



Spectroscopy and Forgery

Edwin Cole had been interested in art since his USC days. When he dropped out of graduate school in 1988, he never imagined that he would become a wealthy collector of fine art. After amassing billions in an Indochinese, then Chinese, telecom venture with a fellow USC dropout, he decided to "give something back."

Edwin found a convenient mechanism for his philanthropy: donating artwork to public museums all over the world. He had traveled extensively with his wife Libby and collected major and lesser-known works. He also developed a keen interest in finding undiscovered artwork. For instance, in 1992 he discovered a new van Gogh that a Japanese businessman had kept private in his family estate for over 50 years.

As his dinner guests arrived on Friday evening, Edwin's eyes were flashing. The guests were buzzing with speculation on what piece Edwin had found this time. Edwin's closest friend, Daniel, made his way across the room.

"You've done it again, haven't you? What did you find this time, another Van Gogh?" chided Daniel.

"Daniel, there are paintings out there that need to be seen."

"Edwin, I think you've already tracked down all the credible leads. Why don't you build another public library or fund more research, put your money into something tangible? Dr. Goode's lab always needs money and you know that he is the person who most influenced your career. It's risky to keep buying these paintings from these shady dealers."

"No, this one is different, and maybe it is the last. You are right, Daniel, that there may not be many more undiscovered works of art. But if I don't seek them, then who will?"

By this time a small crowd had clustered around Daniel and Edwin, listening intently to their conversation. Edwin thought it was the right moment to announce his latest acquisition.

"Ladies and gentleman, thank you all for coming tonight. I am pleased to announce that in my quest to find undiscovered art, I have unearthed another specimen. I plan to donate it Monday to the city's Metropolitan Museum so they will have a complete exposition of the works of..." there

was a dramatic pause and the audience leaned in, "a complete expo on the works of Paul Cézanne." ([See enlargement of the painting.](#))

After the fanfare and the inevitable toasting, Daniel drew his friend aside and pointed out that the existence of a new Cézanne was considered implausible. A French curator had researched the lineage of all known works in 1995 and concluded that no new paintings were likely. "Likely," repeated Edwin. But he appealed to Daniel's artistic tastes, "You saw it, it looks like a Cézanne, it feels right."

Daniel admitted that it looked authentic, but considering that he purchased it from the infamous Jose Burgert, who was known for passing counterfeits (unknowingly, he claimed), Daniel still had his doubts.

Monday evening Edwin received a call from Dr. Winters, the curator of the Metropolitan Museum who was also organizing the Cézanne exhibit. She was a little flustered. "You see, Edwin, the painting, while beautiful and possibly a Cézanne, might be a fake. The Board of Directors had this happen once before and they have indicated in no uncertain terms that they will fire me if a fake makes it into another exhibit. They find this sort of thing very embarrassing. You see, I must be sure..., we must be sure."

"Okay, Dr. Winters, I understand. Daniel shares your concern and now so do I. Let's get this investigated and then make a judgment."

After analysis by her staff and consultants from the university, Dr. Winters arranged for scientists at McCrone Labs to examine the painting. They had done a few investigations previously for the museum and determined, using a combination of spectroscopic techniques, that a Rembrandt hanging in The Hague's museum was painted by one of Rembrandt's students. Dr. Winters thought it was remarkable how the ways of seeing now included most of the electromagnetic spectrum.

On Friday, the four scientists from McCrone Labs gathered in the seminar room at the museum. Edwin and Dr. Winters were there with most of the museum staff. Dr. Winters asked her trusted colleague Dr. Philip to summarize his findings, which were representative of all the art historians that she had interviewed. "Before we discuss the scientific evidence about this painting, let's hear from Dr. Martin about what the art historians think."

Dr. Martin was visibly excited as he took the podium. "Let me say up front that this is the most exciting painting I have ever seen. I think Edwin has purchased a previously unknown Cézanne. The painting is unsigned, but that is not unusual since Cézanne only signed a few of his paintings. This painting is very similar to a Cézanne at the Ramon Barn Foundation in Massachusetts. It is a little smaller, about 55 by 125 centimeters, and has many of the same visual elements, but these are composed into a different arrangement. Cézanne did not paint from nature, but composed in his studio using elements that he had seen and sketched separately earlier. It is a brilliant composition, very characteristic of his constructivist phase in the late 1880s. The brushwork is characterized by solid groupings of parallel, hatched brushstrokes that build up a sense of mass within each visual element in the composition. Under low

magnification in the microscope the fine structure of the brushwork is indistinguishable from other paintings of his in our collection from that period. In short, I would stake my reputation that this is a previously unknown Cézanne, probably painted in the late 1880s. All of my colleagues agree."

Dr. Winters took the podium again. "Thanks, Dr. Martin. Your analysis is extremely helpful and furthermore it helps date the painting to the late 1880s. Now, let me introduce the scientists from McCrone Labs: Dr. Pryde, heading up the investigation with Drs. Anderssen, Montrose, and Simon."

After the introductions, the chief scientist, Dr. Pryde, stood up and spoke. "We have decided to present our findings first before making any final conclusion. I investigated the ultraviolet (UV) spectrum of a paint chip collected from the upper right corner, and the UV spectrum of incident light showed a substantial absorption from a polyene present in the paint material. For you non-specialists, a polyene is an organic constituent of the oil base used in this painting. Typically polyenes are oxidized over time, which causes their absorption to decrease. For paintings that are a century old, the absorbance at 300 nm is typically around 0.15. However, this painting shows an absorbance of 0.6, suggesting that it is not likely to be a hundred years old." ([See spectroscopic analysis.](#))

"Dr. Pryde, this is convincing, but the polyenes could be contaminants caused by soot or burning lamp oil or even cigarette smoke, isn't that true?" asked Dr. Winters.

"That is true. We have no way to know how this painting was cared for. The environment could contribute polyenes. To control for possible contamination, four different strata were taken from another paint sample, which was 120 microns thick. Each layer was analyzed by UV spectroscopy and produced nearly identical absorption spectra," explained Dr. Pryde.

Dr. Anderssen was the second to speak. "This is a good place for me to jump in. Like Dr. Pryde, I used a spectroscopic technique to examine the painting. I used infrared spectroscopy (IR). We use IR to detect anomalies beneath the paint, such as the presence of other paints, the types of binders used, and so forth. The data from IR spectra obtained from both IR reflectance and transmission spectra indicate that this might not be a Cézanne at all. It is true, as Philip Martin pointed out, that the heavy strokes applied with a palette knife, which are especially characteristic of Cézanne's early period, are there. But the analysis of the yellow areas shows indirectly that they could be cadmium-based, maybe composed of Cadmium Yellow Lithopone (a mix of cadmium sulfide and barium sulfate). This pigment mix wasn't widely used until 1927, and yet Cézanne had died some 20 years *earlier*. However, IR spectra do not directly detect metal nuclei, so the presence of barium and cadmium must be confirmed by another technique." ([See spectroscopic analysis.](#))

"There is another more interesting fact I'd like to mention. By IR reflectivity there is an indication that there is an underdrawing, probably charcoal. The image looks like a male figure. But this is difficult to claim with certainty due to the thickness of the paint."

"Last, the binder used is an animal glue binder. There are signals in the transmission IR spectrum that indicate particular functional groups that are characteristic of amino acids. The carbonyl (C=O) signal is present at 1760 cm^{-1} together with an N-H stretch at 3250 cm^{-1} . These are sufficient for me to claim that the binder is based on animal glue. This binder was used widely in the late nineteenth century until the 1940s."

Dr. Winters leaned forward over folded hands. "If the underpainting is authentic, what would this suggest?"

"Well, Cézanne is known not to have done any underdrawings. If it is true, then it is not likely to be a Cézanne," replied Dr. Anderssen.

Dr. Montrose stood up next and described her findings. "I examined the elemental composition of three samples taken from different colored areas of the painting, yellow, blue and green, by x-ray fluorescence (XRF). For the non-specialist, XRF involves irradiating a sample with x-rays to excite the element's inner electrons. As the atoms get de-excited, they emit x-ray frequencies that are characteristic of that specific element. The emission of x-rays can be detected for most metals and certainly for any element of atomic number 14 or larger.

"After reviewing the XRF data of all three samples, I conclude that the elemental composition of the painting matches the composition of the pigments used during the period 1839-1906, and therefore there are no pigment anachronisms. For instance, the yellow pigments are consistent with a mix of Chromium Yellow (lead chromate) and Yellow Ochre (ferric oxide hydrate). The blues are in agreement with a mix of Azurite (basic copper carbonate) and Cerulean Blue (cobaltous stannate) and the green areas show cobalt, zinc, chrome, and lead emission lines in agreement with Cobalt Green (cobalt zinc oxide), Chrome Green Oxide, Lead White (basic lead carbonate), and Cerulean Blue.

"All these pigments were known and widely used before and *during* Cézanne's life span. In addition, the absence of titanium, cadmium, barium, and manganese lines is also good news! Pigments containing those elements were not available until the 1920s and 1930s. Therefore, from an x-ray spectroscopist's point of view, this painting is an original nineteenth century painting in agreement with the compositions of pigments available during Cézanne's time.

"We cannot exclude the possibility, however, that it was painted by some kind of twentieth-century unscrupulous genius who not only is a skilled painter and art historian, but also a material scientist. Unfortunately it is much easier to de-authenticate a painting by finding anachronisms that it is to authenticate it." ([See spectroscopic analysis.](#))

Dr. Winters was impressed with the conclusions suggested by the data. "Very lucid summary. Thank you. Now turning to the last member of your team, Dr. Simon. What did you find from the luminescence images, Dr. Simon?"

"Well, let's see. I examined fluorescence from the surface of the painting using both short-wave and long-wave UV excitation from a mercury lamp. With our spectrometer we can collect a full emission spectrum from any area of the painting, collecting emission from an area as small as a 2

mm square. As you know, Dr. Winters, this provides only information from approximately the top 50 microns of the painting's surface due to the low penetrating power of the UV light.

"Some of the areas of the painting, particularly the dark green areas in the trees and the orange in the rooftops, do show brighter fluorescence than the remainder of the painting. Such bright areas are also found in another painting by Cézanne called *Gardanne* now at the Brooklyn Museum of Art and they are found in the same visual elements: the trees and the rooftops. The emission spectra of both the green pigment and the orange pigments in Mr. Cole's painting are very similar to those found in the Brooklyn Cézanne."

"So the fluorescence data support an attribution to Cézanne?" asked Dr. Winters.

"Yes. Agreement with this degree of confidence is strong support that the pigments were made in the same studio and even by the same artist because of the variability in hand-ground pigments. But I should add that I find no evidence from fluorescence for polyene emission from the painting, even though fluorescence should be clearly more sensitive than UV absorption."

Dr. Winters shifted uncomfortably. "Doesn't the fluorescence data contradict the ultraviolet data of Dr. Pryde?"

"Yes it does," replied Dr. Simon, "but it is possible that some other compound present in the pigment is quenching the polyene fluorescence enough to lower the signal into the background."

Philip Martin spoke up. "Dr. Pryde was only measuring absorption in an isolated region of the painting, and we know that Cézanne was constantly redoing his paintings. Perhaps the regions examined by the two techniques had different ages."

Dr. Pryde pointed out that different regions of the painting could also "age" at different rates and also that part of the painting might have been exposed to light.

Edwin, who had been sitting quietly, shared his view. "There is no clear conclusion here." He turned to Dr. Winters. "Since you have so much at stake here, I think it's your call."

Questions.

Provide well-reasoned and substantive answers to the following ten questions. Make sure that your statements refer to, and are supported by, the relevant evidence.

1. What is the evidence suggesting that the painting might be authentic? Summarize the case for authenticity thoroughly.
2. What is the evidence suggesting that the painting is a fake? Summarize the case for forgery thoroughly.
3. What parts of the electromagnetic spectrum were used by the different spectroscopy techniques applied in this case? Specify the wavelength, or frequency (as appropriate), ranges employed in each case.

4. What is the difference between the spectral regions employed in terms of energies involved?
5. Explain the kinds of chemical information you can get from the types of spectroscopy techniques employed in this case study.
6. How can spectroscopy tell us anything about a painting?
7. What is the difference between absorption and fluorescence spectroscopy techniques?
8. Why does UV light only penetrate 50 microns into the painting?
9. Why can IR be used to look beneath the painting?
10. Can a painting truly be authenticated?

References

Electromagnetic Radiation

- <http://www.lbl.gov/MicroWorlds/ALSTool/EMSpec/EMSpec2.html>
- <http://www.physics.sfasu.edu/astro/color.html#spectra>

Art Analysis

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UV-Vis Spectroscopy

- <http://www.chemistry.ccsu.edu/glagovich/teaching/472/uvvis/uvvis.html>
- <http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/UV-Vis/spectrum.htm>
- <http://accept.asu.edu/PiN/rdg/color/color.shtml>
- <http://accept.asu.edu/PiN/rdg/visnxyray/visnxyray.shtml>
- <http://accept.asu.edu/PiN/rdg/irnuv/irnuv.shtml> (Fluorescence)

IR-Spectroscopy

- <http://wwwchem.csustan.edu/Tutorials/INFRARED.HTM>
- http://arte.ino.it/sitoEN/riflettografia_IREN.php
- <http://www.artmuseums.harvard.edu/renaissance/noframe/nIRR1.html>

X-Ray Fluorescence

- <http://ie.lbl.gov/xray/>
- <http://accept.asu.edu/PiN/rdg/electrons/electrons.shtml>
- <http://ie.lbl.gov/xray/mainpage.htm>

Art Forgery

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Pigments

- <http://www.webexhibits.org/pigments>
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- <http://webexhibits.org/pigments/intro/paintings.html>
- <http://www.sewanee.edu/chem/Chem%26Art/default.html>

Cézanne

- <http://www.ibiblio.org/wm/paint/auth/cezanne/>
- <http://www.albrightknox.net/>
- <http://www.nga.gov/>

Example of a painting analyzed by X-rays and IR spectroscopy (Bellini's "Feast of the Gods")

- <http://webexhibits.org/feast/analysis/xrayinfrared.html>

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