

Precipitate Replications: The Cognitive Analysis of Michael Faraday's Exploration of Gold Precipitates and Colloids

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Abstract

In 1856, Faraday conducted a long series of experiments on the color of gold. We report replications of some of his experiments, permitting an understanding of his response to an important anomaly and the resulting conceptual reorganization of his ideas.

Introduction

In 1856, Michael Faraday (1791-1867) carried out nearly a year's worth of research on the optical properties of thin gold films (Faraday, 1857). In the course of this work, he discovered colloidal gold (the first metallic colloid) and what is now known as the "Faraday-Tyndall Effect," the fact that colloids scatter light. Colloids were an unexpected consequence of his attempts to understand the unusual color properties of thin films of gold. These, in turn, were an important extension of his earlier attempts to understand the interaction of light and matter, and his speculations about the force-centered character of matter (James, 1985; Tweney, 2002).

The present project was initiated by the discovery of over 600 surviving microscope slides and other specimens made by Faraday as part of his research, and now held at the Royal Institution in London (Tweney, 2002). The slides are numbered and indexed in Faraday's Diary and represent nearly the complete set of metallic film specimens used by Faraday in 1856. However, only a few of his colloidal specimens (and none of his precipitates) survived; thus, one goal of the present effort is to restore lost specimens for analysis. Replication is also important even for specimens that still survive -- Faraday often subjected the specimens to destructive and/or damaging manipulations, and these manipulations also need replication. Four general procedures used by Faraday are currently being replicated by our group: (1) Precipitation of gold from solution, (2) "Deflagration" of gold wire, that is, exploding gold wire using sudden surges of current, (3) Producing colloids using reduction by phosphorous,

and (4) Producing thin metallic films of gold using reduction by phosphorous.

Here we present our replications of Faraday's precipitates. Besides restoring for analysis certain lost specimens, these allow insight into the "tacit knowledge" implicated in their preparation. More importantly, preparation of our own precipitates allowed analysis of aspects of Faraday's research previously hidden from view, helping to account for an important conceptual change.

In earlier accounts of Faraday's research, our group examined the way in which Faraday experimentally traversed a problem space of hypothesized and real results during his discovery of electromagnetic induction in 1831 (Tweney & Hoffner, 1987). Our analysis suggested that Faraday used a relatively narrow search strategy in the 1831 experiments, one in which potentially disconfirming evidence was initially ignored and only evidence which supported expectations was pursued. In later stages of the research, he made explicit attempts to disconfirm. This "confirm early-disconfirm late" strategy resembled heuristics observed by Klahr in the "Big Trak" studies (Klahr, 2000) and by Dunbar (1995) in an "in vivo" study of laboratory molecular biologists.

Not all aspects of scientific thinking can be characterized as search through multiple problem spaces (Kurz & Tweney, 1998), and this is especially true of Faraday's work. For example, Gooding (1990) replicated Faraday's 1821 discovery of electromagnetic rotations and argued that identification of circular rotatory motions could only have come about by means of an "eye-hand-brain" interaction of a very dynamic character. Rather than "testing hypotheses," Faraday instead had to make the meaning of the otherwise chaotic appearances presented by the experimental apparatus. Similarly, Cavicchi (1997), partly by conducting replications, showed that Faraday's experimentation during his 1845 discovery of diamagnetism proceeded "not by progressively refining

explanations, but by exposing previously unnoticed ambiguities in the phenomena, and uncertainties in interpretation. This exposing deepens the space of [his] confusions" (1997, p. 876). For Cavicchi, such "confusions" (perhaps in response to a surprising result) are a crucial aspect of the pattern-finding involved in discovery. She was further able to show that Faraday's "confusions" resembled those of a student exploring the relationships between bar magnets and iron needles.

Our earlier examination of two of Faraday's papers, one on acoustic vibrations and one on optical illusions of motion, suggested that Faraday's constructive perceptual processes imply a continuum of developing representative explicitness. This continuum began with the perceptual rehearsal of remembered events, proceeded through the construction of "inceptual" representations (that is, representations that abstract away potentially irrelevant features, with an effort to "see" what the results would look like), and finally resulted in a mental model that even included non-perceivable features of phenomena (Tweney, 1992; Ippolito & Tweney, 1995). Again, Faraday appeared to be using an "eye-hand-mind" dynamic in constructing new spaces. Similarly, Nersessian (1999) argued that Faraday and Maxwell used analogies and imagery in a process of generic abstraction, itself important in conceptual generation and change.

Andersen (2002) argued that conceptual reorganization in science often requires a semantic shift, in which exemplars change category. She showed that such change was an important part of the resolution of anomalies in particle physics in the 1930s. The present paper extends the scope of Andersen's argument, by showing that Faraday's work on precipitates was an active source of a crucial conceptual change near the beginning of his 1856 research on gold, perhaps dependent upon the "confusions" engendered by some of the appearances of gold (described below). The dynamics of the reorganization depended upon "epistemic artifacts" constructed by Faraday to serve as active agents in exploration of a new domain.¹

A distinguishing feature of all of Faraday's research was his determination to produce phenomena of such clarity that his explanations of the phenomena would be transparent to his audiences. "Seeing was believing" in a deep sense for him (see, e.g., Fisher, 2001; Gooding, 1990), and his attention to anomalies in the present case is especially important in explaining the cognitive dynamics of the research. Thus, our replications can potentially contribute to the understanding of the cognitive dynamics of visual representation in scientific

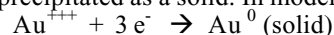
¹ The term "epistemic artifact" was used by Tweney (2002) to suggest a blending of the term "cognitive artifact" used by Zhang & Norman (1994) and "epistemic thing" used by Rheinberger (1997).

research generally (see, e.g., Kulkarni & Simon, 1988; Trickett, et al., 2000).

Why Gold?

Gold films interested Faraday because thin transparent gold films manifest a different color by transmitted light than by reflected light; green, blue, and purple are the most frequent transmitted colors for gold leaf. Faraday thought that gold was therefore a good place to look for insight into the interactions of matter and light. For him, the profoundly interesting question concerned the manner in which such very thin (and apparently continuous) films could so alter light. Although he failed to achieve a definitive answer to this question, he successfully showed that many of the optical properties of metals in general could be produced by the interaction of discrete particles with light. His discovery of gold colloids was an integral part of this argument.

A colloid is a suspension of finely divided particles of a substance held in suspension in a fluid. Colloids differ from solutions in that solutions represent ionized particles of atomic size, carrying an electrical charge. Ions, the particles that form a solution, are much smaller than colloidal particles and affect light in different ways. Faraday's discovery that metals could form colloids was a breakthrough, especially since he also showed that the particles were pure gold, chemically identical to the metal films. Note also that colloids differ from precipitates, which are formed of even larger particles than colloids. If a reducing agent is added to a solution of a gold salt, then metallic gold (Au) is precipitated as a solid. In modern notation;



Because the particles in a precipitate are far larger than those in a colloid (sometimes being visible to the unaided eye), they settle quite quickly. Colloidal particles (which are far too small to be visible) do not settle because, as Faraday speculated, they are lightly bonded to a "cloud" of ionized particles that repel the surrounding fluid media.

The chemistry of precipitates is more complex than the formula given above suggests, since gold chlorides exist in solution as $[\text{AuCl}_4]^{-}$ ions and various hydrolyzed ions as well.² These more complex species and reactions were not known to Faraday. As we discovered, however, the complexity of the reactions is reflected in a very complex phenomenology when gold salts are actually used. We had expected precipitating a gold salt to be a simple and straightforward process -- a "warm-up" exercise for us (as we thought it may have been for Faraday). In reality, our replications opened a new aspect of Faraday's work on gold, one not visible in the text of the diary itself. In the present paper, we describe our replications of Faraday's precipitates and compare them to colloids and solutions.

² See Puddephatt, 1978, for this and other details of the reactions of gold.

Faraday's Diary

Faraday's diary is well known because of its relative completeness, an aspect which permits reconstruction of his research practices (e.g., Steinle, 1996). In some cases, however, as in the case of his research on gold, much of the diary is hard to interpret by itself, since the visual context of Faraday's work is absent. As we show, even with that visual context present (in the form of the surviving specimens), there is more to be learned from the "manual" aspect.

Faraday wrote 1160 numbered entries on his gold research, roughly 300 manuscript pages dated from the 2nd of February, 1856 to the 20th of December (Martin, 1936). The distribution of entries (Figure 1) is roughly bimodal, the greatest density of entries occurring at the beginning of the series and toward the end. The first 47 entries (in the first peak of the distribution) are summaries of previous notes. They also include several dozen entries in which Faraday speculates on possible experiments, much as he had earlier kept an "idea book" to record possible studies (Tweney & Gooding, 1991). Faraday's (1857) published paper on the topic was submitted on November 15, 1856 and read before the Royal Society on February 15, 1857. Indeed, the character of the entries in the second peak suggests that he was "mopping up" prior to ending the research -- conducting some necessary control experiments, trying again to resolve some inconsistencies, replicating key preparations, and so on. His work with precipitates occurs near the beginning of the series, on February 5, and appears to record the first laboratory work on gold conducted in his own laboratory (earlier entries describe gold film preparations made at the home of a friend, Warren De La Rue; see Tweney, 2002). Thus, one question is why precipitates constituted the first task undertaken by Faraday.

It has been suggested (e.g., Williams, 1965) that Faraday's work on gold in 1856 manifests his "declining powers" (whether due to aging alone or to the effects of the many toxic exposures he was subjected to over the years). This judgement may stem,

in part, from the seeming aimlessness of the precipitation experiments, especially since these occur at the beginning of the first burst of activity. Since the precipitation reaction of gold was long-familiar by 1856, Faraday could learn nothing new here and the text of the Diary alone does not indicate why he initiated his gold research with what seems like a rather prosaic procedure. As we show, however, the experiments with precipitates were far from trivial -- by conducting the replications, we were able to detect a "confusion" that served a heuristic role in the important step of arguing that the colors of gold are due to particles interacting with light.

Method

Faraday is vague about exactly how he prepared the precipitates used in his research. In the Diary he indicated only that he "Prepared a standard weak solution of Gold" and a "standard solution of proto sulphate of Iron ... consist[ing] of 1 vol. saturated solution at 54° F. plus 2 vols. Water, and a little sulphuric acid to keep all in solution during the changes" (Entry #s 14291 & 14292, 5 Feby. 1856). "Proto sulphate of iron" is "Ferrous Sulfate" in modern terms, and the fact that it was saturated allowed reproduction of the exact substance used by Faraday. But no clue is offered about the "standard weak solution of Gold." Thus, its concentration is unknown and, more importantly, because of the complex chemistry of gold salts and the solution processes by which they dissolve, several possibilities had to be explored for how to prepare the precipitates.

Today, "Gold Chloride" is typically sold in one of two forms; as "Gold (III)," that is, as gold in the valence state +3, in the form of "Tetrachloroauric Acid" (HAuCl_4), a yellow crystalline substance, or as "Gold (I) Chloride" (AuCl ; valence state +1), in the form of yellowish-white crystals. Each was tried in turn as the basis for gold ion in solution, but neither proved satisfactory, in part because each is unstable. Further,

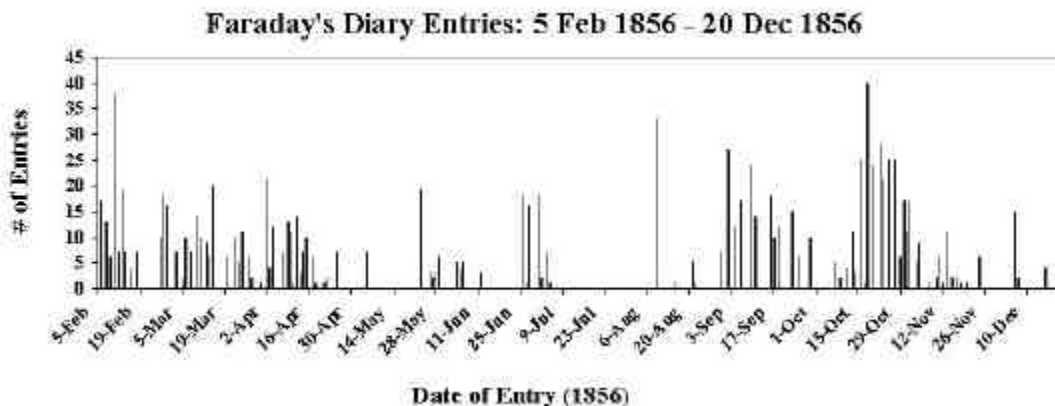


Figure 1

dissolving each in water is problematic; each leaves a precipitated deposit. In the case of tetrachloroauric acid, this is probably pure gold, an expected product when the substance hydrolyzes, but (barring extensive analytic procedures) we were unable to determine if the deposit was the expected gold or simply an undissolved portion of the original crystals. As a result, we could not be sure of the strength of the solutions we were preparing. "Gold (I) Chloride" (AuCl), in the presence of water, oxidizes to the III valence state. This substance seemed to dissolve readily, but again with traces of a deposit. Here again, knowing the strength of the resultant solutions was difficult. Accordingly, we decided to begin with pure gold, dissolving it in such a way that we could be sure of at least the quantity of gold in the solution.

Pure gold wire (0.025" diameter, 99.99%) was obtained from a vacuum technology supply house.³ Aqua Regia, a 3:1 combination of hydrochloric acid and nitric acid, was used to dissolve a 3.5 cm length of the wire, weighing 217 mg, to create gold chloride solution.⁴ Fifteen minutes after addition, the gold wire completely dissolved in the acid. The solution was then boiled in order to remove the hydrochloric and nitric acid. Water was added as needed to keep a constant volume of about 10 cc. The solution was boiled until the odor of the acids and the nitric oxide byproduct (all of which are pungent in even slight quantities) was no longer present.

To produce a gold colloid we used a modern method, the reduction of gold chloride solution by citrate ion (producing such colloids using Faraday's methods is part of an ongoing study and will be reported later). Gold (III) chloride (i.e., tetrachloroauric acid) (3 mg) combined with 10 ml of water produced the gold chloride solution. Gold and excess gold chloride remained at the bottom of the container. Ten mg of sodium citrate, a source of citrate ion, was dissolved in 10 ml of water. The gold chloride solution was agitated with a magnetic stirrer and heated to boiling temperature. Citrate solution (0.015 ml) was slowly added to the gold chloride and reacted immediately, producing a very pale slate-blue solution. Over the course of forty seconds the color of the solution evolved from slate-blue to amethyst to ruby red. When cooled, the product proved stable over many months. Although we cannot be sure of the quantities of gold that are actually in colloidal form, the properties of our colloid were exactly as described by Faraday.

³ Gold wire, because of its malleability and lack of reactivity, is used as a component in high-vacuum O-ring seals. Jewelry gold, unfortunately, is always alloyed with other metals.

⁴ Unlike other metals, gold will not dissolve in hydrochloric acid (HCl) alone because it requires both an oxidant and a ligand donor (Cl^- , in this case). When Aqua Regia is used, the result is AuCl_4^- in solution and gaseous nitric oxide (NO).

The reduction of gold chloride solution by ferrous sulfate solution was used to form gold precipitates. A saturated solution was prepared by dissolving crystalline ferrous sulfate (FeSO_4) in heated water. When cooled, three drops of ferrous sulfate solution were added to 5 ml of gold chloride solution. No immediate reaction was apparent, but on the following day a yellow-orange residue of metallic gold had settled at the bottom of the experiment tube and could be re-dispersed by shaking.

Results

The three preparations showed the expected appearance in ambient (room) light; the solution was a clear, deep yellow fluid, the colloid was a clear ruby-red fluid, and the precipitate, when shaken, was a cloudy yellow-gold suspension in which individual particles could be seen in motion, and in which occasional glints of bright metallic gold could be seen. Except for the overall color, the solution and the colloid appeared to be very similar, while the shaken precipitate had a very different appearance.

The relative similarity of the three changed, however, when directional lighting was passed through the fluids. The principal results are summarized in Figure 2, which shows the effect of a parallel beam of light produced by a fiber-optic illuminator (entering from the left) on our prepared gold colloid, a solution of gold chloride, and the precipitated gold preparation, respectively. The overall colors of the preparations are not shown here, but can be viewed at <http://personal.bgsu.edu/~tweney>. The precipitate was shaken just before the photograph was taken. Note that the colloid shows a bright "Faraday-Tyndall Effect," that is, light is scattered to the side, illuminating the path of the beam through the colloid.



Figure 2. Colloid, Solution and Precipitate

The colloid (a ruby-red transparent fluid) tinges the scattered light a faint pink. The solution scatters no light, only some small reflections from the sides of the glass test tube being visible in the photograph. The precipitate scatters light rather more broadly than the colloid, although some of that is an incidental result of the widening of the initially parallel beam of light into a cone, as a result of its passage through the two prior

preparations. The overall color of the scattered light from the precipitate is a yellowish-gold, and individual particles are easily visible. Obviously the colloid and the precipitate resemble each other most closely under these optical conditions, in contrast to the appearances in ambient light. Although there is no record in the diary of Faraday placing these three in one context (as we have done in Figure 2), it is clear that he was attending these differences very carefully -- they constituted part of the basis for his conclusion that the colloids were in fact metallic particles of gold.

Conclusions

The change in apparent similarity of the three kinds of preparations when transmitted light is compared to ambient light (Figure 3) suggests a possible “confusion” (Cavicchi, 1997), and the need for a reorganization of the phenomenological domain of “divisible gold” (as Faraday referred to it in the 1857 paper). This confusion suggests an explanation for why Faraday began with precipitates on February 5, an explanation that corresponds with what Faraday does say in the Diary.

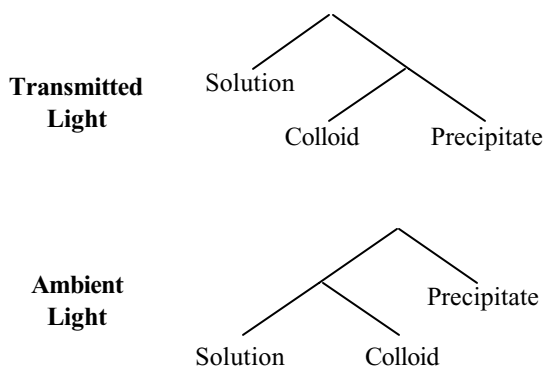


Figure 3. Taxonomy of Similarities

From the Diary, we learn that Faraday had visited De la Rue the week prior to February 5th, and the two had examined some gold leaf through the microscope; Faraday recorded this visit in his first diary entry on gold (#14243, 2 February 1856). On the 2^d, Faraday received some thin gold films prepared by De la Rue, who had used phosphorous to reduce the gold. On the 6th (one day after preparing his precipitates), Faraday established a careful optical method for the examination of precipitates, and recorded that, in the evening, he went to De la Rue’s again, and observed how the thin gold films were made. At this point, Faraday noticed something odd; “A very fine red fluid is obtained [from] the mere washing” (Diary, #14321). This, of course, was a colloid, and Faraday saved the fluid,

returning to it two weeks later on the 18th (#14437), after his experiments with precipitates and his first examinations of thin films. At that point, he was able to ask; “... the question is, is it [i.e., the gold] in the same state as whilst apparently dissolved in the fluid” (#14437, emphasis in original). It is interesting to note that during this 16 day period he referred to the red fluid using two terms interchangeably, “fluid” and “solution”. Only later could he be sure that the red fluid was not a solution, although he must have had the idea very early.

The sequence of his ideas then must be something like the following. He first compares thin films (which he suspects are gold in a continuous state) to the precipitates, which he knows to be discrete particles. Since gold in a continuous state changes appearance in transmitted light and reflected light, he develops an “optical method” for examining precipitates under the same two conditions. Note that, to prepare the precipitates, he must have had before him the clear solution of gold chloride. Then, at De la Rue’s, he explicitly notices the clear red solution and this must have suggested a comparison. He knew that the substances used to produce the clear red solution (phosphorous, carbon disulfide, and a gold chloride solution) produced metallic gold. But why then did it look like a solution? Resolving this “confusion” led him to examine the red fluids more closely – and it would be a natural extension to use both transmitted and ambient light, just as he had done with the precipitates. And the transmitted light (as our Figure 2 shows) would make the red fluid look very different from the clear solution. A real anomaly had been found, and a reorganization became necessary; the “red fluid” must be gold in a “divisible state,” like the precipitates.

There was, of course, still much to do. More work was needed to explore the new optical effects, to examine other kinds of divisible gold (e.g., that produced by exploding gold wires), to examine other substances, and, most importantly, to explain the differences in the color of light produced by gold in different states (a goal only partially realized). Yet the anomalous appearance of the red fluids at the beginning of the series of experiments provided Faraday with a first important clue to the kind of inquiry he would need to make. Far from constituting a record of “declining powers,” the replications allow us to see that Faraday’s ability to notice and exploit an anomaly was undiminished in 1856.

Further, our replications revealed that the precipitation experiments are more important than can be discovered by examining the diary records alone, because their role in recognizing the divisible state of colloidal preparations is not evident otherwise. The text of the diary alone does not reveal what was obvious, visually, to Faraday – and was obvious to us only when

present as the result of our own “makings.” Only in this fashion could we have noted a conceptual change reminiscent of that seen by Andersen (2002) in her analysis of 20th century particle physicists.

Faraday’s gold research in 1856 provided Faraday with mental models based upon new conceptions about the interaction between thin gold films and light. And the differing visual properties of colloids, solutions, and precipitates were a crucial first step, because they showed that the particles of gold had specific optical properties. These in turn led Faraday to reevaluate his previous views of the distinction between continuous and “divisible” matter. Thus, there are similarities between the conceptual reorganizations we observed by replicating Faraday’s precipitation experiments, and the larger reorganizations that constituted the outcome of the entire 1856 series of studies. Further replications and text analysis are in progress to extend the reach of this conclusion.

Acknowledgments

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