The early history of the first chemical reagent

The black colour produced when gallnuts are treated with salts of iron was known quite early in the history of chemistry and references to dyes and inks from misy, chalcanthum and nutgalls are frequently to be found (1). The first scientific application of this phenomenon is due to PLINY (2), who recommends the use of a papyrus treated with gallnuts for the detection of iron in verdigris. He states :—« Deprehenditur et papyro, gall prius macerato ; nigrescit enim statim aerugine inlita » (3). KOPP (4) writes enthusiastically of the reagent : « Die Galläpfel boten also das erste Reagens dar, und mittels ihrer bereitete man auch das erste Reagenspapier ». Although many ancient authors wrote about atramentum sutorium and scriptorium (5), no interest seems to have been paid to this phenomenon until ALBERTUS

(1) DIOSCURIDES, I, 146, states that galls macerated with vinegar or water turn the hair black, but he makes no reference to iron salts in this connection. The *Hortus Sanitatis* (Mainz 1485), Capt. 203, gives the following particulars :—« Item wer do wil schwartz hare machen der neme goloepfel die do dicht und swere synt und mit lochericht und syede die in oelen und syhe dan diss oele durch eyn duch und laiss ess darnach drucken werden an der sonnen und nym dan diss pulueres und syede diss mit regen wasser und wesche dyn hare do mit oder den bart er wirt schwartz. » It is noteworthy that in the chapter on galls references are made to PLINY, SERAPION and PLATEARIUS, none of whom mentions iron. The only ancient reference to the use of iron salt in this connection seems to be in the BOWER M. S., which gives a formula for a hair-dye consisting of copper sulphate and iron sulphate boiled with myrabolanes, which are rich in tannins, see RAY, *A History of Hindu Chemistry* I, p. 53, Calcutta.

(2) *Hist. Nat.*, XXXIV, 11.

(3) KOPP, *Geschichte der Chemie* II, p. 51 (1843), in transcribing wrote « illita » in place of « inlita », and this error has found its way into other writings on the history of chemistry.

(4) KOPP, *loc. cit.*

(5) See CANEPARIO, *De Atramentis*, Londini (1660), for a list of authors who dealt with the subject.

MAGNUS (6) drew attention in his botanical writings to the black colour conferred on galls by vitriol. None of the subsequent ancient writers on botany (7) refers to it, however, with the exception of CLUSIUS (8), who seems to have vaguely connected it with the fact that bread made from gallnuts produces black faeces (9). The most important event in this chapter of chemistry was the observation made by PARACELSUS (10) that gallnuts may be used as a means for the detection of iron in water. To summarise therefore, it is found that the reaction was known to PLINY, that its theoretical aspect (11) was first commented on by ALBERTUS MAGNUS and that its introduction into analytical chemistry was due to PLINY and PARACELSUS. From the time of PARACELSUS onwards galls became a reagent in water analysis, being used contemporarily with PARACELSUS by THURNEYSSER (12) and LIBAVIUS (13), both of whom acknowledge PARACELSUS.

The whole problem was attacked from quite a different point of view by TACHENIUS (14), who was mainly interested in the astringent principle present in the gall. TACHENIUS may thus

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(6) Beati ALBERTI MAGNI, Ratisbonensis episcopi, *Ordinis praedicatorum opera, quae hactenus haberi potuerunt...* Studio et labore R. A. P. T. PETRI JAMMY, Vol. IV, p. 367, Lugdini (1651).

(7) The herbals by MEGENBERG, BOCK, MATTIOLI, LONICER and the *Hortus Sanitatis* (1485) mention gallnuts but make no reference to the black colour produced by iron salts.

(8) CLUSIUS, *Rariorum aliquot stripium per Hispanias observatorum historia* I, p. 21, Antverpiae (1576).

(9) See also CASPARI BAUHINI, *ΠΙΝΑΞ Theatri Botanici...* p. 421, Basileae (1671).

(10) PARACELSUS, *Bäderbüchlein oder sechs köstliche Tractate von Wasserbädern*, Mülhausen (1562) and *De Thermis*, Colon. (1570) where several references to this reagent are given.

(11) According to MIRIAM : « The conjoint aggressive properties of iron and astringent matter manifest themselves in the black colour of their offspring. » As regards the time when MIRIAM wrote, see LIPPMANN, *Entstehung und Ausbreitung der Alchemie...* p. 43, Berlin (1919).

(12) THURNEYSSER, *Pison, von kalten, warmen, minerischen und metallischen Wassern*, Frankfurt (1572), and Strassburg (1612) pp. 17-23.

(13) LIBAVIUS, *De judicio aquarum mineralium* in I) *Commentationem metallicorum*, p. 317, Francofurti (1597); and II) *Commentariorum Alchimiae*, p. 157, Francofurti (1606).

(14) TACHENIUS, *Hippocrates Chymicus*, pp. 124-125, Brunsvigae (1666). English translation by J. W., pp. 56-61, London (1677). The original Latin is in 12°, the English translation in 4°.

be regarded as the founder of the chemistry of the tannins. The elegance with which TACHENIUS dealt with the whole question is so striking that the following of his observations and remarks, which may be described as the incunabula of the whole problem, are here reproduced :

« I have formerly told you, That neither Acid nor Salt, nor any other Sapor, doth overcome and destroy Vitriol, but Alcalyes alone, but the Juice of unripe Galls, falls in with Vitriol, and makes a coalition therewith into black, destroying and absorbing the Acidity thereof, and therefore this Juice is to be reckoned amongst Alcalyes » (15); « after this manner, Ink, and all Black Tinctures are made : yea, when the Acidity of the Vitriol is not, to suffiency, combibed by the Alcaly of the Galls; which comes to pass, when the Galls are too ripe, and are washed by the rain; then the Alcaly doth expire, as it happens to all vegetables, of which hereafter in its place; then the Vitriol erodes and eats out the Cloth, and it becomes as rotten; whence the Vulgar say, *La robba e brusada, nella tinta.* So also, Letters written with Ink, boiled with the aforesaid Galls, do wax pale, because the prevalent Acidity of the Vitriol, consumes the weak Alcaly of the Galls, being washed with the Rain, after the same manner as any Acid Spirit spread upon a writing, presently destroys the Black Colour (i.e.) the Alcaly, which another fixed Alcaly doth again recover and reduce. So if you write with water, wherein Vitriol of Iron hath been dissolved, when it is dry, no sign of any Writing

(15) It will be realised that according to TACHENIUS the astringent principle of the gallnut possesses alkaline properties, and this view was quite independently expressed by LEMERY in his *Sur la Composition des différentes espèces de Vitriols naturels, et explication Physique et Sensible de la manière dont se forment les Ancres vitrioliques*, in *Hist. de l'Acad. Roy. des Sciences*, pp. 538-549 (1707). LEMERY's alkalinity hypothesis had its followers in NEUMANN (1759), LEWIS (1765), BERGMANN (1778), GIONATTI (1779) and BERGIUS (1782), although the Appendix : *Sur le principe astringent végétal* in Vol. III, pp. 403-420 of the *Éléments de Chymie, théorique et pratique...* Dijon (1778) already ascribed acidic properties to the astringent principle of gallnuts. The acidic property of gallotannin does not however agree with the modern views on the chemistry of gallotannin as propounded by EMIL FISCHER from 1912 to 1918, with the result that most fantastic explanations have been put forward, as, for example, those by FISCHER and FREUDENBERG in the *Berichte der deutschen Chemischen Gesellschaft*, Vol. 45, p. 922 (1912). These explanations of FISCHER and FREUDENBERG for the acidic properties are as sound as the alkalinity theory of TACHENIUS and thus history repeats itself.

will appear, but if you smear over the Writing with a simple infusion of Galls, in a moment the Alcaly of the Galls makes the Writing Black, which by a powerful *Acid* or *Aqua fortis*, is presently blotted out, *viz*. The Alcalyes being consumed by the *Acid*. Again, smear over the paper with fixed Alcaly, this will again consume the *Acid*, and the *Writing* will re-appear. By what hath been said, it appears, that Vitriol doth not dye Black, unless its Acidity hath been absumed by some Alcaly or other.

« But that the Alcaly of Galls may be made more perfect, anoint them over, at least with some Fat, or with some Oil, the hidden Acidity of which enters into the Galls, being placed in a pot, in a slow Fire of Ashes, leave them there till you see the Galls become Blacker, but not so as to be reduced to Coals; then their Alcaly will be more fit for Colouring, and an Ounce of such burnt Galls, doth more than a pound of others; yea it colours of it self, because the Acidity of the Fat, by the Fire, hath acted upon its Alcaly.

« Very many Vegetables do abound with the like Volatile and Occult Alcaly, as the greater Housleek, Sage, Rinds of Pomegranates; all which do spend and absume the Acid of the Vitriol, and cause the Colcotar to be much less black...

« But you must note, that Artificial Vitriol of an Azure colour, (which is falsly called *Cyprus Vitriol*) doth not become black, with Galls, though they be burnt, but with Rinds of Pomegranates it tinges obscurely Yellow : Now it is made of the spangles or thin flakes of Copper, by Spirit of Sulphur, or of common Vitriol; both which in a cold place, are Coagulated into somewhat long-angular little stones, hardly dissolvable, and unfit for Distillation, because it wholly wants that *Cupreous Sulphur*. This, with Urine, waxeth green, and with the Alcaly of Urine, is cast into an Azure bottom, which by Fusion returns to Copper.

« So also *Verdigrease* (as proceeding from ripe Copper and Vinegar) doth not wax black with Galls, but becomes of a light red or Spadiceous colour, and, by the Reformers leave, I know, and have experimented, that nothing but Vinegar will be distilled from thence, because the remaining *Caput Mortuum*, after Distillation, by the fire of Fusion, is reduced to pure Copper, of which more hereafter.

« Whence it appears, that burnt Brass, with tosted Galls,

produceth not a black tincture, as *Alexius* of *Piedmont* (16) promises with which process the Women of this Country do wonderfully vexe themselves, that therewith they may black their hair; for as far as this composition tinges any thing, it ownes that Vertue to the tosted Galls; the burnt Brass contributing nothing thereunto ».

Independently from PARACELSUS galls were used by DUCLOS (17) for the detection of iron in water. DUCLOS was therefore generally regarded in France as having discovered this reagent. Thus FOURCROY (18), to quote from the English translation of his textbook, states : « This reagent has been known and employed with success in the analysis of mineral waters since the time that DUCLOS recommended it in 1667. » BOYLE (19), who wrote on the subject in the same year as DUCLOS, deals with it under the title « Experimental remarks upon the (usual) way of examining mineral waters by the help of galls », as follows :

« Since the change of colour, that mineral waters produce in the infusion or tincture of galls, is the most usual way, that many physicians, and the almost only, that some of them endeavour to discover or examine mineral waters by, it may be worth while, in this place, to set down some remarks, that I have made about this way of probation; and the rather, because it may, *mutatis mutandis*, be not unusefully applied to the exploring the qualities of mineral waters by colorations, though made with other materials than galls. First then it may be observed, that one need not make an infusion or tincture of galls in common water, to try if, by their means, a new colour will be produced : for I am wont to beat them to powder (20), and keep them in a glass (not

(16) TACHENIUS refers here to *Les Secrets*, Part II, fol. 47, Paris (1561), where details are given « pour faire la barbe noire, les cheveux noirs », etc.

(17) DUCLOS, *Observationes super aquis mineralibus diversarum provinciarum Galliae in Academia Scientorium Regia in annis* 1670 *et* 1671 *factae, et Dissertatio super principiis mixtorum materiallum habita* 1677. Lugd. Batv. (1685). FOURCROY's statement that DUCLOS had recommended the reagent in 1667 apparently refers to an earlier paper by DUCLOS which I have not seen.

(18) FOURCROY, *Elements of Natural History and of Chemistry*, Vol. III, p. 478, London (1787).

(19) BOYLE, *Short Memoirs for the Natural Experimental History of Mineral Waters*, London (1685). Collected Works, Vol. IV, pp. 231-250, London (1744).

(20) After BOYLE the use of powdered galls became quite general, although it is noteworthy that as late as 1808 PFAFF, *Journ. Chem. und Phys.* v, 331, regarded it as a novelty.

too big) exactly stopped, by which means I have them always in readiness to mingle with the mineral water, and alter the colour of it, if galls be able to do it, almost in a trice; whereas, to draw the tincture of galls with simple water, often takes up several hours and the tinging parts are much weakened by being diluted by the menstruum. If you would have a tincture, the powder of galls, tied up close in a rag, and with it hung in the liquor, makes the infusion less muddy. If you be in haste, and have none of the powder in hand, you may scrape as much of a gall-apple, as you need, into the mineral water.

« 2. I have observed those parts of the infusion of galls, (especially if made by heat) that produce the new colour with ferruginous waters, to be more apt to fly away than one would think, the infusion becoming often unfit to alter the colour of martial waters, whilst yet itself appears sufficiently high coloured. Upon which account I chuse to make a tincture of galls not long before I mind to use it; and if I employ dry galls, to take powder, that is not stale.

« 3. 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. To obviate which inconvenience, I take this course, when the occasion deserves it; I make my infusion of galls with a certain weight of the powder in a determinate weight of water. As for instance, I put about five gr. of powdered galls, to steep for so many hours in an ounce of water : but if I make use of the dry powder, then I am wont to put three or four grains into an ounce of the liquor to be examined; which is a way far more certain, than the common, wherein the ingredients are estimated but by guess. I have mentioned various proportions of powdered galls to the same quantity of liquor, because I have observed, that there is really a great inequality among the mineral waters, in which it may be put; and I have found by trial, that in an ounce of the *German* Spa, a single grain of powder would immediately produce a sufficiently deep purple colour.

« 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 waters.

« Though it be useful, yet it is not necessary, to employ galls to produce a colour in the mineral water proposed; for besides that it is known, that usually, (though not always, as I have tried) the same thing may be done, but somewhat more faintly, with oaken leaves, we may successfully enough substitute, for the same purpose, some other astringent vegetables, as dried red-rose leaves, the peel, and (as we have tried) the juice of pomegranates; and (what I find to be a notable stiptick) the blossoms of the same plant, (which are vulgarly called in the shops *ballaustium* :) to which may be added myrobolans, logwood, and some others, that need not now be mentioned, whose strong infusions have yielded me a tincture very dark and blackish with some martial liquors ».

BOYLE's observations were soon afterwards extensively made use of by LEIGH (21), VICARIUS (22) and NEUMANN (23). The latter used BOYLE's experience in a manner which is most attractively told of by THOMSON (24) :

« Some merchants in Holland, England, Hamburg, and Dantzic, were in possession of what they considered an infallible test to distinguish French brandy from every other kind of spirit. It was a dusky yellowish liquid. When one or two drops of it were let fall into a glass of French brandy, a beautiful blue colour appeared at the bottom of the glass, and when the brandy

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(21) LEIGH, *Tentamen de aquis mineralibus*, London (1694).

(22) VICARIUS, *Hydrophylacium novum, seu discorsus de aquis*... Ulmae Svenorium (1699). VICARIUS assigns (p. 70) the discovery of the reagent to PARACELSUS and THURNEYSSER and makes no reference to BOYLE. Similarly LENTILIUS, in his *Miscellanea curiosa*... Observ. 201 (1686) mentions PARACELSUS only as having discovered this test.

(23) NEUMANN, *De experimento probandi spiritum vini Gallici, perquam usitato, sed revera falso et folici*, No. 391, in the *Trans. Royal Society of London*, pp. 398-408 (1724-1725).

(24) THOMSON, *History of Chemistry*, Vol. I, p. 264, London (1830).

is stirred, the whole liquid becomes azure. But if the spirit tried be malt spirit, no such colour appears in the glass. NEUMANN ascertained that the test liquid was merely a solution of sulphate of iron in water, and that the blue colour was the consequence of the brandy having been kept in oak casks, and thus having dissolved a portion of tannin. Every spirit will exhibit the same colour, if it has been kept in oak casks ».

In addition to the workers mentioned galls were used for the detection of iron in water also by HIERNE (25), HOFFMANN (26) BRANDT (27), TEICHMEYER (28), WALLERIUS (29), BERGMANN (30), STRUVE (31), BRUGNATELLI (32) and many others (33).

In conclusion it is perhaps interesting to state that ELLER (34) used gallnuts for the detection of iron in the calx of human blood, thereby proving for the first time the presence of iron in blood.

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(25) HIERNE, *Brevis manuductio ad fontes, et aquas minerales*.. .Holmiae (1707).

(26) HOFFMANN, *Acta Laboratorii chymici Aldorfini* Norimb. (1719).

(27) BRANDT in *Acta Litt. et Scien. Sulliae*, Vol. III, pp. 39-43 (1723). See also CRELL's *Neues chemisches Archiv* 1784 pp. 274-279. BRANDT expresses the hope that a test for arsenic will be found which will compare with the reliability of the gallnut test for iron.

(28) TEICHMEYER, *Institutiones chymiae*... Ienae (1729).

(29) WALLERIUS, *Hydrologie, nebst Anleitung zur Anstellung von Wasserproben*... Berlin (1751).

(30) BERGMANN, *De analysi aquarum*, Upsala, (1778).

(31) STRUVE, *Von den Reagentien und ihrem Gebrauche bey der Zerlegung der Mineralwasser*, Jena (1786).

(32) BRUGNATELLI, *Elementi di Chimica*... Pavia (1795). CRELL, who reviewed the book in the *Chemische Annalen* for 1796, Part I, p. 661, points out that BRUGNATELLI does not mention that BERGMANN had discovered the test !

(33) GMELIN, Geschichte der Chemie, Vol. I, pp. 740-790, Göttingen (1798), gives a large number of publications which deal with water analysis. Of these I have had the opportunity of examining some 30 odd, in all of which I have found that iron is detected with powdered gallnuts as recommended by BOYLE.

(34) ELLER, in *Hist. de l'Acad. Royale de Berlin*, 1751, p. 11.