Recreating Edmond Becquerel’s electrochemical actinometer

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Abstract
This article reports on the replication of a series of experiments carried out by Edmond Becquerel with the help of his electrochemical actinometer. We focus principally on the difficulties that were met and the problems that had to be solved. They provide an important source of information on the conception and specifications of Becquerel’s instruments and make explicit some underlying links between Becquerel’s different research works.

Keywords: Actinometer, Edmond Becquerel, photography, theory of light

We will expose in this article the replication activity carried out using Edmond Becquerel’s electrochemical actinometer. We shall focus principally on difficulties we met, the problems we had to solve and the setbacks that we suffered. In fact, our failures were the most important source of information we had during the replication. While successes showed us how Becquerel treated his measurements, failures taught us much about instrument conception and specifications and made us realize some underlying links between Becquerel’s different research works.

Introduction
Edmond Becquerel, the father of Henri, the famous Nobel Prize winner, had his professional and personal life drawn out before his birth (Fig. 1). As Antoine César Becquerel’s first son, he had to continue the family’s social ascension, through scientific practice, as his father had done before him. He also had to follow the particular scientific method proposed. In fact César Becquerel considered that scientific practice had to be essentially an experimental one, respectful of facts and experimental results, and prudent with regard to theories (Becquerel 1842).

Edmond Becquerel remained faithful to these family precepts all over his career and experimental work, and published many results, sometimes totally disconnected from any theory.

The works of Edmond Becquerel that we analyze here concern the research he conducted between 1839 and 1843, in his father’s laboratory at the French Muséum national d’histoire naturelle. These works try to investigate, using new instruments and experiments, how matter, principally silver halogens, reacts to light influence. These experiments began in 1839 with Edmond Becquerel’s double thesis in physics and chemistry (Becquerel 1840). This year corresponds to the publication of the first description of the photographic process, named daguerreotype\textsuperscript{1}. As an eighteen years old young man living in the Parisian

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\textsuperscript{1} This work plays indeed an important role in the debate about the nature of light that took place during this period. The scientific quarrel engaged between Biot and Becquerel, at first sight of principally experimental nature, entailed disagreements about theory, see Fatet & Viard 2004.
high society, Becquerel got immediately fascinated by photography. Since then, his interest never faded; he participated in the creation of the first French photographic society, the Société française de photographie, in 1851, and used photography and photographic techniques to develop his scientific work. Considering that Edmond Becquerel’s work was principally an experimental activity, using techniques from photography - a non-theorized domain, we chose to analyze it in technical and experimental terms. To understand and explain precisely what he did, we had to reconstruct the instruments he used, and replicate the experiments he carried out.

The results we present here are part of a thesis studying what Edmond Becquerel did, investigating the nature of light, between 1839 and 1843, and which contains a controversial analysis and an epistemic research (Fatet 2005). We shall only survey here our replication activity.

**What did Edmond Becquerel do?**

In 1839, working on his double thesis, Edmond Becquerel tried to understand how chemical substances can react under the influence of light. To reach this goal, he constructed a first instrument using chemical substances dissolved in liquids, and proposed measuring the electrical modification caused by light effects with the help of a galvanometer. He published the description of his instrument in the Comptes-rendus de l’Académie des sciences (Becquerel 1839a). We represent this unnamed apparatus in Fig. 2, and present the one we replicated in Fig. 3.

It is composed of a jar, containing two superposed liquids. A chemical substance is dissolved in each liquid. The two dissolved substances react, under the effect of light, at the interface between the liquids. When the photochemical reaction occurs, an electrochemical imbalance can be registered on the galvanometer connected to platinum electrodes which are immersed in the two liquids.

This experiment as well as the next ones he conducted can be considered as based on the following reasoning:

- **Light ray quantity**: exactly \(\propto\) proportional
- **Chemical substance that reacts quantitatively**: exactly \(\propto\) proportional
- **Maximum deviation of the galvanometer pointer**

Using this method, Edmond Becquerel obtained results that showed a regular variation between the quantity of substance that reacts and the deviation he measured. To complete his results and to test other substances, he needed to find a new way that could be used to measure the currents created when photochemical reaction occurred. He had to answer an important question too. In fact, Jean-Baptiste Biot, a famous physicist, known at the time for his fight against the wave theory of light, asked Becquerel to verify if light effects exist on the platinum electrodes which participate in the measurement of the currents. This intervention was the first that engaged a scientific quarrel between both men. The only way to check if a parasitical effect was affecting Becquerel’s results was through a differential process. He consequently published a new description of an apparatus using two platinum plates immersed in a box divided in two compartments full of acidified water (Becquerel 1839b). Each plate was connected to a galvanometer. When the box was closed, no light could penetrate inside. Becquerel exposed one plate to light using a hatch, the second plate staying in obscurity. If a light effect occurred on platinum, it would occur on one plate and create an imbalance that could be seen on galvanometer. He initially observed an effect, but repeated experiments with red-hot platinum plates provided no further results and he concluded that a thin layer of impurities on the surfaces of the plates produced the first currents. This result crucially shaped his experimental evolution. The desire to obtain results drove Becquerel to construct a link with the metallic plates covered with a thin silver halide layer he had used in photography. He thus tried to use photographic plates immersed in his apparatus.

When Edmond Becquerel obtained in 1841 the measurements with photographic plates, he began with their help the study of the solar spectrum. He made there a complete inversion of his research object:
until this moment, he had studied photochemical reactions, but then he started to study light through photochemical reactions.

He published in 1841 a description of a third apparatus (Becquerel 1841), named an electrochemical actinometer (*actinomètre électrochimique*). This device consisted of a wooden box divided in two compartments containing acidified water. In each compartment was immersed a silver plate covered with a thin silver chloride layer, prepared as a photographic plate. Each plate was connected to a very sensitive galvanometer. As in the previous device, a hatch gave the possibility of lighting one plate, leaving the second in its dark compartment (Fig. 4).

Verifying a result obtained by a totally different way (Fraunhofer used his eye as a light detector) was, in Edmond Becquerel’s terms, the proof of the efficiency of his device. He began then to study the solar spectrum’s invisible extremities, especially the extremity beyond violet. In 1843 he announced he had discovered 3 Fraunhofer’s black lines beyond violet (Becquerel 1843). The identity of properties between this area and those in the visible solar spectrum drove him to consider the nature of this area as corresponding to light too. This result was to become an important clue in extending the definition of light beyond its visible limits.²

To explore the principles and specificities of Becquerel work, we replicated his instruments and experiments. We were particularly eager to verify a hypothesis concerning the role and the place that photographic principles played in the invention of the electrochemical actinometer and its uses.

**Our replication and its results**

We replicated the three devices and most of the experiments Becquerel performed with their help. We will however focus here principally on the replication work we did using the electrochemical actinometer.

**The problem of location**

The first question we had to solve concerned the room where to install our devices. Becquerel’s experiments took place in the dark room of the Museum’s physics laboratory. This kind of room, useful a century ago, does not exist anymore in the local physics laboratories. We needed a room with a window exposed to the sun for several hours a day, giving possibility for total darkness and that could be ventilated to expel toxic gases such as dibromine.

We chose to install our laboratory in an old photographic lab. We constructed a wooden hatch, totally closing the room’s only window, and allowing us to choose when we needed a direct solar ray to enter.

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² Original title: *Recherches sur les effets électriques produits au contact des solides et des liquides en mouvement.*
We met the first major difficulty right at the outset of our experiments. Becquerel and the scientists of the time were used to work in this kind of place, in total darkness, but the long experience of working in such environment is lost today. Organizing the tools and the chemical substances needed for the experimental manipulations requires special attention when the only light one can use is a small candle flame, far away from the apparatus. We had to find ways of working, moving, and manipulating toxic substances. The photographic dark room experience acquired before proved here really helpful.

The choice of galvanometer

At first, we wanted to use a genuine galvanometer from Becquerel’s times to reproduce precisely his work. Unfortunately the old galvanometers we could find were all out of use or unused since a century. To repair this kind of apparatus with modern materials is quite difficult and there is no warranty as concerns correct functioning: one cannot then trust their efficiency.

Becquerel used his galvanometer in a specific way. He did not read off currents in units, but was just interested in current variations. His result boards contained numbers noted in degrees of pointer deviation. He just analyzed differences between two deviations produced by two solar spectrum areas.

Given this, we decided we could use a very simple modern galvanometer with no electronic system provided we took care to work with the same gauge every time. We never read off currents, but only, as Becquerel did, spot deviations. We chose to use a Verivrac™ galvanometer shown on Fig 6. We first tested current intensities, and chose to use the 500 µA gauge.

We consider that, given its purpose, a modern galvanometer doesn’t disturb the studied phenomenon. We placed it as far as possible from the actinometer tank containing the two silver plates connected to the galvanometer.

Rebuilding instruments

The wooden tanks that Becquerel used to analyze light have since disappeared. We did found their traces in the Museum biophysical laboratory inventory book (Becquerel 1864), Becquerel’s laboratory logbook, started in 1864, and ended in 1951. The author mentions these boxes in the “before 1864” section. Although there is no outgoing inventory line concerning these tanks, we could not find them anywhere. We had thus to rebuild them using the brief descriptions Becquerel gave in his publications. We constructed a first wooden box, using Becquerel’s descriptions, as a cube of 10 cm each side. We chose oak wood, because of its density and hardness. We fixed each face to the next using nails, and improved its watertightness with Arabic gum. However, when we filled it with water the wood warped, and the box started to leak slowly. During the final installation, a long time was required for the spot to stand still, corresponding to the imbalance of the electrochemical silver plates. Because of the leaks, the box would get empty before reaching this stage. We definitely needed a new way to adjust the box sides, but Becquerel’s writings were not giving any further clue about the construction.

We tried a new method, consisting of a mortise and tenon joint, as shown on Fig 7. When the wood warped, the tenon in the mortise warped too and watertightness was thus improved. We used Arabic gum too. In this way, it was possible to wait for the electrochemical imbalance several hours before starting measurements.

We realized our first electrochemical actinometer replication using this tank. An oak partition separated the box in two compartments. Each compartment had a hatch on the box top, enabling to introduce the silver plate and, when closed, to secure darkness. Another hatch at the front of the box covered a window pane. We used this hatch to light one of the two silver plates, keeping the second in obscurity. Fig. 8 and Fig. 9 show the hatch disposition and the
Preparing the plates

Edmond Becquerel does not give any information about the size of the silver plates in his first publications dealing with the electrochemical actinometer. He just describes his silver halide layer preparation method. We used, as an information source, a description he wrote twenty years later in his book *La lumière, ses causes, ses effets* (Becquerel 1868). His electrochemical actinometer appears to have changed during this time. The tank conception has changed, and so perhaps has the plate size. Since we had no further clue, we ended up using two 5x2.5 centimeter silver plates.

The silver plates Becquerel used in the last actinometer version were covered with a thin silver chloride layer. But before this choice he tried different silver halides. We replicated each method and each substance he used. In the sequel, we report only on the silver chloride results, but here we describe both the silver chloride and bromide preparation.

In what concerns chloride, a very simple method consists in covering the plates with liquid silver chloride, and then warming them with an alcohol lamp. The difficulty of this method is that the only light source one can use is the blue flame of the alcohol lamp. In the case of bromide, one has to expose, in total darkness, the silver plates to dibromine gases. The latter are extremely toxic: there is a definite danger to manipulate them in obscurity and in a confined space.

These methods are actually quite close to what is used in daguerreotype preparation. Place, obscurity, substances and methods are the same. As a matter of

Fig. 8. Top of the tank, hatches and partition.

Fig. 9. Front hatch of the tank.

entire wooden tank. Two metallic bars crossed one box side, entering in each compartment, and allowing the connection between each silver plate and the galvanometer.
fact, Edmond Becquerel proposes to use for his actinometer commercial daguerreotype plates which existed for photographers who did not have the practical possibility of preparing their own.

After the difficult process of preparing the plates, we still had to go through other risky manipulations: we had next to introduce them, avoiding any exposure to light, in the tank containing acidified water, and then close the hatches.

**The first experiments**

The next step was to set up the complete electrochemical actinometer, including prism, tank and galvanometer. The excellent and big prism we used is shown on Fig. 10. We further used an adjustable split (Fig. 11) to select the rays we would analyze, and a converging lens to secure a good quality spectrum (Fig. 12).

When the installation is achieved, the solar light crosses the room window split, and then the lens. It gets further dispersed by the prism, forming an eighty centimeters wide spectrum. Using the adjustable split, the experimenter can then select a thin part of it, which is finally projected on the front tank hatch. The tank, full of water, contains the silver plates connected to the galvanometer. When the experimenter is ready, he opens the hatch, exposing one plate to the selected light; this causes a photochemical reaction to occur, creating an electrochemical imbalance between the lighted plate and the other one kept in obscurity. This imbalance can then be measured by means of the galvanometer. The experimenter must, as quickly as possible, select the light, open the hatch, go to the galvanometer that is far from the tank and read the information then go back to the tank and close the hatch. All this has moreover to be done in quasi-darkness. If measures are quickly done, this can be repeated over ten hours with the same pair of plates. The results can then be compared. The experimenter can thus explore the differences in the action of the spectrum light by means of the photochemical reaction. The results he records are current values, and so are totally independent of human perception, namely human vision.
When we started the experiments, using an electrochemical actinometer equipped with silver chloride layer plates an unexpected difficulty occurred. Oak wood contains tannins of very high coloring power. The water inside the oak box gets then quickly violet colored (Fig. 13). The light passing through this colored water to interact with the silver chloride is then necessarily changed. This in turn influences the results. However, Becquerel never mentions this effect. To solve this problem using just traditional methods, we contacted a cooper factory in Bourgogne. Indeed, cooperers still use traditional methods to eliminate oak tannins when they construct wine barrels.

Although we tried different methods in use, we describe here only the one that we think has been used by Becquerel himself. It consisted of warming the inside of the box with an alcohol flame for an hour. Heat destroys tannins and transforms them into gallic acid and phenol-ketones. After this treatment the inside of the box is blackened and no color appears anymore in the water over the time of the experiment. The artifact is thus corrected.

Now, the wooden tank description Becquerel gave in 1841 contains an expression that seemed mysterious before we started replication. His box, which was totally dark when closed, was, in his words, *blackened in its interior* (*noircie dans son interieur*). He gives no explanation for this, and we could not find one either, safe that his box must have been blackened inside precisely because of the tannin treatment the manufacturer used, just as we did with our tank. This probably means that Becquerel never met this difficulty, and probably did not know this treatment: he thus probably did not construct his box himself.

We could not find any trace of a scientific instruments manufacturer order. We know that Becquerel's father and his son, a laboratory professor, collaborated with the famous Parisian instruments manufacturer Chevalier. It could be that Chevalier constructed this box; however, he never mentioned it in his catalogues. Be it as it may, once this problem was solved, we could finally start the experiments.

**Liquid movements and currents**

After days spent trying to achieve an efficient laboratory organization, repeating the experimenter displacements sequences and learning how to manipulate the instrument in obscurity, we were eventually able to obtain the first experimental series. The results, which we shall not discuss here much further, corresponded indeed to Becquerel's. However, after hours of manipulation using the wooden tank, a new and unexpected problem occurred.

During the manipulation the oak wood warped: after three hours, the front hatch was warped too and it became harder to slide. When the experimenter was opening and closing this hatch, he was then causing tank movement, which then provoked turbulence within the liquid. As it turned out, the turbulence near the plates created currents as intense as the analyzed effect. It eventually made light effect measurements totally impossible.

Edmond Becquerel did not mention this problem in his publications between 1839 and 1843, but he published in 1855 an article in the *Annales de chimie et de physique* with the title “Electric effects produced by contact with solids and liquids in motion” (Becquerel 1855). In the introduction, Becquerel states that he discovered this effect (currents caused by liquid agitation) about fifteen years before, but since had never time to investigate it. This suggests then that he met the same agitation problem we did. He just did not mention it in publications. This artifact made us realize a connection between two scientific subjects, and two periods of Becquerel's experimental work. This connection could not have been realized without our replication activity. Now, since Becquerel continued his experiments after this discovery, we had to find out how he managed to solve the problem.

In *La lumière* he published in 1864 the description he gave of the electrochemical actinometer is different. He used a blackened glass tank. This new material, well adjusted, solved the agitation problem. We decided to build such a new tank (Fig. 14). We chose to use plexiglass® instead of glass, using glass for the tank window. The hatch this time slid perfectly. We did not meet any agitation problems and could then replicate the experiments.
Replication results

We replicated every experimental series Becquerel described in his publications between 1839 and 1843. We shall only describe here some results obtained with the electrochemical actinometer using silver plates covered with a thin layer of silver halide layer, which corresponded with Becquerel’s results. One of the latter consisted in observing different maximum sensitivities for each silver halide. He showed that silver bromide light sensitivity is maximal with violet light, and important beyond violet, where no light is visible. This compound can be used to explore invisible spectrum extremity. The silver chloride’s best sensitivity corresponded instead to green light. This compound can then be used to explore the visible spectrum. In what concerns silver iodide, it has quite the same sensitivity area but the effects are more intense and shorter.

We realized, for each substance, 10 current measurements for 10 spectrum areas equally shared. The spectrum was 80 cm long. The results we obtained are shown in Table 1. The numbers in the chart correspond to the deviation in the number of marks.

<table>
<thead>
<tr>
<th>Light color</th>
<th>Silver bromide</th>
<th>Warmed silver chloride</th>
<th>Silver iodide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dark red</td>
<td>3</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Red</td>
<td>7</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>Orange</td>
<td>7</td>
<td>7</td>
<td>5</td>
</tr>
<tr>
<td>Orange-Yellow</td>
<td>6</td>
<td>6</td>
<td>11</td>
</tr>
<tr>
<td>Yellow</td>
<td>7</td>
<td>7</td>
<td>12</td>
</tr>
<tr>
<td>Green</td>
<td>9</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>Blue</td>
<td>11</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>Violet</td>
<td>14</td>
<td>4</td>
<td>14</td>
</tr>
<tr>
<td>Dark violet</td>
<td>14</td>
<td>3</td>
<td>8</td>
</tr>
<tr>
<td>Near UV</td>
<td>18</td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td>Far UV</td>
<td>6</td>
<td>0</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 1: Measurements obtained in electrochemical actinometer replication

Our results correspond with Becquerel’s discoveries. Minimum and maximum sensitivities are different for each substance. Another result Becquerel obtained motivated him to propose a new kind of light rays. He discovered that the red spectrum extremity cannot initiate a silver chloride reaction, but can nevertheless continue a reaction initiated by the violet spectrum light (Becquerel 1842b). Becquerel referred to these effects using the names “continuator rays” (rayons continuateurs) and “exciter rays” (rayons excitateurs). He verified those effects, measuring currents, and scanned the entire spectrum several times. He showed that these effects increase after several spectrum scans. We replicated as well this series of experiments, and verified this discovery.

Becquerel extended his measurements using silver chloride and was able to considerably reduce the size of the areas he studied. He obtained for instance such fine results as detecting Fraunhofer’s black lines in the solar spectrum. Our experimental organization and our four-month only experience of manipulation, to be compared with Becquerel’s four years, must have hindered our precision. Indeed, we did not manage to achieve, over the entire spectrum (80 cm) more than 10 roughly equidistant measures: this should be compared with Becquerel’s achievement where he reached, detecting black lines, a resolving precision of the order of a tenth of a millimeter. Fraunhofer’s lines remained thus definitely out of our experimental reach and it proved equally impossible to measure those lines behind violet, as Becquerel did. This failure, despite repeated attempts, makes clear the precision and the quality of Becquerel’s experimental work.

He was used to work in a dark room, as was every physicist at this time, and he received a rigorous experimental training; this is probably still not enough to explain the enormous difference between his precision and ours. This drove us to consider his work as extremely rigorous and precise.

Conclusion

In our thesis, we used two tools to explore Edmond Becquerel’s work. A controversy analysis, which surveys the debate between Jean-Baptiste Biot and Edmond Becquerel, and a replication activity concerning the experiments that generated and fueled this controversy. Using both in a same context can cause difficulties, as noted by Dominique Pestre (Pestre 1994). According to him, whereas a controversy analysis requires caution with respect to anachronism, replication activity is necessarily anachronistic. Our work about Edmond Becquerel shows that some cases can nevertheless be studied using the association of both methods. The results we obtained were actually made possible because of this association.

3 The question of the sense one can assign to the word “ray” is complex, and played an important role in the running quarrel between Biot and Becquerel. We cannot develop it here: let us just note that this word doesn’t necessarily mean “corpuscular”. This issue is discussed in Chappert 2004.
We only reported here the different results of the replication. It could appear odd that we choose principally to present the difficulties and the failures we met. But those failures, both the resolved ones or not, proved more informative than some results which fit with Becquerel ones.

Becquerel did not report most of the problems we met, but elements of his instruments descriptions drive us to think most probably he must have met them too. Conception difficulties, such as water leaks, or tannin dispersion conduct us to postulate he did not technically construct his boxes.

The discovery of the currents produced by the liquid agitation helped us to establish a connection between two of Becquerel's research domains, which seemed totally disconnected before our replication.

One the most important information obtained with the help of the replication is the role of the photographic processes in Becquerel's work. To start with, we used in the actinometer black room the same habits we acquired in a photographic black room. The space organization and the movements are similar. Next, the chemical processes used in the silver halides plates' preparation are really close to photographic chemical processes. Becquerel himself mentions this link.

The actinometer owes a part of his efficiency to photography. In turn, the results obtained with it opened new perspectives to the latter. The use of the “exciter” and “continuator” rays, discovered by Becquerel, simplified photographers’ work. Soon, the actinometer was modified and readily used to select the exposure of photographic plates. It changed and ended up becoming one of the first sensitometers.

References:

