

## SOME NOTES ON THE EARLY HISTORY OF NITRIC ACID: 1300 – 1700

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### Introduction

Nitric acid is one of the compounds that have played an important role in alchemy, chymistry, and crafts. The first clear European recipe for its preparation is in the Latin treatise *Liber de inventione veritatis*, which appeared around 1300. Together with four further works, this treatise formed a corpus initially considered to be of Arabic origin, compiled by Jābir ibn Hayyān, known in Europe under the Latinized form of his name Geber. In the medieval Arabic world doubts had already been expressed as to whether this alchemist had actually ever lived. Confusion concerning the authorship of the works under Jābir's name continued well into modern times. H. Kopp, who dealt extensively with the history of nitric acid, originally considered Jābir to be the author of the corpus and thus of *L. de inventione veritatis*. It has been recognized subsequently that these books are of European origin, influenced by Arabic sources. Called the Pseudogeberian corpus, it was then generally accepted as a source that had introduced nitric acid in Europe.

This compound brought deep changes in alchemy and in crafts, especially what concerned new approaches to assaying, because it allowed the separation of gold from the rest of metals in a wet process. Simultaneously, reactions of nitric acid with these metals led to new compounds and thus to the broadening of knowledge that gradually contributed to the development of chemistry (1). Yet, further studies of alchemy and early chemistry have revealed that

the history of nitric acid is more complicated. As will be shown, a serious obstacle in this study is old terminology, which makes it difficult to decipher texts with sufficient reliability. With these problems considered, there appear signs that nitric acid could have been known before 1300 and not only in Europe. The history of this compound is therefore not a closed chapter.

### In Search of Nitric Acid

Nitric acid was no exception in the confusing language of early-modern chemistry. There are two principal problems in analysis of old chemical terminology (2). In some cases, one name was assigned to several different substances; in the particular case of nitric acid it was, for example, the term *aqua corrosiva* that reflects the ability of this compound to “corrode” or dissolve metals. Yet, other mineral acids possess this same property as well. As a result, “corrosive water” sometimes stood for sulfuric acid, but this expression could also denote mixtures of mineral acids that originated from a combination of various compounds.

The second problem is the use of many different terms, sometimes chosen arbitrarily, for one substance. This too is the case with nitric acid: the earliest known recipe calls it *aqua nostra dissolutiva* (“our dissolving water”), but during the subsequent centuries a variety of terms appeared. Some of these are summarized in the table. They can be roughly divided into three groups.

The first of these includes the word “aqua,” an allusion to one of the quartet of Aristotelian elements. The second, more complex group includes three terms. “Spirits” denoted vapors in general and also various volatile substances (such as mercury). Thus, fumes escaping from an acid were also considered to be spirits. “Oleum” referred to the consistency of a liquid compound, which could resemble that of oil. Eventually the term “nitri,” derived from *sal nitrum* (known as saltpeter, mostly potassium nitrate), was introduced as the ingredient from which nitric acid was made (3). The term “aqua nitri” therefore belongs in both the first and second groups.

The third group comprises the potentially confusing code names that alchemists often used in their texts. For example, *aqua mercurialis* seemingly hints at mercury rather than at nitric acid, but was used for this acid (4) and sometimes for  $\text{SbCl}_3$  (the latter compound was also known as *butyrum antimonii*, for its butter-like consistency).

**Table.** Names of Nitric Acid as they appear in Old Sources

Aqua fortis
Aqua acuta
Aqua calcinativa
Aqua caustica
Aqua dissolutiva
Aqua gehennae
Aqua gradatoria
Aqua mercurialis
Aqua nitri (sometimes used for sal alcali, $\text{K}_2\text{CO}_3$ )
Aqua nostra dissolutiva
Aqua solvens
Aqua stygia (sometimes used for a. regia)
Aqua valens
Oleum nitri
Rubigo nitri
Spiritus acidus nitri
Spiritus fumans Glauberi
Spiritus nitri
Chrysulca
Draco
Protheus
Roter Löwe
Salamanderblut
Stomachus
Struthionis
Sudor hermaphroditici

## European Origins

The oldest known unambiguous European recipe for nitric acid is found in the *Liber de inventione veritatis*, a part of a corpus originally assumed to be translations of the works of Jābir ibn Hayyān, Arabic alchemist known as Geber in Latin Europe (5). However, it has been suspected since the late 19<sup>th</sup> century that these works are of European provenance, compiled by an unknown author sometime around 1300. The authorship of this corpus was consequently attributed to an anonymous Pseudogeber (6), and speculations as to the exact dates and authorship of these works continue today (7). According to Newman, *Liber de inventione veritatis* was written shortly after *Summa perfectionis* as a commentary on this book (8). A more precise dating of these works is problematic, as is the dating of the discovery of nitric acid. As will be shown, this is not the only confusion in the early history of this compound.

The recipe in *L. de inventione veritatis* is as follows (9):

In the first place I will speake about our solvent [*aqua nostra dissolutiva*] that I had mentioned in our ‘Summa,’ there, where I had spoken about dissolving with strong liquids. First take one pound of vitriol [ $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ], one half of a pound of salt-peter [ $\text{KNO}_3$ ], and one quarter of a pound of alum [ $\text{KAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ ]. Prepare this liquid with red [color ?] of alembic, because it has a high solvent action. Use it, as was given in the preceding chapters. It will be yet much stronger if thou dissolveth a quarter of a pound of sal ammoniac [ $\text{NH}_4\text{Cl}$ ] in it. This liquid then dissolves gold, sulfur, and silver.

The reference to *Summa* was obviously an intentional attempt to link both treatises, but there is no mention of any “strong water” in the *Summa* (10). In fact, the cited recipe leads to two potent solvents: the beginning describes the preparation of nitric acid, whereas the subsequent addition of sal ammoniac turns it into *aqua regia*, a mixture of hydrochloric and nitric acid, which indeed dissolves gold. The expression “red [color ?] of alembic” suggests that a high temperature is necessary, that the alembic (distilling apparatus) should glow red. With the discovery of *aqua regia*, gold ceased to be the “immortal” metal that it had long been considered to be because of its low chemical reactivity. Yet, the formulation of this recipe does not suggest that its author had discovered the acid.

It should be stressed that the recipe for nitric acid in *L. de inventione veritatis* is currently accepted as the first unambiguous one, which had appeared in

Europe. Discovery of strong mineral acids, particularly nitric acid and *aqua regia* derived from it, had likely occurred repeatedly as independent acts, but this knowledge did not spread; it remained unnoticed or maybe it was not understood correctly. Nitric acid could have been prepared unintentionally since the necessary ingredients, potassium nitrate and iron or copper sulfate, had been known from ancient times, and alchemists especially used distillation as one of their essential techniques (11).

It is difficult to trace these discoveries, because before introduction of nitric acid in mediaeval Europe no special term for this compound was used. The allusions to “strong waters” that occur sometimes in old texts could be confusing. They could stand both for acid and alkaline solutions. These “waters” could also denote such solutions produced by hydrolysis of suitable salts. Furthermore, the passages in question could be later insertions into an older text.

According to Multhauf (12), mineral acids were not implied in the meaning of this word, but they have been gradually recognized over two centuries beginning *at least* as early as 1300. He points out that neither Albertus Magnus (before 1200-1280) nor Roger Bacon (1214/1220-after 1292) knew of these substances, in spite of the fact that it was Bacon who was the first to mention saltpeter, Albertus also did not mention Pseudogeber’s work — what is considered a sign that it appeared later, and its dating around 1300 can be accepted as correct. These facts, however, do not prove unequivocally that mineral acids had not been prepared before this time.

On the contrary, Multhauf supposed that alchemists were familiar with mineral acids earlier. According to this author these substances had appeared in their treatises in a broad span of time, from the twelfth-century *De aluminibus* (attributed to Pseudorhazes) to Pseudolullian *Testamentum* that in Multhauf’s words appeared two centuries later (13). Nitric acid in more or less pure form could have been prepared incidentally as a byproduct or intermediate substance in some process. Only later properties of this substance were sufficiently recognized, and the technique was worked out for its production. The technical problem of preparation of nitric acid was obviously the obstacle that slowed down its introduction into wider use (14). Although the earlier occurrence of this acid might sound plausible, this statement remains hypothetical unless new information is uncovered.

Occasional references to nitric acid appeared soon after 1300. For example, the cardinal Vitalis de Furno (1260-1327) is also supposed to have prepared this acid (15). According to his recipe *sal petrae* and *corprosse* (copper sulfate) mixed with *aqua ardens* (alcohol) should be distilled. This process should be repeated and the “water” made in this way was said to dissolve all metals. The recipe is problematic, because gold, too, is mentioned among these metals; but no further ingredients are given in the text that could have produced *aqua regia*. Nevertheless, the original inorganic ingredients and description of the effect of the product make it quite plausible that it was nitric acid. The date of Furno’s death helps narrow the possible time when nitric acid appeared in Europe, if *L. de inventione veritatis* were really the first account of it.

As Multhauf further added, from 1350 onwards references to some mineral acid appear more frequently in alchemical literature. In *Rosarius minor*, attributed to Arnald of Villanova (16), “the key to seven gates” of the rose garden should be actually *aqua fortis* produced from vitriol, saltpeter, and alum, denoted as “three herbs” in the text. In his search for “sulphur of philosophers” John of Rupescissa (active around 1350) alluded to nitric acid and concluded that this substance is humidity or spirit drawn from saltpeter and Roman vitriol (copper sulfate).

A later account appeared in *Das Buch der Heiligen Dreifaltigkeit*, an anonymous German alchemical manuscript, the oldest version of which was compiled between 1410 and 1415/17. Nitric acid is mentioned here as *aqua fortis*. This treatise was influential especially because of its symbolical approach to alchemical topics (17).

These references document that nitric acid entered alchemical laboratories first; only later did craftsmen, too, employ this substance. Because of technical problems, originally only small amounts of this compound were prepared.

### Possible non-European Origins

The Indian alchemical treatise *Rasarnava* is supposed to have been compiled around the twelfth century A.D., but this dating is doubtful. Because of their philosophical views, Indians were not especially concerned with time, and therefore did not often date their texts. If the age of *Rasarnava* were accepted, any discussion about

mineral acids should be more complex. The text in question is a dialogue between Bhairava (the god Shiva) and his consort Parvati, both of whom are crucial figures in Indian alchemy (18). Bhairava first lists the metals known to him: gold, silver, copper, iron, tin, and lead. He adds that their resistance to waste decreases in that order. He continues (19):

Hear attentively as I shall now speak of the killing of metals. There is no such elephant of a metal which cannot be killed by the lion of a sulfur.

In the language of European alchemy “killing” denoted a process in which metals lose their metallic appearance through their transformation into some compound (20).

Bhairava gives the following recipe ingredients: “Green vitriol, rock-salt, the pyrites, stibnite (21), the aggregate of the three spices (black pepper, long pepper, and dry ginger), sulfur, saltpeter” and some plant juices, which surely did not play any real role in the process. But when this mixture was processed in the proper way, “...it makes a vida, which would kill all [the metals]” (22). It is not easy to decipher this text, because the crucial information about how this mixture was to be treated is not described. If it were distilled, then, pepper and ginger aside, the product would have resembled the mixtures that European alchemists used for the process of gradation (discussed below).

In the same treatise, there is also a recipe entitled “killing of gold” (23):

Saltpeter, green vitriol, sea-salt, rock-salt, mustard, borax, sal ammoniac, camphor, the pyrites – all these are taken in equal parts. The crucible is to be smeared with the milky juice of *Euphorbia nerifolia* and *Asclepia gigantea*; then having added the power of the aforesaid ‘vida,’ the gold is to be killed, my beloved!

Killing of gold could be comprehended as its dissolution. Depending on the quantity of the combined substances and their processing, the Indian recipe could indeed have led to *aqua regia*, even though it would likely have contained other compounds as well. Indian scholars (24), careful in their conclusions, nevertheless admit that although the old texts do not mention mineral acids explicitly, it cannot be excluded that they had been prepared (25). Otherwise, the intentional use of these acids for dissolving metals seems not to have appeared in India before the sixteenth century. The “vida” thus remains a mystery.

The allusion to a substance that could dissolve wood, gold, and iron already appeared in the Chinese

account written by Tuan Chhêng-Shih in 863 A.D. (26). According to this source, an Indian prince captured by the Chinese claimed to know the *Pan-Chha-Cho Shui* (Punjab “water” or “liquid”) that must be handled with extreme care since it “melts and destroys hands.” The old accounts should be taken cautiously; yet in this particular case the “water” able to dissolve gold could have been *aqua regia*. On the other hand the Indian prince could have exaggerated in his statements. In any case, the Chinese source points to India.

In the Arabic world, too, some early allusions appear that could be explicated as recipes for nitric acid or *aqua regia*. A recently analyzed work entitled *Kitāb Thahīrat Al-’Iskandar* (“The Book of the Treasure of Alexander”), supposed to be of Harrānian origin, was compiled probably in the 9th century A.D., but the oldest known manuscript is from 904 A.D. (27). Among various alchemical recipes dealing with typical procedures for purification of different substances or transmutation of metals, there is a text under the heading “Recipe for the grand softening water which Hermes called Kālīānūs, meaning the one that removes dryness” (27):

A mixture of horse-hooves scraps, donkey-hooves scraps, scraps of goat horns, and similar ingredients should be buried in dung for two days. On the third day vitriol and sal ammoniac were to be added dissolved beforehand in water, and finally this mixture was distilled in a cucurbit. The obtained water of golden, bright color allegedly softens “white copper.

The recipe is not quite clear, but as the authors of this study suggest, it could have produced *aqua regia*. Decomposition of organic matter (hooves, horns) could result in nitrates if the process took longer than a few days. Subsequent addition of vitriol and sal ammoniac could then lead to a mixture from which a strong mineral acid could be isolated by distillation. Problematic is “white copper;” should it be copper or one of its alloys, this material would likely dissolve in *aqua regia* rather than be softened, unless “softening” would denote dissolution.

Mansur al-Kamily, chief chemist at the Egyptian mint at Cairo in the 13<sup>th</sup> century, wrote a practical handbook on the extraction, purification, and assaying of gold. According to Holmyard (28) who mentions this person, Arab chemists were already well acquainted with parting of gold and silver by nitric acid by that time, a century before *L. de inventione* was compiled.

## Two Nitric Acids?

In 1735 the Scottish scientist William Cullen (c. 1710 – 90) remarked (29):

It is certainly improper to support... different names where there is no real difference of the thing. How really these different names mislead may be observed from hence that in almost every table of specific gravities there occur in two distinct articles the specific gravities of spirit of nitre and aqua fortis.

Both terms stood for nitric acid, but in former times two basic kinds of this compound were distinguished.

This distinction depended on the ingredients used for their preparation, as Johann Rudolf Glauber (1604-1670) had introduced it. He called *salis nitri spiritus* (later only *spiritus nitri*) nitric acid prepared from saltpeter and alum, whereas this same acid made from saltpeter and vitriol was *aqua fortis* in his terminology (30). Glauber, however, noted that both acids serve the same purpose — dissolution of metals — and concluded that they are obviously “almost one thing and have the same effect” (“bey nahe ein Ding [sind] und gleiche würckung haben”).

Later he worked out a method of direct production of relatively concentrated nitric acid by distillation of saltpeter with sulfur; yet he did not publish this process. It was said that he communicated it only by word of mouth in exchange for payment (31). In this process sulfuric acid is formed, which reacts with saltpeter to produce nitric acid and *nitrum vitriolatum* (potassium sulfate). According to other sources (32), Glauber performed this reaction directly with sulfuric acid and sodium nitrate. As a byproduct he obtained sodium sulfate, later known as Glauber’s salt (33).

In his textbook *Cours de chymie*, Nicolas Lemery (1645-1715) described the preparation of both *spiritus nitri* and *aqua fortis* (34). The first procedure took about 14 hours (35), the second only eight to nine hours; but as Lemery stated, in this process the resulting product was a mixture of *spiritus nitri* and *spiritus vitrioli* (nitric and sulfuric acid) (36). In Lemery’s opinion, the vitriol and the earth added in the second process only served to separate the particles of *sal nitrum* tightly bound together in the original substance.

### Reconstruction of Nitric Acid Production

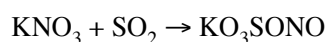
In the 1950s Schröder (37) attempted to reproduce the preparation of nitric acid according to some original

recipes. To simulate the conditions of the old laboratories, he preferentially used minerals from deposits mined in the past, or substances preserved in old collections. The joints of the laboratory apparatus were “luted,” tightened with a mixture including clay, straw, horsehair, egg white, and other substances, as was common practice in earlier centuries. The temperature regime closely simulated the heating produced by wood- or charcoal-burning furnaces. In this way, Schröder followed two basic procedures described in old literature and paraphrased below (38):

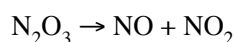
*Aqua fortis*: The dry distillation of a mixture of 150.0 g of saltpeter, 150.0 g of vitriol, and 50.0 g of alum was performed in an earthen vessel at approximately 800°C. The resulting 70.0 g of HNO<sub>3</sub> corresponded to 74% of the theoretical yield, but subsequent analysis demonstrated that the product contained nitric acid of 51% concentration and a small admixture of nitrous acid of 0.4% concentration. The solution had a blue color when fresh, due to dissolved N<sub>2</sub>O<sub>3</sub>, but this color eventually disappeared.

*Spiritus nitri*: The dry distillation of a mixture composed of 50.0 g of saltpeter and 150.0 g of bolus alba (hydrated aluminosilicate, white clay, kaolin) was performed in an earthen vessel at 800-1000°C. This procedure produced 8.0 g of blue-green distillate corresponding to 32% of the theoretical yield when calculated as pure HNO<sub>3</sub>. The product was, in fact, nitric acid (concn. 53.2%) with a small admixture of nitrous acid (concn. 0.6%). The blue-green color of this solution eventually changed to a light yellow.

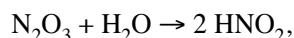
Soukup and Mayer (39) later performed a similar experiment in the interest of explaining its chemistry. They tested a procedure from Agricola’s *De re metallica* (40), using 4 pounds of vitriol, 2 ½ pounds of saltpeter, ½ pound of alum, and 1½ pounds of spring water. In this process, “a blue or intermittently green liquid could be observed in the condenser, which drops into the receiver with vigorous evolution of gases.” This gas was N<sub>2</sub>O<sub>3</sub> produced by the following sequence of reactions:



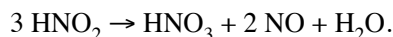
If the cooling is insufficient, N<sub>2</sub>O<sub>3</sub> decomposes:



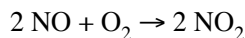
In the opposite case, this oxide dissolves in water to produce nitrous acid



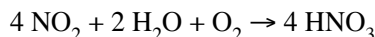
which disproportionates:



Nitrogen (II) oxide reacts with the oxygen produced by the decomposition of  $\text{CuSO}_4$  :

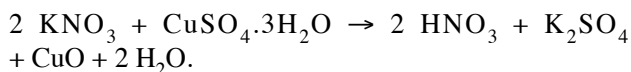


and the  $\text{NO}_2$  formed in this step leads to further nitric acid:



At higher temperatures and insufficient cooling, side reactions accompanying this basic sequence may produce nitrosylsulfuric acid, sulfuric oxide, and water vapor. In these cases,  $\text{N}_2\text{O}_3$  does not always form, and both nitric and sulfuric acids can result. This mechanism explains Lemery's assumption that *aqua fortis* is a mixture of two acids; the French chemist had apparently deviated from the appropriate conditions of his experiment. Furthermore, the contamination of saltpeter by potassium chloride leads to a small amount of hydrochloric acid.

If the vitriol is dehydrated prior to the experiment, the entire process can be expressed by the summary reaction:



### Agricola's Acids

In Book X of *De re metallica*, Georgius Agricola (1494-1555) deals in detail with the parting of gold and silver (40) "by means of aqua valens, and by powders which consist of almost the same things as this aqua." Agricola first describes what this "aqua" is made of and subsequently provides ten recipes. As he states: "almost all these ingredients contain vitriol or alum, which, by themselves, but much more when joined with saltpeter, are powerful to part silver from gold." Yet, there is confusion even in the first recipe, because "one libra of vitriol and as much salt, added to a third of a libra of spring water" would yield hydrochloric, not nitric acid, upon distillation. However, most of recipes he cites would produce more or less pure nitric acid, such as the fourth one, in which the mixture "consists of two librae of vitriol, as many librae of saltpeter, one quarter of a libra of alum, and three-quarters of a libra of spring water."

The tenth composition is difficult to interpret in modern terms. Agricola points out that the mixture lacks both vitriol and alum, but (41):

...it contains three librae of saltpeter, two librae of stones which when thrown into a hot furnace are easily liquefied by fire of the third order, half a libra each of verdigris, of stibium, of iron scales and fillings, and of asbestos, and one and one-sixth librae of spring water.

The fusible stones mentioned in this process are not specified, and the indication of the degree of heat as a "fire of the third order" is too vague a characterization.

Agricola concludes that all these *aquae* cleanse gold of its impurities, but there are "certain compositions which possess singular powers." One of the four recipes for such powerful waters runs as follows:

The second composition is made from one libra of each of the following, artificial orpiment [ $\text{As}_2\text{S}_3$ ], vitriol, lime, alum, ash which the dyers of wool use, one quarter of a libra of verdigris, and one and a half unciae of stibium..

Depending on temperature and other conditions (such as the variously impure compositions of the ingredients), the distillation of this mixture could have produced sulfuric and perhaps even sulfurous acid containing various volatile contaminants (such as compounds of arsenic, and maybe of antimony).

Although the examples in this section are from Agricola's *De re metallica*, the works of alchemists abound in similar recipes. Vannoccio Biringuccio (1480-1539), the first of three important metallurgists of the European Renaissance (the other two are G. Agricola and L. Ercker) already noticed this variation of ingredients in alchemical recipes for acids (42). In the first chapter of the eighth book of his work *De La Pirotechnia* (1540) he describes the preparation of "common parting acid" from saltpeter and vitriol, or from alum, which was a more expensive ingredient. Then he turned attention to approaches in which various further ingredients were added (42):

Alchemists make infinite varieties of acids for their solutions and the aforesaid minerals are the basis of all. It is indeed true that they add sublimes and various salts and other corrosive materials according to their opinion

Yet, he does not elaborate with further details. Various recipes given by Agricola thus stem from other sources, although he drew substantially from Biringuccio.

Indeed, Agricola appears to have copied these recipes from experienced persons and written sources, and is not thought to have necessarily tested them

himself. This raises an important point as to who made such mixtures, and what were their uses. The explanation lies in procedures utilized by alchemists and craftsmen alike; in early-modern Europe there was often no hard and fast distinction between the two, with ‘alchemical’ and ‘metallurgical’ activities being performed sometimes in the same laboratory, especially in connection with the processing of precious metals (43, 44).

### Nitric Acid in the Parting of Gold

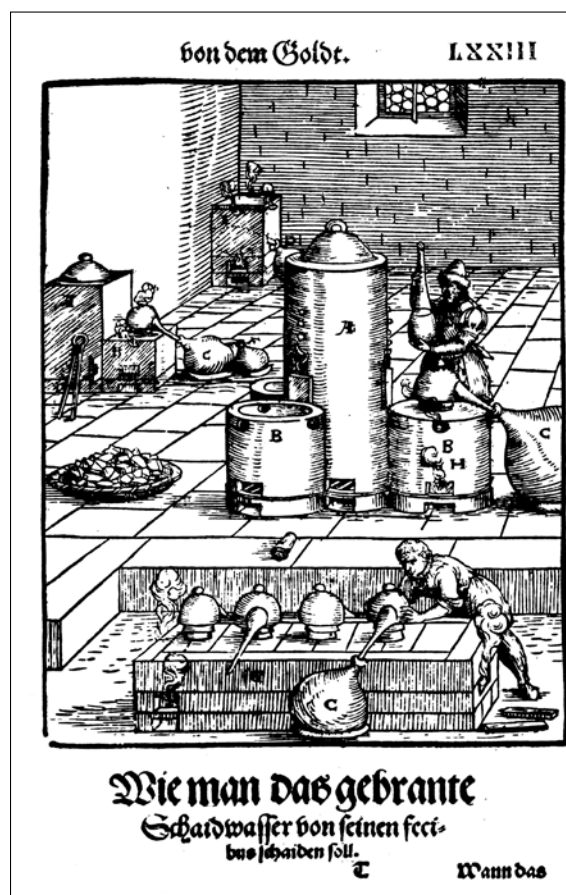
Nitric acid is notable for its ability to dissolve all metals except gold, and this property makes it ideal for the separation of the precious metals. The origin of this understanding cannot be dated reliably, but it seems that alchemists were pioneers of this approach. The preparation of nitric acid was not easy, and as mentioned above, it is likely that originally only small amounts of this compound were available, thus allowing only small-scale experiments in laboratory conditions.

Increasing nitric acid production to quantities sufficient for the large-scale isolation of gold was a question of time. Numerous *Probierebüchlein*, assayers manuals, which began to appear from the beginning of the 16th century, indicate that this process became standard practice (45). Later metallurgists described the isolation of gold in greater detail; Biringuccio’s *De La Pirotechnia* was the first example of such works. Two points concerning the processes described by Biringuccio are particularly significant. First, he recommended building a large furnace “for holding three or four pairs of cucurbits or as many as you wish.” This clearly reflects that a large-scale production of nitric acid was already common by his time. He also brought attention to safety concerns, remarking that the vessels must be of high quality, and their glass must be without bubbles, “for they would be dangerous” if they broke (46). This warning indicates why the production of larger amounts of nitric acid appeared only gradually.

The second point concerns the subsequent cleaning of the product “if you wish this acid to be good.” Pure silver should be added and “you will see the acid begin to grow turbid.” This step had the effect of removing traces of hydrochloric acid that were often present because of the contamination of saltpeter by potassium chloride. In this way, hydrochloric acid was precipitated as silver chloride (47).

A quarter century after Biringuccio’s treatise Lazarus Ercker (? 1528/30-1594) published his work, *Bes-*

*chreibung Allerfürnemisten Mineralischen Ertzt* devoted to assaying (48). In the second book of this treatise the most detailed contemporary account on making of both nitric acid and *aqua regia* appears. The preparation of starting substances, vitriol and saltpeter, is described first. Vitriol should be calcined (heated to remove crystal water), whereas saltpeter must not be heated, but it should be cleaned of impurities as described in the fifth book of Ercker’s treatise. A typical contaminant was common salt; quite a simple technique was employed based on different solubility of potassium nitrate and sodium



The equipment for nitric acid production as shown in Ercker’s *Beschreibung* (Fig. LXXIII). The furnace in the center was known as “Heinzen.”

chloride in a hot, almost saturated aqueous solution of the former (49).

Ercker describes various materials suitable for reaction vessels, glass, clay, or iron, and specifies conditions for distillation. He gives two basic recipes. According to the first procedure, four pounds of saltpeter and four and a half pounds of calcined vitriol are used (50). For “remarkably strong Scheidewasser” three pounds of both calcined vitriol and saltpeter, one pound of calcined alum,

and two pounds of “burnt silicious stone” (*gebrannte kislung* in the original, perhaps roasted iron pyrite, which surely contains sulfates) should be selected (51). One recipe describes preparation of *aqua regia*. Removal of hydrochloric acid by silver, as described by Biringuccio, appears in Ercker’s treatise as well.

Separation of gold became one of the techniques alchemists employed for the alleged transmutation of metals. The alchemist Wenzel Seiler (? 1648-1681) successfully applied this approach in a famous transmutation performed in 1677 (52). He dipped an allegedly silver medallion weighing 4200 grams into a colorless liquid “tincture,” after which the immersed part seemed to become gold. An analysis of this artifact performed in the twentieth century revealed it to be composed of a gold-silver-copper alloy (53), which resembles silver, even though it has a yellowish hue. The tincture was most likely diluted nitric acid, which dissolved all the metals from the surface except for the gold. This spectacular experiment attracted wide attention, and even Robert Boyle inquired in his letters about details of this supposed transmutation (54). It can thus be seen that both alchemists and craftsmen made use of the same processes.

### Graduatio and Gradatio

In Agricola’s description of the “parting” of gold, he briefly mentions that it can be done with a powder. This is an allusion to a method of gold refining that had been known to the ancients (55), but the confusing terminology of European craftsmen and alchemists has led to the result that two terms, *graduatio* and *gradatio*, have sometimes been used interchangeably. However, these were actually two separate processes, both of which employed nitric acid.

**Graduatio:** The specificity of this technique was the addition of another metal to the gold. Two distinct approaches existed, denoted as a dry (a) and wet (b) process in the present article. Nitric acid was used only in the wet process.

a) The oldest known European description of this process occurs in the treatise *De diversis artibus* (approximately 12th century A.D.) attributed to Theophilus Presbyter (56). Impure gold was hammered into thin sheets and cut into square pieces with a hole in their center. These sheets were interlayered with a powder made of clay and salt, moistened by urine, and placed in an earthen crucible. This is the powder mentioned in *De re metallica*. The filled crucible was closed by placing

another one on top, dried, and strongly heated day and night. Then the gold was removed, hammered again, and the process was repeated (40):

After another day and night take it out again, mix a little copper with it, melt as before, and put it back in the furnace. And when you have taken it out for the third time, wash it carefully and dry.

This is actually a cementing process that, in its typical form, had been performed without the addition of another metal.

b) The principle of adding another metal to estimate the purity of gold was introduced sometime after the discovery of nitric acid. In this method, three parts of silver were added to one part of gold, and it was these proportions that gave the process the name *quartatio*, or *analysis per quartam* (57). *Quartatio* is mentioned in numerous sources, such as the “Testimony of Helvetius” (58), but we will consider the brief description of this process that occurs in Agricola’s *De re metallica* (59). Gold weighed at the beginning was refined by cupellation during which a threefold quantity of silver was added, and to which was later joined a small amount of copper. If necessary, this operation was repeated to obtain a pure alloy of both precious metals. The resulting buttons of the alloy “are hammered and flattened out, and each little leaf is shaped in the form of a tube, and each is put into a small glass ampulla. Over these there is poured one uncia and one drachma of the third quality aqua valens.” When heated, “small bubbles resembling pearls in shape will be seen to adhere to the tubes. The redder the aqua appears, the better it is judged to be; when the redness has vanished, small white bubbles are seen to be resting on the tubes, resembling pearls not only in shape, but also in color.” The nitric acid had to be replaced several times, and finally the sheets were washed and weighed. The difference between the original and final weight reflected the amount of impurities in the gold.

The success of this operation depended on the skill of an assayer, the crucial factors being the gold content of the original sample, the amount of added silver, and the quality of the nitric acid. This method worked by allowing maximum contact between the alloy and the acid: the silver dissolved, and the resulting cavities in the alloy allowed the acid to enter and dissolve more silver, eventually leaving behind mostly gold. As Agricola mentioned, a small amount of silver remains undissolved, and therefore a correction should be introduced into the final assessment. The recipe of Theophilus cited above also works by maximizing the access of reagent to the



inside of an alloy by a small admixture of copper, though in that case the reagent was common salt.

**Gradatio.** According to the *Alchemia* (1597) of Andreas Libavius (? 1560-1616), *gradatio* was one of two processes that are kinds of *exaltatio* (Erhöhen) (60). In alchemy, *gradatio* was sometimes used to denote the alleged transmutations in which the appearance of metals was changed to look like gold or silver. One of these techniques (61) employed various mixtures containing nitric and sometimes also sulfuric acid among other ingredients (62). Such mixtures appear in Agricola's tenth *aqua fortis* recipe, and especially in the separate group of four "compositions."

Libavius describes *gradatio* as the "raising of metals" to a higher degree of quality, which concerns their weight, color, and durability. However, he emphasizes that *gradatio* does not have the power to "transfigure" a substance, despite the opposite claim made by Paracelsians. In Libavius' opinion, such a claim would be mendacious and fraudulent. He goes on to mention examples of the capabilities of *gradatio*, such as the reddening of white gold, the fixing of a volatile substance, and the purification of an impure one (63). Purification, however, is an allusion to the process known as *graduatio* (or *cementatio*) described above. This further documents the degree of confusion that could exist in using such terminology. Libavius, nevertheless, admits that the treating of common metals by *gradatio* can so closely approach transmutation that it can be even considered as such a change. Moreover, in this we can see the difficulty that even he faced in defining what constituted a true transmutation, as it is supposedly only by the "exalting" of metals (*exaltatio*) that "matter is made nobler in its substance," i.e. transmuted.

Libavius gives a recipe for nitric acid (64), but he states that there are other known kinds of *aqua fortis* as well. Together with the standard ingredients, such as vitriol and saltpeter, further substances are also used in the preparation of *aqua fortis*: "once it is any salt, another time hydrargyrus sublimatus, cinnabar, 'rust of copper,' gypsum, burnt lime, arsenic, 'federalaun,' colcothar, fel vitri, red sulfur, etc." (65) It is hardly possible to judge what the product would have been after adding such diverse materials, but it is likely that in some cases the resulting mixtures could have dyed the base metals to resemble precious ones.

## Conclusions

As has been shown, nitric acid played an important role in both alchemy and crafts. Still, various questions concerning its history remain unanswered. It is sometimes claimed that nitric acid had been discovered earlier than in the Middle Ages, or that it was not discovered in Europe, or not only in Europe, as the Indian treatise suggests. In fact, the widespread technique of distillation could have led to this product even in the more distant past, as the crucial ingredients, vitriol and saltpeter, were certainly available. It would also be of interest to investigate in deeper detail the alchemical technique of *gradatio*, and to determine what the products of these processes could have been. Likewise, it would be important to explore the relations between the impurities that were often present in the original ingredients and in the final products. It could be that impure nitric acids led to reactions that were subsequently explained in terms of metallic transmutation.

## ACKNOWLEDGMENT

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## REFERENCES AND NOTES

1. The history of nitric acid is dealt with in several works, among others H. Kopp, *Geschichte der Chemie*, Dritter Theil, Braunschweig, 1845, 225; E. O. von Lippmann, *Entstehung und Ausbreitung der Alchemie*, G. Olms, Hildesheim, 1978 (reprint of the J. Springer edition, Berlin, 1919), 363; J. M. Stillman, *The Story of Alchemy and Early Chemistry*, Dover, New York, 1960, 276ff.; R. J. Forbes, *A Short History of the Art of Distillation*, E. J. Brill, Leiden, 1948, 86-87. The modern use of nitric acid with a brief excursion into its history is covered in T. H. Chilton, *Strong Water. Nitric Acid: Sources, Methods of Manufacture, and Uses*, The MIT Press, Cambridge, MA, 1968.
2. M. P. Crosland, *Historical Studies in the Language of Chemistry*, Heinemann, London, 1962.
3. The term *sal nitrum* descended from ancient Egyptian  $n^e-t^e-r$ , which had originally denoted impure sodium carbonate; later, in mediaeval Europe it began to be used for potassium nitrate. Modern terms *nitric acid* and *nitrogen* stem from the ancient Egyptian word. This history is briefly described in M. R. Feldman, "N and Na – The Egyptian Connection," *J. Chem. Educ.*, **1980**, 57, 877-8.

4. This term appears in *Testamentum novissimum*, attributed to Ramon Lully (ca 1232 – 1315/16), in reality a spurious work by unknown Pseudolully (On Lully see A. Clericcuzio, *Lullus, Raimundus (Lull, Ramon)*, in C. Priesner and K Figala, *Alchemie. Lexikon einer hermetischen Wissenschaft*, C. H. Beck, München, 1998, 224). Alchemical writings under Lully's name are briefly analyzed and listed in M. Pereira, *The Alchemical Corpus Attributed to Raymond Lull*, The Warburg Institute, London, 1989. Pseudolully gives a recipe for nitric acid in which he used cinnabar in place of alum (Kopp, *Geschichte*, p 227).
5. A detailed analysis of the Jābir problem can be found in P. Kraus, "Studien zu Jābir ibn Hayyān," *Isis*, **1931**, 15, 7-30; P. Kraus, *Jābir ibn Hayyān: Contributions à l'Histoire des Idées Scientifiques dans l'Islam*, Mémoires de l'Institut d'Égypte, Cairo, 1942; some corrections are in Syed Nomanul Haq, *Names, Natures and Things. The Alchemist Jābir ibn Hayyān and his Kitāb al-Ahjar (Book of Stones)*, Kluwer, Dordrecht, 1994, Ch. I. Doubts concerning the very existence of Jābir had already been expressed in the medieval Arabic world. See J. W. Fück, "The Arabic Literature on Alchemy According to An-Nadīm (A.D. 987)," *Ambix*, **1951**, 4, 81-144.
6. The Pseudogeberian corpus comprises five treatises: *Summa perfectionis magisterii*, *Liber de investigatione perfectionis*, *Liber de inventione veritatis*, *Liber fornacum*, and *Testamentum Geberi*.
7. For example, Holmyard had proposed several explanations for the origin of this corpus. He did not exclude the possibility that it is a genuine translation of Jābir's works, or a translation of the works of other Arabic authors. As another explanation, this author proposed that these works could be summaries of Jābir's books compiled in Europe or medieval European forgeries written by an unknown author (E. J. Holmyard, *Makers of Chemistry*, Oxford University Press, Oxford, 1953, 63; E. J. Holmyard, *Alchemy*, Penguin, Harmondsworth, 1957, 79).
8. W. R. Newman, *The Summa Perfectionis of Pseudo-Geber*, E. J. Brill, Leiden 1991, p 81.
9. A German translation of the whole Geberian corpus, with commentary, occurs in E. Darmstaedter, *Die Alchemie des Geber*, Springer, Berlin, 1922, 113. The recipe cited is translated from this book.
10. The preparation of nitric acid is briefly mentioned in the *Liber fornacum*, a later work of the Pseudogeberian corpus. In Chapter 18, titled "Dissolution of Prepared Metals," the unknown author states, "Our method is: dissolve granulated or filed metal in our solvent that is prepared from sal nitrum and vitriol ..." This formulation indicates that preparation of nitric acid was known by that time and, therefore, the author did not go into the details of the process. The dating of the *L. fornacum* is problematic; it appeared after *Summa* (Ref. 9, p 118).
11. Leicester briefly mentions a Byzantine manuscript from the end of the 13<sup>th</sup> century that describes the preparation of nitric and sulfuric acids (H. M. Leicester, *The Historical Background of Chemistry*, Dover, New York, 1956, 77). The same statement appeared earlier in G. Fester, *Die Entwicklung der chemischen Technik bis zu den Anfängen der Großindustrie*, Springer, Berlin, 1923, 75.
12. R. P. Multhauf, *The Origins of Chemistry*, Franklin Watts, New York, 1966, 179.
13. Multhauf's statement should be corrected, because *Testamentum* appeared later, after 1300. No known Pseudolullian alchemical manuscript dates back to the 14<sup>th</sup> century (see Ref. 4, Pereira, *The Alchemical Corpus*, 22).
14. Ref. 12, pp 196, 197.
15. Ref. 12, p 207, n. 23.
16. Another problematic personality in the pantheon of alchemy, Arnald (ca.1240-1311) was a physician and diplomat; but according to some modern authors he was not an alchemist, and alchemical works under his name would be later forgeries (G. Keil, *Arnald von Villanova*, in C. Priesner, and K. Figala, *Alchemie*, 62; see Ref. 4).
17. W. Ganzenmüller, *Beiträge zur Geschichte der Technologie und der Alchemie*, Verlag Chemie, Weinheim, 1956, 234.
18. P. Ray, *History of Chemistry in Ancient and Medieval India*, Indian Chemical Society, Calcutta, 1956, Ch. III.
19. Ref. 18, p 138.
20. It could be achieved, for instance, by strong heating (calcination) or by various chemical reactions and later by using mineral acids.
21. Green vitriol generally corresponds to FeSO<sub>4</sub>. The pyrites cannot be reliably identified, but they were probably mostly sulfides of iron and/or copper. Stibnite, named also antimonite, is Sb<sub>2</sub>S<sub>3</sub>.
22. Ref. 18, pp 138-139.
23. Ref. 18, pp 139.
24. D. M. Bose, S. N. Sen, and B. V. Subbarayappa, Ed., *A Concise History of Science in India*, Indian National Science Academy, New Delhi, 1971, 307.
25. The products could have contained sulfuric acid as well; in the first recipe cited in this paragraph "lion of a sulfur" is claimed to be able to "kill" metals. The term "killing" was used to express the transformation of metals into their salts by sulfuric and/or nitric acid. Some sulfates are less soluble in water.
26. T'sao T'ien-Ch'in, Ho Ping-Yü, and J. Needham, "An Early Mediaeval Chinese Alchemical Text on Aqueous Solutions," *Ambix*, **1959**, 7, 122-155.
27. A. M. Alfonso-Goldfarb, and Safa Abou Chahla Jubran, "Listening to the Whispers of Matter Through Arabic Hermeticism: New Studies on the *Book of the Treasure of Alexander*," *Ambix*, **2008**, 55, 99-121.
28. See Ref. 7, Holmyard, *Makers of Chemistry*, 77.
29. L. Dobbin, "A Cullen Chemical Manuscript of 1735," *Ann. Sci.*, **1936**, 1, 147-148.
30. J. R. Glauber, *Furni novi philosophici*, Johann Fabel, Amsterdam, 1647, Bd. II, 38, 65ff.
31. U. Klein, *Verbindung und Affinität*, Birkhäuser, Basel, 1994, 143.
32. See Ref. 1, Chilton, *Strong Water*, 14.

33. Glauber was apparently the first to prepare sodium sulfate from common salt (NaCl) and *oleum vitrioli* (sulfuric acid); he named his product *sal mirabile*. To keep the process secret he used dispersion of knowledge, common in alchemical works: he wrote this recipe in two parts published separately, and in each part he used different names of reactants (Ref. 2, p 39).
34. The first edition appeared in 1675; the present text is cited from N. Lemery, *Cours de Chymie, Oder vollkommene Chymist*, J. J. Winckler, Dresden, 1726, 522ff.
35. In the German translation of Lemery's textbook, this product is named "Salamanderblut" (blood of salamander).
36. The terminology in Lemery's textbook seems to reflect the problem of the composition of *spiritus nitri*. In Ch. 2, entitled "Silver-crystals, which are called Vitriolum Lunae," the method of preparing such crystals is described: "This operation is dissolution of silver that is reduced into a kind of a salt by acid spikes of spiritus nitri." The product, silver nitrate, is nevertheless called "vitriol" which name was usually applied to what are today recognized as sulfates. It is as if Lemery interchanged both kinds of salts in this case (Ref. 30, p 142).
37. G. Schröder, *Die pharmazeutisch-chemischen Produkte deutscher Apotheken im Zeitalter der Chemiatrie*, Herbig, Bremen, 1957, 59ff.
38. According to this author, the thermal decomposition of potassium nitrate occurs at high temperatures. Not only are nitrogen oxides formed in this process, but also oxygen is directly produced. If an earthen vessel were to be used, potassium nitrate would react with the silicates. This reaction also produces both oxygen and nitrogen oxides, while the surface of the vessel acts as a catalyst and contributes to the processes leading to the formation of nitrogen oxides. These reactions generally occur when earthen distillation apparatus is used.
39. R. W. Soukup and H. Mayer, *Alchemistisches Gold. Paracelsische Pharmaka*, Böhlau, Wien, 1997, 137ff.
40. G. Agricola, *De re metallica*, transl. by H. C. Hoover and L. H. Hoover, Dover Publ., New York, 1950, 439ff.
41. Verdigris denoted a green copper compound, usually basic copper (II) acetate; stibium was antimony (III) sulfide; and asbestos was apparently the substance currently known by this name.
42. *The Pirotechnia of Vannoccio Biringuccio*, transl. by C. S. Smith and M. T. Gnudi, Dover Publ., New York, 1966, 188.
43. T. Nummedal, *Alchemy and Authority in the Holy Roman Empire*, The University of Chicago Press, Chicago, IL, 2007, Ch. 3 and 5.
44. R. W. Soukup, *Chemie in Österreich*, Böhlau, Wien, 2007, Ch. 5.
45. E. Darmstaedter, *Berg-, Probir- und Kunstbüchlein*, Verlag der Münchner Drucke, München, 1926; see also A. G. Sisco and C. S. Smith, Ed., *Bergwerk- und Probirbüchlein*, The American Institute of Mining and Metallurgical Engineering, New York, 1949.
46. Soukup and Mayer (Ref. 39, p 138), point out that gases (especially NO and NO<sub>2</sub>) evolving in this reaction could cause the explosion of the vessel. The old sources recommended leaving a small hole closed by a piece of wood between the vessel and helm. The pressure inside the vessel would push this wooden stopper out when it became too high.
47. According to H. Kopp, *Geschichte der Chemie*, Vieweg, Braunschweig, 1843-1847, Dritter Theil, 228, Paracelsus already knew this technique.
48. Lazarus Ercker, *Beschreibung Allerfürnemisten Mineralischen Ertzt / und Berckwerckarten / ...* Prag, 1574.
49. Ref. 48, fol. 137v. Solubility of potassium nitrate increases with the temperature, whereas solubility of sodium chloride, which is lower from the beginning, remains almost constant. If a mixture of both salts is dissolved at increasing temperature, sodium chloride collects on the bottom of a vessel, whereas potassium nitrate continues to dissolve. Then, solution enriched in potassium nitrate results. The solubility of these salts is [at 10°/ 100°C in grams per 100 g of H<sub>2</sub>O]: NaCl 4/56.2, KNO<sub>3</sub> 21.2/245.
50. Soukup and Mayer (Ref. 46) point out that Ercker's recipe (Ref. 48, fol. 67v) is more comprehensible and leads to stronger acid.
51. Ref. 48, fol. 70v/70r.
52. V. Karpenko, "Witnesses of a Dream: Alchemical Coins and Medals," in S. J. Linden, Ed., *Mystical Metal of Gold*, AMS Press, New York, 2007, 117-160.
53. Microanalysis of four samples from the surface and from the edge revealed the following average composition (in %wt.): Au 47.55, Ag 43.37, Cu 7.56, with traces of tin, zinc, and iron. See R. Strebing and W. Reif, "Das alchemistische Medaillon Kaiser Leopold I.," *Mitt. der Numismatischen Gesellschaft in Wien*, **1932**, XVI, 209-218.
54. L. M. Principe, *The Aspiring Adept*, Princeton University Press, Princeton, NJ, 1998, 95.
55. A. Ramage and P. Craddock, *King Croesus' Gold*, The British Museum, London, 2000.
56. *Theophilus, On divers arts*, transl. by J. G. Hawthorne and C. S. Smith, Dover Publ., New York, 1979, 108.
57. It appears in Martin Ruland's (1569-1611) lexicon of alchemy as "Quartura" (*Lexicon Alchemiae sive dictionarium alchemisticum ... auctore Martino Rulando*, Frankfurt, 1612, 400); nitric acid is named *aqua stygia* here.
58. F. S. Taylor, *The Alchemists*, Paladin, Frogmore, 1976, 143.
59. Ref. 40, p 248.
60. *Exaltatio* denoted the process in which "a higher stage of a substance and its action can be achieved by maturatio (ripening), or gradatio." The latter of the aforementioned processes can be performed by such techniques as *cementatio*, *extinctio* (Ablöschen, quenching), and *coloritium* (coloring). See *Die Alchemie des Andreas Libavii. Ein Lehrbuch aus dem Jahre 1597*, Verlag Chemie, Weinheim, 1964, Ch. LVI, 99.

61. V. Karpenko, "The Chemistry and Metallurgy of Transmutation," *Ambix*, **1992**, 39, 47-62.
62. Ref. 60, p 107: "There is gradatio ... [performed] by means of spirits of 'sharp waters.'"
63. This sentence is a verbatim citation from Ruland's *Lexicon*, the entry "Gradatio" (Ref. 57, p 245).
64. Ref. 60, p 459.
65. "Rust of copper" could be any copper compound probably prepared by the "corrosion" of this metal. Naturally occurring basic copper (II) carbonate seems to be more probable than artificially prepared basic copper (II) acetate, which was also known as verdigris (Ref. 41). Arsenic needs to be specified; it could be an oxide or any sulfide of this element. "Federalaun" was one of several names of alum, and colcothar was usually impure  $\text{Fe}_2\text{O}_3$ .



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