

# An indicator of its time: two millennia of the iron–gall-nut test†

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The reaction between iron salts and the extract or tincture of gall-nuts is a unique example of an analytical reagent, for its use has been known and recorded for around 2000 years. In its time it became an important but controversial method for detecting iron in solution, before being supplanted by more effective reagents. The purpose of this paper is to review the history of the reagent and to show that not only is it an indicator of iron, but also an indicator of the chemical understanding of the times: ‘a litmus test’ of chemical knowledge.

## Introduction

A key principle of analytical chemistry is the use of reagents to react chemically with a target analyte and through physically observable changes generate quantitative or qualitative information. One of the best known of these reagents is litmus, a dye derived from natural sources that turns from blue to red in the presence of acids. The term ‘litmus test’ has entered the language as a colloquial saying. On the other hand, the reaction between iron salts and the extract or tincture of gall-nuts is much less well known and yet it is a unique example of an analytical reagent, for its use has been known and recorded for nearly two millennia. It became an important but controversial method for detecting iron in solution. Indeed even its first literary mention is not without problem. The purpose of this paper is to review the history of the reagent and to show that it is not merely an indicator of iron, but in many ways it is also an indicator of the chemical understanding of the times: a ‘litmus test’ of contemporary chemical knowledge.

## The reagent

Plant galls are excrescences that occur on virtually any part of a plant. The galls are caused by insectal activity, particularly by mites and wasps, although fungal galls are known. Galls vary in size from the microscopic to a few centimetres in diameter and their shape and bitter flavour earned them the name ‘gall-nuts’. Generally, galls from oak trees were used, particularly in the Middle Ages, to form iron based inks. Galls from the city of Aleppo in Syria were particularly sought after. Most authors (with the exception of Boyle; see below) give little detail on the source or preparation of the gall-nut reagent. The earliest accounts<sup>1</sup> seem to indicate that liquid from the gall-nut was expressed on to a plant substrate such as a papyrus leaf. Later references imply the preparation of a *tincture* (literally, a solution that changes the colour of something) by pulverisation or maceration of the gall-nuts followed by infusion with water.

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## Early discussions of the iron–gall-nut reaction

Pliny’s (AD 23–79), description of the reaction, ‘Deprehenditur et papyro galla prius macerato, nigrescit enim statim aerugine inlita’,<sup>1</sup> follows on from and is part of a discussion of the detection of the adulteration of verdigris. Verdigris was an important medicinal preparation. It was used as a salve: a function, no doubt, arising from the biocidal properties of copper salts. Unscrupulous suppliers were known to mix the verdigris with the much less useful and much less expensive ferrous sulfate or shoemaker’s black (atramentum sutorium). Pliny’s comment leaves a lot to be desired in terms of clarity. This section of the text has been variously translated as:

‘It [the adulteration of verdigris with iron sulphate] is also detected by means of papyrus previously steeped in an infusion of plantgall, as this when smeared with genuine verdigris at once turns black.’;<sup>2</sup>

‘Verdigris can be detected by papyrus that has been steeped in an infusion of galls. When smeared with genuine verdigris, the papyrus immediately turns black.’;<sup>3</sup>

‘You may discover likewise the fraud abovesaid with paper [or reed of papyrus], tempered beforehand and soaked in gall-nuts; for besmeared wherewith the verdegrace that is falsified, it will quickly become black.’;<sup>4</sup>

‘Another way to detect the adulteration is by papyrus previously steeped in extract of gallnuts. This blackens immediately if it is smeared with verdigris (containing shoemakers’ black).’;<sup>5</sup>

The parentheses at the end of the last quote are the translator’s own and are most telling. We know (and presumably the translators all knew) that verdigris (basic copper acetate) does not react with plant gall in the way implied by Pliny’s text. Some translators<sup>2,3</sup> have taken a literal view, yielding a text that does not make sense chemically. Others<sup>4,5</sup> have superimposed their view of what Pliny meant, in the light of their own chemical knowledge. Whether Pliny knew exactly what was happening is a moot point. His prior description of another method of testing the adulteration is also inaccurate and has been shown<sup>6</sup> to be due either to Pliny’s mistake in copying from a manuscript of Dioscorides or Pliny’s accurate copying of an incorrect manuscript. Whatever the cause, Pliny’s insufficient knowledge of chemistry did not enable him to recognise the error.

Elsewhere, Pliny describes a similar test employing the skins of pomegranates for the detection of adulteration of (presumably) potash alum.<sup>7</sup> 'An sit adulteratum deprehenditur suco Punici mali; sincerum enim mixtura ea non nigrescit'. There is some debate as to the final phrase of this sentence, other sources give '...mixtura ea nigrescit'; '...mixturam fugit', '...mixtura inficitur'. Ammonium ferric alum (or possibly potash alum, naturally contaminated with iron compounds such as ochre) could be distinguished by its reaction with oak-galls. 'Alterum genus est pallidi et scabri et quod inficiatur galla,...'. Although Pliny's descriptions contain inaccuracies, his intentions are clear. The reaction is presented as a qualitative test, not just an interesting observation. The extract of plant galls is being deliberately used as a reagent to test for a particular chemical species. This reflects a relatively sophisticated attitude towards a chemical phenomenon, which sees beyond the wonder to an analytical utility: an early example of quality control.

In *The Early History of the First Chemical Reagent*, Nierenstein<sup>8</sup> points out the lack of interest shown in the iron-gall-nut reaction in the period between Pliny and the next known comments which occur in the botanical writings of Albertus Magnus (AD 1193–1280).<sup>9</sup> In the context of the times this delay is not remarkable. From the decline of the Roman empire to the middle of the twelfth century,

'...the human mind has, to satisfy its curiosity [for science and philosophy], only the meagre fragments of the Roman schools heaped together in the compilations of Martianus Capella, Bede, Isidore, and certain technical treatises whose wide circulation saved them from oblivion.'<sup>10</sup>

Pliny's *Natural History* was one of these works. Bede is known to have had access to at least a half of the *Natural History* and drew on it substantially for his own *De Rerum Natura*. Healy comments,<sup>11</sup>

'Manuscripts of the *Natural History* multiplied and in the ninth century were to be found at Corbie, St Denis, Lorches, Reichenau and Monte Cassino. Some of its books became an established part of monastic culture, being used for astronomy and medicine...'

However, there is a world of difference between a monastic culture interested in astronomy and medicine and a general intellectual environment in which a chemical test could be seen as significant. The transforming impetus came in the eleventh and twelfth centuries, arising from Arab influence in the Iberian peninsula. Arab and Greek texts translated into Latin disseminated over 1000 years of scientific knowledge, including chemistry, to the European nations. The Arabs had acquired much of this knowledge from contacts with Greek, Syrian, Persian and Egyptian sources. From the middle of the twelfth century onwards and within this culture of classical texts and scientific interest, Pliny was used as source not merely for astronomy and medicine but also for botany, meteorology and pharmacology.

Albertus Magnus was born into and schooled in this intellectual climate: familiar with and sometimes critical of the works of Pliny, Aristotle, Avicenna and many Latin translations of Arabic alchemic works, he wrote copiously on scientific subjects and the natural world.<sup>12</sup> His alchemic interests were tinged with a healthy scepticism towards the scurrilous practitioners of these occult arts, famously describing alchemy as '...a beggarly union of genius and fire...'.<sup>12</sup> Under these circumstances of schooling and familiarity with scientific texts, it might almost be expected of him that he should comment on the iron-gall-nut reaction. From a chemical viewpoint it is disappointing that he reports the reaction as botanical phenomenon rather than as an analytical test. There is a sting in the tail to all this. The chemistry unleashed on the Europe in the eleventh and twelfth centuries was primarily alchemic in nature. Partington<sup>13</sup> comments,

'After the adverse criticism of Albertus Magnus, the schoolmen lost interest in the subject, which was then cultivated mainly by "artists" or "adepts", who wandered over Europe in search of wealthy patrons. Large numbers of books on alchemy written in the period 1250 to 1500 are mostly unintelligible.'

This may have been a climate for great interest in chemical phenomena; it was certainly a climate for chemical trickery and fraud; but it was not a climate for careful, objective and systematic investigation of these same phenomena. It is not surprising that the iron-gall-nut test once again lapsed into obscurity.

### The renaissance of the iron-gall-nut reaction as a chemical test

The rediscovery of the analytical use of the iron-gall-nut reaction owes much to the next mention of the reaction by Paracelsus<sup>14</sup> in 1520, 'Also geht das zu ihr sehend dass Galles und Victriol schwarz gibt...', although he himself failed to give details of a distinct analytical procedure.<sup>15</sup> Once again there is a substantial gap between this text and the previous one; the reasons for this have been mentioned in the previous paragraph. Chemistry in the Middle Ages was predominately descriptive. Many reactions were known or discovered but little emphasis appears to have been placed on chemical analysis. However, in the fifteenth and sixteenth centuries, important new trends in chemistry emerged. Three in particular are noteworthy: (i) physicians began to apply chemical methods to the preparation of medicines and to the understanding of the human body (this approach is often known as iatrochemistry); (ii) Italian physicians became increasingly interested in the composition of spa waters; (iii) the technological and chemical aspects of mining and mineralogy became formalised in major texts. All three of these trends had significant implications for the iron-gall-nut test.

Paracelsus was a prime mover in the field of iatrochemistry. Both his personality and his philosophical outlook were instrumental in the changes he wrought in Renaissance chemistry. Sherlock<sup>16</sup> compares Paracelsus with Luther, a fellow German and contemporary:

'Both possessed a dynamic violence of character which manifested itself in an explosive and often coarse use of the vernacular, in a rich imagery, in a readiness to attack existing views and institutions, and, at times, in the forcible expression of their views by external dramatic action, whether by burning the works of Galen and Avicenna in the market place, or nailing the list of theses against indulgences to the church door at Wittenburg.'

Philosophically, Paracelsus's views encompassed a notion of unity. He saw the actions of nature (life, death, sickness and health) as a type of 'world-alchemy'; man became the alchemist of nature when preparing remedies; within man an inner 'archeus' or alchemist was at work. Although his contributions to medicine were more significant than to chemistry, his writings were known to the medical world: both Libavius<sup>17</sup> and Thurneisser<sup>18</sup> acknowledged Paracelsus; from a chemical point of view, the importance Paracelsus gave to the role of alchemy in medicine was central.

The sixteenth century interest in the composition of spa water shown by iatrochemists can be traced back to the work of Italian physicians and others in the Middle Ages (see Debus's review,<sup>19</sup> 'Solution analysis prior to Robert Boyle'). A succession of texts appeared in the thirteenth, fourteenth and fifteenth centuries describing sensory methods of examination, often made on the distillates or evaporates of the water. An increasing emphasis was placed on colour in analysis. Nor was this approach confined to iatrochemistry, Agricola, in his *De Re*

*Metallica*,<sup>20</sup> emphasised taste and colour when testing waters. He also described the identification of ores by the colour of the fumes produced when placed on a hot shovel.<sup>21</sup> Similarly, Biringuccio in 1540<sup>22</sup> commented on colour and taste, thus:

'There are some who praise highly as a good sign certain residues that water make where they are still and after having stood for several days, frequently warmed by the rays of the sun, they show in some part of their residues various tinctures of metallic substances. There are others who usually take this water and cause it to evaporate or dry up entirely by boiling it in a vessel of earthenware, glass or some other material, and they test the gross earthy substances that remain at the bottom by tasting, by the ordinary fire assay, or in some other way that pleases them.'

Consequently, by the middle of the sixteenth century, there was a scientific-cultural environment in which colour was seen as an important part of water analysis: the iron-gall-nut test had been described by Paracelsus a progenitor of the iatrochemists; the iatrochemists themselves were involved in the analysis of spa waters. The conditions were more than favourable for the reintroduction of the iron-gall-nut test as an analytical procedure.

### The iron-gall-nut test: growth, controversy and maturity

The late sixteenth century was something of a watershed for the iron-gall-nut test. Texts in which the test was described appeared with some frequency. Debus<sup>19</sup> mentions nine references from 1550 to 1600: by modern standards this publication rate may seem a trickle, but when compared with the previous 1500 years it was a torrent! The key works in this period are *De Medicatis Aquis atque de Fossilibus* by Fallopius<sup>23</sup> and *De Judico Aquarum Mineralium et Horum quae cum Illis Inveniuntur* by Libavius.<sup>17</sup> Fallopius's work is significant not merely because of the details of the tests that it contained but also because it was extensively abstracted and translated, thus furnishing French, German, English and Italian chemists with vernacular texts. Libavius presents refined methods of water analysis, based largely on Thurneisser's work,<sup>18</sup> describing the iron-oak-gall test and mentioning that it reacts in the presence of copper as well as iron sulfate. In spite of the ready acceptance of the test, it was not altogether clear to these sixteenth century analysts just what it was they were measuring. The state of chemical knowledge in the late sixteenth century let alone at the time of Pliny was rudimentary. Hindsight enables us to untangle the meaning of Pliny's words (see earlier), but in the sixteenth century it was not clear whether the iron-gall-nut test was detecting vitriol (ferrous sulfate), alum (possibly ammonium ferric alum) or copper vitriol (cupric sulfate). The late sixteenth century use and even abuse of the iron-gall-nut test was entirely

commensurate with the contemporary knowledge of chemistry.

There was continued application of the iron-gall-nut test in the seventeenth century and continued confusion and even controversy.<sup>19</sup> The resolution of this confusion and controversy in the latter half of the seventeenth century owes much to the research undertaken by Tachenius<sup>24</sup> and Boyle.<sup>25,26</sup> These two are an apposite pairing. Tachenius, still strongly imbued with the alchemic philosophy could be seen as a 'typical' member of the iatrochemical school; one might almost say that in his day he was a chemist of 'the old school'. His contemporary Boyle, on the other hand, can be considered 'the founder of modern chemistry'. Partington<sup>27</sup> gives three reasons for this:

'(1) he realised that chemistry is worthy of study for its own sake and not merely as an aid to medicine or as alchemy-although he believed in the possibility of the latter; (2) he introduced a rigorous experimental method into chemistry; and (3) he gave a clear definition of an element and showed by experiment that the four elements of Aristotle and the three principles of the alchemists (mercury, sulphur and salt) did not deserve to be called elements or principles at all, since none of them could be extracted from bodies, e.g. metals.'

Tachenius, who first introduced a definition of a salt as 'composed of two parts, of acid and alkali', described the reaction between vitriol and the juice of galls in a similar manner:<sup>28</sup>

'...but the juice of unripe Galls, falls in with vitriol and makes a coalition therewith into black, destroying the acidity thereof; and therefore this juice is to be reckoned amongst alcalyes; after this manner, ink, and all black tinctures are made:'.

He tested a wide range of salts with the juice of galls, in effect producing a simple qualitative scheme (Table 1) and concluding,<sup>29</sup> 'Wherefore of the seven Metals being dissolved by acids, Iron and Silver, with Galls, do tinge of a black colour.'. Tachenius<sup>30</sup> also described the same sort of 'occult alkalye' in other plant materials such as houseleeks, sage and rinds of pomegranate.

Boyle mentions the iron-gall-nut reaction in his *Experiments and Considerations Touching Colours*, in the section on 'Experiments in consort touching whiteness and blackness'.<sup>25</sup> This is not primarily a discussion of an analytical chemical procedure, but it does elucidate a feature of the reaction that had been known for some time, viz, that the colour could be dispersed by adding oil of vitriol (sulfuric acid) to the reaction and that the colour could be restored using sal tartari (potassium carbonate). This sequence of reactions had been used as a method of producing secret writing. Boyle notes:

'...and in making the first ink mentioned in this experiment, I found that I could by filtration separate pretty store of a very black pulverisable substance that remained in the

**Table 1** Reactions between metal ions and gall-nut extract, according to Tachenius (ref. 29)

Compound name	Modern equivalent	Reaction with gall-nut juice
Cyprian vitriol	Copper sulfate	No reaction
White vitriol	Zinc sulfate	Slow: black colour
Verdigrease	Basic copper acetate	Red colour
Romane vitriol	Ferrous sulfate	Black colour
Crocus martis dissolved with spirit of salts and digested with spirit of wine	Ferric oxide dissolved with hydrochloric acid and digested in ethanol solution	Black colour: on dilution becomes amethyst coloured
Gold corroded by <i>aqua regia</i>	Gold tetrachloride complex [AuCl <sub>4</sub> ] <sup>-</sup>	Yellow amber colour
Silver corroded by <i>aqua fortis</i>	Silver dissolved in nitric acid	Black colour
Mercury dissolved by acid things	Mercuric salts	Slow: yellow colour
Lead reduced into salt or vitriol	Lead salts	White precipitate
Tin reduced into salt or vitriol	Tin salts	White precipitate



filtre, and when the ink was made cleer again by the oyl of vitriol, the affusion of dissolved Sal Tartari seem'd but to praecipitate, and thereby to unite and render conspicuous the particles of the black mixture that had been dispersed into very minute and singly invisible particles by the incisive and resolving power of the highly corrosive oyl of vitriol.'

In other words, Boyle showed that the black colour was due to a precipitate that formed in the reaction between the constituents of the gall-nut juice and the ferrous salts and that this precipitate was dissolved in acid solutions and formed in alkali conditions.

In *Short Memoirs for the Natural Experimental History of Mineral Water*,<sup>26</sup> Boyle deals in more detail with the use of the iron–gall-nut test: his observations on the results and conduct of the test and preparation of the reagent established the true limits of the qualitative and quantitative value of the analysis:

'Though the way of trying mineral waters by the change of colours that galls produce in them, be useful and recommended by being easy, cheap, and expeditious, yet I do not take it to be either of that extent, or of that certainty, that is vulgarly presumed to be of: for its main, if not only considerable use is, to discover by striking, or not affording, a black or blackish, or at least a purple or a purplish colour with a mineral water, to manifest the liquor to be, or not to be, either of a vitriolate or a ferruginous nature. But there are divers metallic ores, and other mineral bodies, which, not participating of iron, will not, by this way, be discoverable, and yet may strongly impregnate the water proposed.... I long since found, upon trial purposely made, that another body of metalline nature, and that did not partake of iron, would with infusion of galls, afford a very dark colour, that might easily, among ordinary beholders, pass for the colour of martial waters.... It is an inconvenience, that not only Galls, but the other drugs hereafter to be mentioned, impart a high tincture of their own to the common water they are infused in; and therefore it were to be wished, and is fit to be endeavoured, that we had some drug, that without imparting a colour to the common water it impregnates, would afford an infusion fit to strike a blackish or a purple colour with martial (iron-containing) waters'.

In these three excerpts, Boyle sounds every inch the analytical chemist. He is concerned that the method is in one respect too specific (other important constituents of the sample water are missed) and in another respect it is too general (interfering species may be misinterpreted as iron). His plea for a reagent that is colourless with an iron-free sample but which yields a strong colour with iron-containing water will strike a chord in the hearts of every analytical chemist pursuing the holy grail of an improved signal-to-noise ratio!

Boyle<sup>26</sup> described methods of obtaining the reagent by pulverising the gall-nut and using the powder directly or by making a tincture from the powder, rather than by making the tincture from the whole nut (a time consuming process). He pointed out that the reagent lost its efficacy over time,

'Upon which account I chuse to make a tincture of galls not long before I mind to use it; and I employ dry galls, to make powder that is not stale.'

Boyle was also concerned with the quantity of reagent added to the water to be tested:

'It is no safe way, and may be very erroneous, that is usually taken in mixing galls, or their infusion with the water to be explored so carelessly, as is wont to be done. For those that are curious to make good ink will easily believe, that much of the deepness of the colour depends upon the proportion of galls to the other ingredient; and accordingly, that by putting a much greater, or a much

lesser, quantity of galls into such a quantity of the mineral water, the resulting colour may be more or less intense.'

He goes on to recommend using fixed proportions of powder to water and to steep for a fixed number of hours when making an infusion or, if the powder is to be used directly in the test, to add a fixed mass of the powder.

Boyle was also concerned with the conduct of the test suggesting to the analyst:

'It seems very fit, if not necessary that he look upon the change of colours, both while it is producing, and when it is produced, in a good light, and with a heedful eye: for by this means he may discover several shades or varieties of the more principal colours and some other circumstances, that he could not else take notice of; and which may yet afford good hints (in reference to other minerals, as well as martial ones) to a sagacious observer....'

It would be fair to say that by the end of the seventeenth century the iron–gall-nut test had become well established as the method of choice to determine the presence, and to some extent the amount, of iron in mineral waters. From a contemporary viewpoint the nature of the reaction had been established: the method of use had become more or less standardised; the target analyte (dissolved iron salts) was known; the colours produced by other salts (interferents) had been established. Consequently, the eighteenth century chemical literature contains numerous references<sup>8</sup> to the use of the test. To the early eighteenth century chemist, the only poorly understood part of the test was the nature of the material in the gall-nut that caused the formation of the black product with iron salts. The solution to this problem emerged during the latter half of the eighteenth century, mainly because of the interest shown in the reaction by chemists whose principal concerns were not analytical. The product of the reaction between iron and gall-nuts was of interest to ink and dye makers, whilst the astringent principle of gall nuts and other plant species was significant to the tanning industry. In his two volume work entitled *Commercium Philosophico-Technicum, or the Philosophical Commerce of the Arts, Designed as an Attempt to Improve the Arts, Trade and Manufacture*, Lewis<sup>31</sup> discusses the use of nut-galls to produce ink and of the black colour produced with iron salts; he says

'The power by which they produce this blackness and their astringency, or that by which they contract an animal fibre, and by which they contribute to the tanning of leather, seem to depend upon one and the same principle and to be proportional to one another. Of the other properties of this astringent and colouring matter, little more is known, than that it is dissolved and extracted both by water and spirit of wine, and that it does not exhale in the evaporation of the liquors by heat.'

This was not the first mention of a link between astringency and the iron–gall-nut reaction. Boyle<sup>26</sup> also had made the connection between the astringency of plants and their reaction with iron salts. He pointed out that other astringent materials (such as the juice of pomegranates which he knew to be a good styptic) reacted with dissolved iron to give a black coloration, although he does not appear to link the property of astringency with a substance or component of the plant.

The idea that a principle (or component) of the vegetable matter was responsible for the formation of the black colour with iron salts was an important step in the understanding of the iron–gall-nut test. It was also an idea consonant with the times. Although the understanding of organic chemistry prior to the early nineteenth century (with a few notable exceptions<sup>32</sup>) was poorly developed, a wide variety of organic substances or principles were known, even if their chemical compositions were not. Lewis's 'astringent and colouring' matter mentioned

earlier consisted of what we would now call the hydrolysable polyesters of gallic acid or gallotannates.

In 1778, Guyton de Morveau showed that an infusion of galls was feebly acidic.<sup>33</sup> Eight years later, Scheele<sup>34</sup> made the following observation:

'I became aware, by chance, some time ago that a peculiar sediment had deposited in an infusion of gall-nuts prepared with cold water. This sediment was grey and had a crystalline appearance when it was observed in sunshine. It had a sour but not an astringent taste and was quickly dissolved by hot water, while it precipitated vitriol of iron black.'

Scheele went on to obtain this precipitate in a more systematic way and to investigate its properties. He allowed a fresh tincture, which he said had the colour of French wine, to age over a period of 3–4 months, and during this time a mould formed on the surface and a series of sediments were formed. Scheele, as was the practice of the time, also followed the progress of the experiment by taste, noting that the astringency of the infusion decreased, to be replaced by a sour flavour. He was able to crystallise a grey salt that was moderately soluble in water but which dissolved easily in alcohol. The salt solution reacted with a range of metal ion solutions giving colours typical of the gall-nut reaction. Inadvertently Scheele had brought about the hydrolysis of the gallotannates in the gall nuts (a process which is expedited by certain types of mould) and had released gallic acid. Subsequently, Lavoisier<sup>35</sup> included gallic acid in his *Traité Élémentaire de Chimie*:

'The Gallic acid, formerly called Principle of Astringency, is obtained from gall nuts, either by infusion or decoction with water, or by distillation with a very gentle heat. This acid has only been attended to within these last few years. The committee of the Dijon academy have followed it through all its combinations, and given the best account of it hitherto produced. Its acid properties are very weak, it reddens the tincture of turnsol, decomposes sulphurets, and unites to all the metals when they have been previously dissolved in some other acid. Iron, by this combination, is precipitated of a very deep blue or violet colour.'

At the end of the eighteenth century and in the early nineteenth century, the iron–gall-nut test was reasonably well understood. The seventeenth century knowledge of the test was augmented by the new organic information. The active ingredient of the gall-nut had been identified as gallic acid, which was known to be an organic acid composed of carbon, hydrogen and oxygen. The gallic acid was associated with a sour taste in solution but was shown by Berthollet<sup>36</sup> not to be associated with the true astringent principle (the 'astringent and colouring' matter of Lewis). Deyeux<sup>37</sup> suggested that a peculiar extractive principle in galls combined with gallic acid to give the astringent principle. It was clear that this astringent principle also reacted with iron salts and the salts of other metals and could be found in a range of other plant materials. The paragraphs on 'Iron gallates' in Henry and Hare's 1823 edition of *The Elements of Experimental Chemistry*<sup>38</sup> sum up the contemporary knowledge:

'When sulphate of iron is mixed with an infusion of galls, we obtain a black solution which is a new combination of oxide of iron with the gallic acid and tan... in order that the iron may quite with the gallic acid or tan, it must be combined with the sulphuric acid in the state of red oxide; for the less oxidised iron in the green salt does not form a black compound with these substances.'

Elsewhere the authors write,<sup>39</sup>

'Tincture of Galls is the test most generally employed for discovering iron; with all combinations of which it produces a black tinge more or less intense according to the

quantity of iron....By applying this test before and after evaporation or boiling we may know whether the iron be held in solution by carbonic acid or a fixed acid. For, 1. If it produce its effect before the application of heat, and not afterwards, carbonic acid is the solvent. 2. If after as well as before a mineral acid is the solvent. 3. If by the boiling, a yellowish powder be precipitated, and yet galls still continue to strike the water black, the iron, as often happens, is dissolved both by carbonic acid and by fixed acid.'

This was the zenith of the iron–gall-nut test: not only could the test distinguish iron (if used with care) but it could also be used to provide speciation information.

## Decline and fall

The supremacy of the iron–gall-nut test was not to last much longer: by the end of the nineteenth century its use had all but disappeared. Watts' *Dictionary of Chemistry*,<sup>40</sup> published in 1875, mentions three tests for iron, the gall-nut test, the formation of Prussian Blue from the reaction between iron(III) and potassium hexacyanoferrate(II) and the iron thiocyanate reaction. The last reaction was identified as the most sensitive of the three. Bernay's *Notes on Analytical Chemistry*<sup>41</sup> in an edition published 14 years later mentions only the potassium hexacyanoferrate(II) and the iron thiocyanate tests, a state of affairs unchanged in twentieth century books.<sup>42</sup> The decline of the iron–gall-nut test, in part, can be traced back to the comments of Robert Boyle mentioned earlier in which he decries the colour of the unreacted reagent. It will be recalled that Scheele described the tincture of galls as having the colour of wine. The ideal reagent is one which is colourless when unreacted, but which gives an intense colour when it combines with a target analyte. Tincture of galls is obviously not such a reagent. On the other hand, potassium hexacyanoferrate(II), to a certain extent, and potassium thiocyanate, in particular, approach the ideal more closely. There were other problems with gall-nut tinctures too, related to its plant origins: these are neatly summarised by Burns *et al.*:<sup>43</sup> '...extracts in solution would not keep, and the coloured part of a plant would usually be available during a short season'. In these respects, once again, both potassium hexacyanoferrate(II) and potassium thiocyanate were advantageous. Finally, there were problems concerning the specificity of the iron–gall-nut reaction: such concerns were diminished for the other two iron tests.

There is a certain irony (and a pun) that both potassium hexacyanoferrate(II) and potassium thiocyanate were known in the eighteenth century (although in the case of the potassium thiocyanate reaction that's only just true), an era which could be described as the heyday of the iron–gall-nut test. Prussian Blue appeared in Berlin in 1709: its manufacture was documented by Woodward<sup>44</sup> in 1724 and in the same journal Brown<sup>45</sup> established that it was the addition of iron to the potassium hexacyanoferrate(II) that yielded the blue colour. The reagent was not well received at first: early batches prepared by the method of Macquer<sup>46</sup> were often contaminated with iron(III) and so produced Prussian Blue when acidified even in the apparent absence of iron.<sup>43</sup> (Incidentally, Macquer makes brief mention of the iron–gall-nut reaction<sup>47</sup> but only to report the reaction, not to discuss any analytical possibilities.) Marggraf<sup>48,49</sup> in 1751 made extensive use of the reagent for the determination of iron in water and a variety of other samples; Bergman<sup>50</sup> gave details of both the potassium hexacyanoferrate(II) and the gall-nut method for the determination of iron. The red colour arising from the reaction between iron and potassium thiocyanate was observed by Winterl<sup>51</sup> towards the end of the eighteenth century, although Winterl was not aware that the colour was due to iron. Porret<sup>51</sup> established the role of

iron in the reaction early in the nineteenth century and by the middle of the century a semi-quantitative method using calibration standards had been developed.<sup>52</sup>

Not only the rise but also the fall of the iron–gall–nut test are indicative of the chemistry of the day. The use of seasonal, variable natural products as indicators for the sensitive detection of chemical species is of limited value to an industrialising society. The nineteenth century saw a move away from natural products to manufactured chemicals. The new reagents had advantages of availability and performance. Analytical chemists are not sentimental about chemical reagents. A reagent offering improved detection limits and better selectivity will soon supplant one that falls short in either of these key characteristics. So it was with the iron–gall–nut reaction.

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