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

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AFAHA regional meeting – 4 December 2022

Projet Simon Le Noir

LGPM
GÉNIE DES PROCÉDÉS ET MATÉRIAUX

# 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**

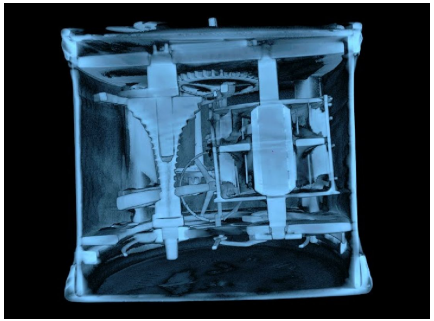
# The question of authenticity: two examples

- 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

# The question of authenticity: two examples

- 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 & 2014 [3]
- 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

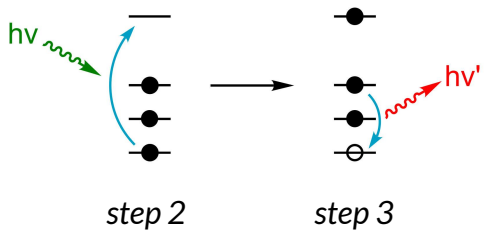


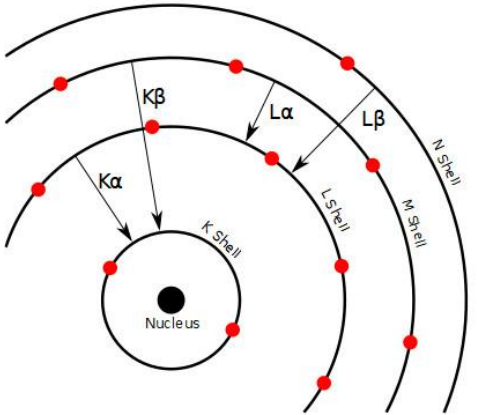
[3] J. Ehrt, *Ein Mythos auf dem Prüfstand - Die Untersuchungen an der sogenannten Peter Henlein-Uhr des Germanischen Nationalmuseum Nürnberg* (Restaurierungsatelier Jürgen Ehrt, 2021) – photographies from https://artsandculture.google.com/story/LAXxeqppGOtCLA

# 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*)

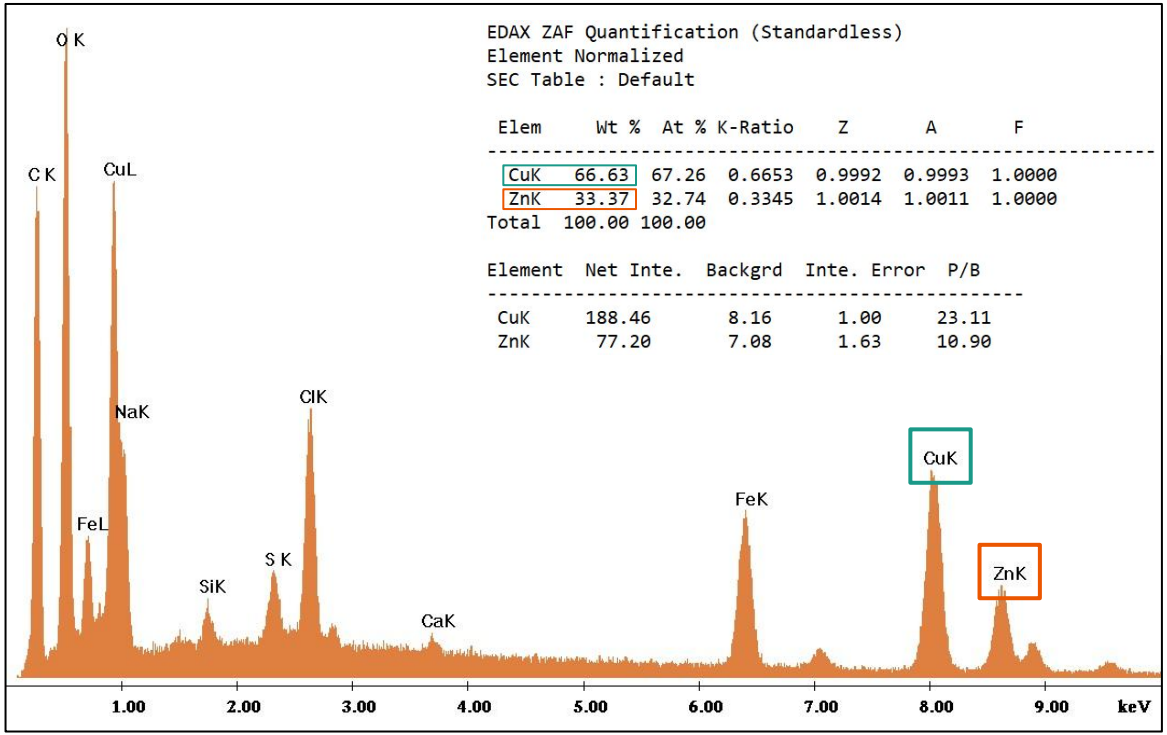



Images: https://fr.wikipedia.org/wiki/Spectrométrie_de_fluorescence_des_rayons_X
Image from the top by Calvero, public domain.
Image from the bottom by HenrikMidtiby, CC BY-SA 3.0

# Principle of XRF analyses: example of spectrum

*number of photons detected*

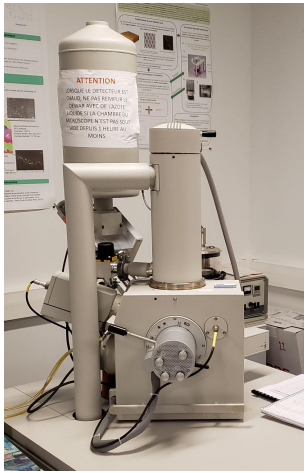



*energy of the photons*

# Experimental protocol

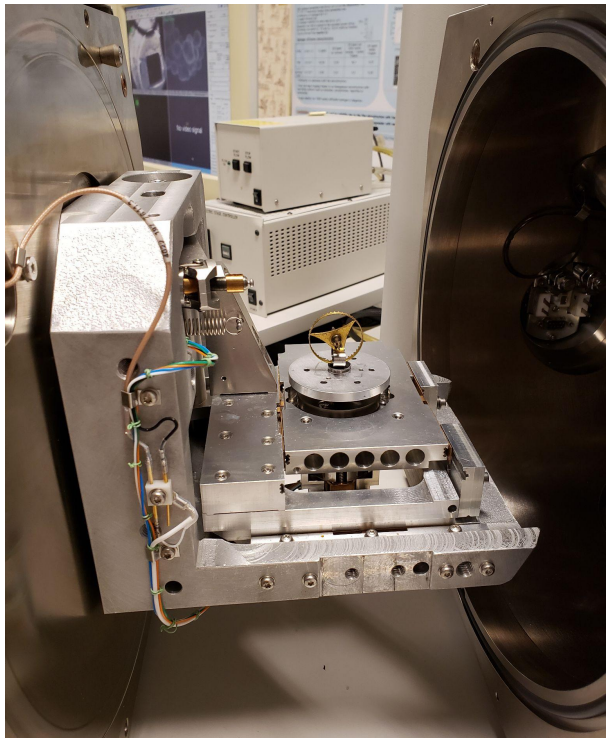
- Measurements done with the scanning electron microscope of the LGPM of CentraleSupélec [4]
- Protocol:

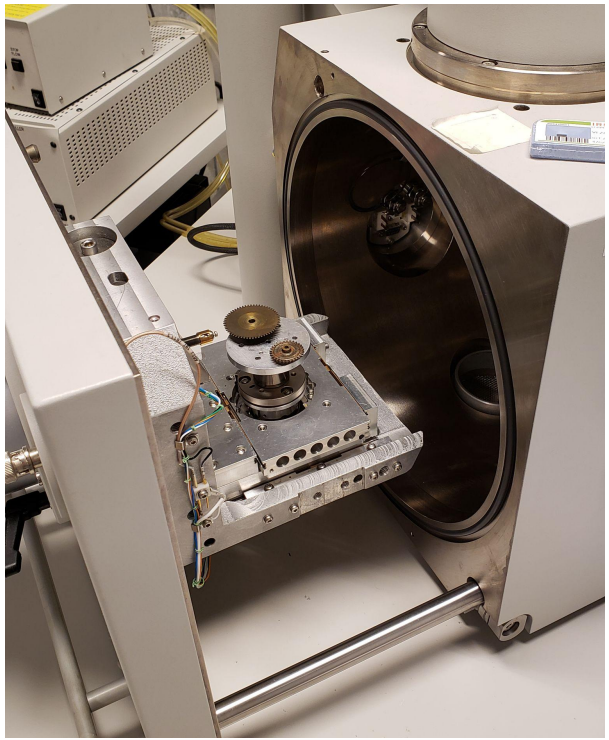
1. The parts were scraped with a piece of wood to remove surface impurities (when needed)
2. The parts are installed on aluminium studs with carbon pastilles and steel springs




[4] https://lgpm.centralesupelec.fr/sites/lgpm/files/inline-files/ESEM.pdf

# Experimental protocol





# 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.

- <u>Purpose of the analyses</u>:

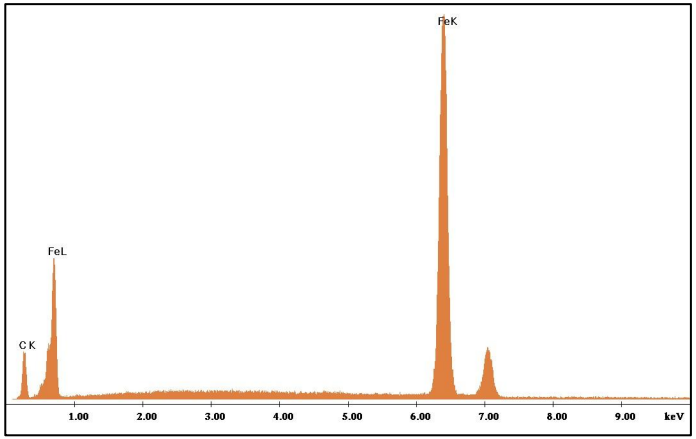
- composition of the steel and the rust → classical steel with only iron & carbon? natural rust?
- composition of the gilding → presence of mercury?
- composition of the brass parts → consistent with the brass used in the 17$^{th}$ century?

+ comparison with other results gathered on clocks & scientific instruments of the same era (ongoing).

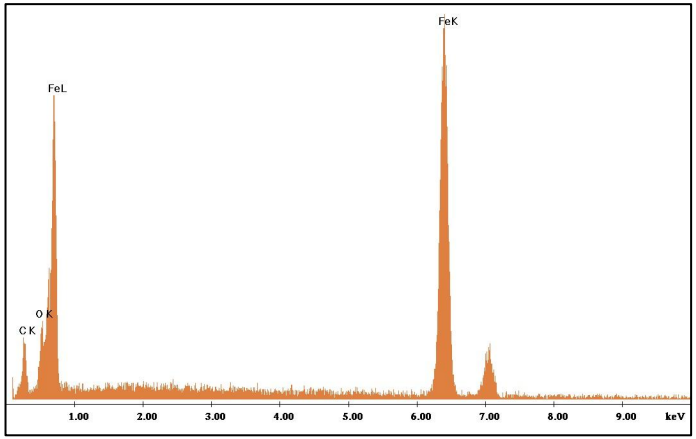
- **<u>Ultimate objective</u>: check the authenticity of the mechanism with a scientific & objective method**

# 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 century [5], hence **"simple" steel** as expected




*Verge*

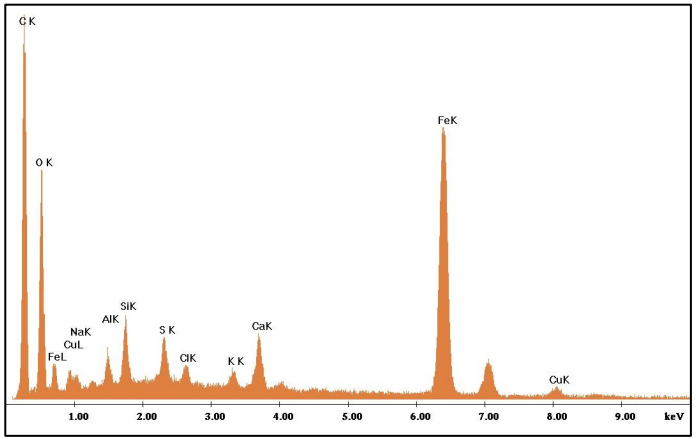



*Contrate wheel*

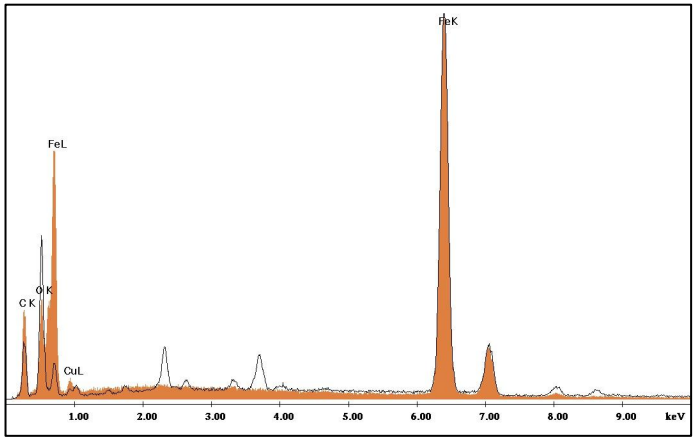
[5] N. Chezeau, *De Réaumur à la Première Guerre Mondiale : les étapes de la maîtrise de l'acier, l'essor des aciers spéciaux*, Comptes Rendus de l'Académie des Sciences – Chimie, vol. 15, July 2012

# 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?



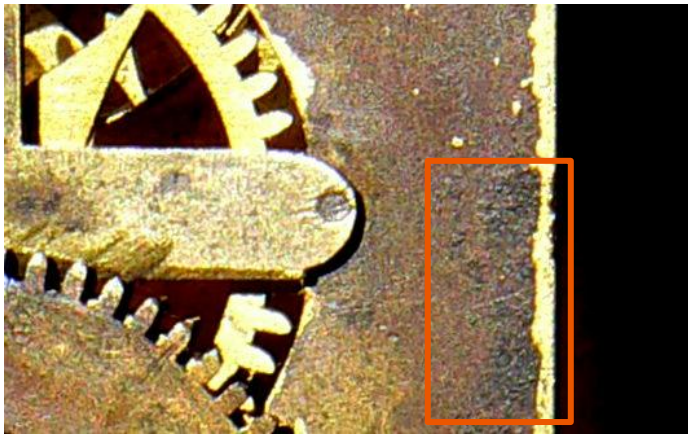

*Right winding wheel*



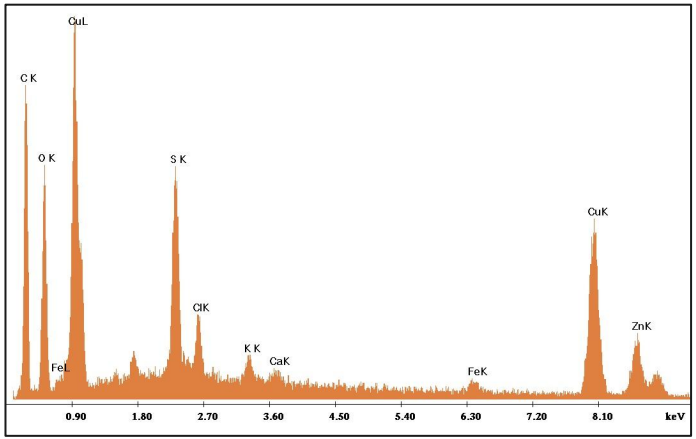

*Superposition of the spectra of the ratchet (black line) and the winding arbor (orange)*

# 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



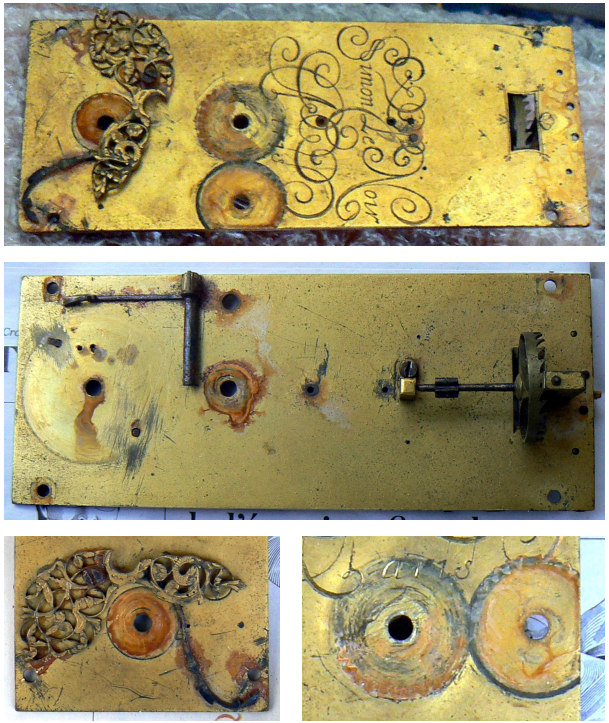
*Sediment agglomeration on front-plate*




*Spectrum of the "sedimentary" area*

# Steel and rust: 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**



*Rust on back-plate before cleaning*

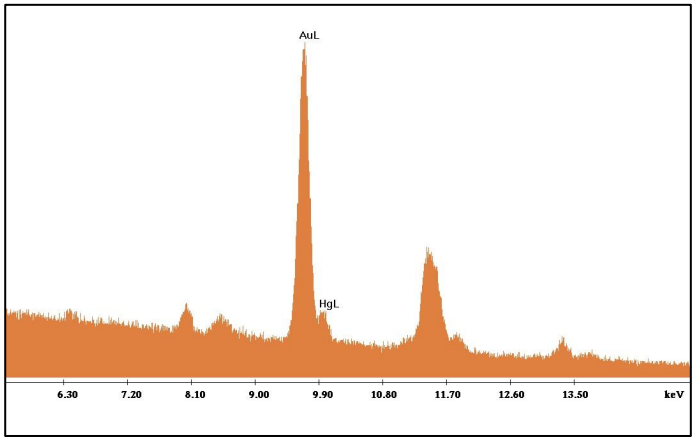
# Gilding: the process of fire gilding

- 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 19$^{th}$ century by electrolytic gilding
- To see the process in action: https://www.youtube.com/watch?v=ES_NKoVW7Vo

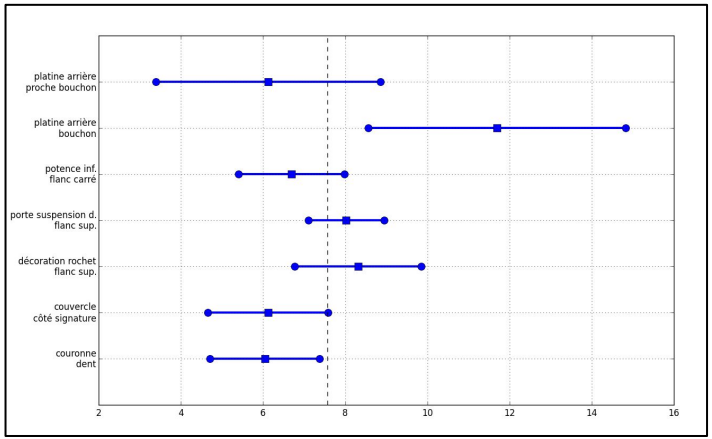
Captures from the video (link above), © Dirk Meyer

# 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 method [6], consistent with the expectations




*Upper side of the right suspension cock*




*Mercury concentrations measured*

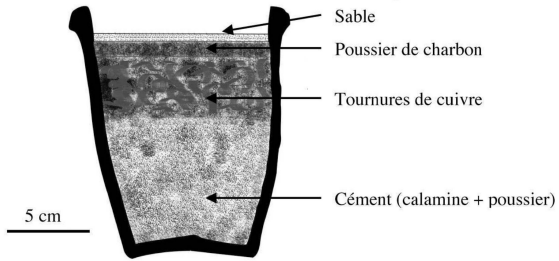
[6] R. Margreiter *et al.*, *Investigations on fire-gilding*, Archaeometry, June 2022

# Brass parts: making brass in the 17th century

- Cf. the *Dictionnaire de Chymie* from Macquer [7]:

"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 can incorporate only a limited amount of zinc: ~28% if the copper is in plates, ~33% if it is granular
- Experiments conducted recently [8] 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

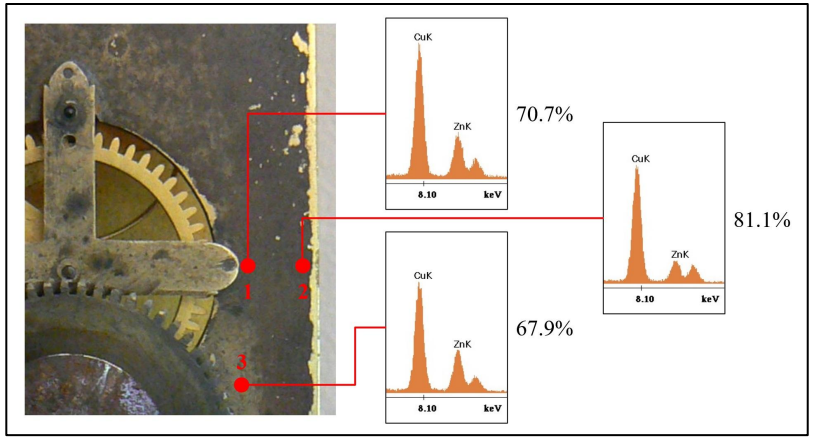
[8] A. Doridot, L. Robbiola & F. Tereygeol, *Production expérimentale de laiton par cémentation en creuset ouvert, avec du minerai de zinc, selon les recettes médiévales et modernes*, ArcheoSciences

# Brass parts: analyses – limitation & uncertainties

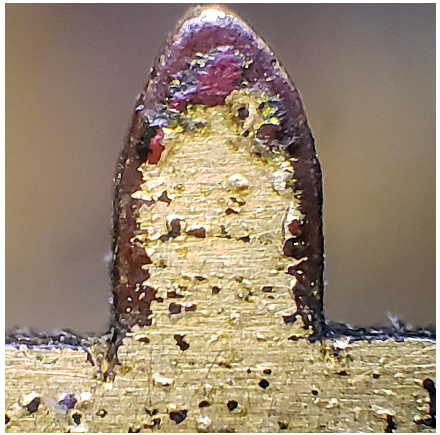
- Geometric constraints of the microscope: some parts could not be analyzed (*e.g.* the teeth filed on the intermediate wheel → insufficient inclination)
- Alteration of the original zinc composition because of **dezincification** = differential corrosion process that causes brass to lose more zinc than 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

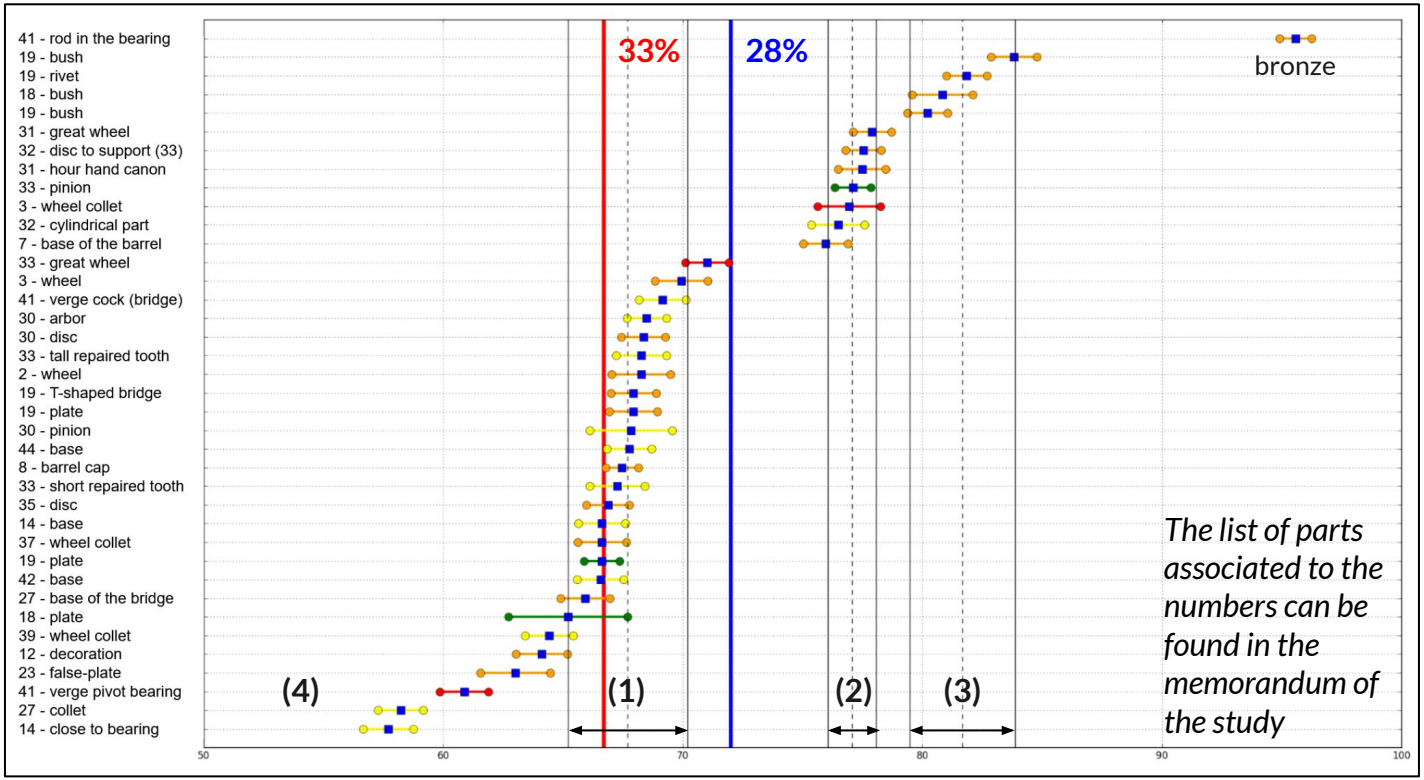



*Dezincification brought to light on the front-plate*



*Copper behind the gilding on the contrate wheel*

# Brass parts: analyses – global results



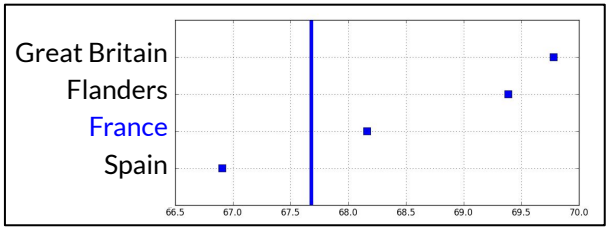
# Brass parts: detailed analyses

- 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

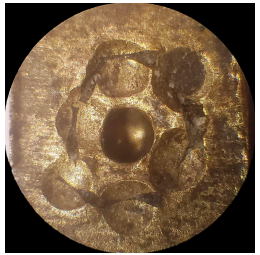
  → brass made from remelting of old brass material = higher dispersion of concentrations & less zinc content (because it evaporates during the melting process)

  → **use of “raw” copper quite common during the Renaissance as it was cheaper** (also on Coster D4 [10])
- 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”*

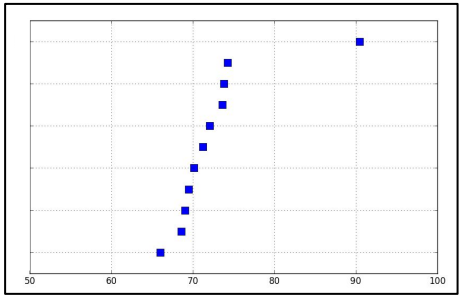


*Lower potence of the crown wheel*

[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**




*Clock from Johann Scheirer – XRF analyses*

[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

# Conclusion: summary of the analyses

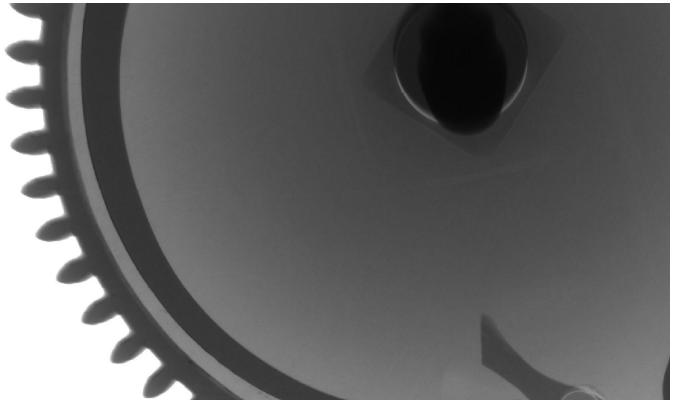
- Steel without added elements detected (below the limit of detection)
- Fire-gilding used, mercury concentrations consistent with the supposed manufacturing date
- Different brass used:
  - **68% Cu / 32% Zn:** high quality brass for structural parts and gilded parts, as used in the 17$^{th}$ century 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 20$^{th}$ century, or 17$^{th}$-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**

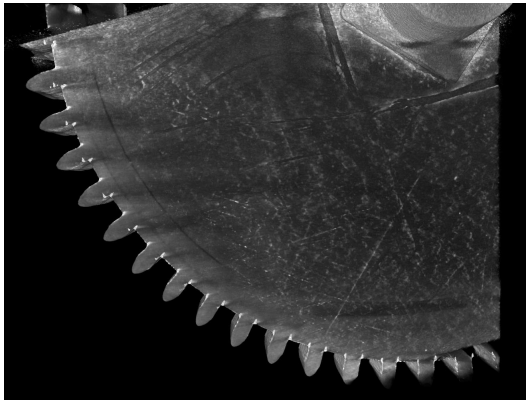
- Bonus: storage of the mechanism over the last decades → probably in a garage where it underwent daily temperature variations, hence condensation + cracks on some parts

# 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



*X-ray radiograph of the fusee wheel*



*3D reconstruction of the wheel*

# Bibliography

Bibliographic resources in order of citation in the text:

1. A. Gomand, *Simon Le Noir et l'application du pendule aux horloges : une histoire parallèle ?*, Horlogerie Ancienne, 91, June 2022, online: https://agomand.github.io/asln/en/documents.html
2. S. Whitestone, *The van Call, a modern forgery*, Antiquarian Horology, 34-1
3. J. Ehrt, *Ein Mythos auf dem Prüfstand - Die Untersuchungen an der sogenannten Peter Henlein-Uhr des Germanischen Nationalmuseum Nürnberg* (Restaurierungsatelier Jürgen Ehrt, 2021), online: https://www.uhrenrestaurator.de/de/ein-mythos-auf-dem-pruefstand
4. https://fr.wikipedia.org/wiki/Spectrométrie_de_fluorescence_des_rayons_X
5. https://lgpm.centralesupelec.fr/sites/lgpm/files/inline-files/ESEM.pdf
6. 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, 15, July 2012, online: https://doi.org/10.1016/j.crci.2012.04.008
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The figures that are not associated to any reference are from the author.