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Historical Article

Martin Heinrich Klaproth (1743-1817), a Great, Somewhat Forgotten, Chemist

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Abstract. For various reasons, some of them linked to the evolution of the historiography of Chemistry, many recognized and important chemists in their time – and in ours, because of the legacy they left – are relegated to some degree of oblivion. One of these chemists, dead just over 200 years ago, is Martin Heinrich Klaproth (1743-1817), a key figure in the transition from phlogiston theory to Lavoisier's new chemistry and one of the creators of modern analytical chemistry, an empiricist who discovered many elements and polymorphism, author of remarkable chemical and mineralogical analyses and creator of archaeometry. This article presents the life, training and scientific production of a great, but less remembered, chemist, crossing the frontiers of Chemistry in many cases.

Keywords: history of chemistry, Martin Heinrich Klaproth, history of analytical chemistry, history of the discovery of the elements, mineral and mineral water analyses, archaeometry.

> As much as I worried about meeting the obligations that the chemist owes to Science, for whose progress he responds to, and the audience, to whom he reports the fruits of his labor; as much as I myself committed to imprinting on my analyses the greatest possible degree of accuracy and truth; many were the occasions when I realised how difficult this goal is.
> (Martin Heinrich Klaproth)

FORGETFULNESS

A little more than two hundred years ago, on January 1, 1817, died Martin Heinrich Klaproth, one of the most important, respected and productive chemists of his time. In the posthumous opinion of August Wilhelm von Hofmann (1818-1892), Klaproth was "for all times a model of the true scientist"[1], and yet today he is not remembered as deserved. Despite his great importance for the consolidation of Lavoisier's new chemistry, especially in the German-speaking academic world, even with the discovery or confirmation of new elements (uranium, zirconium, cerium, tellurium, titanium, strontium, chromium), with a systematic work in the fields of analytical chemistry (gravimetry, data processing) and of inorganic chemistry, with the creation of archaeometry (application of chemical procedures in archaeology), Klaproth's name is now not very common even among chemists. How is it possible that a researcher of enormous importance and influence in his own time is now somewhat forgotten? Forgetting would even be understandable if his proposals were currently not valid, or their empirical data wrong, but this is not the case.

Georg Edmund Dann (1898-1979), historian of pharmacy and professor of history of pharmacy at the University of Kiel, biographer of Klaproth, wrote about it in 1958:

> No chemical law, no theory, much less a hypothesis are associated with Klaproth's name. With his exact works of investigation he participated personally like few others in the establishment or confirmation of the bases of the new Chemistry. But from the results of his researches he did not develop any regularity or general law, he did not himself develop any theory from his data[2].

Brita Engel adds that Klaproth did not leave any longer text exposing in an integrated way his ideas and conceptions about the new antiphlogistic chemistry, to whose dissemination he contributed so much. He did not even write a textbook, which could offer an idea of his lectures, which can, however, be evaluated through an extensive manuscript of 588 pages, left by Arthur Schopenhauer (1788-1860), who studied at the University of Berlin in 1811/1812, not only with Fichte and Schleiermacher, but also with Klaproth. Another manuscript, by the physician Stephan Ferdinand Barez (1790-1858), complements Schopenhauer's. Both were transcribed and studied by B. Engel in 1987/1989[3].

A law. or theory, or reaction or reagent linked to the name of a chemist certainly perpetuates his memory along with the application that is made, to this day, of his law, theory, reaction, or reagent, even if the researcher who created them occupies a less prominent place in the general context of our science. Every chemist, and probably researchers from other areas, will know the names of Guldberg and Waage, Proust, Fehling or Mohr, but the aforementioned Klaproth, or Torbern Bergman, or Wollaston are less remembered. Although present in almost all histories of Chemistry, cited and quoted in papers, the real importance of his work should, in our opinion, be the subject of more detailed discussion.

Pharmacist, chemist and member of the Berlin Academy, Klaproth was self-taught. Has this fact contributed to some marginalization? This seems unlikely, considering Dalton, Davy and Faraday were self-taught, and obligatorily figure in all history of science texts, irrespective of ideologies. On the other hand, the academic community seems to value graduates from the academy itself: Mitscherlich, Klaproth's successor, coming from Göttingen and from Berzelius' laboratory, deserved a statue at the University of Berlin, but not Klaproth, whose contribution to Chemistry, however, far surpasses Mitscherlich's.

There may be extra scientific motivations minimizing Klaproth's contribution to the whole history of chemistry. Perhaps the most obvious case of forgetting and excluding scientists for unscientific reasons is the ostracism to which brilliant Austrian chemists were condemned after Austria's political and economic downturn in 1918: where do we still find figures such as Loschmidt, Rochleder, Lieben, Hlasivetz, Pfaundler, Redtenbach, authors of extensive empirical and theoretical work? The scientific isolation of Germany and Austria after the First World War (1914/1918) may have contributed to the ostracism or even oblivion of many scientists. Needless to say, opinions fluctuate with time and context, and sometimes the version is worth, not the objective fact.

There are reasons for some marginalization which are inherent to the scientific activity, and as such justifi-

Figure 1. Valentin Roses's pharmacy 'Zum weissen Schwan', in the Nikolaiviertel, in Berlin, lithograph, c. 1840, where Klaproth was assistant. (Edgar Fahs Smith Collection, University of Pennsylvania, Philadelphia).

able. But there are also reasons unrelated to science, arising from historical-political contexts, and thus not always justifiable. What matters is keeping, within the limits where this is possible, the historical records of a great man, and that is what we intend to do succinctly in this article. It does not intend, and should not be, a hagiography, but Klaproth's scientific activity and practice are such that few criticisms can be made. Of course there are controversies and questions of priorities, but these are normal in periods of great expansion of scientific knowledge. But there are other, much deeper – and more dangerous – motivations for the ostracism to which Klaproth and many other chemists were relegated, which we will present at the end of this essay; The importance of uranium, which Klaproth discovered in 1789, for nuclear energy, contributes to preserve his memory.

THE ORIGINS AND FORMATION OF KLAPROTH

Of humble origins, Martin Heinrich Klaproth was born on December 1, 1743 in the small town of Wernigerode, in the mountains of the Harz, the second son of the tailor Johann Julius Klaproth (? – 1767). The medieval town of Wernigerode was nominally part of the county of Stolberg-Wernigerode, but Count Christian Ernst of Stolberg-Wernigerode (1691-1771) ceded his lands in 1714 to the Kingdom of Prussia. The modest birthplace, narrow and 3 meters wide, was rebuilt after a great fire that devastated a large part of the town in 1751. With the destruction of his family's house, he moved to the home of relatives. His childhood was unhappy. Of his four brothers, one died young; Julius Christoph (1739-....) studied theology and was a Lutheran pastor and teacher, and Christian August (1757-1812) held a public office. From 1755 to 1758 Martin Heinrich Klaproth attended the *Gymnasium* (*Lateinschule*), but abandoned it before completing his studies, because of the rigor observed by some teachers. In Dann and Schwedt's current critique, instruction at the *Gymnasium* was comprehensive and modern, similar to Halle's famous *Franckesche Stiftung*. For C. Friedrich, the professor Johann Christian Meier (1732-1815), from the *Gymnasium*, aroused Klaproth's interest in Pharmacy. To ensure his livelihood, he participated in the church choir (*Chorus symphonicus*), giving rise to the deep religiosity that accompanied him throughout his life. Even with little education, from 1759 to 1766 he was apprenticed in Pharmacy at the *Adler und Ratsapotheke* (founded in 1575), with the pharmacist Friedrich Victor Bollmann (1712-1789), in the nearby city of Quedlinburg, becoming a pharmacist in 1766, at the age of 23. Between 1766 and 1771 he went to work as a pharmacy assistant at the *Hofapotheke* (Court Pharmacy) in Hannover, at Gabriel Heinrich Wendland's (1730-1796) pharmacy *Zum Engel* (located on *Mohrenstrasse* and now disappeared) in Berlin, and at the *Ratsapotheke* in Danzig (present-day Gdansk, Poland), then owned by the physician Johann Alexander Hevelke (1731-1806). He decided in 1771 to return to Berlin, to study with Johann Heinrich Pott (1792-1777) at the *Collegium Medico-Chirurgicum*, with Andreas Sigismund Marggraf (1709-1782) at the Academy of Sciences, and with the pharmacist Valentin Rose the Elder (1736-1771), with whom he learned not only chemistry, but also Latin and Greek.

The year 1771 marked Klaproth's professional life: he became Valentin Rose's assistant at his *Zum Weissen Schwan* (To the White Swan) pharmacy in Berlin, located on *Spandauerstrasse*, no longer in existence today. Rose, who had been a student of Marggraf and versed not only in pharmacy but also in chemistry (inventor of Rose's metal, a low melting point alloy) and in metallurgy, acquired the pharmacy in 1761. There worked and studied not only Klaproth, but also Sigismund Friedrich Hermbstaedt (1760-1833), who would take over the pharmacy in 1783, Conrad Heinrich Soltmann (1782-1859), Johann Daniel Riedel (1786-1843). Rose's pharmacy was a sought-after center of research and study. Still with Wilhelm Rose (1792-1876), grandson of Valentin the Elder, came to study pharmacy (1836/1840) the novelist Theodor Fontane (1819-1898), fellow countryman of Valentin Rose (in his novel "Effi Briest", from 1896, Fontane speaks of Carl Wilhelm Scheele and the discovery of oxygen, in the wake of manuscripts from Scheele's time then discovered by Adolf Erik Nordenskiöld). In his biographical writings "Von Zwanzig bis Dreissig" (1894), Fontane tells in a casual way his formation with Wilhelm Rose. The pharmacy, which in 1802 gained a new building designed by Karl Friedrich Schinkel (1781-1841), an exponent of classicist architecture that would characterize Berlin. The pharmacy was completely destroyed in 1945[4].

With the death of Valentin Rose the Elder in 1771, Klaproth took over the "White Swan" pharmacy, and the education of Valentin's four children, including Valentin Rose the Younger (1762-1807), later an important chemist and co-author with Klaproth of several articles. He also took care of the education of the children of Valentin the Younger, who died of cholera in 1807, Heinrich Rose (1796-1864) and Gustav Rose (1798-1873), later professors of chemistry and mineralogy, respectively, at the University of Berlin.

In 1780, Klaproth carried out the rigorous examinations required for the profession of pharmacist,

Figure 2. Martin Heinrich Klaproth (1743-1817). Engraving by Ambroise Tardieu (1788-1841), after a portrait by Eberhard Siegfried Henne. Public domain.

with a paper entitled "Treaty on Phosphorus, plus an annex on the preparation of the best distilled waters" (published in 1782). The year 1780 was another decisive year in Klaproth's career: in February he married Christine Sophie Lehmann (1748-1803), daughter of the famous mineralogist Johann Gottlob Lehmann (1719-1767), active in Saint Petersburg, and Marggraf's niece. Klaproth thus entered the Academy's innermost circle. In the same year, Klaproth bought the pharmacy *Zum Goldenen Bären* (To the Golden Bear) or simply *Bärenapotheke* (Bear's Pharmacy) pharmacy, located on the same street as the White Swan Pharmacy, right next to old *Nikolaikirche*. Klaproth renovated the pharmacy and installed a private laboratory there, in which he analysed dozens of minerals and discovered uranium. A plaque shows today the location where this discovery, so crucial in the future and for the future of Humanity, took place. Klaproth sold the pharmacy in 1800. The building was replaced in 1898 by a modern one, which in turn was destroyed in 1945. The complex of houses was restored to recall, although not reproduce, its original appearance in the popular *Nikolaiviertel*.[5]

In 1787 Klaproth was admitted to the Berlin Academy of Sciences, succeeding in 1802 Franz Carl Achard (1753-1821) as director of the laboratory. He began teaching at the *Collegium Medico-Chirurgicum* (1782), at the Mining School (1784), at the Military Academy (1787), and finally, in 1810, self-taught in chemistry and without a university degree, he was chosen to be the first professor of Chemistry at the new University of Berlin, on the recommendation of Wilhelm von Humboldt (1767-1835), the founder of the university. His colleagues were the physicists Paul Ermann (1764-1851) and Karl Tourte (1776-1847), the mathematician Johann Georg Tralles (1763-1822), the zoologist Martin Lichtenstein (1780-1857), the botanist Karl Willdenow (1765- 1812) and the mineralogist Christian S. Weiss (1780-1856)[6]. Klaproth's renown had crossed borders: he was a member of the Royal Society (1795), the Paris Academy (1804), the Stockholm Academy (1804), and the St. Petersburg Academy (1805). Fortnightly, he taught public Chemistry classes, in the spirit of the Enlightenment, approaching current topics, and spoke about chemical subjects at meetings and private events. After successive attacks of apoplexy (he had already suffered a heart attack in 1814) he died in the modest residence reserved for him at the Academy, on January 1, 1817, at the age of 74. He was buried in Dorotheenstadt cemetery, but his tomb, for which Schinkel had drawn a cross cast in iron, has not been preserved. In 1993, on the 150th anniversary of his birth, a plaque was placed in the cemetery. His successor at the university was Eilhard Mitscherlich (1794-1863), recommended by Berzelius (who had refused the post to which he himself had been invited). The university honors Mitscherlich with a bronze statue by Carl Ferdinand Hartzer in front of the side façade (1894), but does not honor Klaproth. Signs of an (almost) forgetting. Many of the places where Klaproth worked no longer exist – another factor that leads to oblivion – but other important places of interest for the scientist's life interested admirers can still be visited: the university, Wernigerode, Quedlinburg. The site of the old Academy building (on *Dorotheenstrasse)*, built in 1711 and destroyed in 1944, today is occupied by a parking building. In 1996, an iron monument by Ralf Sander (*1963) in homage to Klaproth, in the form of a stele, was installed next to the main building of the Technical University in Berlin. Johann Friedrich John (1782-1847) called *klaprothium* the element cadmium, discovered as an impurity of zinc (1817, Stromeyer; Klaproth had died shortly before). A crater on the moon was named Klaproth.

The infrequent citing of Klaproth is, perhaps, only paralleled by that of Marggraf – but in this case the sunset can be attributed to the fact that Marggraf was a phlogistonist, swept away (unfairly) by the 'house cleaning' proposed by some historians[7].

Martin and Christiane Klaproth had a son and four daughters, two died in early infancy. Klaproth's son Julius Klaproth (1783-1835) studied oriental languages against his father's wishes, travelled through Siberia and the Caucasus, was a member of the St. Petersburg Academy and settled finally in Paris. By the end of the 19th century his work was hopelessly outdated. Johanna Wilhelmine (*1787) married the *Bergrat* Heinrich Wilhelm Abich (1772-1844), and Charlotte Ernestine (1790-1868) married the Prussian General Moritz von Bardeleben (1777-1868).

THE WORK – THE THEORY

Considering the stage of development of Chemistry at his time, Klaproth's work is quite comprehensive and diverse. As we have seen, he left few general texts, but his view of Chemistry can be reconstructed from the notes of others (Barez, Schopenhauer), from his 218 articles, and his participation in several collective works, with other researchers, such as the five volumes from the "Chemisches Wörterbuch" ("Chemical Dictionary") written in partnership with Friedrich Benjamin Wolff (1765-1845). He left aside the French and Latin of the Academy's publications, writing exclusively in German.

Klaproth's theoretical contributions to Chemistry are two and they are interconnected: his general conceptions in the field of Chemistry and the necessary replacement of the phlogistonist theory by a more convincing antiphlogistonist theory, essentially that of Lavoisier. The clash provoked by the introduction of Lavoisier's antiphlogistonist theory in Germany is known[8], not a heated clash as is sometimes made to believe, but a clash anyway, using rational and scientific arguments, but also extra-scientific arguments of nationalist inspiration (after all, it was the period of the Napoleonic wars, the occupation of part of German territory by French troops and the dissolution of the Empire by Napoleon in 1806). The first defenders of the new antiphlogistonist theory in Germany were Johann Friedrich August Göttling (1755-1809), thanks to Goethe professor of Chemistry at the University of Jena, and Sigismund Friedrich Hermbstaedt (1760-1833), professor at the *Collegium Medico-Chirurgicum*. Göttling not only defended the new theory, but published a positive critique in 1794, "Contribution to the Corrections of Antiphlogistic Theory", while Hermbstaedt translated Lavoisier's "Traité" into German (1792). Klaproth read Hermbstaedt's manuscript, studied it, and repeated several of the experiments. Klaproth's position would be fundamental, since after becoming convinced of the validity and usefulness of Lavoisier's theory, he led the Berlin Academy in 1792 to officially adopt it. Klaproth was not content with theoretical considerations and the observations of others, but remade part of Lavoisier's experiments (despite the difficulty in acquiring the equipment), for example, the famous "pelican experiment", with which Lavoisier showed that there is no transformation of water into earth (the experiment seems anachronistic in the 18th century, but is linked to several natural observations, for example, rain and its effects on plant growth and nutrition). The experiment was remade, and Klaproth wrote: "*The formerly accepted belief in the conversion of water into earth is unfounded: analyzing the experiments which were intended to prove it, it was found that the supposed earth was glass, detached from the retort by the effect of friction and heat*"[9]. Converted, he wrote in 1792:

> The ease with which it was believed to be able to give from the phlogiston theory a satisfactory explanation for the most important chemical phenomena, led to forgetting that phlogiston is also a hypothetical entity, and that the system built on this theory would be solid and unshakable. With the almost daily increase in the sum of chemical knowledge, and especially in view of the discovery of gaseous species, there should finally be a review of this part of Chemistry. Among the researchers who are responsible for the greatest merits in this regard, Lavoisier is at the forefront, having convinced himself, after years of experience, of the insufficiency of Stahl's theory, overturning it entirely and introducing the current and new system, which it is also called antiphlogistic[10].

Accepting the new theory, the concept of element was also accepted, as proposed by Lavoisier, an element defined a *posteriori*, as the ultimate result of an analysis (Boyle's element was defined *a priori*). Klaproth mentions 51 *Elemente* or *unzerlegbare Stoffe* (= indecomposable substances), including among them light (*Lichtstoff*), heat (*Wärmestoff*) and 'electrical matter' (*Elektrische Materie*). There were 28 metals, 11 of which discovered while he himself was acting as a chemist (Lavoisier's table contained 33 elements, also including light and caloric)[11].

An original contribution by Klaproth to theoretical chemistry was the discovery in 1788 of polymorphism: the same compound can present itself in several different crystalline forms. Klaproth described two crystalline states for calcium carbonate ($CaCO_3$), calcite (trigonal, hardness 3, density 2.7) and aragonite (orthorhombic, hardness 3.5-4, density 2.95). (The hardness and density values are not from Klaproth's times; and the name "aragonite" was coined only in 1797 by Abraham Gottlob Werner [1749-1817] in Freiberg).

Given the above, the idea that Klaproth was averse to theoretical considerations cannot be maintained, and as a proof, B. Engel describes the theoretical conceptions of Klaproth's chemistry as follows[12]:

- he intends in his lectures to explain, clarify, fighting the view of chemistry as a "secret science";
- chemistry is not a rigid system, but an evolutionary path destined to approach the truth;
- the guideline of his work is clear objectivity, simplicity and accuracy – only experiments that can be repeated are of value as a proof;
- his own contributions are important to him as steps towards the apprehension of reality;
- his work is always descriptive, and whenever possible, quantitative.

Seen today, it is an almost positivist recipe, and certainly an empirical one, averse to unverifiable theorizations – it is in this sense that Klaproth is averse to theories. Consistent with its scientific beliefs, he abhors Alchemy, and unmasks many of the miraculous "elixirs" then in vogue. For example, he called into question the alleged alchemical transmutations in the famous case of Johann Semler (1725-1791), professor of theology at the University of Halle, who claimed to have been successful in obtaining gold: without knowing the "aid" of his servant, who had added traces of the precious metal to the jars. The mysterious "elixir" unmasked were the "Bestuscheff drops" (*Tincture Ferri Chlorati Aetherea*) for "evils of the nervous system", which were just a solution of $FeCl_3$ in ether dissolved in alcohol... the belief in miracle drugs is not of today.

Klaproth's theoretical stance can be understood from the way he converted from the phlogiston theory to the oxygen theory, but it can still be followed in all his "scientific genealogy", in which we can go back to the Paracelsian Daniel Sennert (1572-1637) , putting us in front of a current question: does the evolution and modification of chemical theory necessarily lead, in the creation of chemical knowledge, to ruptures (or new "paradigms", in the Kuhnian nomenclature)? Or, as we have said before, the development of new experimental techniques and methodologies (such as replacing the idea that chemical analysis is a 'comparison of samples' by 'searching for sample components') would not more likely lead to new 'paradigms'?

Sennert → Rolfinck → Wedel → Stahl →
Neumann → Marggraf → V. Rose → Klaproth
KLAPROTH'S SCIENTIFIC GENEALOGY

In Klaproth's case, the adoption of a new theoretical model did not change his laboratory procedures, but it did change the causality and interpretation of the empirical facts studied, excluding *a priori* experiments considered to be meaningless, and including others that his predecessors considered unnecessary. Klaproth became a phlogistonist not only with his teacher Valentin Rose the Elder, but with readings from his apprenticeship as a pharmacist, such as the texts of Johann Friedrich Cartheuser (1704-1777) and Jakob Reinhold Spielmann (1722-1783), and the option for the new theory did not change his practices: uranium and zirconium were discovered in the context of the phlogiston theory, cerium and tellurium already under Lavoisier's theory, without changing laboratory methods. At the time, there was a tendency to consider, alongside "theoretical chemistry" (the analyses referring to the 'system of chemistry'), also a "rational chemistry", which dealt with all aspects capable of 'converting chemistry into science'. The search for rational chemistry dates back to the times of Georg Ernst Stahl's theory of phlogiston (1660-1734) – the theory of phlogiston was a rational theory, albeit based on false premises – and Klaproth's and his contemporaries strong opposition to Alchemy is also owed to the phlogistonists.

Klaproth is directly associated with the discovery or confirmation of the discovery of seven elements. Uranium and zirconium are unanimously mentioned as discovered by Klaproth, in 1789. In the other cases – cerium (discovery simultaneously with Berzelius), titanium, tellurium, strontium, chromium – questions arise about priorities, but it is up to him to confirm the discovery and the characterization of the element. Klaproth's generosity made him give up many disputes, leaving to his colleagues the credit for the discovery. He had only had to confirm it, because, as James Marshall mentions, his articles were in any case appreciated, for the guarantee of a good analysis. Klaproth's righteous character did

Table 1. Elements discovered or confirmed by Klaproth.

Element	Discovery	Independent Discovery or confirmation
1782 Tellurium	Müller v. Reichenstein	Klaproth (1788), Kitaibel (1789)
1789 Uranium	Klaproth	
1789 Zirconia	Klaproth	
1790 Strontium	Crawford, Cruikshank	T.C. Hope, Klaproth
1791 Titanium	Gregor	Klaproth
1797 Chromium	Vauquelin	Klaproth
1803 Cerium	Klaproth	Berzelius

not want to anticipate Henry de Montherlant's (1895-1972) saying that the glory of the great corrodes and destroys that of the small. At a time of great expansion of chemical knowledge, the simultaneity of discoveries is inevitable, giving rise to the consequent disputes over priorities. Klaproth's work with the elements is closely related to the improvements he introduced in Analytical Chemistry, and by extension in chemical analysis.

THE WORK – THE ELEMENTS

Of all these discoveries, the one with the greatest repercussion – not only in the history of chemistry, but in the history of Humankind – was the discovery of uranium. The prehistory of uranium begins in the 16th century, when in the inhospitable and sparsely inhabited mountains and forests of the Metalliferous Mountains (*Erzgebirge*), on the border between Saxony (Germany) and Bohemia (Czech Republic) began an intense mining activity, of silver, tin and other metals, which quickly turned the region into Europe's largest mining center (Freiberg, Annaberg, Aue, Johanngeorgenstadt in Saxony, Joachimstal [Jachymov] in Bohemia). Despite depleted silver veins and competition from silver from the New World, the mines (then owned by the Austrian crown) continued to be explored in the 18th century, producing mainly cobalt and bismuth. There was in these mines a black mineral, which apparently had nothing to do with the silver ores, which the miners called *Pechblende* (from the German *Pech* = pitch, *Blende* = ore, literally 'pitch-colored ore'). The first to describe pitchblende was the naturalist Franz Ernst Brückmann (1697-1753) in 1727. Axel Frederick Cronstedt (1722-1765) considered it a silver mineral (1758), and Abraham Gottlieb Werner (1749-1817), a mineral associated with iron (*Eisenpecherz*). Klaproth, using new analytical procedures he had developed, analysed a Johanngeorgenstadt mineral in the laboratory of his "Bear Pharmacy" (July 1789), and found it to be a compound of a new element, which he called uranite, later uranium, in honor of the discovery of the planet Uranus, in 1781 by Sir William Herschel (1738-1822), his compatriot living in England since 1757. Altogether Klaproth analysed about 300 samples of minerals from Johanngeorgenstadt, today exhibited at the Museum of Natural History in Berlin, which also preserves the more than 4800 pieces from Klaproth's mineralogical collection.

Briefly, he dissolved pitchblende (some say it was a sample of torbernite, phosphate of uranyl and copper, $Cu(UO_2)_2(PO_4)_2$,) in nitric acid, and treated the solution thus obtained with potash (K_2CO_3), obtaining a "yellow precipitate", which redissolves with a new amount of potash. Heating the yellow precipitate with linseed oil gives rise to a black mass, which on further heating turns into a black powder; this, when heated in an oven with coal, leads to a brittle black powder, which Klaproth considered to be the new metal (uranium), but was actually its oxide UO_2. No other element known to Klaproth presented such properties, hence his conclusion that pitchblende contained a new element. The results of his experiments were reported by Klaproth to the Academy of Sciences at the session of September 24, 1789[13]. At a scientific meeting in a building that no longer existed, the Atomic Age was born, and as I have written elsewhere[14],

> in the year of the Fall of the Bastille, when Humanity began to glimpse the spirit of Freedom, Equality, Fraternity, the first seed of a spectrum that more than a century and a half later seriously threatened the future of Humanity was also (innocently) planted. And if, to our unhappiness, the dream of Freedom, Equality, Fraternity has not yet materialized, we are consoled by the fact that the specter is also dead or at least asleep.

Klaproth isolated the oxide from a new metal, and obtained several of its compounds, such as uranium acetate (1793). Metallic uranium was only isolated in 1841 by Eugène Melchior Peligot (1811-1890), reducing UCl_4 with potassium (UCl_4 was also synthesized by Peligot). It was necessary to await the discovery of a stronger reductant than those known at the time, like potassium (Davy, 1807), to reduce certain metal oxides to the corresponding metal (Berzelius developed a reduction procedure with potassium).

For most historians, two conditions are necessary to consider a "discovery" of a new compound: obtaining it in pure state, and its perfect characterization by analysis. I add a third observation: the existence of resources that allow obtaining chemically the element. In Klaproth's time there were no resources to chemically obtain metallic uranium, so Klaproth is its discoverer. (Lavoisier considered the "earths" as elementary – lime, magnesia, soda, potash, barite – as there were no resources to isolate the metal from them, but he suggested the possibility that in the future they would prove to be composed). There is a controversy between Klaproth and the Hungarian chemist Antal Ruprecht (1748-1814) about the conversion of oxides into metals, the "metallization" or thermal reduction of the "earths"[15]. Considering that the *calces* are metal oxides, and given the then-known possibility of obtaining the metals manganese (Gahn, 1774) and molybdenum (Hjelm, 1781) by reduction with coal, Ruprecht, a professor at the Schemnitz School of Mines, intended to be this reaction a general reaction of metal oxides. He built a furnace with which he obtained temperatures of 1600 °C, and claimed to have reduced barite, lime and magnesia to their respective metals (1790). Klaproth was unable to repeat Ruprecht's experiments, and the analysis showed that the supposed metals released in the three cases were impure iron fragments, probably released by the equipment. Klaproth considered the "metallization" as the "Schemnitz Illusion", *Schemnitzer Illusion*, and it would be "impossible in principle" to obtain the metals from these earths (1791). Szabadváry draws attention to the care that we must take in science with statements such as "impossible in principle", because by electrolysis Sir Humphry Davy (1778-1829) managed to obtain the metals from the aforementioned earths, a result that Klaproth, somewhat grudgingly, ended up accepting. The controversy is an example of a dispute in which both sides are right: Ruprecht was right because the "earth" actually contains a metal, Klaproth was right because it is really impossible to get the metal with chemical resources. At the time of the clash, Klaproth's empiricism had won.

Pitchblende is an emblematic mineral in the history of science. In the same pitchblende, now from Joachimstal (provided by the Vienna Academy, through its president Eduard Suess [1838-1914]), Pierre (1859-1906) and Marie Curie (1867-1934) isolated in 1898 polonium and radium.

Another element discovered by Klaproth in 1789, again as its oxide form and again in his pharmacy, was zirconium. After platinum, it was the first element to be isolated from a non-European mineral, zirconite (zirconium silicate, $ZrSiO_4$), a semi-precious stone from Ceylon (present-day Sri Lanka), already mentioned in the Bible. It was not the first time that an eminent chemist had studied zirconite: Torbern Bergman (1735-1784) isolated from it an "earth", which actually was a mixture of alumina, iron oxide and lime. Klaproth analysed the zirconite, noting that 70% of the mineral was constituted by a new "earth", the *Zirkonerde* or zirconia, ZrO_2. Isolation was quite difficult, especially separating the contaminating iron. Although Klaproth believed he had obtained an element, metallic zirconium was only obtained by Berzelius in 1824, by potassium reduction of $K_2[ZrF_6]$.

The discovery of cerium[16] (or *cererium*, as suggested by Klaproth) in 1803, simultaneously and independently by the teams of Klaproth and Jöns Jacob Berzelius (1779-1848), led to the single most serious controversy in Klaproth's career, leading to a harsh exchange of correspondence between the two, interrupted by Klaproth, as it was not leading to anything positive. The incident had a banal origin: when Berzelius and his collaborator Vilhelm Hisinger (1766-1852) sent the journal *Neues Allgemeines Journal für Chemie*, edited by Adolf Ferdinand Gehlen (1775-1815), their article communicating the discovery of the new element, the editor replied that he had already received an identical communication from Klaproth and Valentin Rose, and that, for reasons of chronology, he would first publish Klaproth's work in the current issue of the magazine, and Berzelius' in the next edition. Gehlen's correct decision (although he attributed the discovery of cerium to Berzelius) angered Berzelius' disciples active in Paris, who started a fierce controversy, finally appeased by Louis Nicolas Vauquelin (1763-1829): Klaproth, a man of righteous character and already an experienced and famous scientist, had no need to appropriate the discoveries of others, and from what he had been able to observe during the controversy, Berzelius and Klaproth independently discovered the new earth, practically at the same time. In his view the two researchers should to be considered the discoverers of the earth "ceria", an opinion today accepted by most historians of chemistry. Klaproth himself calmly accepted the priority given to the Swede. The element's name is an allusion to the asteroid Ceres, discovered in 1801 in Palermo by Giuseppe Piazzi (1746-1826).

Both Berzelius and Klaproth isolated the ceria earth from bastnaesite (name given by Berzelius, Klaproth called it ochroite), a mineral found by Frederick Cronstedt (1722-1765) in 1751 in the Bastnaes mines, which belonged to the Hisinger family. For the history of chemistry, more important than assigning the priority of the discovery to Klaproth or Berzelius, is the finding that both ceria and yttria, the latter discovered by Johan Gadolin (1760-1852) in 1794 (from a mineral found in the Ytterby feldspar mines, which Klaproth named in 1801 gadolinite) are sources for the future discovery of new elements – real elements, such as the rare earths, elements never confirmed, discovered twice or more, spurious or non-existent, but nevertheless extremely valuable empirical searches in the historical context of chemistry. For the methodology of scientific work, error or failure can be as illustrative as success.

Of the other elements mentioned, the most complex case is that of tellurium. In 1782, Austrian chemist Franz Joseph Müller von Reichenstein (1742-1824), mine inspector in Transylvania (then part of Hungary, now in Romenia), among deposits of gold discovered a mysterious mineral he called (1795) *aurum problematicum*, possibly an antimony mineral (it is now known to be $(Ag,Au)Te_2$, telluride of gold and silver, silvanite). Müller was averse to analyses, and the mineral was studied, among others, by Antal Ruprecht and Torbern Bergman, who also supported the thesis of an antimony mineral.

Finally Müller von Reichenstein sent samples of *aurum problematicum* to Klaproth. In general terms, Klaproth's analysis involves the dissolution of the mineral in nitric acid, the precipitation of gold and iron by adding potash, neutralization of the solution with hydrochloric acid: it precipitates the oxide of a new "semimetal", as yet unknown; we know today that it is tellurium oxide, TeO. In 1796 Klaproth visited Vienna, and there learned of the analyses of a mineral found by Paul Kitaibel (1757-1817) in 1789 in Hungary (manuscript, the article was never published). Klaproth, who was then busy with Müller's samples, confirmed them, but did not realize at first that they were the same oxide that existed in the *aurum problematicum* sample. Once confirmed the identity, Klaproth called the new element tellurium, in 1798 (from *Tellus* = the Earth, "our dear mother earth"), and was a kind of godfather to the tellurium.

The discoveries of the elements strontium (1790), titanium (1791) and chromium (1797) were confirmed by Klaproth. Klaproth was an independent discoverer of strontium in 1793, but he was not the first to obtain it (always in the oxide state, SrO, metallic strontium was only obtained by Davy in 1809, by electrolysis). Klaproth prepared, however, several strontium compounds (chloride, nitrate, acetate, tartrate) and definitively differentiated $BaCO_3$ from $SrCO_3$, and consequently BaO from SrO. Klaproth was studying at the same time the properties of $BaCO_3$ and $SrCO_3$. The name strontium is an allusion to the lead mines of Strontian, Scotland, where in 1787 William Cruikshank (c.1745-1810), a chemist from the Woolwich arsenal, found a new "earth", so he is known, next to Adair Crawford (1748-1795), also from Woolwich, as the discoverer of this element (1790). A more detailed study of the new species, even before Klaproth, is that of Thomas Charles Hope (1766-1844), professor at the University of Edinburgh (successor to Joseph Black). Hope obtained strontium oxide by heating the Strontian mineral, $SrCO_3$, which he named strontianite. Klaproth confirmed in 1793/1794 the discovery of titanium, isolating titanium oxide, TiO_2, from rutile or *schörl* (a kind of tourmaline). In other analyses, in 1797, Klaproth also isolated strontium from the mineral celestine, $SrSO_4$. The original discovery of titanium, in 1791, is due to William Gregor (1761-1817), in a Cornish mineral, menachite or ilmenite, from which he isolated a new "earth". The name "titanium" was given by Klaproth, a tribute to the Titans, children of Titania, the Earth goddess.

The history of chromium begins with the discovery in 1766 of the mineral crocoite (lead chromate) in the lead mines of Beresoff, near Yekaterinburg in Siberia, by Johann Gottlob Lehmann (1719-1767) (Klaproth's father-in-law). Louis Nicolas Vauquelin (1763-1829) analysed the mineral in 1789, but discovered nothing new. Only a further analysis by Vauquelin in 1797 led to a new metal, chromium (the name was suggested by Haüy and Fourcroy). In the same year, Klaproth isolated the same element from crocoite, but historiography generally attributes the discovery to Vauquelin, because of his previous experiments; others, like Gmelin and Kopp, consider it a simultaneous and independent discovery. For Dann, there is no reason to create a matter of priority Vauquelin – Klaproth about the discovery of chromium, as already in 1791 Johann Jakob Bindheim (1740-1825), then in Moscow, had analysed a Siberian mineral (crocoite), in which would exist a metal, maybe molybdenum; Vauquelin later identified the metal as chromium.

As for beryllium, even before knowing the element beryllium or glucinium, discovered by Vauquelin in 1802, Klaproth had analysed chrysoberyl[17], a mineral discovered in Brazil, first described by Christian August Hoffmann (1760-1814) and Dietrich Ludwig Karsten (1768-1810), both from Freiberg. Klaproth's (1795) analysis provided 71% alumina, 18% silica, 6% lime, 1.5% iron and 3% losses, total 99.95%. The current formula is $BeAl_2O_4$ (Seybert's analysis, 1824)[18].

Beryl, a silicate of aluminum and beryllium (emerald and aquamarine are variants containing metallic impurities) was analysed by Vauquelin, Klaproth and Bindheim.

THE WORK – ANALYTICAL CHEMISTRY

Anyone - like this author - who went through the banks and laboratories of Chemistry courses in the 1960s will recognize in Klaproth's discussion on Analytical Chemistry many of the operations he performed in practice, and much of the reasoning behind them. I think we are few survivors of an era of Analytical Chemistry in which exhausting manual labor performed the task of today's sophisticated instruments and techniques. I think – without nostalgia – that much of the magic of scientific practice has been lost...

Klaproth inherited an already reasonably well-structured Analytical Chemistry, fruit mainly of Torbern Bergman's (1735-1784) activity in this field. After Bergman, Klaproth joined Vauquelin as the greatest exponent of Analytical Chemistry of his time. According to Bergman, chemical analysis has as its purpose the search for the truth, and the analyses must be carried out with the greatest possible rigor. Analytical data already available should be reviewed with the utmost exemption. The analysis of the components of a compound should not be based on comparisons, but on independent identifications in each case. For that, the "wet route" methods are more indicated. Here are the general lines of Bergman's "philosophy of chemical analysis", for which he developed scripts and introduced new reagents. Bergman's conceptions in turn were influenced by earlier work by Marggraf, and many of his reagents already come from Boyle and Friedrich Hoffmann (1660-1742).

Following Bergman, Klaproth structured Analytical Chemistry on strong empirical bases, mainly gravimetry, which he structured as a scientific method of analysis. He emphasized some aspects he considered essential:

- to be subjected to analysis, chemical substances must be in the purest possible state;
- he emphasized the purity of reagents and developed procedures to purify them;
- the equipment must be chosen properly (he was perhaps the first to use agate and silica mortars).

In the particular case of gravimetric analysis, he introduced:

- heating the precipitates to constant weight;
- the precipitate of the reaction is not always the most suitable compound for weighing, and if ignition results in a more stable product, this should be used to determine the weight.

Regarding data processing, Klaproth was the first chemist to record exactly the data obtained, without the "corrections", which even chemists like Bergman and Lavoisier did when the sum of the data did not reach 100%. Precisely the reactions that do not reach 100% lead to the discovery or confirmation of new elements: the "correction" of the analytical data made the discovery of zirconium elude Bergman. In the aforementioned analysis of chrysoberyl, among the "losses" is the element beryllium, later isolated by Vauquelin (1802).

In the qualitative analysis, he made intensive use of hydrogen sulphide (H_2S) to obtain precipitates, a procedure later expanded by Heinrich Rose, and finally systematized by Remigius Fresenius (1818-1897).

In analytical practice he introduced potash fusion in a platinum crucible to convert minerals difficult to decompose into suitable analytes (1802).

THE WORK – CHEMICAL ANALYSIS – MINERALS

Having commented on Klaproth's contributions to Analytical Chemistry, and considering that Analytical Chemistry and chemical analysis are distinct concepts, some comments on the analyses carried out by Klaproth are also appropriate. According to Paschoal Ernesto Senise (1917-2010), Analytical Chemistry is a branch of chemical science and as such deserves a study with all the methodological rigor that characterizes a science; chemical analysis, on the other hand, is the simple routine, "*a set of methods and operations necessary to arrive at the determination of the composition of a compound*". Of course, chemical analysis does not dispense with rigor either, and Klaproth writes about it in the preface to the manual "Anweisung zur Chemischen Analyse" by the pharmacist Johann Friedrich John (1782-1847), professor at the University of Frankfurt/Oder until 1811 and later in Berlin:


Figure 3. Martin Heinrich Klaproth. Bust by Eduard August Lürssen (1840-1891), 1882. Courtesy Museum für Naturkunde, Berlin.

> […] it is not enough to follow in an analysis a theoretical procedure that gives a correct impression of the object [= analyte] to be worked on, but the experiments must be such that in repetition by several chemists, all working with the same accuracy, they always get the same result. The acumen of a chemist can easily be seen by reading his works, but we can only assess the accuracy with which he

> performs his experiments if we are present when he performs them, or if we repeat them. The two qualities are not always present at the same time. There is no lack of chemists who easily know how to solve the most complex problems, without apparently having to confirm a priori; but if we direct our attention to his skills as an experimenter, things soon take on a different image[19].

Here are the conditions that are still valid today for a correct chemical analysis, introduced as an obligatory systematic by Klaproth, and also allowing us to foresee the verification by other analysts defended by the empirical science of the nineteenth century. The difference, for the chemist, between accuracy and precision is also explicit**.**

Klaproth analysed a large number of minerals, among them, in addition to the aforementioned chrysoberyl (from Brazil), chrysolite[20] (brought from the Levante by his friend Hawkins), criolite (originating in Greenland, from where it came into the hands of Professor Peter Abildgaard [1740-1801]; Klaproth mentions the analyses of José Bonifácio de Andrada e Silva [1763-1838], who had received Abildgaard's samples) [21], olivine, alum, apatite, fluorite (previously studied by Scheele, Marggraf, Wenzel and Richter)[22], lepidolite, emerald (from Peru, a gift from Prince Dimitri Gallitzin [1723-1803])[23], topaz[24], opal[25], sapphire, garnet from Bohemia and the Orient[26], dolomite[27], lapis lazuli[28], borax or tincal[29], and mainly pitchblende. The samples were collected by Klaproth himself on excursions through the Dresden and Freiberg region, to Bohemia, to Pomerania; others were sent to him from around the world by friends, such as geologist John Hawkins (1761-1841), or researchers, like Alexander von Humboldt (1769-1859), and even by his son Julius Klaproth, who travelled the Caucasus and in Georgia.

Of Klaproth's mineral analyses, the most famous is certainly that of pitchblende, mentioned above, not only for the future consequences of the uranium discovery, but for the chemical aspects of this analysis, in addition to theoretical aspects, such as the "Schemnitz illusion". The qualitative detection of uranium, as practiced until the 20th century, was, in general, Klaproth's (little practiced in chemistry courses, not because of the risk, but because of the high cost of uranium). The various chemical treatments to which pitchblende was subjected resulted in a solution, identified in 1842 by Eugène Melchior Peligot (1811-1890) as uranyl nitrate, $UO_2(NO_3)_2$; the addition of NaOH leads to precipitation of sodium diuranate, $Na_2U_2O_7$, and H_2S precipitates uranyl sulfide, UO_2S. Briefly, Klaproth indicates in Table 2 the following composition of pitchblende, converted into percentage:

Table 2. Composition of pitchblende according to Klaproth.

Uranium Oxide	86,5%
Iron Oxide	2,5%
Galena (lead sulfide)	6%
Silica	5% (Total 100%)

All these mineral analyses are described in "Beiträge zur Chemischen Kenntnis der Mineralkörper" (1795/1815), with a great wealth of experimental details, the repetition of which would be idle here. A patient reading of all these analytical works, however, shows not only the rigor of Klaproth's work, but especially the ingenious use of the chemical and analytical resources then available.

Some of these mineral analyses are of special importance in the History of Chemistry, for example, that of leucite, a volcanic mineral from Italy, analysed in 1797. At the time, two "soft alkalis" were known, mineral mild alkali, or soda (Na_2CO_3), and vegetable mild alkali, potash (K_2CO_3), the latter obtained exclusively from vegetable ashes (from algae or marine plants). Although the elements sodium and potassium were only isolated in 1807 by electrolysis (Sir Humphry Davy), chemists were able to distinguish perfectly between soda and potash (1736, Duhamel de Monceau), as well as between sodium salts and potassium salts (Stahl). Klaproth discovered potash in leucite, and obtained for the first time in a mineral the "white plant alkali" (leucite is an aluminum and potassium silicate, according to Klaproth containing 53.750% silica, 24.625% alum and 21.350% of ' vegetable alkali')[30].

There is the curious case of siderite or hydrosiderite, a supposed element. In 1777/1778, Torbern Bergman in Uppsala and Johann Karl Friedrich Meyer (1733-1811) in Stettin were studying a curious variety of cast iron, which after being treated with sulfuric acid and further reduced, gave rise to a greyish-white powder, a possible element, siderite. The same variety of iron was also analysed by Klaproth, who found in 1783 that it was an alloy of iron and phosphorus (as phosphoric acid or phosphide)[31].

Another analysis of importance for the evolution of chemistry was that of guano, brought from South America by Alexander von Humboldt on his return to Europe in 1804. Humboldt entrusted samples for analysis to Fourcroy and Vauquelin in Paris, and to Klaproth. The French published their analysis in 1806, Klaproth in 1807[32]. Klaproth found in guano 16% of ammonium urate, 12,75 % of calcium oxalate and 10% of calcium phosphate. The results were similar, but far from those of a modern analysis (Klaproth found phosphates, oxalates, urea, ammonia). Guano has been known since the

16th century, but the first more detailed descriptions are by Amédée François Frézier (1682-1773), in his 1712/1714 travels, and by Antonio de Ulloa (1716-1795). In addition to Klaproth, Louis Nicolas Vauquelin (1723-1829) and Wilhelm August Lampadius (1772-1842) also chemically analysed guano. Other exotic materials brought by Humboldt were also subjected to analysis by Klaproth, such as the “pacos” from Peru (supposed silver mineral, actually 71% iron, 14% silver)[33] and the “mocha” from Quito, a volcanic material[34].

THE WORK – CHEMICAL ANALYSIS – MINERAL WATERS

The analysis of mineral waters, especially those that present a supposed or real curative aspect, attracted the attention of analysts and assayers since the Middle Ages, and with the improvement of analytical techniques these analyses multiplied from the beginning of the 18th century, involving many chemists, from Hoffmann and Bergmann to Berzelius, Liebig and Fresenius. Oskar Baudisch (1881-1950), an analytical chemist, dedicates an essay to the “magic and science of healing mineral waters”. The “magical” aspect of the “cure” is, on the one hand, psychological, involving the entire atmosphere reigning in the mineral resorts, and on the other, even scientific, with the discovery in the waters of chemical principles that could account for certain medicinal effects (iodides, sodium sulfate, lithium salts) [35]. Klaproth also analysed mineral waters, two of which we will present here: the waters of Karlsbad, in Bohemia (today Karlovy Vary, in the Czech Republic), and the waters of the Dead Sea, the first due to the great importance of Karlsbad in the cultural context of the 18th and 19th centuries, attended by the European elite (Goethe, Beethoven, Berzelius, Chopin, Turgenev were regulars), and the second for the emblematic value for Christianity of the waters of the Jordan and the Dead Sea.

The first analysis of Karlsbad thermal waters is due to the spa’s physician, David Becher (1725-1792), in 1770. Klaproth analysed them during his stay there in June 1789, in the company of his friend Count Carl Friedrich von Gessler (1752-1829). Klaproth determined the following components of Karlsbad water: 1000 parts by weight of water contains 5,478 parts of solids, distributed as per the table; the analysis generally confirms Becher’s.

Table 3. Klaproth analysis of Karlsbad mineral waters[36].

Sodium sulfate (Glauber’s salt)	2,431 parts
Sodium bicarbonate	1,345 parts
Sodium chloride	1,198 parts
Calcium bicarbonate	0,414 parts
Silica	0,086 parts
Iron oxide	0,004 parts

A new analysis was carried out in 1809 by the chemist Ferdinand Friedrich Reuss (1778-1852), professor at the University of Moscow. As early as 1802, Klaproth had published a recipe for making ‘artificial Karlsbad water’. The production of artificial mineral waters was described in 1783 by Johann Carl Friedrich Meyer (1739-1811), a pharmacist in Stettin (now Szczecin, Poland), but even earlier Priestley and Bergman had already produced artificial waters. Berzelius published in 1823 a long article discussing the analysis of the waters of Karlsbad, in which he criticizes aspects of Klaproth’s analysis, despite the usual rigorous procedure of the latter[37].

The Dead Sea is *par excellence* a sacred place for Judaism and Christianity, and its waters have a high symbolic value for Western Christian-Jewish civilization: their analyses combine the history of Humanity, the presence of mythical and transcendental values, the ‘magic’ side of science, and chemical analysis figures as a kind of ‘centralizer’ of the discussion. For centuries, pilgrims and explorers visiting the Holy Land brought back bottles with water from the Dead Sea and the Jordan River, and a first qualitative analysis of these waters was carried out by the English physician Charles Perry (1698-1780) in 1742. The first quantitative analysis was that of Pierre Macquer (1718-1784), in 1781 (it is the second quantitative analysis of natural waters, preceded only by seawater). After Macquer, many chemists occupied themselves with the emblematic water: Alexandre Marcet (1807 and 1813), Klaproth (1809, 1813), Gay-Lussac (1819), Hermbstädt (1822), Christian Gmelin (1827), Boussingault (1856)[38]. Table 4 shows Klaproth’s data from 1813.

Klaproth’s data broadly confirm Macquer’s, but they were contested by Marcet.

In 1792/1793 Klaproth analysed the waters of Iceland’s hot springs. John Thomas Stanley (1766-1850) had

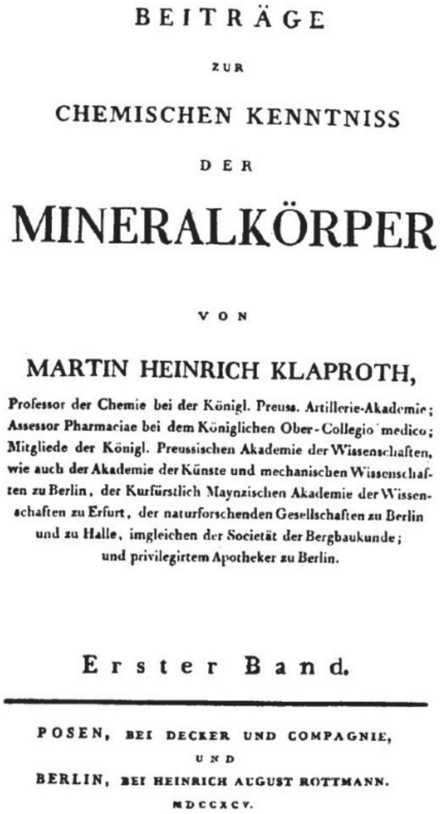
Table 4. Klaproth analysis of Dead Sea waters.

Chloride	206,5 g/liter
Sodium	38,2
Magnesium	35,9
Calcium	24,3
Potassium	traces

brought bottles of these waters from his expedition to the Faroe Islands and Iceland in 1789 and forwarded the samples for analysis to Klaproth and Joseph Black. The results of both are almost coincident (presence mainly of silica, sodium chloride, sodium sulphate)[39].

THE WORK – ARCHAEOMETRY[40]

Analyst that he was, it did not take long for Klaproth to apply chemical analysis to antiquities and archaeological objects: coins, metals, bronze and other metallic alloys, glass, ceramics, pigments, dyes, an applied branch of chemistry known today as Archaeometry. The term 'Archaeometry' is not Klaproth's, it was used for the first time in 1953, in a journal published by the Research Laboratory for Archaeology and the History of Art in Oxford. There are some analyses prior to Klaproth, e. g. the analysis of Chinese *paktong* by Gustav von Engeström (1738-1813) in 1776, and some 'archaeometallurgical' studies mentioned by T. Pownall in 1775[41]. Archaeometry is one of Klaproth's most interesting contributions, not only to Science, but to History itself[42]. Archaeology, erected in science essentially thanks to the efforts of Johann Joachim Winckelmann (1717-1768) in understanding Classical Antiquity, had an auxiliary arm in archaeometry, which allows not only to study the technological resources available to the ancients, but also to make inferences, such as determining trade routes, cultural influences, colonization start dates and others. Knowing the composition of ancient objects, it is also possible to restore works of art from the Antiquity. Klaproth had a special interest in history, and had a valuable collection of antiquities, thus being interested in the analysis mainly of metals (coins, weapons), but also of glass and medieval metallic objects. Klaproth began these analyses in 1785, and Earle Caley (1900-1984), a modern authority on the subject, considered them of great importance, as never before had anyone analysed such objects from a chemical, scientific point of view, nor was there a script until then, for the analysis, for example, of old coins[43]. It is no longer possible to confirm Klaproth's data, but modern analyses of coins from the same time and place confirms his results: for example, for a Roman coin from the times of Emperor Claudius, Klaproth found a composition of 77.9% of Cu and 21.1% Zn, and in 1869 the self-taught writer and chemist Ernst von Bibra (1806-1876), also interested in this subject, found for a coin of the same period the values 77,44% Cu and 21.50% Zn (the difference corresponds to traces of metals that escape the analytical procedures of Klaproth and Bibra)[44]. It is thus known, thanks to archaeometry, that the Roman coins of the 1st century were minted in brass and not in bronze. Josef Riederer (1939-2017), a chemist from the Berlin museums, repeated some analyses of Roman coins (1974), with results very similar to those of Klaproth. Table 5 shows some of the results.



BEITRÄGE

ZUR

CHEMISCHEN KENNTNISS

DER

MINERALKÖRPER

VON

MARTIN HEINRICH KLAPROTH,

Professor der Chemie bei der Königl. Preuss. Artillerie-Akademie;
Assessor Pharmaciae bei dem Königlichen Ober-Collegio medico;
Mitgliede der Königl. Preussischen Akademie der Wissenschaften,
wie auch der Akademie der Künste und mechanischen Wissenschaften zu Berlin, der Kurfürstlich Maynzischen Akademie der Wissenschaften zu Erfurt, der naturforschenden Gesellschaften zu Berlin
und zu Halle, imgleichen der Societät der Bergbaukunde;
und privilegirtem Apotheker zu Berlin.

Erster Band.

POSEN, BEI DECKER UND COMPAGNIE,
UND
BERLIN, BEI HEINRICH AUGUST ROTTMANN.
MDCCXCV.

Figure 4. Cover page of Klaproth's most important publication, 'Beiträge zur Chemischen Kenntnis der Mineralkörper'.

Table 6 compares the data of the analysis of an ancient mirror by Klaproth and Bibra.

In the case of studying old glasses, the weight of the sum of the weights of the components found does

Table 5. Analyses of Roman coins by Klaproth and Riederer[45]

Elements	Klaproth (1795)		Riederer (1974)	
	(sample 1)	(sample 2)	(sample 1)	(sample 2)
Copper	77,9	83,0	77,5	83,0
Tin	-	1,9	-	0,7
Lead	-	-	-	0,62
Zinc	15,5	15,15	22,1	14,45

Sample [1]: coins from the times of Claudius (41/54); sample [2]: coins from the times of Vespasian (98/117).

Table 6. Analyses of the metal of an ancient metal mirror, by Klaproth and Bibra[46].

Elements	Klaproth	Bibra
Copper	62	64,46
Tin	32	28,36
Lead	6	7,13
Iron	-	traces
Nickel	-	0,05

Table 7. Composition of old glass according to Klaproth.

Components (grains)	Red	Green	Blue
Silica	142	130	163
Lead oxide	28	15	-
Copper oxide	15	20	1
Iron oxide	2	7	19
Alumina	5	11	3
Limestone	3	13	0,5

not match the original weight of the sample, a fact that Klaproth does not explain, although he knew the fundamental aspects of glass technology since Antiquity. It is now known that the difference is due to the presence of sodium and potassium oxides, compounds not known in Klaproth's time. The importance of the knowledge of the basic theoretical aspects for correct chemical practice is evidenced in Klaproth's analysis of glass: for him copper was responsible for the color of red and green glasses, but different "forms" of copper. We would say today, different oxidation states of copper, Cu(+II) in red, Cu(+I) in green glass. Table 7 shows data from Klaproth's analyses[47].

In 1798 Klaproth published more detailed glass analyses, from glasses collected at the Villa of emperor Tiberius in Capri. Compounds in bold were in Klaproth's opinion responsible for the color of the glass. Klaproth found out that different 'kinds' of copper are responsible for both red and green color, a fact we explain today considering different oxidation states of copper.

It is worth mentioning the analysis of the ancients' electrum (in this case, a mineral sample from Siberia) [49], and, in the course of the analysis of many "earths", the analysis of the "earth of Lemnos" (*Lemnia Sphragis*), used by the ancient Greeks as antidote for poisons, and whose composition is, according to Klaproth: 66% silica, 14.5% alum, 6% iron oxide, 3.5% soda, 0.25% lime, 0.25% talc and 8% water[50].

Table 8. Analyses of Roman Glasses from Capri (Klaproth, 1798)[48].

Color	SiO_2	PbO	Cu_2O	CuO	Fe_2O_3	Al_2O_3	CaO
Red	72,8	14,4	**7,7**	-	1,0	2,6	1,5
Green	66,3	7,7	-	**10,2**	3,6	5,6	6,6
Blue	87,4	-	-	0,5	**10,2**	1,6	0,3

Other early 19th-century chemists were concerned with archaeometry: Jean Antoine Chaptal (1756-1832) analysed pigments found in Pompeii (1809), and Sir Humphry Davy (1778-1829) analysed the pigments used by the ancients in paintings[51].

And as we said, archaeometry ended up leading to the possibility of restoration and conservation of archeological objects and ancient works of art, today a routine in the laboratories of specialized museums. The first laboratory along these lines was that of Friedrich Rathgen (1862-1942), the "father of modern archaeological conservation", in the Berlin Museums (1888)[52].

THE WORK – ORGANIC CHEMISTRY.

Most of the history of Chemistry treatises consider Klaproth's contribution to Organic Chemistry to be minimal. They limit themselves to mentioning the discovery, in the mineral mellite (*Mellit, Honigstein*), of mellitic acid (*Honigsteinsäure*), $C_6(COOH)_6$, in 1799 (mellite is the aluminum salt of mellitic acid, $[Al(H_2O)_6]_2C_6(COOH)_6$, discovered in Artern, Germany, in 1789 by Dietrich Ludwig Gustav Karsten [1768-1810]) [53]. Mellytic acid is obtained by treating mellite with ammonium carbonate and precipitating alumina with ammonia. In 1776, Klaproth examined copal, a vegetable resin of various origins, used in the manufacture of varnishes. Copal was considered sometimes as a mineral, sometimes as a semi-fossilized resin (*succinum vegetabile indicum*) similar to amber[54].

In fact, Klaproth's interest was great not only in Organic Chemistry, but also in Physiological Chemistry, but as both were still taking their first steps, they hardly appear in his writings. However, they occupy an appreciable space in his lectures, as B. Engel discovered to her surprise when transcribing the aforementioned manuscripts by Barez and Schopenhauer. Surprising is the space given to the "components of organic bodies", almost 28% of the manuscript, almost the same extent as that devoted to minerals (30%), Klaproth's main field of research. "Organic bodies" include "flammable substances" and "substances from the animal kingdom". It is clear, according to Engel, that Klaproth not only taught his students Inorganic Chemistry, but also the knowledge taken as fundamental requirements for understanding Organic Chemistry and Physiological Chemistry that were beginning to develop, a particularly important aspect in courses that prepared physicians and pharmacists, still in the opinion of B. Engel[55].

THE WORK – PUBLICATIONS.

In addition to the routine publication of the results of his investigations – mainly chemical analyses – in various scientific journals, such as Crell's *Annalen der Chemie*, in Scherer's *Allgemeines Journal der Chemie* and in Rose's and Gehlen's *Neues Allgemeines Journal der Chemie*, there are also more comprehensive publications, some in partnership with other chemists. The most important of these works is undoubtedly "Beiträge zur Chemischen Kenntnis der Mineralkörper" (Contributions to the Chemical Knowledge of Minerals), in six volumes, published between 1795 and 1815 in Berlin, devoted the first five volumes successively to John Hawkins, Dietrich Ludwig G. Karsten, Vauquelin, Berthollet and A. von Humboldt. Also important is "Chemische Abhandlungen gemischten Inhalts"[56] (Chemical communications on various contents), Berlin 1815. In this book he describes, for example, the analyses of ancient coins[57] and glasses, Belustscheff's dye[58], analyses of minerals and products of plant origin, analysis of salt, ozokerite, meteorites[59], sugars and many other subjects. In 1797 the King of Prussia Frederick William III (1777-1840) commissioned a new pharmacopoeia, the *Pharmacopoeia Borussica*, which was developed by Klaproth, with the collaboration of Valentin Rose the Younger and Sigismund Friedrich Hermbstaedt (1760-1833). The *Pharmacopoeia* was developed according to the Lavoisierian theory, including nomenclature. Chr. Friedrich notes that the new pharmacopoeia already contains data on the chemical composition of the *simplices* as well as quality tests.

Klaproth wrote in partnership with Friedrich Benjamin Wolff (1765-1843) the "Chemisches Wörterbuch" (Dictionary of Chemistry), in five volumes (1807/1810), dedicated to Tsar Alexander I (1777-1825), translated in 1812 into French by Heinrich August Vogel (1778-1867), professor at the *Lycée Napoléon* in Paris; later four volumes of "Supplements" (1815/1819) were added. Wolff was Kant's student in Königsberg and for a long time taught Mathematics and Physics at the *Joachimstaler Gymnasium* in Berlin, and also wrote a didactic "Handbook of Chemistry". The "Systematisches Handbuch der Chemie" (Systematic Handbook of Chemistry) by Friedrich Albrecht Carl Gren (1760-1798), published in 1787/1794, merited a new revised edition by Klaproth in 1805 (Gren was an ardent advocate of phlogiston, but convinced of the assertion of Lavoisier's theories, sought to reconcile the two theories).

THE STUDENTS.

Raised to the university chair at the age of 67, Klaproth had there few students (we mentioned Arthur Schopenhauer before), but many studied with him at the *Collegium Medicum,* and in what Aaron Ihde considered the "best place to learn Chemistry" in the 18th century, the pharmacy[60]. Klaproth did not form a school, but his biographer Dann mentions 32 names he considers of some relevance who were his students, starting with Heinrich Rose and Gustav Rose, sons of Valentin Rose the Younger and later professors at the University of Berlin. Important was Adolf Ferdinand Gehlen (1775-1815), editor of several scientific periodicals and, since 1807, chemist at the Bavarian Academy of Sciences in Munich (where he died of intoxication while researching arsenic compounds). Johann Jakob Bindheim (1740-1825), about whom little is known, studied with Klaproth in the White Swan pharmacy, and later worked in Russia (1795/1804). Also should be mentioned Carl Willdenow (1765-1812), later professor of Botany at the University of Berlin, the pharmacists Johann Heinrich Julius Staberoh (1785-1858) and Johann Christian Schrader (1768-1826), active in the public health service in Berlin, and Jacques Peschier (1769-1832), the latter from Geneva[61].

A TENTATIVE EVALUATION

Looking at the life and work of the pharmacist and chemist Klaproth, it remains for us to assess the figure of the scientist at the time he was active. In Hufbauer's opinion, at the end of the 18th century the situation in German Chemistry was chaotic, and we can say that in the midst of this chaos, Klaproth's figure is a lone star[62]. In the 18th century there were outstanding and influential personalities in German Chemistry, coming essentially from Pharmacy and Medicine: the theorist Stahl, the empiricists Friedrich Hoffmann and Andreas Sigismund Marggraf, the technologist Johann Beckmann, but the situation deteriorated at the end of the century, not only because of the controversy between the "French chemistry" (read Lavoisier) and "German chemistry" (read Stahl's followers), a controversy fueled not only by scientific arguments, since it was predictable that the German chemists defended first the theory of their countryman Stahl. One cannot forget the influence of nationalist factors and especially the reflection of the decadence of academic chemistry, exhausted and without perspectives, revived in the end by the adhesion of Hermbstaedt and Klaproth to the new Lavoisierian theory, and, in Homburg's opinion, also by the radical reformulation of university laboratories. If at the end of the 18th century there were undoubtedly competent chemists such as Georg Ludwig Claudius Rousseau (1724-1794) or Heinrich August Vogel (1778-1867), there were also exotic characters such as Gottfried Christian Beireis (1730-1809) in Helmstedt, and Ferdinand Wurzer (1765-1844) in Bonn. Thanks to the rationality and empiricism that he imprinted on his scientific activities, Klaproth reversed the situation, just when the chemical community in Germany was beginning to organize itself, around 1790. After a youth of "suffering and hope", in his own words, the self-taught Klaproth raised all the steps of the Prussian medical bureaucracy and academic activity; as an internationally recognized scientist, he gave a new start to the chemical activity in Germany and influenced the pharmaceutical activity for 30 years. We conclude with the assessment that the chemist and historian of chemistry Thomas Thomson (1778-1842) made of his legacy[63]:

> Among the outstanding traits of his character is the incorruptible respect he had for all that was true, honorable and good; his pure love of science, without any reference to feelings of selfishness, ambition or avarice; his rare modesty, unaffected by the slightest boasting or arrogance. He was benevolent to all men, and he never uttered a word of spite or even offense directed at anyone around him. When forced to censure, he did so quickly and without bitterness, for his criticism was always directed at facts, never at people. His friendships were never the result of selfish calculation, but were based on his opinion of each individual's personal worth. […] To all this we can add a true religious feeling […] of the obligations of love and charity […] demonstrated, for example, in the commendable care he devoted to the education of Valentin Rose's children.

Here is the life, character, and work of our somewhat forgotten honoree.

EPILOGUE - A NECESSARY FINDING.

Why was Klaproth forgotten? The evils that affect historiography in general today also affect the historiography of Science: a refusal to accept causality, the gradual replacement of the Philosophy of Science by a Sociology of Science, the abandonment of a logically ordered method, the neglect of primary sources (which could lead to a historiography that is too "positivist", or even Rankean). In the case of the historiography of Science, there are also two dangerous trends: the mistaken belief that scientific creation is socially conditioned, and not by the logic underlying a method, and the appreciation of facts not for what they mean in terms of advances in scientific knowledge, but for the importance attributed to them in the social context. Many "theorists" of the History of Science, in their practice, no longer differentiate between objective science and subjective "doing science", are ignorant of the very notion of "science", and often forget that Chemistry is, after all, an experimental science. And many "theorists" of Science defend more and more the idea that knowledge is a "social construction" and not the consequence of the rigorous application of a pre-established scientific methodology that is periodically tested through the results obtained. Thus, they open the doors for the return of pseudo-sciences and for the emergence of themes that do not exist at all, such as a supposed "pre-Columbian science" (there were pre-Columbian techniques), or others that should already be buried, such as "Occult Chemistry".

The necessary integration of scientific culture to the Culture of Humanity as a whole is unfortunately done at the expense of scientific knowledge. Thus, names like Klaproth, like Bergman, Gadolin, Trommsdorff, Runge or Kolbe, all empiricists, left the scene. They are all deserving of a return. And in this regard "[*History] can help to better understand the scientific discovery itself, verifying the factors that acted in it, the figures that remained behind the scenes. Perhaps this way scientists and historians can rectify many glories and unearth many forgotten skeletons*"[64]. And the biographies serve as a backdrop against which all the events that led to a particular scientific discovery unfold, going beyond the limits of science itself. Biographies, far from hagiographies, make it possible to establish contacts between people – scientists and non-scientists – places and times, assess the spread of ideas and theories, in addition to allowing the identification of influences and scientific schools[65].

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