

Quinacridone Red and Violet: An Infrared Surprise

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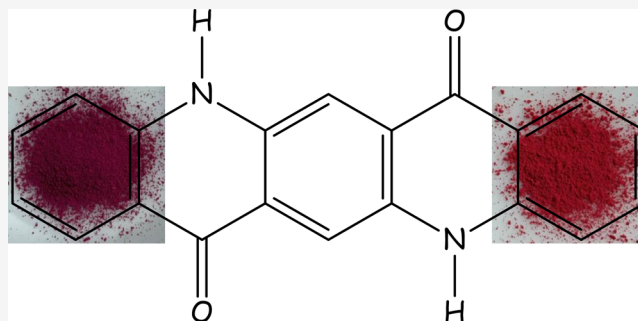
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ABSTRACT: Quinacridone red and violet are visually different colors, an observation confirmed by their visible reflectance spectra and CIE $L^*a^*b^*$ coordinates. However, their IR spectra are extremely similar. Though chemically identical, the two quinacridones are polymorphs. In this experiment, designed for and tested by nonscience majors, the pigments are extracted from oil paints with hexane in a short procedure involving sonification and centrifugation. ATR-FTIR spectra of the recovered brilliantly colored powders reveal the presence of a calcium carbonate filler in one of the two paints. Factoring out the carbonate bands, the spectra are nearly identical. Students must reconcile the evidence of color and the evidence of the spectra.

KEYWORDS: Nonmajor Courses, Laboratory Instruction, Hands-On Learning/Manipulatives, Applications of Chemistry, Dyes/Pigments, UV–Vis Spectroscopy, IR Spectroscopy



INTRODUCTION

The experiment described in this article is inspired by a recent paper in this *Journal* about isolating and identifying two quinacridone pigments in dried paint films using FTIR, FT-Raman, and powder XRD.¹ The original experiment, designed for students interested in conservation science in an advanced analytical laboratory, has been redesigned here to make an instructive, and even delightful, laboratory experience for nonscience majors in a course about artists' pigments and paints.

Long a popular subject in courses for nonscience majors and as topics within courses for chemistry majors, the chemistry of artists' materials has seen a resurgence of interest.^{2,3} An entire volume in the *ACS Symposium Series* was recently dedicated to ways in which art and chemistry have been incorporated at different levels of the undergraduate and high school curriculum.⁴ The experiment described here gives nonscience majors hands-on experience with a mid-20th-century synthetic organic pigment and ATR-FTIR, a technique generally only made available to students in organic chemistry or higher-level courses.

A first version of this experiment was tested by 28 students. The revised version described here was tested by 30 students. Typically, about one-fourth of the students are studio arts majors and one-fourth are art history majors, with the rest drawn from other majors outside science; all are sophomores or above.

In the first version, students extracted pigments from tubes of oil paints (arylide yellow, phthalocyanine blue, quinacridone red, and quinacridone violet) and identified structural features of the pigments from the infrared spectra. Students were entranced by the brightly colored powders they recovered from the paints and excited to use the FTIR spectrophotometer by themselves,

but this initial version lacked punch. In the absence of a specific goal, the laboratory reports were correspondingly diffuse.

In the second year, the samples were narrowed to quinacridone red and violet for reasons explained below. The procedure was almost the same as that used in the original work,¹ but the goal of the revised experiment was very different.

Quinacridones were first produced for industrial applications, such as automobile paints, in the late 1950s.⁵ Their first documented appearance as artists' pigments dates to 1964. Quinacridones are angular or linear aromatic pentacyclic compounds; all artists' quinacridones are linear (Figure 1). Their colors are mostly red, with some inclining toward orange and others toward purple depending on the ring substituents.

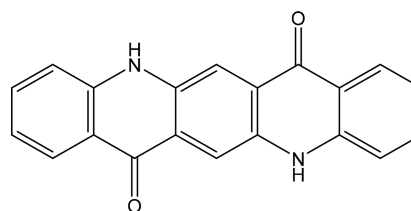


Figure 1. Quinacridone red and violet are polymorphs of linear *trans*-quinacridone.

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The colors are vibrant, transparent, and lightfast. Acrylic, oil, and watercolor tube paints and even the pigments themselves are available from art supply shops.

The paint swatches of the two quinacridones used in this experiment, shown in Figure 2, are readily distinguishable by

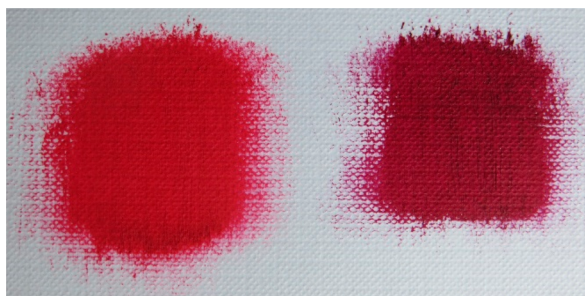


Figure 2. Quinacridone red (left) and violet (right) oil paint swatches on canvas paper.

eye. One is orange-red, the other violet-red. However, and this is the reason for choosing them, they are polymorphs, i.e., they are the same compound but with different crystal structures. The violet phase is designated β , while the more stable red phase is designated γ . In both, quinacridone forms four $\text{N-H}\cdots\text{O}=\text{C}$ hydrogen bonds. In the violet β phase, each quinacridone is hydrogen-bonded to one neighbor above and one below (see Figure 3). In the red γ phase, each quinacridone is hydrogen-bonded to two neighbors above and two below. References 6 and 7 show views of the crystal structures along different directions.

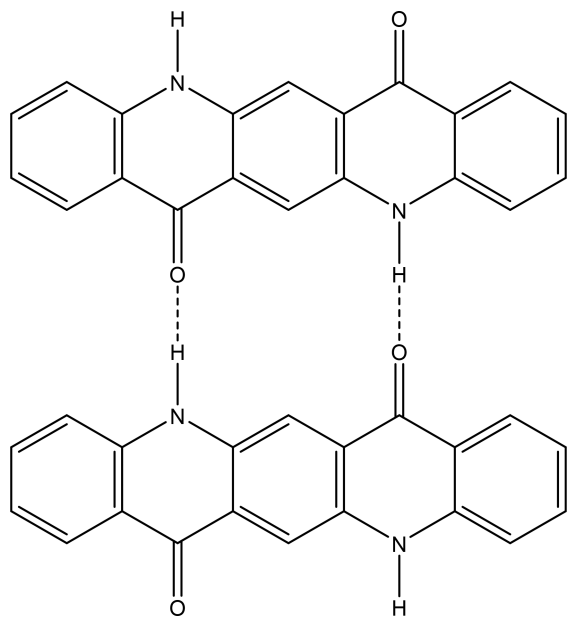


Figure 3. In red γ -quinacridone, each molecule forms hydrogen bonds to two neighbors (one shown), forming ribbons.

Pigments are identified by their common name and Color Index (C.I.) number. C.I. numbers are a more reliable guide to content than names, but they do not always distinguish between polymorphs.⁸ For instance, Gamblin's quinacridone red and quinacridone violet are both Pigment Violet 19 (PV19).⁹

In the experiment of Longoni and Bruni,¹ students were given the task of identifying which dried acrylic and oil paint films

contained PR122 (quinacridone magenta, 2,9-dimethylquinacridone) and which contained PV19 (quinacridone red). Interference from silica and calcite fillers and, to a lesser extent, traces of the acrylic binder that remained after solvent extraction made it difficult to make an identification based on the IR spectra alone; hence, the need for FT-Raman and powder XRD, which are not widely available in the undergraduate teaching laboratories.

Discovering that two visually distinct paint pigments are chemically *alike* rather than distinguishing between paints is the aim of this experiment. The data that lead to this conclusion are the CIE $L^*a^*b^*$ coordinates and reflectance spectra of paint swatches and the FTIR spectra of the pigments extracted from oil paints. The principal goal is to guide students to make the surprising discovery that, notwithstanding their color difference, the evidence of the infrared spectra shows that quinacridone red and violet are the same compound.

Although starting with samples of artificially aged paint is attractive because it simulates the type of samples conservation scientists work with, we decided to use fresh tube oil paints. We found that acrylic and oil paint films on glass slides remained tacky even after heating at 50 °C for an entire day, much longer than the couple of hours that were sufficient for drying in the original work.¹ Either our films were too thick, or the paints we used were formulated differently from those used in the original work. In that work, ethyl acetate was used as the solvent for the acrylic paint films and 1:1 chloroform/methanol for the oil paint films.¹ Perhaps because our aged films were overly hardened, the solvents were not as effective at removing the binders. As a result, the extracted pigments were not loose powders but tiny bits of slightly tacky film. Even quinacridone red pigment extracted directly from a tube of acrylic paint (Golden Acrylics) and extracted twice with ethyl acetate formed a film upon grinding with a mortar and pestle; the IR spectrum confirmed the lingering presence of the acrylic binder in the sample.

In contrast, linseed oil was easily removed from quinacridone red and violet paints using hexane.¹⁰ Moreover, the miscibility of triglycerides and hexane was easy for students to understand because dispersion forces were covered earlier in the course, and both of these molecules are small.

Extracting pigment from paint neatly mirrored the previous experiment in the course, namely, making paints from pigments students had prepared earlier in the course. Students took paint directly from a tube, mixed it with hexane, sonicated the mixture at room temperature to disperse the blob of paint in the solvent, and then centrifuged the mixture. The recovered pigments were bright and powdery in texture.

Students recorded the ATR-FTIR spectra of their extracted pigments. The presence of calcium carbonate in quinacridone violet, a fact omitted from the manufacturer's label, added an interesting twist. That only the pigment (PV19) and vehicle (linseed oil) were named on the label was eye-opening, especially for painters in the course. Fillers like CaCO_3 are added to adjust the consistency of a paint without adding more pigment or to simply create more volume. Students were told in advance that this additive was present in one paint but not which paint. Since CaCO_3 was used to demonstrate the operation of the ATR-FTIR spectrophotometer to students and its spectrum was posted to the Learning Management System (LMS), it was not difficult to identify in quinacridone violet's spectrum.

While waiting to use the centrifuge and the FTIR spectrometer, students measured the CIE $L^*a^*b^*$ coordinates

of the paint swatches using a reflectance spectrophotometer. A sample pair of reflectance spectra were posted to the LMS.

Students' Learning Goals

In summary, the principal goal of this experiment is to let students make the discovery that apparently dissimilar paints contain chemically identical pigments, thereby giving them firsthand experience with polymorphism. A second goal is to introduce students in an interesting way to infrared spectroscopy as a tool for the identification of polyatomic ions and organic compounds.

EXPERIMENT

Instruments

Color measurements were made by using an X-Rite Ci52 sphere spectrophotometer with the standard D65 illuminant. The CIE $L^*a^*b^*$ coordinates are generated from reflectances measured at 10 nm intervals from 400 to 700 nm. Students were familiar with the device, having used it regularly in the course.¹¹

FTIR spectra of the powdered samples were collected from 4000 to 650 cm^{-1} on a Thermo Scientific Nicolet iS10 instrument with a diamond ATR accessory. Although this was the students' first experience with the spectrometer, they navigated the process of recording a spectrum fairly independently following a demonstration and by observing their classmates at the instrument; written instructions provided additional support.

Experimental Overview

Students, working in pairs, chose either quinacridone red or quinacridone violet. A pea-sized blob of paint (100–200 mg) was transferred to a 50 mL polypropylene centrifuge tube. To this, they added 6 mL of hexane, shook the tube to mix any paint clinging to the sidewall into the solvent, and sonicated the tube in a room-temperature water bath for 5 min; at this point, the contents appeared homogeneous. The mixture was then inserted into a tabletop fixed-angle centrifuge and spun for 15 min (maximum rpm = 4400). Since the precipitate became firmly compacted at the bottom of the tube, students simply decanted the entire supernatant (which was colorless) into a beaker for later disposal. A gentle flow of compressed air was used to evaporate any residual solvent. The pellet was then dislodged from the tube by firmly tapping the inverted tube on a piece of filter paper and scooping out any remainder with a spatula; about half the initial mass was recovered as pigment. The pigment particles and flakes were then ground using an agate mortar and pestle, and about 10 mg was transferred to cover the diamond crystal of the ATR accessory. Students recorded the spectrum, labeled the peaks, and saved their file on the computer. Any unused pigments were collected in vials; the brilliantly colored powders are shown in Figure 4.

All seven student pairs were able to complete the above procedure from start to finish within 2 hours. Pairs first in line to use the single FTIR spectrometer finished earlier. Unless a pair inadvertently exited the software, it was not necessary to recollect a background spectrum, which saved time.

In the next class, the spectra were distributed to students in two formats. The first displayed two spectra, one each of quinacridone red and quinacridone violet, with their peaks labeled (Figure S1). During class discussion, it became apparent that the detail in this close-up view was overwhelming; students dwelt on comparing the peak labels and amplified the significance of minor shifts. The second format displayed all

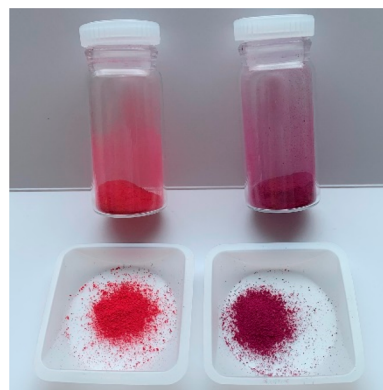


Figure 4. Quinacridone red and violet powders extracted from tube oil paints.

seven spectra collected by the class with the peak labels omitted (Figure 5). This ensemble, with its bird's-eye view, made an immediate, striking impression. The quinacridone red spectra were seen to be all alike, as were all the quinacridone violet spectra. Importantly, the two different sets were seen to be alike except for the strong band at 1404 cm^{-1} and the sharp band at 872 cm^{-1} . (Reference IR spectra of calcium carbonate, linseed oil, and PV19 are available from several sources.^{12–14}) With some prompting, students recollected that they had seen this pattern not only in the demonstration calcium carbonate sample in the laboratory but also in a recent class. (By design, in the class introducing infrared spectroscopy, several examples of IR spectra of samples containing carbonates were illustrated and discussed, e.g., in a chalk–glue ground,¹⁴ a Tibetan thangka,¹⁵ and Stuart Semple's "colouriest" powders.¹⁶ The CO_3 stretching and OCO bending vibrations were discussed at that time.) Students were left to ponder the meaning of all of this in their laboratory reports, whose results were discussed in the next section.

Full instructions from the laboratory manual distributed to students are included in the [Supporting Information](#).

HAZARDS

Quinacridone is mildly irritating to the skin with prolonged exposure and irritating the eyes. Hexane is flammable and can cause drowsiness or dizziness. Prolonged exposure should be avoided. Hexane was transferred to the centrifuge tube in a fume hood. The supernatant consisting of hexane and linseed oil was collected in a hazardous waste bottle, and the precipitate was dried in a fume hood.

DISCUSSION

For the laboratory report, students were asked to interpret the colors of the paint swatches based on the reflectance spectra and CIE $L^*a^*b^*$ coordinates. As for the IR spectra, students were asked to identify the paint containing calcium carbonate and compare features that are not due to the filler. Direction was purposely loose, as class discussion had virtually led students to the doorstep, and their task was to take the final step.

Color

In the discussion section of their laboratory reports, students readily established that quinacridone red and violet are different colors from visual observation and comparison of the $L^*a^*b^*$ coordinates of the paint swatches (Table 1) and reflectance spectra (Figure 6). Quinacridone red is lighter than

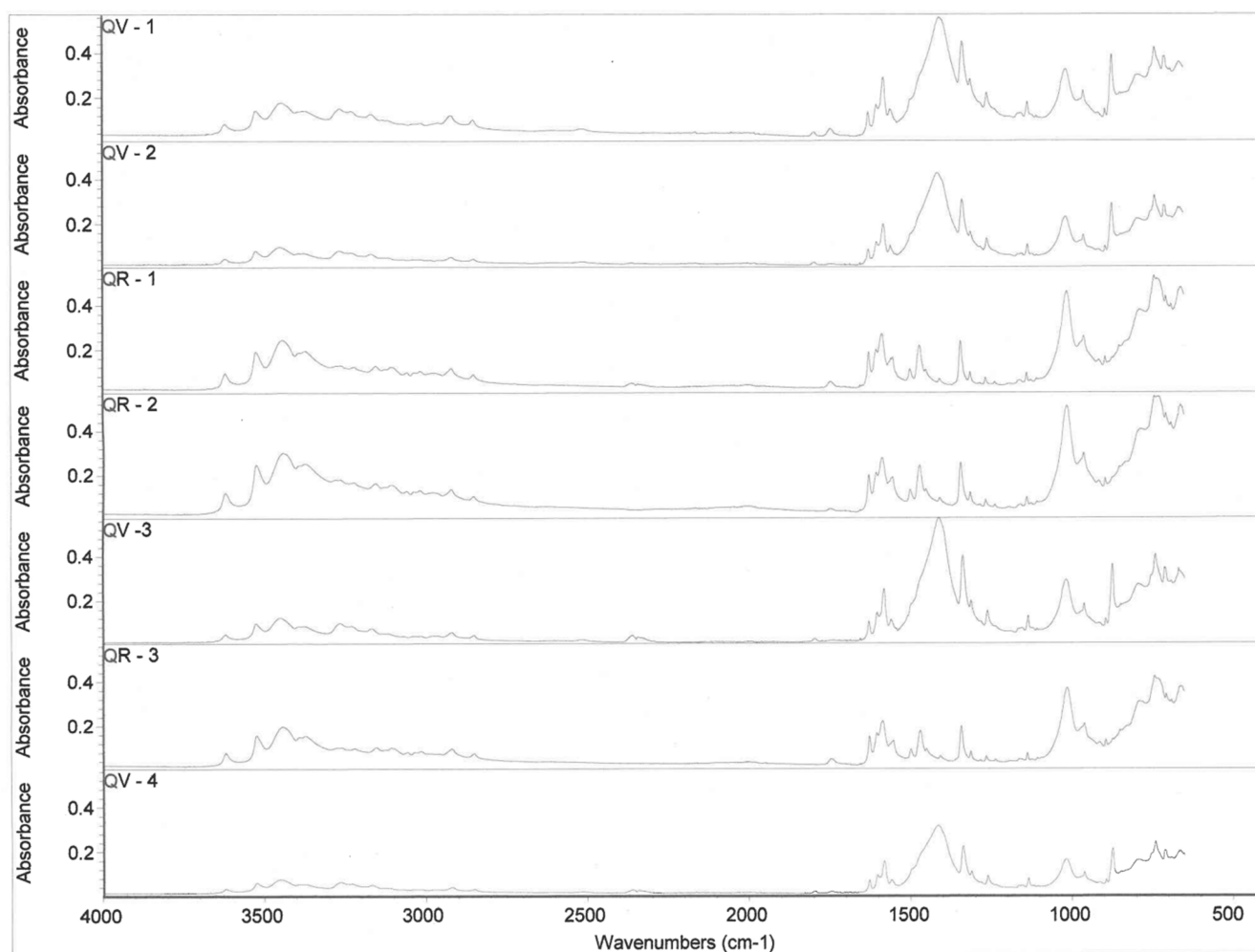


Figure 5. IR spectra of the pigment powders. They were not sorted by color to prompt students to look at them closely. The most prominent traces of the linseed oil vehicle may be seen in the C–H stretching region (2850–3000 cm^{-1}), but the strong C=O stretching band (1730–1750 cm^{-1}) is almost undetectable.^{12–14}

Table 1. Color Characteristics of Painted Swatches of Gamblin Artist's Oil Colors Quinacridone Red and Quinacridone Violet^a

Quinacridone	L^*	a^*	b^*	C
Red	43.0 ± 0.7	54.7 ± 0.7	24.9 ± 0.3	60.1 ± 0.6
Violet	31.1 ± 0.7	35.7 ± 1.4	8.3 ± 0.3	36.7 ± 1.4

^a L^* measures lightness on a scale of 0 to 100; positive a^* and b^* values indicate that the colors have red and yellow components, as opposed to green and blue components. C is the chroma, the radial distance of the a^* and b^* components from the origin located along the L^* axis. The averages and standard deviations are computed from measurements at five different spots on the swatches shown in Figure 1.

quinacridone violet (higher L^*) and more red (higher a^*) and more yellow (higher b^*). In other words, quinacridone red is a lighter orange-red, while quinacridone violet is a darker, nearly pure red. With higher a^* and b^* values than quinacridone violet, quinacridone red also has greater chroma, $C = (a^{*2} + b^{*2})^{1/2}$, or a richer color.

The reflectance spectra are very similar, with a high plateau in the red and orange regions (600–700 nm) and a broad, weak band in the blue (near 420 nm). However, the reflectance of

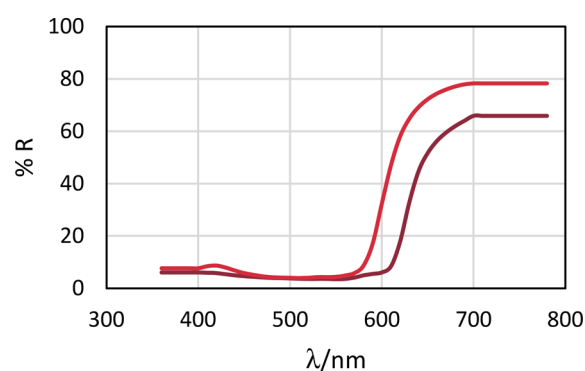


Figure 6. Reflectance spectra of the paint swatches shown in Figure 2: quinacridone red (upper curve) and quinacridone violet (lower curve). The RGB colors of the lines were calculated from the $L^*a^*b^*$ coordinates.¹⁷

quinacridone red is higher and shifted toward the left into the yellow region (550–600 nm), accounting for its lighter, more orange color.

IR Spectra

Interpretation of the spectra is at the heart of this experiment. With Figure 5 in hand and access to the spectrum of CaCO_3 , and

following the in-class discussion described above, students needed to take just one more step to come to the realization that quinacridone red and quinacridone violet are the same compound.

Although this is a big leap, it was not the first instance of polymorphism that students had encountered. Earlier in the course, they had prepared two varieties of lead chromate,¹⁸ one yellow, one orange, and looked at them under an optical microscope. The yellow crystals were bunches of long needles, while the orange crystals were much smaller particles.¹⁹ Students later encounter a third example of polymorphism, medieval frescoes in which vermilion α -HgS had blackened to β -HgS.^{20,21} Thus, quinacridone red and violet are not unique examples of polymorphs among artists' pigments.

DESCRIPTION OF ASSESSMENT OF LEARNING OUTCOMES

The effectiveness of this experiment hinged on whether students in their laboratory reports concluded that notwithstanding the measurably different colors of quinacridone red and quinacridone violet, the IR spectra showed that they were the same compound. In all of the 23 laboratory reports submitted, students correctly characterized the colors of the paint swatches based on the reflectance spectra and CIE $L^*a^*b^*$ coordinates. By this point in the semester, students were accustomed to interpreting these data; therefore, this outcome was expected.

Examining and interpreting the IR spectra (Figure 6) were a new challenge. Of the 23 reports, 19 discussed the IR spectra, 18 noticed that two bands present in the spectra of quinacridone violet were absent from those of quinacridone red, 13 attributed these bands to calcium carbonate, and 12 concluded that quinacridone red and violet were identical compounds. Disconcertingly, of the 18 who noticed that two bands present in one set of spectra were absent from the other, five did not know what to make of them, despite the laboratory manual noting that one paint contained a CaCO_3 filler and class discussion on this very point. Only half the students made the connection that quinacridone red and quinacridone violet are the same compound because their IR spectra are nearly identical, except for the peaks associated with the calcium carbonate filler. Considering that the evidence of the spectra contradicts the visual evidence, this was a difficult conclusion to reach. It must be remembered that the laboratory manual only asked students to (1) identify the paint containing filler and (2) compare the IR spectra; more direction was purposely omitted.

A sampling of the conclusions reached by students is given in the Supporting Information.

To bring the experience to a satisfactory conclusion for everybody, when the corrected laboratory reports were returned, the line of reasoning was reviewed with the whole class. In addition to discussing the IR spectra, the line bond structure of quinacridone (students had learned how to interpret them earlier in the course) and crystal structures of quinacridone red and violet were discussed. Students were reminded of the yellow and orange lead chromates they had made some weeks earlier, and the term polymorphism was added to their vocabulary. Also introduced was the Color Index system along with its limitations (quinacridone red and violet sharing the same C.I.) and the unreliability of descriptive paint names. Not only might different manufacturers give the same pigment different color names, but the same manufacturer might give different names to the same pigment in acrylic, oil, and watercolor.

CONCLUSION

About half of the students in the two trials of this experiment were able to overcome the evidence of their eyes and conclude that quinacridone red and quinacridone violet are chemically identical compounds. All students learned how to extract pigment from tube paint and record an ATR-FTIR spectrum. Continued discussion of this experiment introduced students to the term polymorphism and the Color Index system.

In retrospect, some changes might have resulted in a greater number of students drawing the correct inference from the set of IR spectra. One change would be to give greater emphasis to polymorphism earlier in the course and discuss both lead chromate and mercuric sulfide together instead of separately. A second change would be to eliminate CaCO_3 from the quinacridone violet powder, so that its IR spectrum matched that of quinacridone red. In the original work,¹ CaCO_3 was removed from the extracted pigment by treating it with 2 M HCl. Acid treatment works very well; a pair of infrared spectra taken before and after treatment are shown in Figure S2 along with an outline of the procedure. However, it does add time.

A third change that would not add much time would be to determine the mass percent of the pigment in the paint. Students would need to record the masses in three stages: the mass of the empty centrifuge tube, its mass with the initial paint sample, and its mass after centrifugation and drying. Gamblin's quinacridone red and violet are about 60–65% pigment (including CaCO_3 in the latter case). The calculation would exercise students' quantitative thinking, and students, especially the painters, would find the result quite interesting. Typical results are shown in the instructors' notes.

This experiment would make a thought-provoking addition to any course in which infrared spectroscopy is introduced as a means of identification.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available at <https://pubs.acs.org/doi/10.1021/acs.jchemed.3c00316>.

Supplies, chemical hazards, laboratory equipment, instructors' notes, IR spectra with peak labels, IR spectra of quinacridone violet before and after acid treatment, reference spectra, and excerpts from laboratory reports (PDF, DOCX)

Laboratory procedure for students (PDF, DOCX)

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Notes

The author declares no competing financial interest.

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