

VITRIOL IN THE HISTORY OF CHEMISTRY

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1. Introduction

Although chemistry is widely considered among its practitioners to be a modern science, technological processes based on chemical reactions have been in standard use from the distant past. The production of salts, dyes and paints, cosmetics, and fermented beverages made use of techniques and reactions common to chemical experimentation (such as filtration, dissolution, and sublimation). Among these early crafts, metallurgy involved a widening knowledge of metals and their alloys, and entailed the recognition of certain stones as metallic ores. However, these activities seem to represent only a practical, applied use of chemical processes. Although craft-workers may have developed their own concepts regarding the substances involved in a given process, records of such ideas have not come down to us, and the discoveries and improvements they made seem to have been based largely on a trial-and-error approach.

The ancient considerations on the nature of matter that have come down to us were composed by philosophers who considered the problem of change. In attempting to understand the objects of the natural world and the changes these objects undergo, the idea of earth, air, fire, and water as material elements was first postulated by the Greek natural philosopher Empedocles (492–432 BC), and was brought into its most well known form by Aristotle (384–322 BC). Analogous theories appeared around the same time in China (fire, earth, water,

metal, and wood) and India (earth, water, fire, air, and space)¹. Western alchemy appears to have arisen in Hellenistic Egypt and the Near East during the last couple of centuries BC, in conjunction with several mystical sects and the increasingly common craft practices of creating imitation precious stones and metals². Although it lacked the logical rigor of earlier Greek philosophies, alchemy nonetheless attempted to engage the complex world of chemical processes and mineral substances in a scientific way, which eventually led to ideas involving the transmutation of base metals into precious ones and the preparation of a substance for extending the human life-span. The term protochemistry is often used to refer to some of these activities, and it is this aspect of alchemical activity with which the present work is concerned.

Many chemical and mineral substances known to the ancients were of great importance to civilization. The most ancient literary evidence of familiarity with such substances is from Sumero-Assyrian dictionaries that include some chemical terms. By the time of the rule of the Assyrian king Assurbanipal (668–626 BC), these lists of chemical terms included several kinds of common salt (NaCl), gypsum (CaSO₄ · 2 H₂O), and substances recognized today as metallic sulfates and sulfides^{3,4}. In ancient Egypt an impure form of sodium carbonate was particularly important in mummification. The discovery of gunpowder in China around the ninth century AD led to an increased interest in saltpeter (KNO₃). Other substances were recognized to have remarkable physical properties, such as the easily sublimated sal ammoniac (NH₄Cl). The extraction of elemental mercury from cinnabar (HgS) seems to have become common practice by the end of the fourth century BC. The earliest extant description of this process is in the treatise *On Stones* by Theophrastus⁵ (c. 372 – c. 287 BC), while the laboratory synthesis of cinnabar by combining and then subliming mercury and sulfur seems to have been known⁶ before AD 400. A group of mineral substances that probably attracted attention due to their often striking blue and green crystals and their distinctive chemical properties were the sulfates of divalent metals (principally of iron and copper), commonly known in early terminology as *atrament* and *vitriol* (the latter of which will be used in this paper). In this paper we will attempt to trace the history of vitriol as revealed in chemical literature from antiquity to the early modern period, and discuss some examples of its uses and opinions about its nature and effects.

The mineral substances referred to here as vitriol are recognized in modern science as hydrated sulfates of iron, copper, and even magnesium and zinc, all of which form as secondary minerals within the weathering zones of metallic sulfide deposits. These sulfides were generally referred to as “pyrites” during antiquity. Use of this term became more restricted by the sixteenth century to refer mostly to sulfides of metallic luster which yield little or no metal, although more minerals than the one currently called pyrite were still included under this term. The name marcasite was used by the Arabs in referring to these same minerals, and became used synonymously with pyrites in much of the literature of the sixteenth

century Europe. It was probably during the course of mining such sulfides that vitriol became noticed. The iron and copper varieties of vitriol were widely recognized and utilized in antiquity, and were commonly referred to respectively as green and blue vitriol. In modern mineralogical terminology⁷, the green and blue vitriol correspond to melanterite ($\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$) and chalcantite ($\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$), respectively. The blue and green varieties were known to form spectacular crystals of a vitreous luster, although their formation in botryoidal, granular, or stalactitic masses is more common. In these latter forms, these sulfates often appear in dull shades, and the iron sulfate often appears in shades of blue, yellow, or even completely white. These sulfates are highly soluble and prone to degradation by absorbing water. As such, their occurrence is ephemeral, and the vitriol of commerce was that extracted from the earthy masses and solutions of decomposing sulfide and sulfate minerals.

2. Vitriol in Antiquity

The antiquity of familiarity with vitriol is shown by a Sumerian word list dating from around 600 BC, in which types of vitriol are listed according to color⁸. However, the earliest surviving discussions of vitriol in the literature of antiquity are the works of the Greek physician Dioscorides (first century AD) and the Roman naturalist Pliny the Elder^{9,10} (AD 23–79). Referring mainly to the vitriol produced in the vicinity of the copper ore deposits on Cyprus, both authors describe vitriol forming as white dripstones in caves, mine tunnels, and along the sides of pits dug into the aforementioned ‘vitriolous’ earths. They also mention artificial vitriol obtained from the congelation of both naturally occurring and artificially prepared solutions of these sulfates. In all cases, the origin of vitriol from a liquid, or a solution as we would say (Pliny called it a *limus*), was definitely recognized.

Dioscorides indicates that vitriol was considered as a mineral genus encompassing a number of varieties that he designates by mode of origin. We can thus see that vitriol had already attracted enough attention by workers in the mineral industries to be considered unique among minerals and to be recognized by its chemical qualities despite its various manifestations. Perhaps because of its usual association with sulfide ores that were mined mainly for copper, vitriol was commonly thought to be a cupriferous substance. By virtue of this supposedly cupriferous nature, the Greeks called vitriol by the name *chalcantion*, while in Latin it was called *atramentum sutorium* with reference to its principal commercial use as a blackening agent for leather. However, as this property of blackening leather can only be accomplished by the iron-rich vitriol, and in consideration of the composition of the sulfide deposits on Cyprus¹¹, it is probable that most of the vitriol used in antiquity was actually iron-rich in spite of its association with copper ores (the presence of iron in these substances appears to have remained unrecognized until the sixteenth century).

As mentioned above, commercial vitriol was obtained through lixivation techniques¹² that probably originated with similar processes for obtaining alum in ancient Mesopotamia¹³. These processes entailed the dissolution of vitriolous material or the collection of naturally occurring vitriol solutions, followed by the concentration of the solution (or *lixivium*)

and its subsequent coagulation in open trenches or vats. Both Dioscorides and Pliny designate these vitriolous materials by the terms *chalcitis*, *melanteria*, *misys* and *sorys*. Although both authors attempt to describe each of these vitriolous earths in detail, it seems doubtful that they had personal experience with them. Moreover, as these materials were mixtures of sulfides, sulfates, oxides and clays in varying degrees of chemical and physical condition, and containing varying degrees of sulfate enrichment, it is doubtful whether these names could have been used in a strictly uniform sense even among the vitriol manufacturers themselves. Nonetheless, we must note the significance of such subdivision among these substances, for it further demonstrates that vitriol was considered to comprise a group of related substances, among which workers attempted to make qualitative distinctions.

So far, this discussion has shown that already from the beginning of the current era, vitriol was characterized as being compositionally related to copper, forming from a solution, and as representing a specific mineral group. Vitriol and its related substances continued to be commonly used throughout later antiquity. Dioscorides' medical interest in these substances was followed up by the Graeco-Roman physician Galen (c. AD 129 – c. 200), who discusses these vitriol substances in Book 9 of his tract *On Medical Simples*¹⁴. These substances also found their way into various metallurgical processes, being used in the purification of gold and in the fabrication of imitation precious metals. The routine empirical use of these substances in such operations are recorded in the *Physica et mystica* of Bolos-Democritus¹⁵ (c. 300 BC), the third century AD writings of Zosimos¹⁶, and in the roughly contemporaneous¹⁷ Leyden Papyrus X, all of which reflect vitriol's involvement in the early development of alchemy in Hellenistic Egypt.

3. Vitriol in Arabic Alchemy

An early attempt to systemize the classification of mineral substances beyond the level of metals, stones, and earths is that of the Persian physician and alchemist Muhammad ibn Zakkarīya ar-Rāzī (c. AD 854–925/935). In his *Book of Secrets* (*Kitāb al-asrār*), written around 900, he classified all substances known to him, first dividing them into four main groups: mineral (Table I, as given by Newman¹⁸), vegetable, animal, and derivatives of these. The latter included substances that ar-Rāzī was unable to include into any of the three preceding groups, as for example litharge (basic lead carbonate), verdigris (basic copper acetate), and tutia (zinc oxide).

Among ar-Rāzī's table of mineral categories vitriol appears as a class of six substances. This grouping testifies to the continued recognition of the qualitative and chemical relations among vitriol and its related substances despite their various appearances and chemical effects. He included alum among the types of vitriol, probably due to the similarities in their adstringent qualities and mode of occurrence; for although alum had industrial and medical uses different from those of vitriol, both were manufactured by similar means and sometimes even occurred together. Otherwise, the remaining five types of vitriol in ar-Rāzī's group seem to be various derivatives of the copper and iron sulfates, distinguished roughly by color, most of which he referred to by Arabic transliterations

Table I

Rázi's classification of minerals in an abridged latinized form; in some cases one substance is classified as more types in the original version. The difference was often only in purity of such a substance, but sometimes they are quite different compounds.

Terrena ("Earthy things")

- A. Four Spirits [volatile substances]
1. Quicksilver
 2. Sal ammoniac (NH_4Cl) (three types)
 3. Auripigment (six types distinguished by their color; this group includes both As_2S_3 and As_4S_4)
 4. Sulfur (five types, including black one which was either sulfur mixed with asphalt or iron sulfides)
- B. Seven Bodies [i.e. seven known metals]
Gold, silver, copper, tin, iron, lead, and "Karesin" or "Catesin" [the Arabic *khár síní*, "Chinese iron", possibly a bronze composed of copper, zinc, and nickel]
- C. Thirteen Stones
1. Marchasita [= Arab. *marquashítá*: the minerals now known as "pyrites", including "fool's gold" (FeS_2). Four types mentioned by ar-Rázi cannot be positively identified]
 2. Magnesia [= Arab. *maghnísiyá*: an old alchemical "cover-name" used to denote various substances; three types]
 3. Edaus (or daus) [= Arab. *daus*: either an iron ore composed of iron oxide, or iron fillings, or even iron slag]
 4. Thutia [= Arab. *tutíyá*: usually zinc carbonate and oxide]
 5. Azur [= Arab. *lázward*: lapis lazuli]
 6. Dehenegi [= Arab. *dahnaj*: malachite; $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$]
 7. Ferruzegi [= Arab. *fírúzaj*: turquoise]
 8. Emathita (elsewhere *sedina* or *sedena*) [= Arab. *shádanaj*: hematite or bloodstone]
 9. Cuchul [= Arab. *kuhl*: antimony sulfide and lead sulfide (galena), often confused].
 10. Spehen [apparently a misreading of Isfahan]
 11. Funcu [= Lat. *succen* < Arab. *ash-shukk*, arsenic oxide]
 12. Talca [= Arab. *talq*: not our "talc", but mica or layered gypsum]
 13. Gipsa [= Arab. *jíbsín*: gypsum; CaSO_4]
- D. Six Atraments [the class of "atraments" contained metallic sulfates and their impurities]
1. Black atrament [impure FeSO_4]
 2. Alum [a rather vague category including $\text{KAl}(\text{SO}_4)_2$ in varying degrees of purity as well as other metallic sulfates]
 3. Calcandis or white atrament [= Arab. *qalqant*: weathering product of copper/iron ores or alum]
 4. Calcande or green atrament [= Arab. *qalqádis*: iron and/or copper sulfate]
 5. Calcatar or yellow atrament [= Arab. *qalqatár*: "decomposition product of sulfide- and sulfate rich copper/iron ores on the one hand, and burnt

Table I – continued

- iron vitriol < i.e. iron sulfate >, thus iron oxide on the other"]
6. Surianum or red atrament [= Arab. *súrí* or *súrín*: same as *calcatar*]
- E. Six Boraces [= Arab. *bauraq* (i.e. $\text{Na}_2\text{B}_4\text{O}_7$); 7 types, in this group also Na_2CO_3 and K_2CO_3 were included]
- F. Eleven Salts
1. Common salt [presumably NaCl]
 2. Bitter salt [perhaps a type of rock-salt]
 3. Salt of calx [slaked lime; $\text{Ca}(\text{OH})_2$]
 4. Pure salt [presumably NaCl]
 5. Sal gemma [rock-salt; NaCl]
 6. Salt of naphtha [presumably NaCl contaminated with asphalt]
 7. Indian salt [not identifiable]
 8. Salt effini [= Lat. *essini* < Arab. *as-síní*: Chinese salt. Not identifiable]
 9. Sal alkali [= Arab. *al-Qali*: soda]
 10. Salt of urine [$\text{NaNH}_4\text{HPO}_4$, produced by decomposition and drying of urine]
 11. Salt of cinder [potash; K_2CO_3]

of the Greek names *chalcanthon*, *chalchitis*, *colcothar*, and *sory*.

The fact that ar-Rázi designated vitriol as a special group speaks for the interest in and importance of these materials in the eyes of as skilled a chemist as he undoubtedly was. As a physician his activity in alchemy was of a practical nature, and he declined from speculating on the mineralogical origins of the substances he used. As Multhauf¹⁹ has pointed out, one of ar-Rázi's most significant contributions to chemistry was this systemization of mineral substances. Ar-Rázi's categorization of the vitriolous substances among the other types of minerals was an important step in codifying the recognition of the compositional similarities and relations between these substances, while his mineral system was so apt that it remained in use for several subsequent centuries.

The importance of ar-Rázi's consideration of vitriol comes into sharper focus when compared with those of other Arabic authors²⁰. For instance, Jabir ibn Hayyan in his *Great Book of Properties* (*Kitáb al-hawass al-kabir*). He is a mysterious figure in alchemy; doubt still persists as to whether there was ever an actual person of this name. The supposed dates of his life are AD 710/30 – c. 810. A detailed discussion of this problem is given by Haq²¹. Jabir divided all mineral substances into three groups: spirits (substances that completely evaporate when heated), metallic bodies (metals), and mineral bodies. This third group contained malleable mineral bodies that either melt or remain unchanged in fire. This author included vitriol in a subcategory of the mineral group for substances that contain only a very small proportion of "spirit" (the separable, volatile part), and which also included shells, pearls, and "flower of copper" (*qualquant*). Another author, Muhammad ibn Ibrahim al-Watwat (1234–1318) divided mineral substances into seven groups in his treatise *Mountains and Minerals* (*Mabahig al-fihar*). Vitriol appears in the group called "stones whose nature changes that of other stones", along with borax,

magnesia, and potash. Although this categorization does not seem to entail the degree of chemical understanding implied in ar-Rázi's system, it nonetheless betrays a certain metallurgical rationality in that all of the aforementioned substances were used in the purification and coloring of metals. Such categorization could also suggest that this author was familiar with the reaction in which solid iron immersed in a vitriol solution seems to change into copper (this reaction is further discussed below). Lastly, the Arabic author Abdallah ibn Síná (commonly known as Avicenna, 980–1037) divided minerals into stones, sulfurs, salts, and metals in his *Book of Remedy* (Kitáb aš-šifá). He included vitriol and its related substances in the category of salts, as he considered them to be composed of saltiness, sulfurness, and stoniness.

Ar-Rázi's influence in the recognition of various types of vitriol appears in the work of an anonymous eleventh century Spanish Arab known to modern scholarship as Pseudorhazes (because the thirteenth century Latin copies of this work were attributed to ar-Rázi). This book, known in its Latin version as *De aluminibus et salibus* (On Alums and Salts), contains a chapter about vitriol, which begins as follows²²: “*Know that there are many kinds of vitriol, and their places of occurrence are numerous. These vitriols are water and color that have coagulated by the dryness of earth, and there is something hot and dry in their nature. And one of their kinds is Colcothar and [further kinds are] Sory and Calcythis and Calaminaris [?] ... And these vitriols blacken [metallic] bodies and give to the red [body] yet more redness and blacken the white; and the finest of it is Colcothar and the coarsest is Sory.*”

Although this description of vitriol is brief, it contains significant information on how vitriol was characterized on a qualitative level. The moist yet earthy nature of the vitriolous earths, and their often striking colors, are addressed with reference to their coagulative mode of origin, while the “something hot and dry in their nature” refers to the sulfurous character of these substances. The inclusion of *calaminaris* among these vitriolous earths is strange, as it is probably a reference to a hydrated oxide of zinc often associated with the weathering zones around silver mines. If so, this author must have included it due to its earthy nature and its “coagulative” mode of occurrence, similar to that of the vitriolous substances.

The following example of the laboratory treatment of vitriol is given in the subsequent paragraph of *De aluminibus*. Although this recipe appears to be somewhat corrupt, and although we cannot be sure of the intended result, it nevertheless reflects a chemical procedure: “... *thou takest as much as thou wilt of [vitriol]; and put [it] into a vessel, and let it stand one night in a hot furnace. Thereafter vitriol gets out red, of very strong redness. And then let it remain covered by a four-fold amount of pure sweet water, and let it stand until it dissolves, and it settles down as a sediment on the bottom. Then let it trickle off [distillatio per filtrum], and return it [sediment] for future use.*” Here, it seems that an iron-rich vitriol was strongly heated, with the resulting slightly soluble, red iron oxide being rinsed with water.

Although we have said almost nothing about the industrial and medical uses to which vitriol was applied, we have attempted to show by the above examples that the origin and chemical nature of vitriol did engage the thought of early workers in the chemical field. Thus far, this attention culminated in regarding

vitriol as a distinct group of mineral substances. These materials continued to acquire extraordinary importance in both practice and theory. As will be discussed below, further attempts to explain the nature of vitriol on a chemical basis appeared in Europe during the sixteenth century, when alchemists and other workers in the mineral industries sometimes recorded their knowledge and ideas about these strange substances.

4. Vitriol in Indian Alchemy

The alchemy that developed in India contains features that are characteristic of the philosophical and religious background of that region. As such, Indian alchemy was more focused on a practical approach to human health, and to this end it widely utilized substances made from plants and inorganic compounds. The interpretation of such recipes is often problematic, as is dating many of the works and identifying their authors²³.

Mention of vitriol in Indian alchemy does appear in some late medieval writings²⁴, but often only the blue or green varieties are included. For example, inorganic substances are classified in part IX of the *Rasahridaya* attributed to Bhikshu Govinda (c. eleventh century AD). The most important of these groups in Indian alchemy was the *rasas*. This word originally meant “juice”, was later used to refer to mercury, and in the present sense seems to indicate a group of minerals whose origin or composition were supposed to have involved a liquid component. This group includes blue vitriol (*sasyaka*), pyrites, cinnabar, calamine, and an unidentifiable variety of iron. There is no mention of any perceived similarities between these substances, nor is there any mention of green vitriol. The twelfth century *Rasarnava* lists a group of eight *maharasas* (or “great” *rasas*) similar to that of the previously mentioned work, and in which green vitriol is likewise absent.

Conversely, both blue and green vitriol are mentioned in a *Rasakalpa* (a part of *Rudrayamala Tantra*) written around AD 1300. Yet blue vitriol is classified among *maharasas*, while green vitriol is included among the *rasas* in this work. Both substances appear again in this *Rasakalpa*, but this time as a special group: *kasisa* (vitriol), *pushpa kasisa* (another vitriolous substance; *pushpa* meaning “flower”), and *hirakasisa* (green vitriol; *hira* means “precious stone”, and was perhaps used with reference to green vitriol by virtue of this mineral's striking green color and crystalline appearance).

We can only speculate as to why more importance was ascribed to blue rather than green vitriol in Indian literature, as both materials seem to have been generally known. Perhaps this was partly because the blue and green varieties have quite distinct chemical effects. A possible explanation is that familiarity with the chemical reaction in which solutions of blue vitriol deposit copper onto solid iron surfaces caused the blue vitriol to be considered as a special substance, while the iron-rich green vitriol undergoes no such spectacular reaction. This reaction was described in the *Dhatuvada*, dated around the eighth or ninth century AD. This possibility gains further support from a passage in the *Rudrayamala Tantra* showing further recognition of the relation between blue vitriol and copper, which reads: “Copper in combination with the ‘burning water’ gives rise to blue vitriol.” Although a discussion

of mineral acids in Indian alchemy is beyond the scope of this paper, the latter example makes it clear that in using copper to create blue vitriol, the Indian alchemists understood that blue vitriol must in some way contain copper. It thus seems possible that these two types of vitriol were categorically separated in Indian alchemy by virtue of their distinct chemical effects and some degree of compositional knowledge of the blue variety.

5. Vitriol in European Alchemy and Mineral Industry

It was through works such as *De aluminibus* that vitriol entered the sphere of Latin alchemy. Here we find vitriol included in such disparate sources as an ink recipe in the twelfth century *On Divers Arts*²⁵, in the laboratory-oriented, gold-making recipes of the late thirteenth century *Liber claritatis*²⁶, and in widespread use in the growing corpus of Latin chemical literature. As will be discussed below, it is from the use of vitriol by the Latin alchemists that sulfuric and nitric acids were discovered. Changes also occurred in vitriol nomenclature during this period. Among the earliest works to use the word vitriol (as opposed to *atrament*) are the eighth century Latin version of the *Compositiones ad tingenda*²⁷, and the thirteenth century *Book of Minerals* of Albertus Magnus²⁸ (c. 1200–1280). The name vitriol comes from *vitrum*, the Latin word for glass, and was coined with reference to its vitreous luster. When the names vitriol and *atrament* remained in use during the later Middle Ages, vitriol seems to have been used with reference to the vitreous, processed substance²⁹. Copper was sometimes used to distinguish naturally occurring vitriol from the refined variety³⁰, although the names vitriol, *atrament*, and copper became used interchangeably by the sixteenth century^{31,32}. Even as late as the publication of *De natura fossilium* in 1546, Agricola, who used the term *atramentum*, notes that the name vitriol was becoming commonly used at the time³³.

Accounts of vitriol production processes appear in the literature of the sixteenth century mineral industry. In *The Pirotechnia*³⁴ (1540) and *De re metallica*³⁵ (1556), the authors describe vitriol manufacturing techniques very similar to those mentioned by Dioscorides and Pliny (discussed above). One notable innovation is found in *De re metallica*³⁶, in which Georgius Agricola (1494–1555) describes a process that goes beyond the use of naturally occurring vitriolous earths and solutions by generating these directly from pyrites. This is the earliest record of the recognition of the genetic relationship between vitriol and the metallic sulfides from which they are generated, and this innovation seems to have entailed an increased understanding of vitriol and pyrites on the compositional level. Lazarus Ercker (1528/30–1594) was an assayer and metallurgist who lived in Bohemia from 1567; the emperor Rudolf II named him master of the Prague mint in 1583. In his *Treatise on Ores and Assaying* (1574) he displays a full understanding of the compositional links between these two mineral substances, for he describes procedures for assaying pyrites for vitriol³⁷, and shows the earliest understanding of the compositional complexity of both substances³⁸.

Interestingly, the addition of solid iron to the vitriol solution during the lixivation process became standard procedure

by the sixteenth century³⁹. This addition would cause most of the copper present in the solution to precipitate onto the surface of the solid iron, leaving an iron-rich vitriol solution and the solid iron coated with copper. Although this practice appears in the lixivation processes described by Biringuccio and Agricola, neither of them remark on its supposed purpose or significance. Ercker mentions the reaction itself, which he believed to be a vitriol-induced metallic transmutation of iron into copper⁴⁰. Ercker was not alone in this opinion, and it is to this aspect of the history of vitriol that we must now turn our attention⁴¹.

The use of solid iron to collect copper from solutions containing copper sulfate was used in the hydrometallurgical production of copper in ancient China, when copper ore deposits became too depleted to yield enough metal for coinage⁴². This process was also used by the Spanish Arabs during the Middle Ages, who appear to have discovered it independently when their copper deposits were also becoming exhausted while iron remained abundant⁴³. In the chemical literature of the sixteenth century, we find that this reaction was cited in support of the possibility of metallic transmutation. Although Paracelsus (1493/4–1541) never claimed to have transmuted metals other than by this single reaction, it nonetheless enabled him to extrapolate the possibility of further metallic transmutations⁴⁴. Paracelsus mentions this vitriol-induced reaction in chapter XV of the *Economy of Minerals*⁴⁵, and in chapter VI of *The Book Concerning the Tincture of the Philosophers*⁴⁶.

In *The Tincture* vitriol is not mentioned by name⁴⁷, but is called a “lixivium of marcasites” (as mentioned above, *marcasite* was a term generally synonymous with pyrites). Two locations cited by Paracelsus at which this vitriol solution occurs naturally are the old Czech mining town of Kutná Hora, and a fountain he designates as the Zifferbrunnen in Hungary. At both of these places, the vitriol solution generated from marcasites was observed to transmute iron into high-quality copper. In a brief discussion of vitriol in the *Economy of Minerals*, Paracelsus⁴⁸ again mentions “a fountain in Hungary, or rather a torrent, which derives its origin from Vitriol, nay, its whole substance is Vitriol, and any iron thrown into it is at once consumed and turned to rust, while this rust is immediately reduced to the best and most permanent copper, by means of fire and bellows”.

The preceding discussion has shown that although vitriol was a substance of considerable interest within the spheres of the mineral industry and alchemy, understanding its composition and chemical effects were important problems in the development of mineral chemistry. It was through the industrial exploitation of vitriol and through further investigations of its mysterious properties that its composition and generation became increasingly understood. Unfortunately, space does not permit a discussion of the significance of these explorations in the further development of mineral chemistry, although it should be mentioned that it was mainly through the work of Angelus Sala^{49,50} (?1576–1637), Nicolas Guibert⁵¹ (?1547–?1620), and Robert Boyle⁵² (1627–1691) that the compositional dissection of vitriol was taken beyond the level reached by Ercker, and the supposed transmutation of iron to copper became understood as a reaction between copper ions in the vitriol solution and the iron of the solid surface. Belief in this reaction as a metallic transmutation nonetheless survived even in the eighteenth century⁵³.

6. Vitriol and the Mineral Acids

6.1. Nitric acid

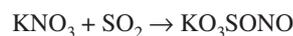
The discovery of nitric and sulfuric acid is often linked with the alchemist known as Geber. This name is the latinized form of Jabir, an Arabic alchemist mentioned above. The appearance of Latin works under the name Geber in the late Middle Ages led to considerable confusion, as this author was identified with the Arabian Jabir for quite a long time. Although modern historiography has shown that the Latin Geber, as he was later called, or Pseudo-Geber in modern literature, was not the Arabian Jabir, the identity of the Latin author yet remained unknown. Newman's recent investigations⁵⁴ on this subject have resulted in two important conclusions. First, the *Summa perfectionis magisterii* of the Latin Geber was probably written around the end of the thirteenth century by the otherwise unknown Franciscan monk, Paulus of Taranto. Second, other works that appeared in print under Geber's name in 1541 were not written by this same author, which is why we speak of a Pseudo-Geberian corpus. Among the other texts that comprise this corpus is the *De inventione veritatis*, in which the earliest known recipe for the preparation of nitric acid is found. As dating the works of the Pseudo-Geber corpus is problematic, dating the discovery of nitric acid is likewise uncertain. It is estimated that this discovery took place after 1300, some two hundred years before it appeared in print.

This recipe, titled *About dissolving liquids and softening oils* reads as follows⁵⁵: "Take a pound of Cyprus vitriol [Fe, CuSO₄], a pound and a half of saltpeter, and a quarter of a pound of alum. Submit the whole to distillation, in order to withdraw a liquor which has a high solvent action. The dissolving power of the acid is greatly augmented if it be mixed with some sal ammoniac, for then it will dissolve gold, silver, and sulfur." The addition of sal ammoniac to the distillate leads to aqua regia (a mixture of HNO₃ + HCl, in proportion 1:3).

Nitric acid had become a commonly used substance by the mid-sixteenth century. Biringuccio⁵⁶ describes its purification by adding a small amount of silver, which has the effect of removing the traces of HCl that originate from the KCl sometimes present as an impurity in saltpeter. And although the term *aqua fortis* was already in regular use, Agricola⁵⁷ interestingly chose to refer to it as *aqua valens* in his *De re metallica*. This latter work contains several recipes for this acid, not all of which actually lead to nitric acid (some resulted in a mixture of all three strong mineral acids). One of his recipes that does yield nitric acid prescribes the following ingredients: "four librae of vitriol, two and a half librae of saltpeter, half a libra of alum, and one and a half librae of spring water."

Agricola also describes "certain compositions which possess singular power", one of which reads as follows: "The second composition is made from one libra of each of the following, artificial orpiment [As₂S₃], vitriol, lime [CaO], alum, ash which the dyers of wool use [K₂CO₃ ?], one quarter of a libra of verdigris [impure basic copper (II) acetate], and one and a half unciae of stibium [Sb₂S₃]." This example is revealing of the attempts that were made in Agricola's time to prepare even more potent solvents.

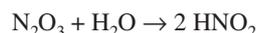
According to Soukup and Mayer⁵⁸, Agricola's correct recipe for nitric acid can be expressed by the following set of consecutive reactions:



If the cooling is insufficient, N₂O₃ decomposes spontaneously:



or otherwise reacts with water:



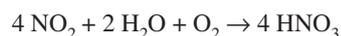
and the subsequent disproportionation of HNO₂ produces HNO₃:



Oxygen produced in the first reaction oxidizes NO:



and the dissolution of the resulting oxide in water yields further nitric acid:



Schröder⁵⁹, who repeated Agricola's experiment, arrived at following result: the dry distillation of 150 g KNO₃, 150 g CuSO₄, and 50 g KAl(SO₄)₂ at 800 °C yielded 70 g of approximately 51 % (wt) HNO₃ and 0.4 % HNO₂.

6.2. Sulfuric acid

The history of sulfuric acid is especially difficult to trace, as no reliable recipe for its preparation is known prior to the sixteenth century. Nevertheless, there are vague allusions to it in the work of Vincent from Beauvais (d. 1264) and in the *Compositum de compositis* ascribed to Albertus Magnus⁶⁰. In both cases, the description concerns the distillation of alum.

A passage from the second part of Pseudo-Geber's *Summa perfectionis*, as interpreted by Darmstaedter⁶¹, was long considered to be the earliest known recipe for sulfuric acid (the chapter in *Summa* is titled "About the medicine of the first order for the yellowing of silver"). In the recent translation by Newman this passage reads⁶²: "Luna is also yellowed similarly with a solution of mars. The method of that yellowing which is perfected by vitriol or copperas is as follows. A specific quantity of either of them should be taken, and the part of that which allows itself to be sublimed should be sublimed until it is sublimed with a total expression of fire. After this, what was sublimed should be sublimed again with a suitable fire, so that it be gradually fixed, until the greater part of it is fixed. Then let it be calcined carefully with intension of the fire, so that a greater fire can be administered to it for its perfection. Then it should be dissolved into a red water to which there is no equal." In a footnote concerning this passage Newman states that "This is not a recipe for sulfuric acid ... Copper sulfate decomposes at 700 °C to cupric oxide; further heating to

1050 °C will produce cuprous oxide, a red compound often used as a pigment. The *Summa's* advice that this be sublimed may be a thought-experiment. Alternatively, if the starting product were iron sulfate, iron oxide would be produced by simple decomposition of the sulfate to the oxide, again brought by heating."

In the interest of exploring this problem, it will be instructive to compare this recipe with others. Andreas Libavius⁶³ (c. 1556–1616) writes at length about spirit of vitriol (*Vitriolgeist*) in his book *Alchemia* (1597), in which he distinguishes a white kind and a red kind. In his opinion, the latter spirit is pure "oil of colcothar", or a red liquor remaining after the separation of a white spirit. As colcothar was usually Fe₂O₃ precipitated during the reaction, it seems probable that this is a description of the preparation of an acid contaminated by a red oxide. Red colors likewise appear in similar recipes in his text.

Another comparable recipe appears in Basil Valentine's treatise *Vom grossen Stein der alten Weisen* dated around 1602. (The author of books published under this name was probably Johann Thölde (? – before 1624), the owner of a salt-works in Thuringia⁶⁴). This recipe is cited from Schwarz and Kauffman⁶⁵: "If you get such a deeply graduated and well prepared mineral, called Vitriol [FeSO₄], ... , put it into a well coated retort, drive it gently at first, then increase the fire, there comes in the form of a white spirit of vitriol [SO₃] in the manner of a horrid fume, or wind, and cometh into the receiver as long as it hath any material in it ... if you separate and free this expelled spirit well and purely per modum distillationis, from its earthy humidity [H₂O], then in the bottom of the glass you will find the treasure, and fundamentals of all the Philosophers, and yet known to few, which is a red Oil, as ponderous in weight, as ever any Lead, or Gold may be, as thick as blood, of a burnt fiery quality."

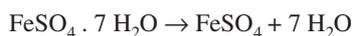
It is interesting to note the remark concerning the red oil in Valentine's description. Its apparent viscosity might lead us to believe that it could have been a suspension of red ferric oxide. Similarly, Paracelsus described the distillation of colcothar that had already been used for the production of *spiritus vitrioli*, and the blood-red, oily liquid (*oleum vitrioli*) evolved therefrom.

In all three of the above-mentioned cases, an acid of a red color was prepared. Valentine's mention of a sediment associated with this liquid could support the suggestion that ferric oxide was present. Yet this oxide would have also contaminated the acid itself, giving it a red color.

The chemistry involved in this method of preparing sulfuric acid is described here according to Soukup and Mayer⁶⁶, in which the old terminology is used. The individual substances involved in this process are as follows:

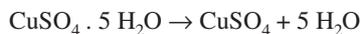
(a) *Ros vitrioli* (Dew of vitriol): the humidity of the salt used in this experiment.

(b) *Phlegma vitrioli*: structural water of the sulfate.



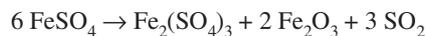
Six moles of water are freed at 115 °C, and the remaining one at a temperature above 280 °C.

The same process, this time using copper vitriol



releases two moles of water at 30 °C, two further moles at 110 °C, and the rest at 250 °C.

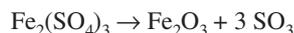
(c) *Spiritus vitrioli*: the SO₂ that reacts with water in a receiver, yielding H₂SO₃:



The slow oxidation in air leads to sulfuric acid:

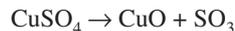


(d) At temperatures above 480 °C, ferric sulfate decomposes in a process known as *Vitriolbrennen*,



leaving behind the *caput mortuum*, which in this case is colcothar (Fe₂O₃).

When copper vitriol is used, it decomposes at very high temperatures,



and in both cases SO₃ reacts with water in receiver, producing sulfuric acid.

Schröder⁶⁷, who analyzed the production of sulfuric acid in detail, distinguished between the *spiritus vitrioli* (or *liquor vitrioli acidus primus*) prepared in step (c) above, and the *oleum vitrioli* (*liquor vitrioli acidus secundus*) from step (d). According to this author, the latter substance is a thick, red-brown, strongly smelling oily liquid comprised of approximately 75 % H₂SO₄. This seems to be the substance that Paracelsus referred to as *oleum vitrioli rubrum*, and it is Schröder's opinion that this oil of vitriol was known as far back as the fourteenth century.

Schröder performed the dry distillation of 200 g of *vitriolum Goslariense* (FeSO₄ · 7 H₂O), gradually elevating the temperature to 1000 °C over a three hour period. As a result, he obtained approximately 8–10 g of "strongly acidic liquid, smelling like SO₂". This liquid turned out to contain 2.9 % SO₂, and on standing it oxidized gradually to 2.75 % H₂SO₄.

With consideration of these facts, we now return to the problem of whether or not the above-mentioned process from the *Summa perfectionis* of Pseudo-Geber resulted in the production of sulfuric acid. It has been shown that a red liquid obtained from vitriol is mentioned both in old and modern works. In these descriptions, both the process used and the color obtained correspond with those described in the *Summa perfectionis*. Although the language of this text is not entirely clear, it nonetheless seems possible that this process did lead to the preparation of sulfuric acid. The red color in question could have resulted from the presence of iron (III) compounds that developed during the process and contaminated the product. However, as alchemists could not use chemicals of analytical grade purity, the influence of unintentional impurities should also be considered. As Mellor⁶⁸ has pointed out, selenium, when present as an impurity in sulfuric acid, imparts a red color to the product. As selenium can substitute for sulfur in the mineral pyrite, it could also be present in natural or

artificially prepared sulfates generated from such selenium-bearing pyrite, and thus could have found its way into the acids prepared using these sulfates. Even though very little is known about the provenance of the vitriol used by alchemists, the possibility of the presence of selenium as an impurity should also be considered when attempting to ascertain whether or not the process described by Pseudo-Geber was an early preparation of sulfuric acid.

7. Conclusions

The goal of this paper is to outline the historical importance of vitriol and to go some way toward illustrating its role in the history of chemistry and mineralogy. These salts, among which alum was sometimes included, were very important substances in the dual spheres of theory and practice. The discovery of strong mineral acids, particularly of HNO_3 , and *aqua regia*, had a strong effect on existing ideas about minerals, metals, and their chemical composition. For example, the discovery of *aqua regia* derived from vitriol and sal ammoniac robbed gold of its status as an indestructible metal, for now it could be dissolved, or “killed” as some alchemists would say. Second, nitric acid was a potent solvent that led to improved methods for parting gold from silver and to the preparation of numerous new salts. Indeed, green vitriol was often referred to as “the green lion” in alchemical terminology, and the corrosive elixirs extracted therefrom caused it to be the subject of much secrecy, allegory, and interesting imagery in fourteenth century alchemical texts. Vitriol’s crucial role in the preparation of nitric and sulfuric acids deserves deeper analysis, particularly concerning the recipe in the *Summa perfectionis* which might actually be a preparation for sulfuric acid.

Meanwhile, familiarity with vitriol resulting from industrial and laboratory practices led to an impressive chemical and compositional exploration of this substance, beginning at least as far back as the first century AD. The spectacular reaction in which solid iron reacts with a vitriol solution, which is understood today as the reduction of cupric ions by iron from a solution containing copper sulfate, was known to the Chinese, Indians, and Arabs. This reaction drew considerable attention in sixteenth century Europe as a process from which both craftsmen and alchemists profited. The former used this reaction in the hydrometallurgy of copper and for enriching their manufactured vitriol in iron, while alchemists cited it as a repeatable and apparently undeniable example of the transmutation of metals. The understanding of vitriol’s composition and chemical effects obtained by the pre-modern workers in the chemical fields constitutes an important chapter in the history of mineral chemistry; for it reveals an interesting interplay between observation (concerning the natural formation of vitriol and its related substances), empirical knowledge (concerning vitriol’s composition, chemical uses, and the development of extraction processes), and theory (concerning vitriol’s mineral identity and its remarkable chemical effects).

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V. Karpenko^a and J. A. Norris^b (^a*Department of Physical and Macromolecular Chemistry and* ^b*Department of Philosophy and History of Natural Sciences, Faculty of Science, Charles University, Prague*): **Vitriol in the History of Chemistry**

Vitriols, known today as sulfates of divalent metals, played an important role in the development of modern chemical and metallurgical practice, and engaged the speculation of alchemists and mineralogists. The natural occurrence of vitriols and its earliest recognition as a distinct group of related minerals is discussed. The unique position of vitriols was codified in al-Rāzī's (854-925/935 AD) classification of mineral substances. On the contrary, although considered to be a noteworthy mineral substance in Indian alchemy, vitriol is not recognized as a distinct mineral, the blue and green varieties being classed separately according to other criteria. The deposition of Cu from a vitriol solution on an iron surface was known in some ancient cultures, and it became even used on an industrial scale in the 11th and 12th centuries AD. These reactions, which were sometimes construed as an apparent transmutation of metals, were further investigated and were significant for European alchemy and mineralogy. The practice of preparation of nitric acid from vitriol, which seems to have begun around 1300, soon increased the number of known chemical reactions. Aqua regia was a further innovation that made possible the dissolution of gold, which had previously been considered as the indestructible metal. Particular attention is paid to the preparation of sulfuric acid from vitriol. Several descriptions of a red solution obtained during this process lead to the consideration of a process from the *Summa Perfectionis* of Pseudo-Geber that could have resulted in sulfuric acid, and in which contamination with Se could have led to the red product.