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(Graphical abstract) *Explosion in the alchemist's laboratory* (Justus van Bentum, 1670-1727).

The ruby-red fumes could be due to fulminating gold.

Fulminating Gold and Silver

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Biography:

Curt Wentrup was educated at the University of Copenhagen (Cand. Scient. 1966 with K. A. Jensen; DSc 1976) and the Australian National University (PhD 1969 with W. D. Crow). After post-doctoral periods with Hans Dahn (Lausanne), W. M. Jones (Gainesville, FL) and Maitland Jones, Jr (Princeton, NJ), he held academic positions at the Université de Lausanne, and a professorship at the Universität Marburg (1976-85), before returning to Australia as Professor (now Emeritus), Chair and Head of Organic Chemistry at The University of Queensland. He is a Fellow of the Australian Academy of Science (AAS) and an awardee of the Australian Centenary Medal, the David Craig Medal of the AAS, the Birch and Leighton Medals of the Royal Australian Chemical Institute, and a *Dr. h.c.* from the Université de Pau, France. His main research is on reactive intermediates. He set up his first laboratory at the age of 13, at first to make rocket propellants, and then progressed to fascinating and energetic compounds like NCl_3 , fulminating gold, fulminates, and azides.

Abstract: This essay deals with the fascinating and highly explosive compounds fulminating gold and fulminating silver, which are easily made by treatment of gold dissolved in aqua regia with ammonia, and by reaction of silver oxide or silver salts with ammonia, respectively. Fulminating gold in particular captivated the alchemists in the 16th to 18th centuries. Numerous preparations were described, as well as numerous attempts to make volatile, sublimable or distillable gold, and to use the products so obtained (which were most likely gold chlorides) to make the sought-after tincture, which would "heal" the

"impure" metals and transform them into gold, and equally be a panacea to cure all human illnesses.

1. Introduction

Fulminating gold and silver have fascinated alchemists and chemists for more than four centuries, including prominent modern-era chemists like Lavoisier, Dumas, Berzelius, Scheele, Bergmann, Raschig, and many others.^[1] Virtually all iatrochemists and alchemists from the 16th century onwards were interested in *aurum fulminans*, because it was intimately associated with the processes of making volatile and drinkable gold (*Aurum volatile* and *Aurum potabile*)^[2,3] required to obtain the Philosopher's Stone and create a wonder-medicine. It is worth noting that gold nanorods and gold compounds are extremely important in medicine today.^[4]

The fact that fulminating gold was capable of volatilizing gold must have been an amazing observation; the red-purple fumes formed actually contain elemental gold, and enormous effort went into experimentation to control the volatilization, usually starting with the dissolution of gold in aqua regia. Much of the ensuing chemistry was undoubtedly that of gold chlorides, examples of which will be detailed below, but the concept of molecular compounds had not yet been developed. It has to be realized that the majority of the work described here was some 200 years before Dalton's atomic theory (ca. 1805-8), Lavoisier's chemical nomenclature (1787), and Berzelius' chemical formulae (1813-26).

The idea to link the heavenly bodies to the metals and indeed to the human body goes back thousands of years to Indian, Babylonian and Arabic writers.^[5] Following these ancient ideas, the alchemists used the same symbol for the sun (*sol*) and for gold (*aurum*), ☉, and the crescent moon ☾ was the symbol for both the moon and silver, while Venus was copper, and Mars iron. Furthermore, the sun and the moon, and hence gold and silver, were considered crucial for the preparation of the philosophers' stone. For example, Roger Bacon (ca. 1219-1292) stated "The Stone hath Father and Mother, to wit, the Sunne and Moone", whereby "the Sunne is his Father, that is, Philosophers Gold".^[6] This was taken nearly verbatim from Hermes Trismegistos,^[7] except that the latter applied this to the whole world, not just the Stone. The alchemists borrowed much from this hermetic philosophy. Bacon further stated that "the stone is often changed by decoction into diverse colours...after putrefaction it waxeth red, but not with a true rednesse..., it is often red, and often of a citrine colour". These are indeed the colours of anhydrous and hydrated auric gold chloride, Au₂Cl₆, respectively; aurous chloride AuCl is yellow, and HAuCl₄ (formed on dissolution of gold in aqua regia) can show various ruby-gold-yellow colors. These compounds are formed in numerous alchemical manipulations, and examples will be described below.

Mirror of Alchimy,

Composed by the thrice-famous and learned
Fryer, Roger Bacon, sometimes fellow of
Martin Colledge: and after wards of
Eriſen-woſe Colledge in
Oxenforde.

Alſo a moſt excellent and learned diſcouſe of
the admirable force and efficacy of Art and Nature,
written by the ſame Author.

With certaine other worthie Treatiſes of
the like Argument.

Vno vendibili non opus eſt hedera.



LONDON
Printed for Richard Oliue.
1597.

Figure 1. The Mirror of Alchimy, by Roger Bacon, 1597.

It should be noted that the capricious fulminating gold is not a fulminate but an amorphous, polymeric condensation product of gold(III) ammine salts containing the $\text{Au}(\text{NH}_3)_4^{3+}$ moiety and varying numbers of Cl^- , OH^- and O^{2-} counterions.^[8] In contrast, "true" gold fulminate would be a salt of fulminic acid, HCNO .^[9] Complexes of $\text{Au}(\text{I})\text{CNO}$ and the explosive salt $\text{Na}[\text{Au}(\text{CNO}_2)]$ are known.^[10]

2. Fulminating gold - Schwaertzer and Valentin

This compound was described by Sebald Schwaertzer^[11] an alchemist under the Kurfürst (prince-elect) of Saxony, already in 1585 in his book *Chrysopoeia Schwaertzeriana*. A copy of this book was published in 1718, and it has been made available on the Internet by the Bayerische Staatsbibliothek.^[12] An English translation of the preparation has been published.^[8] Schwaertzer described on pp. 84-86 a complicated four-day procedure starting with the dissolution of gold in aqua regia, made from nitric acid and *Sal amoniac* (salmiac, NH_4Cl).^[13] This generates HCl , required to make aqua regia. To the resulting mixture Schwaertzer added copper vitriol (sulfate) to precipitate the gold calx, dried it, dissolved it again in aqua regia, and repeated this whole process again. Finally, the *aurum fulminans* was carefully precipitated as a beautiful purple-colored solid with *oleo Tartari* (aq. K_2CO_3). The purpose of this is to neutralize the mixture so that the ammonia set free from the salmiac can react with the dissolved gold. As shown by Glauber^[14] (see below), this cumbersome procedure is unnecessary; simply neutralizing the aqua regia solution with ammonia will produce a pure *aurum fulminans*. If this is not done, then neutralization with K_2CO_3 also works, but only if the aqua regia has been made with salmiac, or at least an ammonium salt has been added. For example, dissolve gold in HNO_3/HCl , add ammonium nitrate, and neutralize with soda ash (Na_2CO_3), as this author confirmed as a teenager using readily available materials.^[15]

It needs to be mentioned that a claim to the preparation of fulminating gold already in the 15th century by a certain Basil Valentin^[16] (Figure 2) was made by Johann Thölde (1565-1614), but in all likelihood he wrote the books attributed to Valentin himself, at least in part, and it is believed that this could not have been earlier than 1590,^[17,18] but Schwaertzer referred to him as Bas. Val. already in 1585 (*Chrysopoeia* p. 97) in the context of volatilization of gold and making crystals by treating a gold (chloride) solution with *Oleo Vitrioli* (sulfuric acid): "as confirmed by Arthephius [Artephius, 12th century alchemist^[19] and likewise by *Bas. Val.*, the *Vitriol* is the best tool for its [the Stone's, presumably] preparation". Schwaertzer's gold was dissolved in *Aqua Regis* and *Spiritus Salis* (HCl) as before and concentrated to the consistency of an oil [this serves to decompose and remove HNO₃], and then treated with purified *Olei Vitrioli* [sulfuric acid; this would generate H₂AuCl₄ from the chloride]. Thereby "the heterogeneous parts of the gold separate from each other" [that is the mercurial (volatile) and sulphurous (solid) parts], and on subsequent distillation, lastly over a strong fire "most of the gold goes over as beautiful flowers like *Alumen plumosum*" [soapstone]. Probably, the volatile material was the red Au₂Cl₆, which is highly hygroscopic, absorbing moisture from the air and becoming slippery like soapstone. Indeed, Robert Boyle reportedly observed that gold chloride formed yellow and red sublimates, sometimes with "the neck of the retort enriched with numerous large, thin, red crystals, very like rubins, and glorious to behold, which would run in the air *per deliquium*."^[20]



Figure 2. The alleged Basilus Valentinus, *Chymische Schrifften*, Samuel Heyle, Hamburg 1717.

Schwaertzer then dissolved the "gold" that had distilled over and concentrated it to the thickness of a strong solution over the fire to remove any remaining *Aqua Regis*. "Put this in the cellar or another cool place, and crystals will form, which are true, natural *Vitriolis Solis*. And this all is done without danger, which is not the case when fulminating gold is made with *Ol. Tartari*, *Spiritus Vini*, and *Spiritus Salarmoniaci* or *Urinae*."

If Schwaertzer's crystals made by adding *Oleo Vitrioli* as above were imbibed with *spiritus salarmoniaci*, and dried over a low heat, a distillate as beautiful as a ruby was obtained. If the crystals were dissolved in *spiritus vini*, the gold goes over blood-red on

distillation and crystallizes in the retort. "Two drops of it gives a strong medicine, capable of curing almost all illnesses and renovate the whole human body, as well as the metals". The ruby-red sublimate was likely anhydrous gold(III) chloride.^[17]

Alternatively, treat the same crystals with *salarmoniac Urinae*, sublime them together, and add *aqua fort* [HNO₃], which due to the *salamoniac* becomes *Aqua Fortis*, or add *Spiritus Salis* (HCl) till all is dissolved, distil off the menstruum till a thick liquor is left behind and extract this with *Spiritus Vini*. "This give a perfect *Aurum potabile* for the human body and metals". It is possible that colloidal gold is formed in some of these destructive distillations, due to the thermal decomposition of AuCl₃ to Au + Cl₂ and the disproportionation of AuCl to AuCl₃ + Au.^[21] Colloidal gold can form a ruby-red liquid and is known to have strong antiseptic properties and thus could be responsible for the ability of the miracle medicines to aid the healing of open wounds. Also fulminating gold itself was used medicinally as a diaphoretic (sweat-inducing) agent, and like all gold medicines it was supposed to be good for the heart, but this was discontinued in the late 17 century.^[22]

Finally, Schwaertzer claimed to be able to transmute silver to gold: dissolve the crystals in water and add as much *Ol. Vitrioli* and distil to dryness. This give a glorious *Sal enixium solare* [sal enixium = strenuous salt; solare = gold], which liquefies in the air and is again coagulated on warming. "With this *sal enixium* you can transmute silver to gold to great use. And if you know how to add the right *Mercurium* in the right weight and then 2 or 3 times dissolve this *Sal mirabile* in ordinary water and add fresh *Olei Vitrioli* in the same weight, then for 3 weeks fixate over light heat, you obtain a true tincture in a short way, which for the most is equal to the age-old *Lapido Philosophico* and has endless power. Pour *spiritus vini* on the so-obtained *Sal enixium solare*, then it extracts only the golden, sweet part, and you get a medicine, which is a true and very strong *Aurum potabile*, which make people quite young and frees them of all illnesses" (p. 105). Johann Kunckel von Löwenstern (see below) held Schwaertzer's chemistry in high regard but was critical of Valentin.^[23] large amounts of gold objects were recorded in the estates of the Kurfürsts August and Christian I, and Kunckel ascribed them to Schwaertzer's craft.^[23]

From Schwaertzer's statement it is clear that the work of *Basil Valentin*, whoever he was, was known to him, and it is unclear who made fulminating gold first or who copied whom. Both used very similar, sometimes identical, experiments and expressions, and both used a system of explanatory *claves* (keys), but so did other writers. It is possible that the scribe who copied Schwaertzer's handwritten manuscript, "unverfälscht durch viele Mühe und Unkosten", or somebody else, added comments or edited the text prior to its publication in 1718. The scribe was the late Herr Tutschky, the former *Fürstlich Sächsischer Stall-Secretarius* (Figure 3).

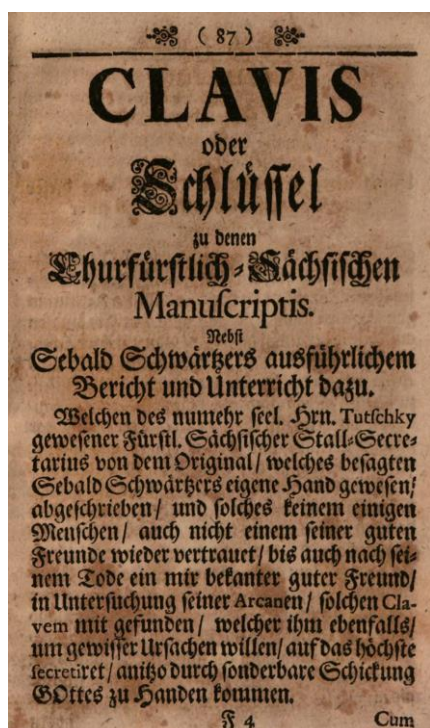


Figure 3. Schwaertzer's *clavis* (key) "in his own hand" copied by the blessed Herr Tutschky.

At any rate, *Bas. Val.*'s description of the preparation of an explosive *Goldkalck* fits the requirements for making fulminating gold.^[3] The procedure has been reproduced in ref. [18]. Basil Valentin's work was reviewed extensively by Angelo Sala^[3] and by Anthony Principe,^[17] but Sala's description of the preparation of *Sol fulminant* is almost identical with that of Oswald Croll.

3. Croll and Hartmann

Oswald Croll provided a detailed preparation of *aurum fulminans* in his *Basilica Chymica* 1609-10 (Figure 4).^[24] Croll (1563-1609) was M.D. from Marburg 1582 and Professor of medicine in Marburg till ca. 1602, when he moved to Prague.^[25] First, on p. 291 the familiar analogy is drawn between the celestial sun (*Sol*) and the terrestrial gold.^[24] He then describes the preparation of *aurum fulminans*, which is needed for the preparation of *Calx Solis subtilissima (aurum volatilis)* and then the powerful medicine *aurum potabile*:

Dissolve gold in *aq. fortis* made from *Sal Armoniac*, evaporate to dryness, dissolve again and evaporate again. Then add good *oleo Tartari* to the acidic solution, and the gold falls to the bottom. Wash it several times with water, then dry it carefully to avoid that it blows up. Thus, Croll essentially used Schwaertzer's prescription but wisely omitted the copper vitriol, which is not important for the reaction.

Croll observed that when the fulminating gold is heated and touched with an iron instrument, it explodes with a loud bang like gun powder and a purple-colored smoke is generated. One skruple (1.2 g) gives a louder bang than 1/2 pound of gun powder, which may cause hearing damage. "Many have through inexperience put their lives in danger," and "Not a single atom is to be found" afterwards. As we shall see below, Glauber was nonetheless able to make good use of the gold in the purple smoke. Croll also discovered that it is soluble in *aqua Salis* (hydrochloric acid). This produces HAuCl_4 , which renders the fulminating gold harmless. It also became harmless by mixing with sulfur.

Croll put forward an anthropomorphic explanation of the formation and explosiveness of fulminating gold, whereby he likened the enmity of *Sal armoniacum* and *oleo Tartari* to the enmity of *Sal nitrum* (saltpeter, KNO_3) and sulfur in gun powder (*pulueris tormentarij* or *Polueris Pyrij*) (p. 293-4). Thus, according to Croll, "when the *Sal armoniac* comes in contact with its enemy, the *oleo Tartari*, their fight results in the precipitation of the gold from the aqua regia solution. The *oleo Tartari* strikes the *Spiritum nitri* which as a result of this battle combines with its opponent, the *Sulphure Solis* [gold sulfur, where the "sulfur" is not to be taken literally]. This gold sulfur is much finer than ordinary, combustible sulfur; therefore it exhibits stupendous power even in small amounts in the same way that ordinary sulfur and *Sal petrae* [saltpeter] in gun powder when combined and ignited produce a loud, banging noise."

A posthumous edition of *Basilica Chymica* was published by Johannes Hartmann in 1658 (Figure 4). Hartmann (Figure 5) was a contemporary of Croll in Marburg, where he was first professor of mathematics (1592) and then *Professor Chymiatricae* (1609) in the Marburg Academy and as such the first professor of (medicinal) chemistry in the world. Since 1621 he was personal physician to the Landgrave of Hessen and professor of medicine and natural sciences in Kassel.^[26] Since both Croll and Hartmann were dead by 1658, Johannes Hartmann's son Georg Eberhard Hartmann published the book together with Iohanne Michaelis, *Philosophiae et Medicinae Doctore*.^[27] Not surprisingly, Hartmann added several of his own medicinal prescriptions such as *Laudanum D. Hartmanni*, *Aqua Benedicta D. Hartmanni* and *Syrupus Vomituus D. Hartmanni* also found in his *Praxis Chymiatricae* (Figure 4).^[28] Croll and Hartmann were paracelsists, i.e. adherents to the Paracelsus school of iatrochemistry (cf. Figure 5), and there are also several prescriptions due to Paracelsus in their works. Hartmann, too, described the preparation of aurum fulminans in his *Praxis Chymiatricae* and used it to make the wonder medicine, *aurum potabile anglicum* according to Francis Anthony (cf. ref. [2]). Hartmann repeated Croll's 1609-10 explanation in terms of the enmity of *sal armoniac* and *oleo Tartari* but added some qualifications of his own, especially that the cause of the fulminating power was to be found in "*Mars nimirum in aqua fortis, quae nullum recipit ammoniacum, solutus & oleo Tartari repercussus eadem fulminandi potestate pollet*" (Mars [is] namely in *aqua fortis*, which does not welcome ammonia & *oleo Tartari*, repercusses them and thus causes fulmination) and "*causa fulminis sola existit in auro, nitro & oleo Tartari*". Further, "namely the spirits of both solutes are contrary, so their mutual action stimulated by heat or fire together wounds the gold" (Figure 6). The conclusion that the cause of the fulmination lies solely in gold, nitro, and oleo Tartari is of course incorrect; the *nitro* only serves to dissolve the gold as Au^{3+} , and the *oleo Tartari* to neutralize it, but it is the ammonia that does the chemistry.

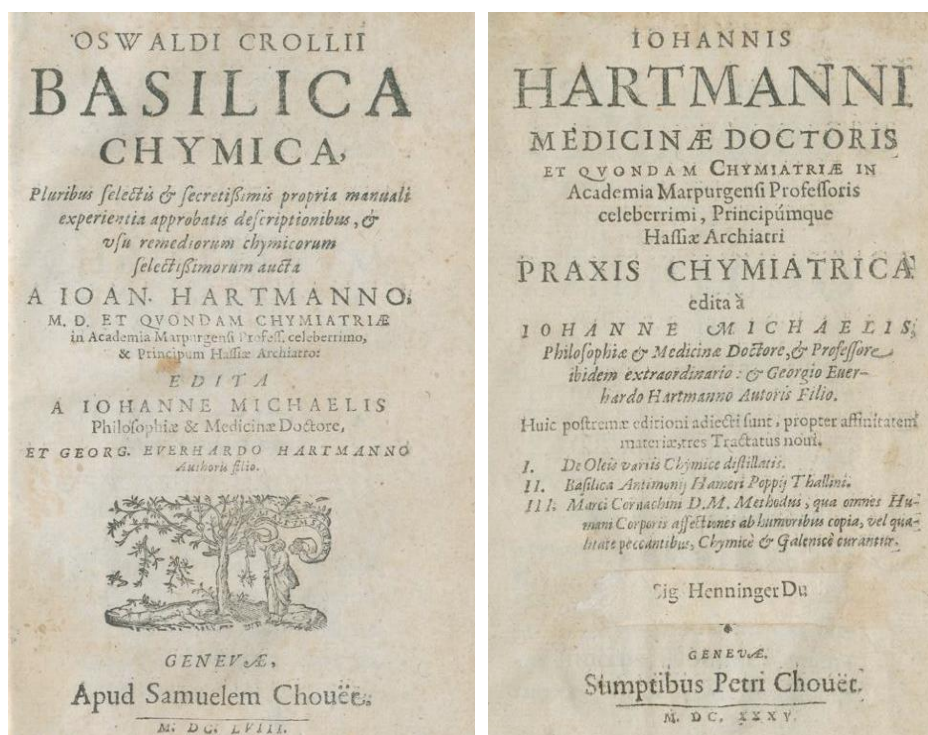


Figure 4. Croll's *Basilica Chymica* (Ed. Hartmann) and Hartmann's *Praxis Chymiatricæ*^[27,28]



Figure 5. Johannes Hartmann (1568-1631)^[26] and Paracelsus, born Philippus Aureolus Theophrastus von Hohenheim (1493-1541).^[25b]

Croll used several names for aurum fulminans, including *aurum volatil*, *aurum tonitruant* (Latin, thundergold), and *Schlaggold* (German, blowing gold) (Figure 6), and Hartmann also used *ceraunocryson* (Greek, thundergold) (Figure 6). An appendix to Hartmann's 1635 edition^[29] of *Praxis Chymiatricæ* by Dr. med. Ioanni Ernesti described fulminating gold as *avrum sonitum vel fragorum edat instar polueris bombardici* (noisy gold crashing like bombarding (cannon) powder).

o Dicitur etiam aurum fulminans, ceraunocryson, Germanis das Schlaggold / ab effectu.

p Negamus. Si nimirum esset causa, utique ad omnem effectum talem requireretur, sed non hoc, Ergo neque illud. Mars nimirum in aqua forti, quæ nullum recipit ammoniacum, solutus & oleo Tartari repercussus, eadem fulminandi potestate pollet.

q Additur Carbo Tiliæ facilioris ignitionis ergo.

r Causa fulminis sola existit in auro, nitro & oleo Tartari. Vtriusque nimirum spiritus arctius cum corporibus solutis hæret. Sunt autem contrarij isti. Igitur omnium mutua inuicem actio, à calore vel igne excitata, simul in ipsum aurum iniuria est.

Figure 6. Aurum fulminans, ceraunocryson, Schlaggold, etc. O. Croll (Hartmann's edition).^[26]

3. Glauber, Brugnatelli and gilding

The German-Dutch apothecary Johann Rudolf Glauber (the inventor of Glauber's salt (Na_2SO_4), in previous times a popular laxative) found in the 17th century that deposition of the beautiful purple fumes generated in the explosions of fulminating gold can be used for gold plating. He published detailed descriptions and illustrations of his "philosophical ovens" and distillation apparatuses including one consisting of two vessels connected with a glass tube (Figure 7). A quantity of 2-4 grains (100-200 mg) of fulminating gold (*Aurum tonitruant*) was placed in the first, thick-walled container, and the object to be gilded in the second. Heating the first container caused the explosion, and the purple fumes streaming through the connector deposited on the object in the second compartment. The first container was fitted with an opening and a lid, so that a new charge could be inserted as soon as the first deposition was completed. One imagines that a fair amount of gold may have been lost on the walls of the equipment, but he may have been able to recycle this or to use it in his preparation of gold tincture, "one of the noblest medicines, strengthens and delights people's hearts, and rejuvenates impure blood, whereby many serious illnesses such as *lepra, morbus gallicus* and the like can be driven off".^[30]



Figure 7. Glauber,^[14] *Operum Chymicorum*, and one of his distillation ovens^[30] (p. 45).

Furthermore, Glauber observed that fulminating gold is made less dangerous by mixing with other compounds (as noted above, Croll had already found that dissolving in HCl or mixing with sulfur made it harmless). This fact was used by goldsmiths and enamellers (e.g. in the Meissen factory).^[18] The firing of enamel painted with fulminating gold flux produced a ruby coloration due to finely divided gold particles. This could lead to explosions in the Meissen factory. It is believed this technique was used widely by decorators and goldsmiths in the 17th-18th centuries.^[18]

In the early 1800's Luigi Valentino Brugnatelli, professor of general chemistry applied to the arts at Pavia, discovered gold-electroplating by electrolysis of ammoniacalized solutions of gold in nitro-muratic acid (aqua regia), which would have generated fulminating gold. The gold deposited on a silver cathode, and he was able to gild large silver medals this way.^[31,32,33] Nowadays gold cyanide salts have replaced the dangerous fulminating gold.^[33]

4. Johann Kunckel von Löwenstern

Kunckel (1630-1703) described the preparation of *Aurum fulminans* much like Schwaertzer, Croll and Hartmann in his 1738 *Collegium Physico-Chemicum Experimentale* (p. 272) (Figure 8).^[23] He specified that, if the *aqua regis* is *not* made with *Salamoniac*, then addition of *Spiritus Urinae* is necessary to make the gold fulminate, but when it is made with *Salmiak*, then addition of *oleo Tartari* will also precipitate the *Aurum fulminans*. He also explained why the *Spiritus Urinae* as well as the *oleo Tartari* can precipitate the gold, although "one is a pure *Sal alcali* [*oleo Tartari*, largely K_2CO_3], and the other (*Spiritus Urinae*) is a volatile *Sal frigidum*" [probably composed of ammonia, ammonium carbonate and ammonium cyanate]: "when the *Sal acidum* comes in the *Terram alcali*, then the *Urinorum* is set free and insinuates itself with [into] the *Terra Solis* [gold], then the *Acidum* can no longer hold the gold but lets it go." However, when *Spiritus Urinae* is poured in, it will be changed by the *Acidum* in the *Aqua Fort*, which no longer can hold the gold because there is an inequality between the *Acidum* and the *Urinosa*." (It is rather the *Urinosa* that changes the acid, i.e. neutralizes it, and the free ammonia produces the fulminating gold.)

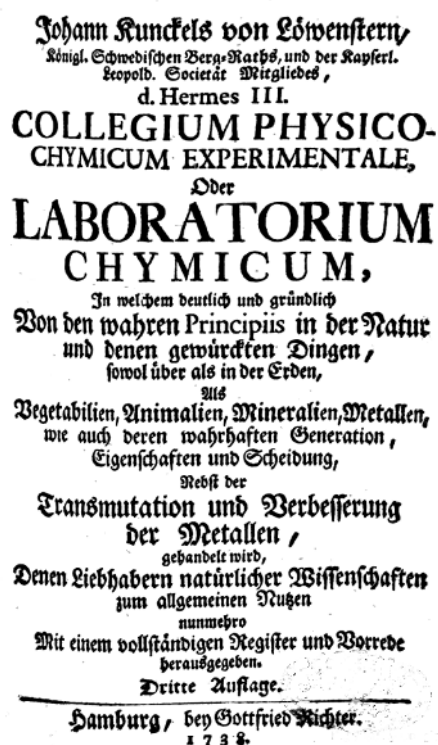


Figure 8. Kunckel's *Collegium Physico-Chemicum*, 1738.^[23]

Following in the footsteps of Schwaertzer and Croll, he also described the beautiful purple-colored *Aurum Sublimans*, which should be much better medicinally than ordinary gold. As mentioned above, this was probably Au_2Cl_6 . *Aurum Potabile* was similarly prepared.

5. Berzelius and modern chemists

Although the interest in fulminating gold in the 16th to 18th centuries was closely related to the efforts of alchemists to find the universal tincture for transforming lesser metals to gold and of the iatrochemists to create a panacea, chemists of the modern era did not lose interest. In ca. 1809 the influential Swedish chemist *Jöns Jakob Berzelius* (Figure 9) was working with an amount of up to 9 g (!) of the material, which blew up in his face when he treated it with too strong hydrochloric acid, blinding him for months and badly injuring his hand, where numerous glass splinters remained embedded for years.^[34] Many other famous chemists have been injured by various explosions in their laboratories.^[35]



Figure 9. Berzelius (1779-1848).

Neither the structure nor the mechanism of formation of fulminating gold are simple. Analyses were performed by Dumas, Lavoisier, Scheele, Bergmann, Berzelius, Raschig, and Weitz.^[1] Jules Jacobsen found that it is formed by treating Au(OH)₃ with ammonia, and therefore assigned the structure Au(OH)₂(NH₂) or alternatively AuN×2H₂O to it. The elemental analysis for nitrogen was correct, but it was 2% too low for gold.^[36] The structure is now considered to be an amorphous poly-condensate containing a square-planar Au(NH₃)₄³⁺. The numbers of Cl⁻, OH⁻ and O²⁻ counterions vary, even within a single sample, and depend on the method of preparation.^[8]

6. Fulminating silver

Fulminating silver (*argentum fulminans*, silver nitride, Ag₃N) is even more dangerous than fulminating gold. It may detonate from the slightest touch or movement, and can even explode when wet. Claude Louis Berthollet (Figure 10) is usually credited with its discovery by treating silver oxide with ammonia,^[37] but in fact it was already described by Kunckel at least 70 years earlier on p. 308 of his *Collegium*:^[23] "Dissolve silver in *Aqua fort* [nitric acid], then precipitate it. There are several methods for the precipitation, whereby *Spiritus Urinae* is very different from other agents (e.g. ordinary salt, *Calce viva* [quicklime, CaO], ash, or *Oleo Vitrioli*" [sulfuric acid], and "the difference lies in the *urin* which can cause the precipitated silver to fulminate. This depends on the right proportions" [presumably of *spiritus urinae* to *aqua regis*], "otherwise it is no trouble and happens rarely, but one has to be wary of it."



Figure . C. L. Bethollet (1748-1822).

Schwaertzer,^[12] too, reported many experiments with silver, similar to those with gold, including dissolution in *Aquafort* or *Aqua Regis* and treatment with various substances, including *sal armoniac*, "but this does not go as well as with gold, only helping to destroy the silver and causing damage"! (*Chryseopoeia*, p. 106).^[12] These are conditions where fulminating silver would be formed, but surprisingly, that is all he said about it.

Bethollet mentioned that dropping "a few atoms" of it on the ground made the black *argent fulminant* explode, and a falling water droplet was enough to set off.^[37,38] Once prepared, one cannot touch it or move it; it has to stay in the vessel where it was prepared, and one should not prepare more than a grain (54 mg) at a time. Berthollet advanced a theory that the force of explosion was due to the rapid expansion of the nitrogen gas formed as well as of the water vapor formed in the combination of oxygen and hydrogen (believing the *argent fulminant* was a compound of silver oxide and ammonia"). According to Berthollet, the silver is recovered after the explosion as metallic silver, "white and brilliant".

Halle^[39] reported a workable procedure for synthesis of fulminating silver in a manner similar to *aurum fulminans* from pure silver and dilute nitric acid made from one

part fuming nitric acid and two parts distilled water, and the calcium salt is precipitated with freshly prepared limewater. This salt is then treated with aq. ammonia, and the mixture is allowed to dry in the sun or by gentle heating. The sun has no effect, it can be dried inside, although not over a fire! It explodes when touching the dry material with a cold instrument. Halle recommends not to make more than two or three grains at a time (that's still ~100-150 mg!).

In a Danish version of Halle's *Fortgesetzte Magie*, Andreas Svendsen^[40] refrained from a description of the preparation of the "terrible" fulminating silver because it is too dangerous, but referred to Halle's volumes^[39] for those who really want to know. Because it is so easily formed from silver compounds and ammonia, reagents readily available in most laboratories, it is important to be conscious of the dangers, especially when using Tollen's reagent for detection of aldehydes or Martin's method for silvering of glassware.^[41]

Liebig repeated the preparation of the "true" silver fulminate, AgCNO,^[42] by the methods of Howard^[43] and Brugnatelli^[44] and also treated this substance with ammonia to obtain a highly explosive compound, detonating with a force "three times higher" than that of AgCNO and exploding even if touched in solution with a glass rod.^[45] Undoubtedly, he had transformed AgCNO into the fulminating silver (silver nitride) of Berthollet and Kunckel. Unlike the case with AgCNO, he refrained from carrying out an elemental analysis for this fulminating silver. Although he was an exceedingly skilful analyst, he still needed gram-quantities of AgCNO for the comprehensive analysis. Handling such an amount of fulminating silver would be unthinkable, even for Liebig.

Faraday did carry out analyses and detected nitrogen but thought nonetheless the compound was a *pre-oxide* of silver and that it gave off oxygen on explosion, although he was unable to confirm this due to the necessity to work with small amounts.^[46] Raschig's chemical analyses indicated the formula Ag₃N, although the silver value was often too high.^[47] Hahn and Gilbert obtained a good nitrogen analysis for Ag₃N, but the silver value was too low. However, they determined the structure as Ag₃N using X-ray crystallography.^[48] Haisa believes the N atoms are statistically distributed in the octahedral interstices.^[49] Recent computational studies have confirmed the experimental lattice parameters of Ag₃N(DO₉).^[50]

Shanley and Ennis^[51] performed valiant experiments attempting to obtain an X-ray structure of fulminating silver (Ag₃N), and reported that "many of the samples ... did not survive the minimum handling required to move them, container and all, to the X-ray stage...Even among supersensitive materials, silver nitride is a striking example of a compound "teetering on the edge of existence",.... Silver oxide exposed to the vapor over strong [aqueous] ammonia converts to explosive silver nitride.... in a closed container [it] usually explodes within 24 h without overt external intervention".

7. Conclusion

Fulminating gold was investigated by many prominent alchemists of the 16th-18th centuries, mainly because it was thought to be an essential step in the preparation of the philosophers' stone and in the wonder medicine *aurum potabile*. The first reported preparations were by Schwaertzer (1585) and Basil Valentin, whereby in the latter case both the identity of the person and the year of preparation are obscure. Detailed descriptions and explanations were published by Croll and Hartmann. Rudolf Glauber was in fact able to gild objects effectively by deposition of the red-purple fumes containing elemental gold on objects, and fulminating gold has been used in gold-painting of enamel, and in gold-

electroplating. The structure is an amorphous poly-condensate of the $\text{Au}(\text{NH}_3)_4^+$ framework with various counterions.

The "terribly" explosive fulminating silver was first made by Johann Kunckel von Löwenstern and Berthollet, and it was probably also formed as an unwanted product by Schwaertzer. Liebig observed that treatment of the "true" silver fulminate AgCNO with ammonia produced the fulminating silver of Berthollet. Chemical analyses were attempted by Faraday, Raschig, Shanley and Ennis, and Hahn and Gilbert, and the latter confirmed the composition as silver nitride, Ag_3N . Faraday reported that it can be used effectively to deposit pure and continuous silver films on objects, which "might be applied in some cases in the arts".

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nunmehr jederman vor Augen geleet, und mit einigen nützlichen Anhängen von verschiedenen curieusen Processen vermehret. Schwaertzer mentions on p 94 that a part of the manuscript was given to Kurfürst August already in 1583.

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