
Physics and chemistry to question authenticity: the case of the Simon Le Noir mechanism

Augustin GOMAND

AFAHA regional meeting – 4 December 2022

Projet *Simon Le Noir*



The question of authenticity

Principle of XRF analyses

Experimental protocol

Steel and rust

Gilding

The process of fire gilding

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Brass parts

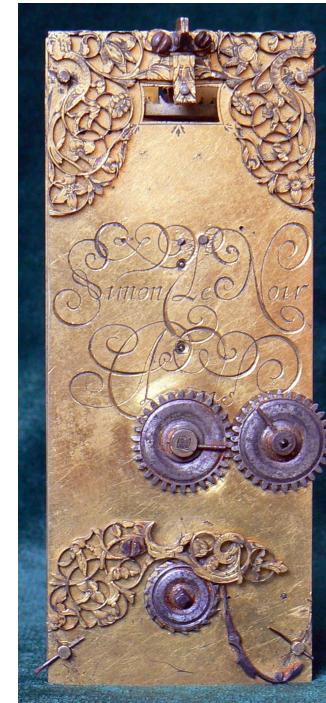
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Introduction: the Simon Le Noir project

- Project initiated in October 2020 following the discovery of a mechanism signed Simon Le Noir (seen from the back on the figure at right)
- The mechanism presents many specificities that makes it quite different from the first French pendulum clocks (the *pendules religieuses*) and seems rather to belong to the Renaissance style & era
- Anecdote reported in a manuscript by Claude Raillard (~1720): Simon Le Noir would have been the first to apply the pendulum in France according to his son, Jean-Baptiste
- Main objectives of the project:
 - Detailed analyses of the mechanism from a technical & stylistic point of view
 - Historical researches on Simon Le Noir and the first pendulum clocks
 - Formulation of hypotheses on the place of the studied mechanism in the history of clockmaking
- First article published in the *Horlogerie Ancienne* journal, June 2022 issue ¹
- Website to follow the work in progress: <https://agomand.github.io/asln/en>
- Other publications to follow in 2023



¹ A. Gomand, *Simon Le Noir et l'application du pendule aux horloges : une histoire parallèle ?*, Horlogerie Ancienne, 91, June 2022

The question of authenticity: a brief history

- Recurring question in the studies of objects that are possibly historically significant: is the object perfectly authentic? was it repaired? reconstituted? or may it be a fake?
- Until now, very few clocks have been submitted to extensive analyses about their authenticity, only some “specimens” related to a great invention or innovation:
 - invention of the portable clock = the watch → portative clock of Peter Henlein
 - application of the pendulum to clocks → Jan van Call regulator, **Simon Le Noir mechanism**
 - invention of the balance spring...
- Analytical methods that have evolved during the 20th century with scientific innovations:
 - stylistic & technical analyses (before the 20th century) → useful to check the consistency with the alleged date of manufacture BUT mainly **subjective** analyses and sometimes not sufficient
 - analyses of materials by direct observation = optical microscopy (20th century) → structure of materials that can be compared with the techniques and uses of the time BUT analyses often **destructive** (cuts / samples necessary)
 - spectroscopic / tomographic analyses (late 20th century) → precise chemical composition (quantified) + internal structure of materials from **non-destructive & objective** analyses → **subject of this lecture**

The question of authenticity: two examples

- Regulator of Jan van Call: presented some time as the oldest pendulum clock ever built
- Sold at Sotheby's in 1986, bought by the Science Museum, studied in the British Museum
- Analyses globally inconclusive ²:
 - signatures engraved after the gilding
 - spectroscopy: no mercury in the gilding
 - gilding possibly electrolytic...
 - anachronism of the secondary cursor of the pendulum
 - no known history before the sale...
- Probably a reconstitution of new and old, or a pure forgery (the most shared hypotheses)

² See the articles published in the *Antiquarian Horology*, vol. 33-6 & 34-1, for the main discussions about this clock – the photography is taken from the article of S. Whitestone, *The van Call, a modern forgery*, AH 34-1, p.48



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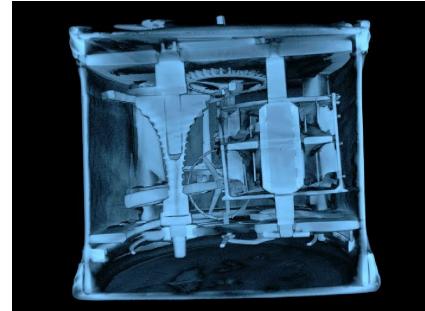
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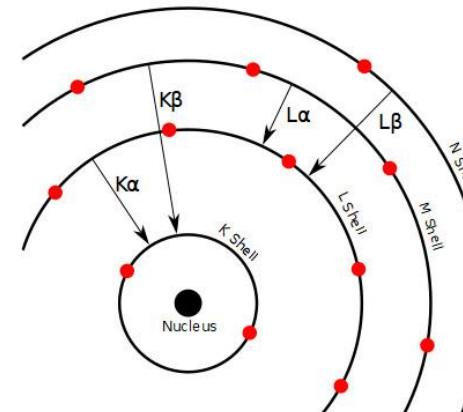
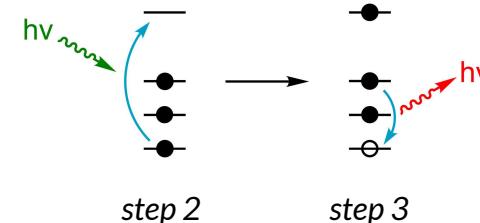
- Small clock engraved “Petrus Hele” for Peter Henlein, the presumed inventor of the watch around 1500
- Clock bought in 1897 by the Germanisches Nationalmuseum
- Early suspicions about its authenticity: signature covering the scratches → not original
- Tomographic analyses conducted in 2013 & 2014³
- Too many adjustments from the 19th century have been found even in the structure of the clock (the plates and some wheel arms recut, some bearings moved...)
- At best a clock that dates from the 16th century but heavily modified in the 19th century (and not by Peter Henlein?), at worst a pure forgery



³ J. Ehrt, *Ein Mythos auf dem Prüfstand - Die Untersuchungen an der sogenannten Peter Henlein-Uhr des Germanischen Nationalmuseums Nürnberg* (Restaurierungsatelier Jürgen Ehrt, 2021) – photographs from <https://artsandculture.google.com/story/LAXxeqppGOtCLA>

Principle of XRF analyses

- XRF = X-Ray Fluorescence: non-destructive technology to perform chemical analysis of materials
 - Principle :
 1. The sample is bombarded with high energy radiation
 2. Electrons are stripped from the atoms by photoelectric effect → the atoms are in an **unstable state**
 3. Electrons of the atoms come to replace those which were ejected = electronic transition → emission of a photon X **whose energy is characteristic of the atom**
 4. Emitted photons captured by a detector that measures their energy (energy analysis = EDS, for *Energy Dispersive Spectroscopy*)



Images: https://fr.wikipedia.org/wiki/Spectrom%C3%A9trie_de_fluorescence_des_rayons_X

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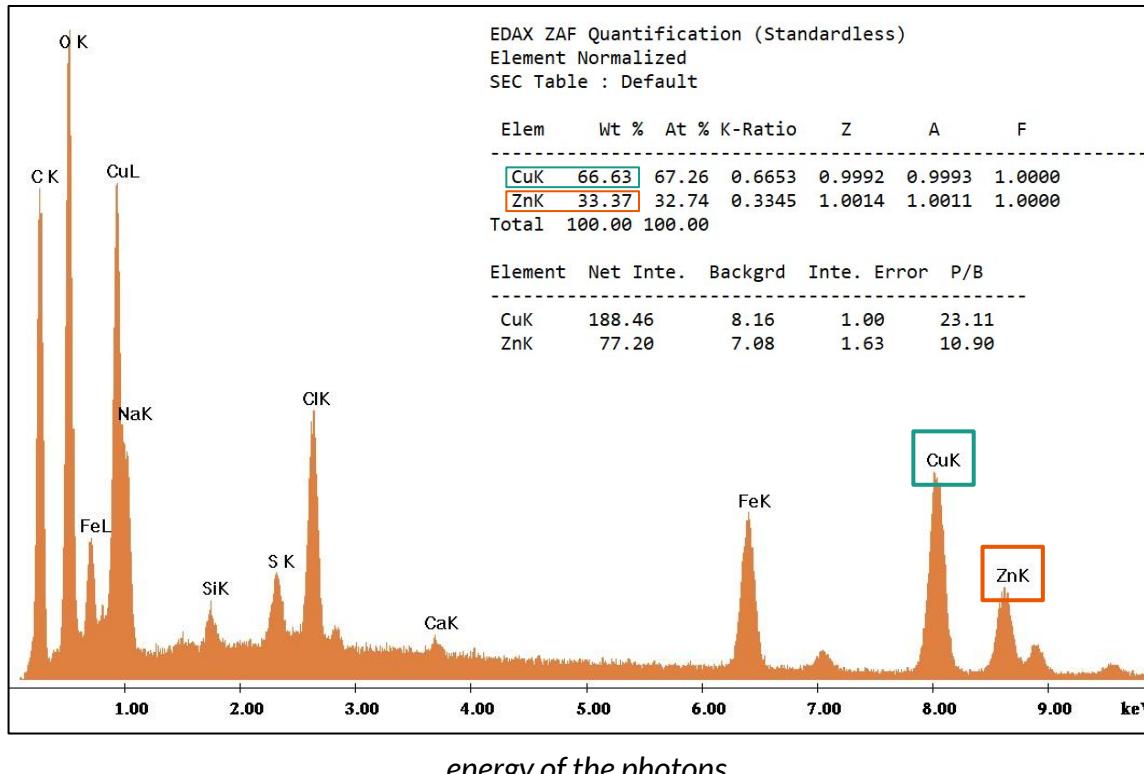
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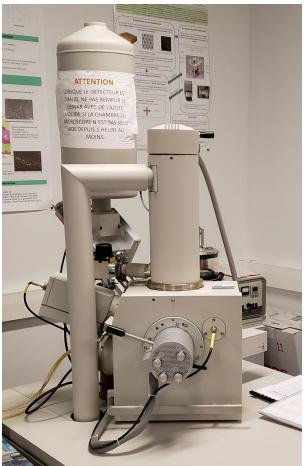
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number of photons detected



Experimental protocol

- Measurements done with the scanning electron microscope of the LGPM of CentraleSupélec⁴
- Protocol:
 1. The parts were scraped with a piece of wood to remove surface impurities (when needed)
 2. The parts are installed on aluminium studs with carbon pastilles and steel springs



⁴ <https://lgpm.centralesupelec.fr/sites/lgpm/files/inline-files/ESEM.pdf>

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Experimental protocol

3. Photons collected during 60 seconds (energy of the beam: 20 keV)
 4. Step (3) repeated on other areas of the part depending on the results obtained.
 - When the rust and the impurities have been analyzed, step (1) (cleaning of the analyzed area) has to be avoided.
-
- Purpose of the analyses:
 - composition of the steel and the rust → classical steel with only iron & carbon? natural rust?
 - composition of the gilding → presence of mercury?
 - composition of the brass parts → consistent with the brass used in the 17th century?
 - + comparison with other results gathered on clocks & scientific instruments of the same era (ongoing).
 - Ultimate objective: check the authenticity of the mechanism with a scientific & objective method

► Steel and rust

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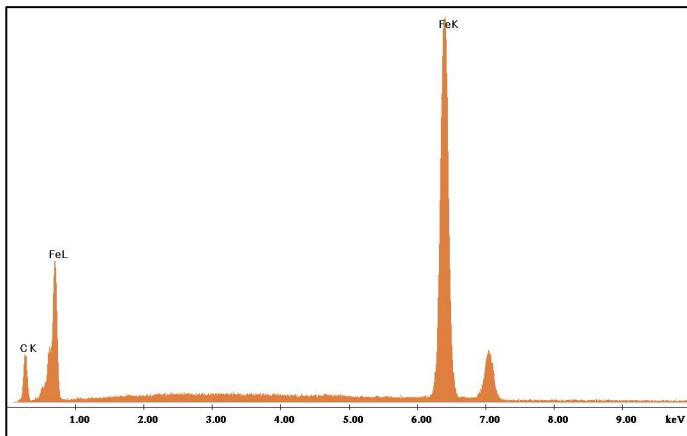
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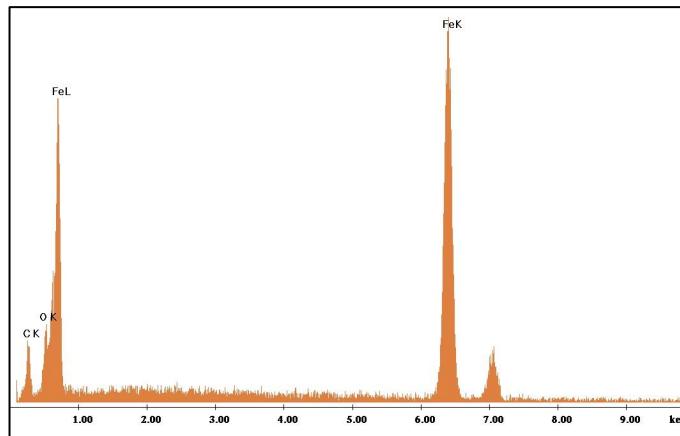
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Steel and rust: measurements on pivots

- First spectra collected on steel parts “polished” by friction (pivots)
- Observation: detectable elements = iron, carbon, oxygen (because of oxidation), sometimes copper (because of friction in brass bearings) → no additional elements like chromium, nickel, manganese... added since the 19th century⁵, hence “**simple**” steel as expected



Verge



Contrace wheel

⁵ N. Chezeau, De Réaumur à la Première Guerre Mondiale : les étapes de la maîtrise de l'acier, l'essor des aciers spéciaux, Comptes Rendus de l'Académie des Sciences – Chimie, vol. 15, July 2012

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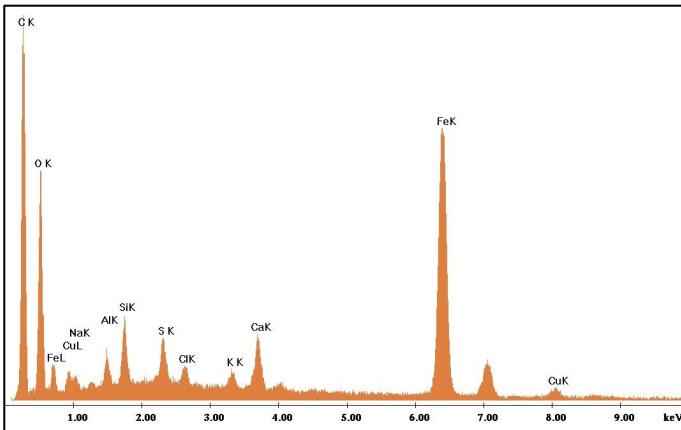
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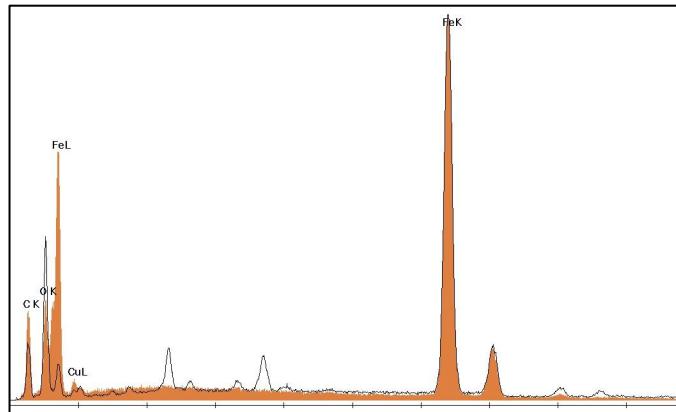
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Steel and rust: corrosion products

- Next spectra collected on the rust that covers some steel parts
- Observation: new elements detected that were not seen before: sodium (Na), aluminium (Al), silicium (Si), sulphur (S), chlorine (Cl), potassium (K) & calcium (Ca)
- **They are no “added elements” from the steel** as they are not detected on “clean” areas + sometimes found on brass parts where no rust is visible → **external origin**, but which one?



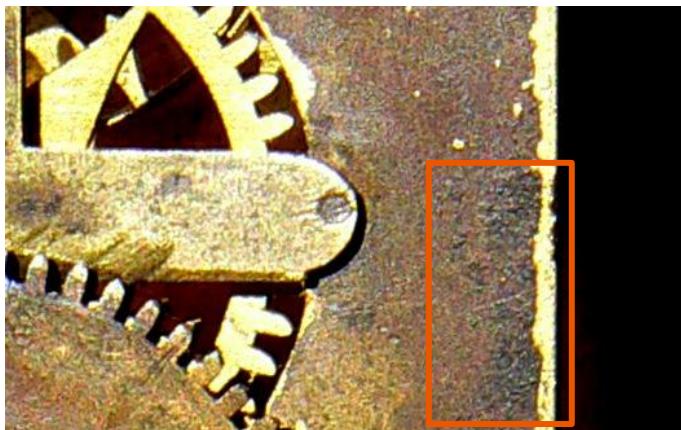
Right winding wheel



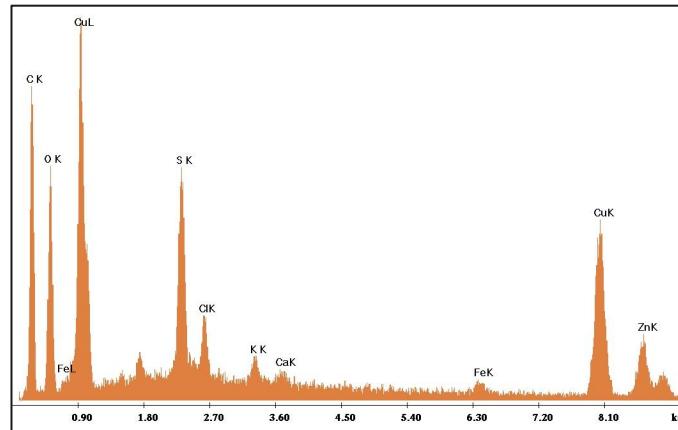
Superposition of the spectra of the ratchet (black line) and the winding arbor (orange)

► Steel and rust: origin of the impurities

- Correlation between some elements, notably the couples Al-Si & K-Ca → aluminosilicates?
- When it was rediscovered, the mechanism was covered with a thin layer of brown granular material, probably earth or clay like that found in cements or bricks
- Material consistent with the presence of couples Al-Si & K-Ca + sulphur & iron oxide
- Hypothesis checked by analysing an area where some dirt was accumulated



Sediment agglomeration on front-plate



Spectrum of the “sedimentary” area



▶ Steel and rust

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The process of fire gilding

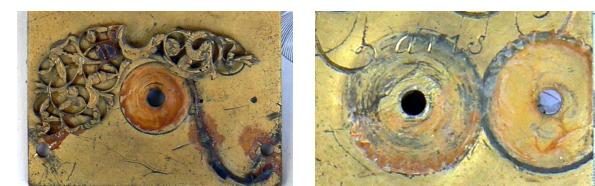
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Rust on back-plate before cleaning

Steel and rust: origin of the impurities

- Would it be possible that brick dust have accumulated in the rust during its formation?
- The rust follows the contour of the parts (e.g. the teeth of the winding wheels and the outlines of the decorations) → formed by **condensation**, repeated hot / cold cycles = water film (dew?) between the decorations / wheels and plates
- Hypothesis reinforced by the presence of cracks on some parts → caused by humidity + chemical reaction with ammonia (traces of nitrogen noted on some spectra)
- Rust propagation in a privileged direction → mechanism stored **horizontally**
- **Conclusion:** the mechanism was probably stored in a garage for several years or decades

Gilding: the process of fire gilding

- Until the 19th century, gilding was performed by mixing gold with mercury to obtain an amalgam that was applied with a brush on the surfaces to be gilded, then the amalgam was heated to evaporate the mercury
- Very aesthetic results but very toxic method... superseded in the 19th century by electrolytic gilding
- To see the process in action: https://www.youtube.com/watch?v=ES_NKoVW7Vo

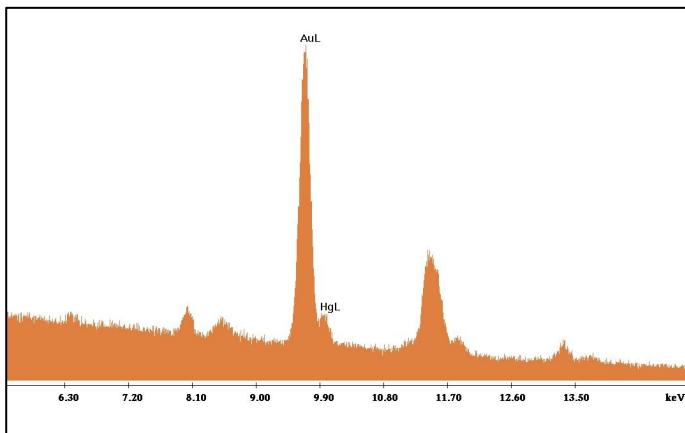


Captures from the video (link above), © Dirk Meyer

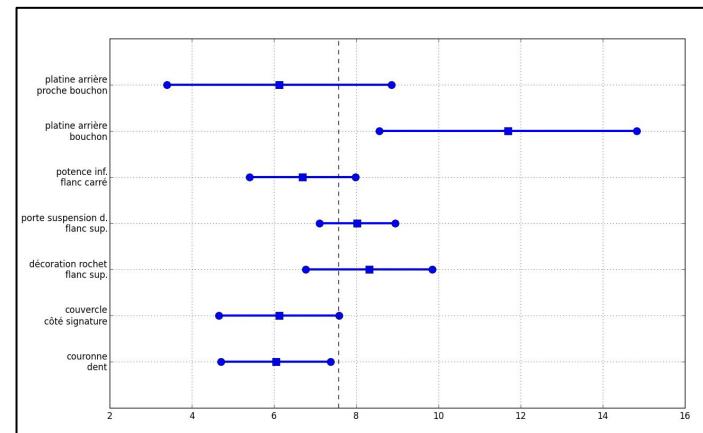
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Gilding: analyses

- Mercury detected in low quantity → “shoulder” near the peak of gold (see left figure)
- Every gilded part analyzed do contain some mercury
- Relative concentrations compared to gold are summarized in the right figure below, always higher than 5% → **it confirms that these parts are indeed fire-gilded**
- Initial concentrations estimated with Margreiter method⁶, consistent with the expectations



Upper side of the right suspension cock



Mercury concentrations measured

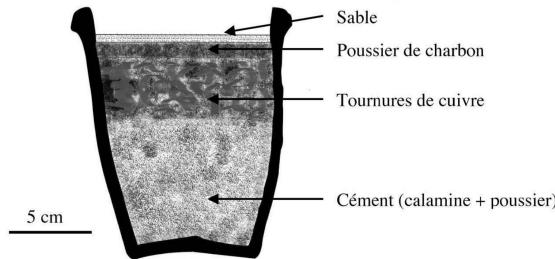
⁶ R. Margreiter et al., Investigations on fire-gilding, Archaeometry, June 2022

Brass parts: making brass in the 17th century

- Cf. the *Dictionnaire de Chymie* from Macquer⁷:

“On fait un **cement** composé d'une partie & demie de bonne **pierre calaminaire**, & autant de poudre de charbon pulvérisés ensemble : [...] on le met dans un pot de terre ou **creuset** : on y introduit une partie de **cuivre très pur, réduit en lames** : [...] on ferme le creuset, & on le chauffe seulement assez pour le faire bien rougir par dégrés. [...] Lorsqu'il est refroidi, on y trouve le **cuivre devenu jaune, augmenté d'un quart, & quelquefois d'un tiers de son poids**”

- “Calamine” brass that can incorporate only a limited amount of zinc: ~28% if the copper is in plates, ~33% if it is granular
- Experiments conducted recently⁸ to reproduce this brass-making process (figures at right)



Arrangement of the elements in the crucible



Metallic conglomerates obtained after cementation

⁷ P. J. Macquer, *Dictionnaire de Chymie* – volume 1 (Paris: Lacombe, 1766), p.320

⁸ A. Doridot, L. Robbiola & F. Tereygeol, *Production expérimentale de laiton par cémentation en creuset ouvert, avec du minerai de zinc, selon les recettes médiévales et modernes*, ArcheoSciences

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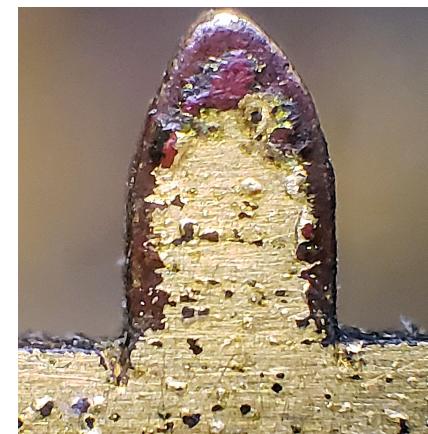
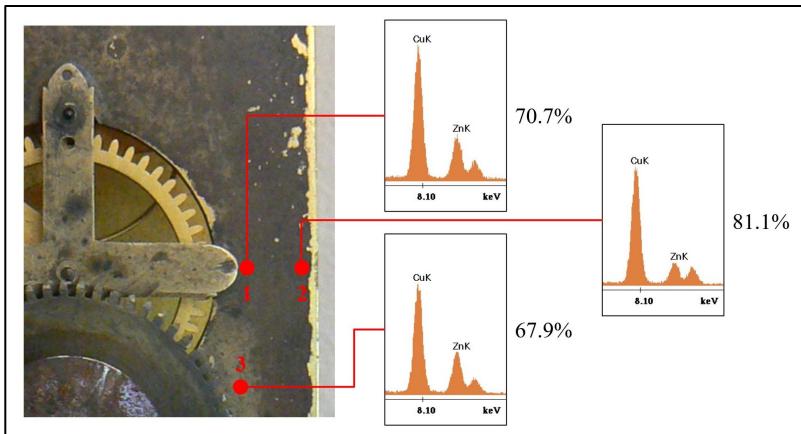
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Brass parts: analyses – limitation & uncertainties

- Geometric constraints of the microscope: some parts could not be analyzed (e.g. the teeth filed on the intermediate wheel → insufficient inclination)
- Alteration of the original zinc composition because of **dezincification** = differential corrosion process that causes brass to lose more zinc than copper
 - phenomenon illustrated by 3 spectra collected on different areas of the front-plate
 - similar surface condition on the brass behind the gold layer, areas difficult to analyze



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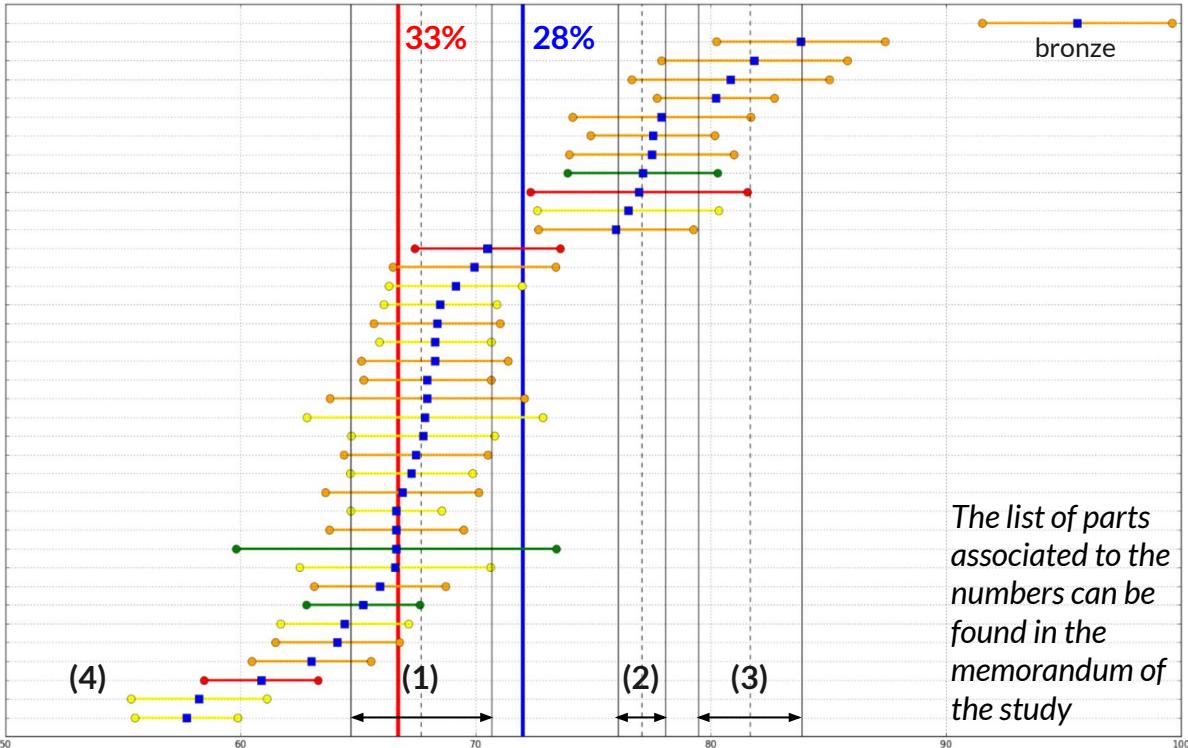
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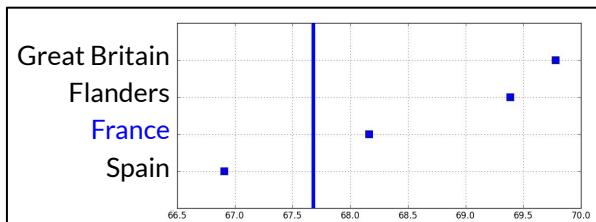
Brass parts: analyses – global results

41 - rod in the bearing
 19 - bush
 19 - rivet
 18 - bush
 19 - bush
 31 - great wheel
 32 - disc to support (33)
 31 - hour hand canon
 33 - pinion
 3 - wheel collet
 32 - cylindrical part
 7 - base of the barrel
 33 - great wheel
 3 - wheel
 41 - verge cock (bridge)
 30 - arbor
 30 - disc
 33 - tall repaired tooth
 2 - wheel
 19 - T-shaped bridge
 19 - plate
 30 - pinion
 44 - base
 8 - barrel cap
 33 - short repaired tooth
 35 - disc
 14 - base
 37 - wheel collet
 19 - plate
 42 - base
 27 - base of the bridge
 18 - plate
 39 - wheel collet
 12 - decoration
 23 - false-plate
 41 - verge pivot bearing
 27 - collet
 14 - close to bearing



Brass parts: detailed analyses

- **Type 1:** most of the structural parts (plates, bridges, some wheels...)
 - high quality brass made from granular copper, used since ~1560 in France and in several countries in Europe to produce scientific instruments ⁹
 - mean concentration seen in Le Noir mechanism close to the French one (cf. figure below)
 - **consistent with the alleged period & country of manufacture**



- **Type 2:** parts not gilded or not visible from the back (wheels of the motion-work...)
 - "classical" calamine brass used during the 16th century, medium quality
 - possibly dedicated here to the non-visible parts of the mechanism? Example of the barrel: cap of type 1 and gilded, base of type 2 and not gilded nor visible... same for the driving wheel: great wheel of type 1 & teeth visible from the back, pinion of type 2 & not visible

⁹ M. Pollard & C. Heron, *Archaeological chemistry – 2nd edition* (RSC Publisher, 2008), p.195 (p.219 for the concentrations by country)

Brass parts: detailed analyses

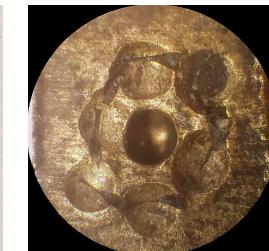
- **Type 3:** parts of “low added value” (rivets, pins, bushes) that make the link between some structural parts (T-shape & motion-work bridges) and the decorations of the verge
 → brass made from remelting of old brass material = higher dispersion of concentrations & less zinc content (because it evaporates during the melting process)
 → **use of “raw” copper quite common during the Renaissance as it was cheaper** (also on Coster D4¹⁰)
- **Type 4:** $[Cu] < 66\%$ (limit of the cementation process)
 → some modern parts (collet added on the motion-work bridge & repair on the lower potence of the crown wheel)
 → other parts that seem original: possibly made of the recently invented “Prince Rupert metal” used to mimic gold? Case of the central winding wheel collet: brass part that could not be gilded (because of soldering) but which is visible from the back... same for the verge bearing



Red-copper pins on Coster "D4"



Lower potence of the crown wheel



¹⁰ K. Piggott, A Royal 'Haagseklok', Appendix Three, Open-Research. MEMORANDUM D4 : A Salomon Coster Pendulum Timepiece

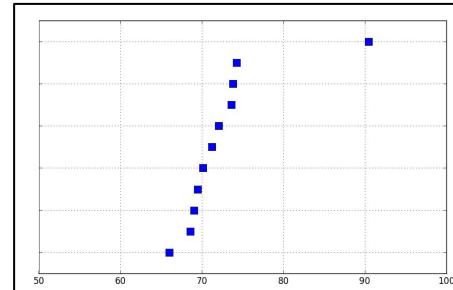
Brass parts: comparative analyses

- Almost no published data on 17th century clocks → some experts and museums contacted to try to gather data
- Study of Gregory Bailey on a German table clock signed Johann Scheirer, circa 1675 ¹¹
→ the 3 main type of brass seem to be used, with type 1 predominant as expected
- Clocks from Thomas Tompion (1709) and George Graham (1722) ¹²: mainly brass of type 2, [Cu] ~ 76% → **this confirms that this type of brass was indeed used by some clockmakers (even the greatest ones)**
- Quid of the simultaneous use of types 1 & 2?
→ French trigometer of Philippe Danfrie (1580) ¹³: both types are present, type 1 with [Cu] ~ 67-68% and type 2 with [Cu] ~ 77-80% → **similar to the Le Noir mechanism**

¹¹ G. Bailey, *About Time: Analysis and Conservation of a 17th-Century Table Clock*

¹² M. Pollard & C. Heron, *Archaeological chemistry - 2nd edition*, p.225

¹³ *ibid*, p.223



Clock from Johann Scheirer – XRF analyses

Conclusion: summary of the analyses

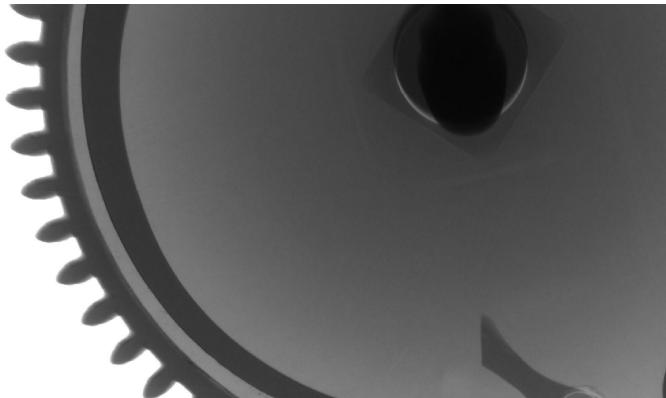
- Steel without added elements detected (below the limit of detection)
- Fire-gilding used, mercury concentrations consistent with the supposed manufacturing date
- Different brass used:
 - **68% Cu / 32% Zn:** high quality brass for structural parts and gilded parts, as used in the 17th century on scientific instruments
 - **77% Cu / 23% Zn:** medium quality brass for non-gilded and non-visible parts
 - **>80% Cu / <20% Zn:** brass from recast? = remelting of old brass for small parts of "low added value"
 - **<66% Cu / >34% Zn:** either modern brass = repairs at the beginning of the 20th century, or 17th-century brass of type "Prince Rupert" recently invented?

→ globally, the analyses are conclusive and confirm the authenticity of (almost) all the parts of the mechanism

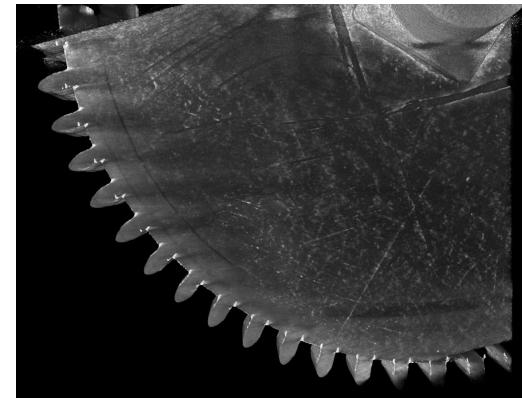
- Bonus: storage of the mechanism over the last decades → probably in a garage where it underwent daily temperature variations, hence condensation + cracks on some parts

Conclusion: way forward

- End of the EDS analyses for some remaining parts + parts of an Isaac Thuret *pendule religieuse*
- Detailed analyses of some trace elements (Ni, Ag, Bi, Pb, Sb) to identify the place where the copper has been extracted & check the total consistency of some parts between them
- Tomographies already carried out with the LMPS of ENS Paris-Saclay → post-processing in progress, useful to analyze previous repairs / engraved inscriptions & the inner structure



Scanner aux rayons X de la roue de la fusée



Reconstitution de la roue en 3D

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