

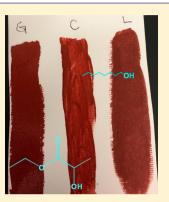
Chemistry and Art: Removal of Graffiti Ink from Paints Grounded in a Real-Life Scenario

Joan M. Esson,*[®] Rachael Scott, and Carrigan J. Hayes

Department of Chemistry, Otterbein University, 1 South Grove Street, Westerville, Ohio 43081, United States

Supporting Information

ABSTRACT: An activity that brings together chemistry and art, incorporates a real-world incident, and asks students to consider concepts of solubility is described. The activity was inspired by the vandalism of a modern art painting with graffiti ink, and it has students (i) determine the solubility of the ink in solvents of various polarity; (ii) predict which solvents would remove the ink while preserving the underlying paints, made using various binders, via the concept of "like dissolves like"; and (iii) conduct an activity to prove or disprove their hypotheses. Students work in groups of two to four on this 3 h activity, which was originally designed as an undergraduate general chemistry laboratory but could be adapted to a high school chemistry classroom or outreach event.



KEYWORDS: First-Year Undergraduate/General, Interdisciplinary/Multidisciplinary, Laboratory Instruction, Hands-On Learning/Manipulatives, Dyes/Pigments, Molecular Properties/Structure, Noncovalent Interactions

INTRODUCTION

Undergraduate laboratory activities and courses at the interface of chemistry and art have been described previously in this *Journal*, and many of these have involved pigment or paint synthesis and analysis.^{1–11} This paper describes a new laboratory activity at the interface of chemistry and art, incorporating noncovalent interactions and the concept of "like dissolves like".

This activity was inspired by a talk given by Mindy Keefe of Dow Chemical at a Columbus American Chemical Society local section meeting. In this talk, Keefe described her collaboration with the Tate Museum, working to identify solvents that would remove graffiti ink from a Mark Rothko painting.¹² In October 2012, the Rothko painting Black on Maroon had been vandalized when someone wrote on it with black graffiti ink. The suspect was caught, and the specific Molotow graffiti ink used was found in his possession. Thus, the conservators knew the identity of the ink, which aided in their search for appropriate solvents that would remove the ink without damaging the painting.¹³ This real-life scenario, which is documented in various media,^{14–17} provides a hook to engage students in the learning experience. In this activity, students are asked to take on the role of the scientist aiding the conservator and to explore (i) the solubility of the ink and (ii) which solvents would remove the ink without damaging an underlying painting.

This activity was developed by chemistry faculty in conjunction with an undergraduate student who provided feedback about time requirements, necessary laboratory materials, and clarity of the provided experimental protocols. Involving undergraduates in the planning/piloting phase was helpful to ensure successful implementation of the activity during a 3 h General Chemistry II laboratory session that was run in five different laboratory sections with a maximum capacity of 24 students each.

■ THE ACTIVITY

Students are introduced to the vandalism of Rothko's Black on Maroon using clips from YouTube videos.^{16,17} Pertinent background information is provided with respect to the basic composition of a painting [canvas, primer, painting (containing pigment and binder), and varnish] and the fact that Rothko used varying techniques and materials, complicating the exploration of solvents that would remove ink from the painting. Thus, in their analysis, students are expected to study the effect of the ink on multiple types of paints. In this exercise, students work in groups of two to four to achieve four objectives. First, they explore the solubility of the graffiti ink in solvents of varying polarity. Second, they create three paints, using a common pigment (red iron oxide B) in each of three binders: casein, linseed oil, and gum Arabic.¹⁸ Third, they use their previous observations of the graffiti ink solubility, as well as their knowledge of the binder and solvent structural formulas, to predict which solvents will remove the graffiti ink from a painting without affecting the painting itself. Finally, they carry out an experiment to examine their predictions. A

Received:July 18, 2017Revised:December 13, 2017Published:January 24, 2018



Journal of Chemical Education

student handout and instructor guide are available in the Supporting Information.

Due to time constraints, it is best if the students create the three paints and paint a strip of each type on watercolor paper before considering other aspects of the activity. While the paint samples dry (this process can be sped up with a hair dryer if desired), the students choose two solvents of various polarity and determine the solubility of the ink in these solvents. Thus, although students are told to determine the ink solubility, there is still some student choice in the procedure, which increases their ownership of the activity. Further, since each group investigates only two solvents, students must discuss results with their classmates to see the full scope of how different chemical structures affect polarity. Five different solvents and their chemical structures are provided to the students: water, benzyl alcohol, ethyl lactate, dimethyl sulfoxide (DMSO), and 1-octanol, most of which were included in the analysis by the Tate staff.¹³ (The solvents used by the Tate staff and employed in our exercise all have measurable dipole moments associated with them; to further explore the effect of solvent polarity, an instructor adapting this activity could also include a nonpolar solvent such as hexane.)

The students are then directed to paint the Molotow graffiti ink over their now-dried paint samples. While the ink is drying, students consider both the structure of the paint binders and their newfound knowledge of the graffiti ink's solubility in order to choose a solvent that will remove the ink without disturbing the painting. In their decision-making process, students discuss noncovalent interactions that would exist between various combinations of the ink, binder, and solvent, and determine which solvent is the best choice, based on the concept of "like dissolves like". [Note that the same pigment is used in all paints to minimize the effect of pigment on the successful removal of the ink: that is, only the binders differ among the different paint samples. In our studies, different pigments were found to affect the results to some extent.] This provides another point at which the students are active decision-makers, increasing their ownership and engagement with the activity. Once the ink is dried, students then dip a cotton swab in their chosen solvents, rub it over the ink, and record their observations regarding ink removal and damage to the paint.

SAFETY

Students should wear appropriate personal protective equipment during the activity, including safety goggles and gloves. The solvents should only be used in well-ventilated areas, such as hoods, and without flame or heat nearby. Students should be encouraged to use minimal amounts of solvent. All solvents should be collected and disposed of properly. If they have severe allergies to dairy, students should only handle the linseed oil and gum Arabic binders.

RESULTS

The Molotow graffiti ink is described by the manufacturer as being an alkyd material; therefore, students should find that it dissolves in octanol, DMSO, ethyl lactate, and benzyl alcohol, but not in water. They should then conclude that water is not a suitable solvent to remove the ink from the painting, but that the other solvents might be. For the oil paints (paints made with linseed oil binder), octanol, DMSO, benzyl alcohol, and ethyl lactate remove the ink but also remove some of the underlying paint. None of the available combinations appear sufficient to remove only the ink from the oil paint in this activity. For the watercolor paints (paints made with gum Arabic binder), octanol, DMSO, and ethyl lactate are all able to remove the ink without damaging the paint. For the paints made with casein binder, only ethyl lactate is able to remove the ink without damaging the paint.

EXTENSIONS

Student groups compare their answers with those of other groups, extending their knowledge of chemical structure and its impact on the removal of ink added over paint layers. Instructors are cautioned that some students struggle with applying the concept of "like dissolves like" to this activity since they are used to looking at far simpler structures in lecture problems. Asking the students to circle polar regions of the molecules and consider the similarities and differences between the solvents and binders is helpful.

To extend the ideas of this activity, students are asked to propose additional experiments that they would do if they had more time. Students may come up with ideas such as considering the number of layers of paint, using different pigments in the paint, exploring the addition of varnish (which was omitted in the sample under study in this activity), and using mixtures of solvents rather than a single solvent for removal.

At the end of the activity, the combination of solvents used by the restorers at Tate Modern on Rothko's *Black on Maroon* is revealed, and students discuss whether or not their results were consistent with the findings of the restoration process.¹³

STUDENT FEEDBACK

This experiment was piloted in Spring 2017. Participating students were administered a survey adapted from the Advancing Science by Enhancing Learning in the Laboratory Student Laboratory Experience (ASLE) survey,¹⁹ which is available in the Supporting Information. The survey results indicated that 100% of students enjoyed the experiment and identified the main lesson to be learned as the relationship of structure and polarity. Further, 90% "strongly agreed" or "agreed" with the survey statement, "This experiment improved my understanding of structural factors that affect solubility", while the remaining 10% neither agreed nor disagreed. With respect to the length of the activity (3 h), 95% of students felt it was appropriate, while the other 5% felt that it was too long.

Since one of the action items for students was to predict which solvent would be best to remove the ink without affecting the paint, the ASLE survey statement "This experiment helped me develop my ability to hypothesize" was especially of interest to examine. Seventy-one percent of students "strongly agreed" or "agreed" with this statement, while the other 29% neither agreed nor disagreed. Last, the survey asked students which aspects of the experiment needed improvement, but no clear trends emerged, suggesting that this activity is appropriate as written and completed.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.7b00536.

Student handout (PDF, DOCX) Instructor guide (PDF, DOCX) Student survey results (PDF, DOCX)

AUTHOR INFORMATION

Corresponding Author

*E-mail: jesson@otterbein.edu. ORCID [©]

ORCID

Joan M. Esson: 0000-0003-1412-826X

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work is an extension of a project started with funding from the National Science Foundation (no. 1347243). The authors are also grateful to Julia Petry for help in conducting initial experiments, additional faculty who used this activity in their courses (Robin Grote, Brandon Crowe, and Wendy Johnston), and the students who took General Chemistry II in Spring 2017 who provided feedback about the activity.

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