to colored solutions. This demonstration looks spectacular up close and also works well with overhead projectors or document cameras. In addition, this paper provides listings of simple recipes to produce many different colors, Figure 2. The combination of multiple colors and spatial distribution enables many different patterns to be produced from colorless solutions. (Note that the gas phase reaction described below starts with solutions that are all yellowish to achieve red, colorless, and blue.) Potential patterns of interest include logos, words, or flags from a multitude of nations.

Experimental

Repetitive filling of the wells in the well plates can be tedious. A conventional eyedropper for dispensing reagents may be sufficient, but for plates with small wells the drops dispensed can be too large. For example, each well in a 96-well plate may only have a capacity of 250 μL. In many cases 50 μL in each well are sufficient for effective demonstrations. For large drops in small wells, the surface tension of the drops can trap air at the bottom of the wells, preventing the drops from completely entering the well and sometimes causing to spill over the edges of the well. A micropipette, with its narrow tip and small dispensing volume is highly recommended for dispensing the appropriate reagents [10]. Once the wells are filled, covering them with plastic wrap will minimize evaporation.

There are multiple methods of activating the solutions in the well plates. These methods range from spray bottles to wash bottles to powder shakers; even reactants in the gas phase can be used. There are advantages and drawbacks to each. All methods are somewhat sloppy; that is, in order to fill all the wells relatively quickly the reagent of choice must be dispensed with some disregard as to whether all of the reagent actually makes it into the wells. To prevent contamination of the demonstration areas, the well plates should be placed on the bottom of a shallow transparent plastic or glass container (a glass cake pan works well). For gas-phase reactants, the cake pan can be covered with transparent plastic wrap to safely trap the gases.

Solutions can be dispensed from a hand-pumped spray bottle, such as one used for window cleaning solutions, or from a wash bottle, such as the deionized water wash bottles that are ubiquitous to every general chemistry laboratory. Powdered solid reagents can be dispensed from a salt-shaker-type device into the solution. A powder shaker can be made simply by poking small holes into the lid of a plastic container. Concentrated (~12 M) hydrochloric acid solution placed near the well plate can supply hydrogen chloride gas as an acidic reactant that diffuses from the acid, through the air, and into the solutions in the wells.

The following are recipes for the production of many colors as well as the reagents and methods used to activate these changes. A large number of reagents are listed, with varying degrees of toxicity. Ammonia and hydrogen chloride are corrosive irritants in both the gas phase and in solution and should be used with caution. The reader should take the time to review safety information such as materials safety data sheets for the particular chemicals to be used. For a 96-well plate with 250 μL wells, 20 to 50 μL of solution is often sufficient to constitute a "part".

Colors Produced by Spraying With Household Ammonia Solution.

Transparent Colors (useful on overhead projectors and document cameras).

- Colorless ("white"): just use water with a white background.

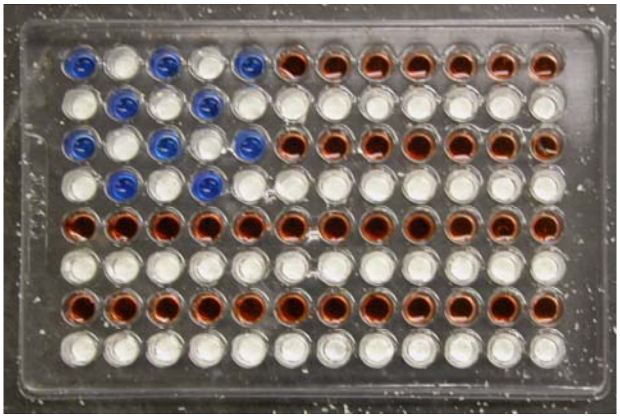

Figure 1. Solid ammonium thiocyanate sprinkled onto a 96-well plate flag reveals the colors red (iron(III) thiocyanate complex), white (silver(I) thiocyanate), and blue (cobalt(II) thiocyanate complex).

Figure 2. A handful of the colors available using base-activated indicators: (left to right) red, orange, yellow, green, blue, purple.

- Magenta: 0.05 g phenolphthalein indicator in 50 mL water and 50 mL 95 % ethanol turns in basic solution [1, 3, 4, 7, 11].
- Red: 1 part phenolphthalein indicator and 5 parts *m*-nitrophenol indicator mix turns in basic solution.
- Orange: 1 part phenolphthalein indicator and 17 parts *m*-nitrophenol indicator mix turns in basic solution.
- Yellow: 0.1 g *m*-nitrophenol indicator in 100 mL water turns in basic solution [1, 11].
- Green: 12 parts *m*-nitrophenol indicator and 1 part thymolphthalein indicator mix turns in basic solution.
- Blue: copper(II) ions form a complex with ammonia [3, 4, 12] .
- Blue: 0.04 g thymolphthalein indicator in 50 mL water and 50 mL 95 % ethanol turns in basic solution [1, 7, 11].
- Purple: 1 part phenolphthalein indicator, 1 part thymolphthalein indicator and 2 parts *m*-nitrophenol indicator mix turns in basic solution.
- Gray: 1 part phenolphthalein indicator, 28 parts *m*-nitrophenol indicator, and 3 parts thymolphthalein indicator mix turns in basic solution. NOTE: This is a difficult color to achieve in a consistent manner and this recipe might vary from batch to batch of solutions.

Opaque Colors (useful on document cameras).

- White: 0.2 M lead(II) ions form a precipitate with hydroxide ions [3].
- White: magnesium ions in saturated solution form a precipitate with hydroxide ions [1, 4, 13]. This works poorly because it requires too much ammonia solution to get even a weak effect.
- Orange: 0.1 M iron(III) ions form a precipitate with hydroxide ions [12].
- Brownish-black: 1 part 0.2 M manganese(II) ions and 1 part 3 % hydrogen peroxide mix precipitate manganese(IV) oxide, which catalyze the decomposition of excess peroxide to produce oxygen and water and create an intriguing foaming effect [12].

Colors Produced by Spraying with Saturated Iron(III) Ammonium Sulfate Solution.

- Transparent red: 0.2 M thiocyanate ions form a complex with iron(III) ions [1, 2].
- Transparent green: 0.1 M tartaric acid forms a complex with iron(III) ions [1, 2].
- Transparent yellow: 0.1 M hydrogen sulfite forms a complex with iron(III) ions [1, 2].
- Opaque blue: 0.2 M ferrocyanide ions form a precipitate with iron(III) ions [1, 2].
- Opaque white: 0.1 M barium ions form a precipitate with sulfate ions [1, 2].
- Transparent black/gray: tannic acid or tea forms a precipitate with iron(III) ions. Various types and quantities of teas give differing shades of gray. [1, 2, 13].

Colors Produced by Spraying with 0.01 M Iron(III) Chloride Solution.

- Transparent red: 0.2 M thiocyanate ions form a complex with iron(III) ions [2, 14].
- Opaque blue: 0.2 M ferrocyanide ions form precipitate with iron(III) ions [2, 14].
- Opaque white: 0.2 M silver(I) ions form a precipitate with chloride ions [14].
- Colorless (“white”): just use water with a white background.

Colors Produced by Spraying with 0.05 M Copper(II) Chloride Solution.

- Opaque red: 0.2 M ferrocyanide ions form a precipitate with copper(II) ions [12].
- Opaque blue: household ammonia forms a complex with copper(II) ions [3, 12].
- Opaque white: 0.2 M silver(I) ions form a precipitate with chloride ions [12].
- Colorless (“white”): just use water with a white background.

Colors Produced by Sprinkling with Solid Sodium Hydrogen Carbonate.

- Opaque magenta: 0.05 g phenolphthalein indicator in 50 mL water and 50 mL 95 % ethanol turns in basic solution [1, 3, 4, 7, 11].
- Opaque blue: copper(II) ions form a precipitate with carbonate ions. Copper(II) nitrate solutions are sufficiently acidic to produce carbon dioxide fizzing as the hydrogen carbonate decomposes.
- Opaque white: solid sodium hydrogen carbonate deposits at the bottom of the wells.
- Opaque yellow: 0.1 g *m*-nitrophenol indicator in 100 mL water turns in basic solution [1, 11].

Colors Produced by Sprinkling with Solid Ammonium Thiocyanate.

- Transparent red: 0.001 M iron(III) ions form a complex with thiocyanate ions [12].
- Transparent blue: 0.1 M cobalt(II) ions in 95% ethanol solution form a complex with thiocyanate ions [6, 12].
- Opaque white: 0.2 M silver(I) ions form a precipitate with thiocyanate ions [12].
- Colorless (“white”): just use water with a white background.

Colors Produced by Sprinkling with Solid Sodium Chloride:

- Transparent yellow: 0.2 M iron(III) ions form a complex with chloride ions [15].
- Opaque white: 0.2 M silver(I) ions form a precipitate with chloride ions [12].

Colors Produced by Contact with Hydrogen Chloride Vapor. 150 μL volumes are recommended for this experiment.

- Transparent red (from yellow): 0.02 g methyl red indicator in 40 mL water and 60 mL 95 % ethanol is diluted 1:4 indicator:water and then made yellow with the addition of a minimal amount of 6 M NaOH. This turns back to red in acidic solution [11].
- Colorless (from yellow): 0.1 g *m*-nitrophenol indicator in 100 mL water is diluted 1:4 indicator:water and then made yellow with the addition of a minimal amount of 6 M NaOH. This turns back to colorless in acidic solution [11].
- Transparent blue (from yellow): 0.1 g indigo carmine indicator in 100 mL water made then made green-yellow with the addition of NaOH. (Add approximately 0.25 mL of 6 M NaOH to 3 mL of indicator solution). The basic (yellow) form of indigo carmine degrades over time, possibly by air oxidation [16]. Therefore it should be used as quickly after preparation as possible (preferably within a half-hour). This yellowish solution turns back to blue in acidic solution [11].

Results and Discussion

There are advantages and drawbacks to each of the activator reagent dispersion methods. The powder sprinkler best enables materials to remain in the demonstration area. Sprinkling baking soda (solid sodium hydrogen carbonate) into the wells of the plate is particularly safe and simple. A potential drawback to this method is that high concentrations of reactant can end up in the wells, making the resulting solution too dark. For example, sprinkling potassium thiocyanate into 0.2 M iron(III) nitrate solution yields an intense, nearly black solution rather than the desired red solution. If a solid reactant is placed in the wells to produce a precipitation reaction, the precipitate may quickly form around the crystal of solid before it can disperse throughout the well and produce a uniform coloration of the well. For example, sprinkling potassium thiocyanate into 0.2 M silver(I) nitrate solution yields a white precipitate, but it is not evenly dispersed throughout the well. To help remediate these problems, finely divided powders should be used. Ordinary saltshakers work well for dispensing finely powdered reagents. A flour sifter can be used to help break up powder clumps. Some salts, such as ammonium thiocyanate, can extract moisture from the air to make salt solutions that corrode metal containers or shaker lids; therefore these salts should be kept as dry as possible. Containers with plastic bodies and lids, with an extra plastic lid to help seal out moisture, are recommended (e.g., from the Tupperware Corporation, Orlando, FL). Aqueous solutions cannot be dispensed by the powder sprinkling method because the solution droplets tend to coalesce into much larger droplets before they leave the container.

Solutions can be dispensed with wash bottles. The solutions in the well plates can be splashed out of the wells if reagent is added with sufficient force; therefore, the droplets of reagent dispensed must be small and must fall gently into the wells. The stream of the wash bottle should not be aimed directly into the wells, but should be angled across the plate so that the droplets fall a short distance to the wells. In many cases, a small amount of cross-contamination between the wells due to splashing is tolerable.

The smallest droplets, produced by a spray bottle, would logically cause the least splashing. Sprays of sodium hydroxide solutions have been suggested for colorizing "invisible painting" demonstrations [1]. The drawback to this method is the small droplets can drift more easily in air currents and also evaporate more easily to introduce reagent into the air. This can lead to release of reagent beyond the demonstration area. For example, many colors can be produced by spraying appropriate solutions in well plates with household ammonia solution; however, dispensing household ammonia solution from a spray bottle releases some gaseous ammonia into the air, which can be an irritant. Appropriate ventilation and brief use of the spray bottle can help minimize this release.

Gas-phase reactants require the more care with respect to containment, but, as noted above, this can be achieved relatively easily with plastic kitchen wrap over a glass baking pan. Spraying the wrap with antifog solution (such as that used for swimming or skiing goggles) helps keep the wrap from fogging up during the demonstration. The well plate with base-treated indicators is placed in the pan and the pan is covered with the plastic wrap. About 25 mL of concentrated hydrochloric acid can then be placed in the pan under the plastic wrap. A large plastic syringe with the tip covered works well to transport the acid to the pan. The acid is injected under a corner of the wrap. (Lift a corner of the wrap to inject the acid and remember to reseal the pan when injection is finished.) The acid will spread across the pan: under, but not covering, the well plate. The hydrogen chloride that diffuses from the acid to the wells will change the colors of the indicators at different rates. The methyl red and *m*-nitrophenol indicator wells change in approximately 3 to 4 minutes, the indigo carmine indicator wells change in about 12 minutes. The basic (yellow) *m*-nitrophenol indicator is also able to change to colorless when dry ice is added to the pan as a carbon dioxide source for the formation of carbonic acid in the wells.

The colors of some of the color-changing reagents appear to continue to slowly shift after the colors have been activated. UV–vis spectroscopy shows that some indicators shift in color over time in basic solutions. The pink color of the phenolphthalein indicator will fade irreversibly over time, apparently due to air oxidation [17]. Much of the color shifting observed in these demonstrations appears to be a result of activator reagent such as ammonia solution initially located at the top of each well and mixing more deeply into the color-changing solutions.

When the demonstration is finished, make sure the well plates are thoroughly cleaned. Some indicators are susceptible to contamination to deposits of acidic or basic material. During cleaning, soap appears to help air bubbles trapped in the wells to be released, enabling more effective cleaning

Conclusions

A number of color-changing reactions and means of initiating these reactions have been described. By distributing these reactions into the wells of 96-well plates, these attractive reactions become even more spectacular. A micropipette is highly recommended for repeatedly dispensing these reagents. Classroom connections that can be made with the demonstrations include topics such as acids and bases and solubility. The ammonia-activated red, white, and blue flag demonstration described in Figure 1 has been used for the last few years to open science demonstration shows at Bradley University. The most striking and chemically interesting demonstration is the red, white, and blue flag made by adding solid ammonium thoicyanate to Fe^{3+}, Ag^{+}, and Co^{2+} solutions on a document camera.

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