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COMMENTARY

The Philosophical Magazine and the Periodic Table of Elements

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The history of the Periodic Table of Elements covers almost 300 years: from the discovery of phosphorus in 1669 to that of Lawrencium in 1961. Before that period, only elements such as copper, silver, gold, mercury, lead and of course carbon were known, which already had accompanied the history of mankind for millennia. The first "wave" of discoveries of new metals occurred at the close of the eighteenth and the beginning of the nineteenth centuries and was almost entirely based on "wet chemistry". Because this period, in which no physics-related techniques of identification were available, seems to be now so remote, it is worthwhile to recall these discoveries in the context and style of their time by making use of the *Philosophical Magazine* archives.

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Nowadays it is extremely easy to get a quick view of the Periodic Table of Elements. All one has to do, is to Google "periodic table" and quite a few web pages [1] pop up yielding lots of information about the atomic weight, properties, isotopes, history, etc., of chemical elements. Usually – displayed in beautiful lay-outs – each element can be clicked-on separately.

In Figure 1, a Periodic Table of Elements is shown using a color code reflecting the centuries in which the various chemical elements were discovered. Quite obviously, besides all those elements that were already known since ancient times[1] such as copper, silver, gold, tin, mercury, lead and carbon, in the year 1800 the number of additional elements was rather restricted. By that time most of the newly discovered metals such as beryllium, titanium, chromium, manganese, strontium, yttrium, zirconium and molybdenum had been found in the second half of the eighteenth century, and quite a few of them only very close to the beginning of the nineteenth century.

In the years from about 1770 to 1820 Nature first became an object of various curiosity collectors and only then a field of interest in certain areas. The *Philosophical Magazine* archives provide a wonderful image of these interests, since the *Philosophical Magazine* was first published in 1798, i.e. only shortly after the

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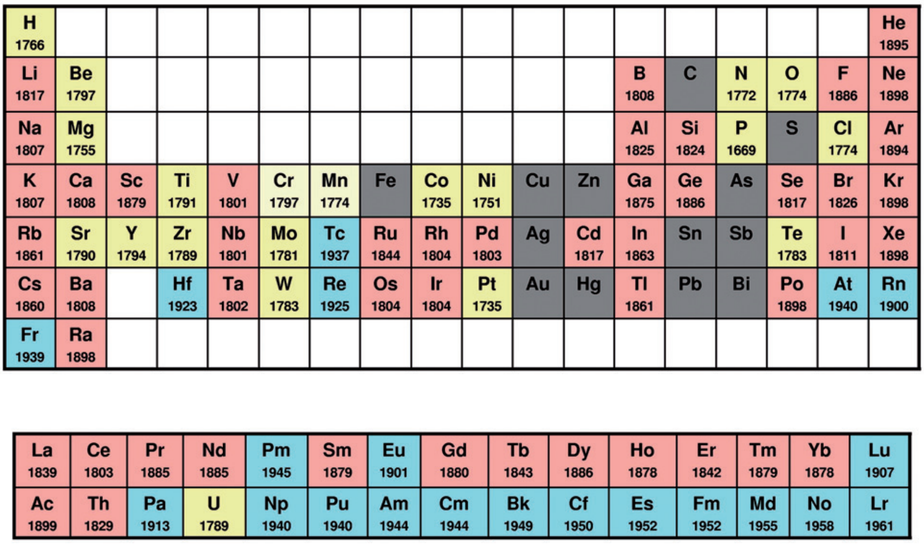

Figure 1. The Periodic Table of Elements. Grey: known since ancient times; yellow: discovered in the seventeenth and eighteenth centuries; pink: discovered in the nineteenth century; blue: discovered in the twentieth century.

French Revolution of 1789 that not only terminated the *ancien régime* but also resulted in an outburst of new ideas, ideas freed of scholastic traditions.

In this period, the start of which is frequently associated with the French encyclopedists, in particular, zoology [2], botany, mineralogy and geography, [3] became the main fields of scientific interest. Even a new field arose, namely chemistry, which had finally succeeded in overcoming the stage of superstitiously minded alchemy, having inherited, however, all its technical skills. With the arrival of "wet chemistry," namely of the idea of characterizing "substances" according to their properties to form various salts, the written history of the Periodic Table of Elements starts. Of course it was partially driven also by the curiosity of dealing with rare or precious minerals, i.e. it was a consequence of interests in mineralogy.

Already, in its very first year, 1798, the *Philosophical Magazine* picked up this new scientific field:

> *The fragility of* ***chrome***,[2] *the resistance it offers to the action of fire, and the smallness of the masses in which it hitherto has been naturally found, do not leave us any hopes that this metal can ever be of great utility in the arts . . . The acid and the oxyd of this metal, however, maybe of the greatest utility* [4].

It is indeed fascinating to imagine that at the beginning of the nineteenth century only "wet chemical" methods were available to prove the existence of a new metal without the help of spectroscopic or other physics-related means of identification as nowadays used routinely. A newly discovered metal had to be characterized only by its chemical properties; its physical properties consisted merely of the specific weight (which was a little bit shaky anyhow, because of incompatible measuring units) and perhaps, if possible, the melting point (also quite ambiguous for the same reason).

The search for new metals was therefore almost comparable to a crime investigation with lots of logical bifurcations. Only after having surpassed lots of "ifs" and "thens" in terms of colors, smells or shapes of crystals, a corresponding claim could be put forward, which occasionally – at least according to present knowledge – sounds completely absurd:

> *I entertain no dread then of being ridiculed by the unprejudiced philosopher, if I call the attention of chemists to a phenomenon in which silver appears to be converted into gold* [5].

In the above case "horn silver" (AgCl), which sometimes is found on gold coins was the cause for this mischief.

Since no chemical nomenclature or chemical formulae were available, every single process had to be described in words. Usually a typical communication would therefore start out in describing precisely what kind of mineral was analyzed. A very characteristic example, involving one of the best known chemists of that time, namely Berzelius, is to be found in a report on the discovery of cerium:

> *The tungsten of Bastnas, which we call cerite, for reasons which will be hereafter mentioned, was found in the year* 1750, *in a copper mine called Bastnas, ... in Westmannia, of which it formed with asbestos*[3] *the matrix; but after that time it was inclosed in quartz and mica,*[4] *at the depth of seventeen toises*[5] ...
>
> *These and the following circumstances have determined us to consider the substance as the oxide of a metal hitherto unknown, to which we have given the name of* ***cerium***, *from the planet Ceres discovered by Piazzi* [6].

In the same year, namely 1804, the discovery of three new metals (iridium, osmium and rhodium) was published in the *Philosophical Magazine* even on consecutive pages.

> *Upon making some experiments, last summer, on the black powder which remains after the solution of platina,*[6] *I observed that it did not, as was generally believed, consist chiefly of plumbago,*[7] *but contained some unknown metallic ingredients* [7].

By simply determining the specific weight of platina Smithson Tennant could easily rule out immediately the presence of "plumbago." After some unsuccessful attempts to combine the black powder of platina with other known elements such as lead or bismuth, he tried to dissolve it in *nitro-muriatic acid*,[8] the remainder being a black powder as before, that, as he noted, *may easily be united, by fusion, with silver or gold*. Then:

> *I put a quantity of the powder into a crucible of silver, with a large portion of pure dry soda, and kept it in a red heat for some time. The alkali being then dissolved in water, had acquired a deep orange, or brownish-yellow colour, but much of the powder remained undissolved. This powder, digested in marine acid,*[9] *gave a dark blue solution, which afterwards became a dusky olive-green, and finally, by continuing the heat, of a deep red colour. Part of the powder, being yet undissolved by marine acid, was heated as before with alkali; and, by alternate action of the alkali and acid, the whole appeared capable of solution* ...
>
> *The alkaline solution contains the oxide of a volatile metal, not yet noticed, but which I shall presently describe, and a small portion of the other metal* ...
>
> *As it is necessary to give some name to bodies which have not been known before, and most convenient to indicate by it some characteristic property, I should incline to call this metal*

> ***iridium***[10] *from the striking variety of colours which it gives, while dissolving in marine acid....*
>
> *When the alkaline solution is first formed, by adding water to the dry alkaline mass in the crucible, a pungent and peculiar smell is immediately perceived. This smell, as I afterwards discovered, arises from the extrication of a very volatile metallic oxide; and, as this smell is one of its most distinguished characters, I should on that account incline to call the metal* ***osmium***.[11] [7]

Finally, after having convinced himself that he indeed found two new metals, Smithson Tennant succeeded in reducing solutions of their salts to the elemental metals. In a similar manner William Hyde Wollaston, who eventually would become the president of the Royal Society, discovered rhodium.

> *Notwithstanding I was aware that M. Descotils had ascribed the red colour of certain precipitates and salts of platina, to the presence of a new metal; and also Mr. Tennant had obligingly communicated to me his discovery of a second new metal, in the shinning powder that remains undissolved from the ore of platina; yet I was led to suppose that the more soluble parts of this mineral might be deserving of further examination, as the fluid which remains after the precipitation of platina by sal ammoniac,*[12] *presents appearances which I could not ascribe to either of those bodies, or to any other known substance.*
>
> *My inquiries having terminated more successfully than I had expected, I design in the present Memoir to prove the existence, and to examine the properties, of another metal, hitherto unknown, which may not improperly be distinguished by the name of* ***rhodium***,[13] *from the rose-colour of a dilute solution of the salts containing it* [8].

Because of the slow speed of communications and exchange of journals occasionally discoveries were made simultaneously. Vauquelin [9], for example, noted that cerium was discovered also by Klaproth at the same time as Hisinger and Berzelius. Sometimes even two names existed for apparently one and the same new metal as was the case, e.g. with tantalum (Ekeberg, 1802) and *columbium* (Hatchett, 1801). A ''wet chemical analysis'' by Wollaston [10] seemed to prove that these two ''substances'' were identical. He actually was wrong. It was only proven more than fifty years later (1864) that *columbium* in fact was what is nowadays called niobium.[14] Obviously Wollaston, the discoverer of palladium[15] (1803) and rhodium had the bigger authority in the scientific community, see also [11].

A few years later the discovery of a new element termed *iode* (iodine) raised quite some interest, mainly since it did not seem to be a new metal:

> *When it is purified by means of potash*[16] *and distillation, it is infusible at the temperature of boiling water, and has nearly the same volatility as this fluid. By no chemical agent does it offer any trace of muriatic acid.*[17] *The iode combines with nearly all the metals; but as it is solid, it does not appear to develop in its combinations so much heat as oxygenated muriatic acid, with which it has much analogy in its general properties ... The action of phosphorus on iode furnishes the means of obtaining the new acid in both its states, gaseous and liquid* [12]; *see also* [13,14].

The above quotes concerning the use of ''wet chemistry'' in the case of iridium, osmium, rhodium and iodine are to illustrate the chemical possibilities of tracing new metals at the beginning of the nineteenth century. The next major breakthrough in completing the Periodic Table only occurred around 1880 with the discovery of the rare earth elements, but at that time line spectroscopy was already a standard procedure of analysis.

Two more aspects characterizing the progress in finding new chemical elements made in the first one or two decades of the nineteenth century have to be mentioned.

First, the use of a new technique to separate metals by means of g*alvanic columns*. In this manner, e.g. sodium (1807) and kalium (1807) were discovered by Sir Humphry Davis and reported in the *Philosophical Magazine*. However, since at that time mostly technical variations of Galvani's newly found effect were of main focus, the results of the electrolysis, namely elementary forms of sodium and kalium, were perhaps only a by-product.

Second, because – from mathematics to technology – French science at that time was so dominant, British scientists mainly looked over the channel to keep in touch with their foreign colleagues. This in particular is also the reason for quite a few "reports" in the *Philosophical Magazine* from French meetings or journals. Despite the persistent resistance by the Select Committee on Weights and Measures in the House of Commons to adopt also the newly defined units of meter and kilogram and the metric system,[18] it is quite obvious that the era of the French Revolution had indeed an enormous impact on science in Britain and subsequently in other English-speaking countries.

Surely, the Periodic Table of Elements was and is one of the major achievements in science in the last almost 300 years. Parts of its written history is to be found in the *Philosophical Magazine* archives.

Notes

1. The history of the last 6000–7000 years can be viewed also using entirely metallurgical terms. Homer's *Iliad*, the fall of Troy, for example, appears to be a metaphorical setting for the transitional period between the Bronze Age and the Iron Age. Very often the rise of a new Middle East high culture was connected with a new metallurgical technique. In some cultures the knowledge of metallurgy is indeed astonishing: *Tumbago*, for example, a copper-gold alloy used frequently in South American precolumbian cultures, corresponds almost exactly to the eutectic point in the phase diagram.
2. Greek: chroma, color.
3. A fine fibrous form of (usually) amphibole or serpentine.
4. Sheet silicates.
5. 1 toise was exactly 6 pieds (feet) (about 1.949 meters) in France until 1812.
6. A platinum-containing ore found in Columbia, South America.
7. Historically, graphite was called blacklead and plumbago.
8. Aqua regia, nitro-hydrochloric acid.
9. Hydrochloric acid.
10. Greek: "with the colours of the rainbow," after Iris, the Greek winged goddess of the rainbow and the messenger of the Olympian gods.
11. Greek: osme, smell, odour. Just as a matter of curiosity, the name of the well-known company providing light bulbs, Osram, is derived from "**Os**mium" and "Wolf**ram**" (tungsten).
12. Sal ammoniac: white crystalline ammonium chloride NH_4Cl occurring as a mineral in nature. It is highly soluble in water.
13. Greek: rhodeos, rose-coloured, "rose-red."
14. From the Greek mythology: Niobe, daughter of Tantalus.
15. Named by Wollaston after the asteroid Pallas, which in turn is derived from the Greek goddess Pallas (Athene).
16. Solid material mostly containing KCl.

17. Muriatic acid: hydrochloric acid.
18. This will be the topic of an upcoming commentary.

References

[1] See for example http://ptable.com
[2] M.M. de Serres, Phil. Mag. Series 1 47 (1816) p.249.
[3] See, for example, Phil. Mag. Series 1 56 (1820) p. 93.
[4] Cit. Vauquelin, Phil. Mag. Series 1 2 (1798) p.74.
[5] Professor Hildebrant, Phil. Mag. Series 1 4 (1799) p.18.
[6] W. D'Hisinger and J.B. Berzelius, Phil. Mag. Series 1 20 (1804) p.154.
[7] S. Tennant, Phil. Mag. Series 1 20 (1804) p.162.
[8] W.H. Wollaston, Phil. Mag. Series 1 20 (1804) p.168.
[9] M. Vauquelin, Phil. Mag. Series 1 22 (1805) p.193.
[10] W.H. Wollaston, Phil. Mag. Series 1 35 (1810) p.201.
[11] M. Vauquelin, Phil. Mag. Series 1 44 (1814) p.33.
[12] See for example Phil. Mag. Series 1 43 (1814) p. 58.
[13] A. Garden, Phil. Mag. Series 1 43 (1814) p.209.
[14] J. Murray, Phil. Mag. Series 1 43 (1814) p.270.