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LECTURE

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Analytical chemistry in the discovery of the elements

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Abstract After a brief introduction to the evolution of the philosophy of matter over the centuries to arrive at the actual concept of chemical elements and "chemical matter" a historical overview is presented on the discovery of new elements within the 17–20th centuries, associated with the development and progress of chemical analysis and analytical chemistry. Some specific details are included in connection with imaginative theories, controversies on precedence of discovery, and spurious discoveries and their discoverers. 16 new elements were discovered in the 18th c., 51 in the 19th c. and 26 in the present c. The influence of some chemical schools, the incidence of conjunctural circumstances, the difficulties implied by some discoveries, serendipitous and fictitious discoveries, etc. are considered focusing on specially remarkable cases of historic interest. Historical and actual controversies related to naming of new elements are briefly considered.

Introduction

Phosphorous was the first element of known discoverer (Brand, 1669) but it took over a century to recognize it as a chemical element (Lavoisier, 1789). Ironically, an alchemist discovered the first element while an advocate by profession classified it as a chemical element.

Thus we come to two very important aspects of a discovery and its discoverer:

- the *consciousness* of the discovery itself
- the *awareness* of its meaning

The concept and types of scientific discovery as well as other aspects related to the discovery itself are well treated elsewhere [1–3]. Another question is the "consciousness" of the discovery by the discoverer. Ulloa discovered platinum in South America, was aware that it was a new *metal* and introduced his knowledge into Europe by 1748. Brand knew quite well that he had discovered a new *substance*, but he did not know that this substance was a new chemical element. After one century Lavoisier resolved Brand's ignorance, not being himself discoverer of any chemical element.

We cannot therefore avoid revising briefly some historical aspects on the philosophy of matter. To begin with we will start by the end of the question: Between Brand and Lavoisier 13 new elements were discovered but their discoverers never talked about new chemical elements but just about bodies, substances, or even metals, simply because the concept of "element" although coined from antiquity and actualised by Boyle and others in the years of Brand's discovery remained vague, metaphysical and unassociated with concrete existing chemical elements. We can therefore conclude that the discoverers of those 13 elements really discovered elements but were unconscious of their elementality. Years, even decades after Lavoisier's definition and classification of "simple bodies" (a fundamental approach to the concept of "chemical elements") a number of outstanding scientists still doubted the "elementality" of a number of true chemical elements, (see below). Looking back we can strictly speak of true discoverers of new chemical elements just after Lavoisier's official tabulation of "corps simples" as organised in his "Traité" in 1789. But even Lavoisier suffered omissions and errors since two elements (U, Zr) were not included in his tabulation probably because of their recent discovery in the same year (1789). What is much worse, because for Lavoisier chlorine was a compound which he named as "oxymuriatic acid", he had not the right to enter it into the table.

A few aspects of the historical evolution of the theory of matter from the point of view of chemists [4–8] deserve to be briefly discussed here.

Historically the philosophy of matter was essentially methaphysics until Lavoisier's definition of *simple bodies*. We can recall the monistic matter theories of ancient Greek philosophers, the four or five metaphysic elements bound to the names of Empedocles, Plato, and Aristotle,

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the Indian *panchatouan* or the Chinese *wu-hsing* theory related to the *yin-yang* doctrine, the dualistic *sulphur-mercury* alchemic Arabian theory deriving from the Aristotelian *two-exhalations* theory and/or from the Chinese *yin-yang* to arrive at the Paracelsian trichotomy of the *tria prima* [13] and the *five-principle* theories of the 17–18th c. based on the interpretation and observation of the products resulting from distillation or fire analysis of matter [9, 12, 15].

For Lomonosov, metal nobility was directly related to the phlogiston content, which was supposed to be generally low for the most common metals. Macquer advanced a curious theory being sceptical about the possibility of total calcination of metals whereby a variable amount of phlogiston would be retained by the calcined resultant earth, specific for each particular metal. He even went so far as to postulate that the "complete" calcination of metals would render a unique final earth, common to all metals, from which the different metals could be obtained through combination with the pertinent amount of phlogiston. Based on these speculations Macquer concluded that metal transmutation was impossible if each particular metal "contains" a specific earth but transmutation should be possible provided that "complete" calcination of any metal could be achieved [18].

Davy postulated soonafter (1807–1814) a dualistic theory for metals aiming at a simplification of the "forms" of "undecompounded bodies" ("simple bodies" for Lavoisier) which he assumed to be composed from a reduced number of protoelements or principles. Davy's dualistic metal theory considered all metals to be composed by hydrogen (the only truly simple, elemental substance for him) combined with certain unknown bases. Such a theory was strongly and belatedly reminiscent of phlogiston at a time when Lavoisier's and Dalton's theories enjoyed nearly universal acceptance [19, 20]. However, not only Davy but a good number of outstanding chemists (Vauquelin, Hatchett, etc.) were reluctant to consider as new elements their experimental discoveries of new metals (Cr, Nb, etc.).

Vague methaphysics bound to sensorial and/or experimental results is mixed systematically in all these conceptions. Backing up again we find Boyle who correctly established the "analytical concept" of elementality of "chemical matter" but was unable to make a further step to materialise matter in concrete terms as did Lavoisier a century later, based on the same conceptual premises, Boyle's "Sceptical Chymist" (1661) establishes a fundamental revision and disqualification of consecrated metaphysical "element" and "principles" but – given Boyle's inner conflict between alchemy and chemistry – he was unable to overcome his own metaphysics which would have implied a concrete connection between his corpuscularianism and his conceptual definition of a chemical element in practical terms. On the other hand his belief in metal transmutation should not have been incompatible with such bridging step, rather his cautious attitude is more likely from his congenital scepticism, self respect and remaining strong ties with traditional Alchemy [21–24].

Lavoisier's operational, pragmatic and concrete definition and tabulation of *simple bodies* was fundamental to eliminate the metaphysics of matter from experimental chemistry. But he too was careful to talk just in "chemical terms" of matter using analytical resolution power as the limit for the *chemical elementality* of matter. He even left a door open towards the foreseeable progress of chemical analysis which could prove that some officially "simple" bodies were not so, as happened shortly afterwards with a number of "earths" included in his tabulation.

Cautiousness and scepticism was also observed by Davy who preferred not to mention "simple bodies" but rather "undecompounded bodies" which contains essentially Lavoisier's concept only expressed more openly and uncompromisingly.

The term *element* is probably the most ambiguous, misleading, and equivocal generic concept in the History of Science, therefore its use was very carefully restricted by most scientists in this epoch to a chemical context.

Another disturbing fact for scientists in this epoch was the growing number of chemical elements being discovered which apparently conflicted with the supposed simplicity of nature and could be interpreted to be an anarchy against natural laws. Such was the case with Davy who never identified the new metals as *true elements*, but went even further to postulate a simplicistic theory of matter which considered *undecompounded bodies* to be composed of two protoelements (hydrogen, electropositive; oxygen, electronegative) and a "base" of unknown nature (19, 20). The concept of *element* was for Davy synonymous with "ultimate particle" (true element) which in line with Prout's reductionistic hypothesis – warmly supported by Davy against Berzelius – should be unique: i.e. hydrogen or Prout's *protyle* [25].

The problem of elementarity of matter within a purely chemical context was finally successfully resolved by Dalton ("A new system of chemical philosophy", 1808) using a synthesis of Boyle's and Lavoisier's theories combining the atomistic discontinuous quantitative aspect of matter with the macroscopic pragmatism defining the simple bodies based on the chemical analytical criteria. By synthesizing the classical quantitative and qualitative aspects of matter Dalton bettered his predecesors by specifying the concept of *chemical elementality* of matter thereby eliminating the traditional confusion posed by the concepts of *absolute matter* (physical, uncompounded, truly simple, rigorously elemental) and *chemical matter* (undecomposable up to the chemical analytical limit, disregarding its potential resolution into more elemental constituents or elementary units by other means outside the resolution power of chemistry). Dalton's comprehensive theory accounts for the main chemical aspects of matter considered from the point of view of chemistry (i.e., "chemical matter"), and can be summed up:

- *qualitative* (specificity, individuality, types, proprieties, "forms")
- *discontinuous* (built by units of "elemental chemical" atoms)
- *quantitative* (specific mass for each "chemical atom")

Table 1 Significant conceptual errors on the elements after the publication by Lavoisier of his classification of elements [29]

Element	Author	Remarks
H	Davy	Accepted hydrogen as possibly the only undecomposable body, as principle (“Urstoff”) or “true element”
O	Lavoisier	Thought of oxygen as being composed of oxygen (unisolated) and “caloric” (justifying the gaseous state of oxygen)
	Davy	Approaching Lavoisier’s ideas he considered oxygen to be composed of unisolated oxygen (i.e., a pure simpler body) and light in order to explain the production of fire in the combustion process. Based on this view he even elaborated a fictitious “phosoxygen” theory for the combustion process which he abandoned quickly [19, 20]
N	Berzelius	Assumed nitrogen to be an oxide of the hypothetical radical “nitricium”
N, H	Berzelius	Based on Davy’s suggestions considered them – as well as ammonia – to be ammonium oxides
Cl	Lavoisier	In line with Scheele’s supposition about its compound nature (“muriatic or marine deflogisticated acid”) Lavoisier named it “oxymuriatic acid”, being followed in this respect by Berthollet, Gay-Lussac and Thénard among others
	Davy	Demonstrated it by electrolysis of HCl not to be a compound body but a “simple body” (not necessarily a “true element”, but just an “undecompounded body”)
	Berzelius	Following Lavoisier he assumed it to be “oxymuriatic acid” up to 1820
	Schönbein	By as late as 1865 he considered chlorine to be a peroxide of “murium”
Na, K	Klaproth	Was reluctant to classify these metals as real metals, because of their strikingly low density
	Gay-Lussac Thénard	Considered these elements to be compounds of a caustic alkali and hydrogen by similarity with the chemical behaviour and existing theories on the ammonium ion
Si, N, P, S	Davy	Doubting their elementality he attempted their chemical decomposition by different means

Another interesting concept is that Dalton’s chemical atoms would not be omnipresent in any type of matter but they would just correspond specifically to the smallest discrete parts of Lavoisier’s “simple bodies” wherefrom Dalton’s concept of “chemical element” becomes absolutely unambiguous implying a restricted aspect of matter, which is the direct concern of chemistry and which represents a syncretic fusion of many of the philosophical aspects of matter held both by ancient Greek philosophers (Democritus, Epicurus, Empedocles, Aristotle) and more modern scientists (Boyle, Lavoisier, Davy).

In spite of the physically demonstrated composed nature of atoms Dalton’s concepts of “chemical atoms” maintain actually their chemical *individuality* as well as their chemical *elementarity*. As a result the cornerstones which are the fundamental quantitative laws of chemistry remain as valid as they were at the time of their experimental establishment and doctrinal formulation. Ironically, such a syncretic theory was not easily accepted by a number of prestigious antiatomists like Ostwald, Davy, Berthollet, and Mach, and even by Mendeleev many decades afterwards.

However, as stated by Guerlac [26] the process of the quantification of chemistry began with the quantitative definition of chemical elements, leading finally to the establishment of the periodic table, the final triumph of quantification of the older chemistry.

Furthermore, as a result of the chemical similarity of the rare-earth elements, which posed specially difficult analyticals separation and identification problems as well as derived from the discovery of helium by spectroscopy in the sun (1868), a number of curious metaphysical theories on the genesis of the elements and the structure of matter appeared in the last decades of 19th c. [27, 28] like Crooke’s *metaelements* or *elementoids* and Mendeleev’s *chemical ether* theories.

Table 1 shows that the problem of the elementality of *chemical matter* took many years for many outstanding chemists to be accepted in the 19th c. More evidence on this subject will be furnished from the examination of Table 5 where a few examples of comparatively recent fanciful theories of matter and spurious discoveries of elements are considered. The foregoing lines are a necessary clarification of the questions posed at the beginning of this introduction as to the decisive importance played by *consciousness* and *awareness* as inescapable premises for the discovery of new chemical elements.

Analytical techniques and methodologies involved in the discovery of elements

With few exceptions, the discovery of new chemical elements is directly related to progress of material assaying techniques, systematic wet and gravimetric analysis and the progressive physicalisation of chemical analysis. Many of the fundamental aspects of the secular evolution of chemical analysis to become finally scientific analytical chemistry have been briefly outlined by the author in a preceding communication [30, 31] making it unnecessary to enter here into specific details. Brief attention will be paid here only to the essential genealogical aspects of the “backbone” of chemical analysis as summed up schematically in Fig. 1 which shows the main names and schools related to the development of chemical analysis in the 18–19th c. directly related to the discovery of elements. In fact the names included in Fig. 1 are directly related to the discovery of 25 new chemical elements from a total of 51 which were discovered in the 19th c. Such a feat was possible because of the development of many diversified and reliable qualitative and quantitative systematic methodologies and particular techniques of chemical analysis. Specific details on this significant development can be found elsewhere [14, 32, 33–39].

A simplified overview is given in Table 2 of the most important identification, separation and isolation techniques and methodologies which have been used for the discovery of chemical elements from the 18th c. to our present time. As can be seen the combination of chemical and physical methodologies shows a continuous increase from the beginning of the 19th c., with the introduction of voltaic electricity into chemistry.

Despite the large number of physical methods, classical analytical dry and wet methods have played a fundamental protagonism throughout the history of the discovery of new elements, especially in the 19th c. (Fig. 1). Even in our century where physical methods of analysis have overshadowed the heroic protagonism of the analytical chemistry of the preceding century, analytical chemistry is as omnipresent as radiochemistry as an essential auxiliary branch in connection with the investigations related to the actinides and the new superactinide elements.

Such a methodological evolution of analytical chemistry is a logical consequence of the increasing complexity of the problems encountered beginning in the second half of the 19th century with the introduction of spectroscopic detection methods and the wide use of physical separation techniques (fractional crystallisation and distillation) which proved indispensable to achieve difficult separations of complex samples of chemically very similar elements as are the lanthanide earths, the noble gases, etc.

To conclude this section we can recall Hevesy's wondering at the accomplishments of analytical chemistry in its heroic period:"... one of the most brilliant achievements of chemistry ever made".

Table 2 Methodologies and techniques used for the identification, separation and isolation of new chemical elements

Period	Methodologies Techniques	Elements	Remarks
18th c.	• dry qualitative (blowpipe) and wet quantitative analysis	Ni, Te, (Ca, Ba, Mn, U, Zr, Sr, W, Mo)	( ) elements identified as oxides
	• high-temperature carbon reduction	Mo, W, Cr, (Ti, Be, Nb, Ce, F)	( ) elements identified as oxides, acids
	• gasometric (bound to calcination, acid attack)	H, N, O, Cl	"pneumatic chemistry"
19th c.	• Electrolysis (fused salts, amalgams, mixed electrolytes)	Li, Na, K, Ca, Sr, Ba, Mg, Si, Al, F,	elements obtained as metals (except fluorine)
	• reduction with alkaline metals	Ti, Zr,U, Th, Ce, lanthanides, Al, B, Si, Be	elements obtained as metals
	• high-temperature reduction (C, H_2) of oxides and salts	Cr, Mo, W, U, Mn, Zn, Ge, Cd, P, V, Ti, Nb, Ta	elements obtained as metals
	• gravimetric systematic analysis	Se, Ge, (Nb, Ta, V, Ir, Os, Cd)	( ) element obtained as acids or oxides
	• calcination of salts	Pt-group elements	metals obtained as spongy masses
	• emission spectroscopy	Rb, Cs, In, Tl, Ga, some lathanides	
	• absorption spectroscopy	He	first discovered in the sun (1868)
	• spark & arc spectroscopy	Sc, most lanthanides	
	• fractionated crystallisation plus spectroscopy	lanthanides	separated as chlorides, nitrates, bromates, fluorides
	• fractionated distillation plus spectroscopy	noble gases	
	• wet systematic analytical separation plus radioactive analysis	Po, Ra, Rn, Ac	first step of radiochemistry development
	• X-ray analysis	Hf, Pm, Re, actinides	except Pm all the lanthanides were identified before X-rays introduction
	• polarography	Re	
	• radiochemical development	actinides, unstable elements	
	• liquid-liquid extraction and ion-exchange chromatography	actinides, lanthanides	
	• nuclear reactions	Ac, Pa, At, Fr, Pm, Tc, actinides, superactinides	different approaches (radioactivity, bombardment with particles, fusion reactions)
	• zone refining, vacuum sublimation (metal halides)	transition metals, Ge, Si, Se	ultrapure elements (99,999% or better)

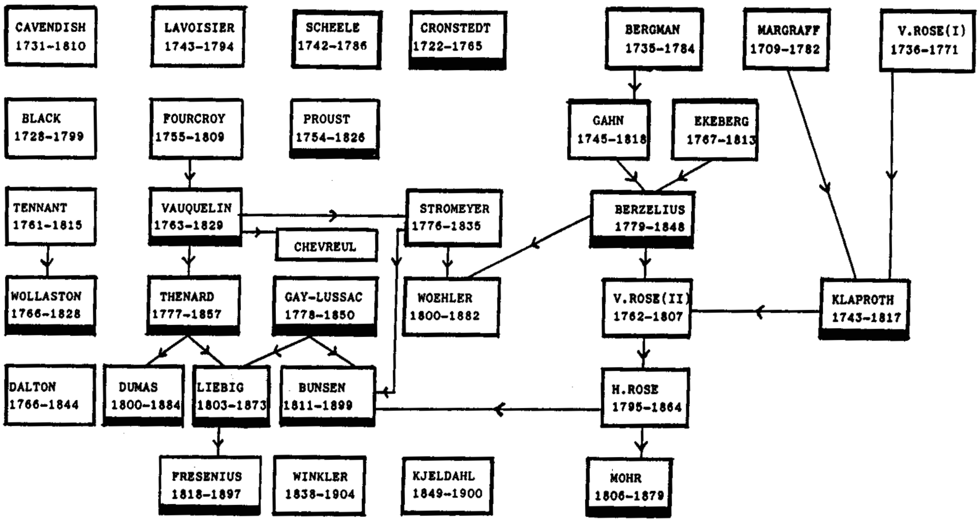

Fig. 1 Outline of the main protagonists and schools involved in fundamental developments of chemical analysis in the 18–19th centuries of direct incidence for the discovery of many new chemical elements

Factors influencing the discovery of new chemical elements

The history of the discovery of new chemical elements contains many factors which influenced, directly or indirectly, their discovery. Without exhaustive claims for the theme a few important aspects of the question follow.

In the 18th c. the fundamental vectors were mineralogical analysis using dry analytical techniques, especially blowpipes as well as the gasometric and calcination work which crystallised in Lavoisier's "chemical revolution".

The progressive quantification of chemistry from the beginning of the 19th century brought about an essential progress in the development of diversified, systematic and accurate analytical methodologies which were essential for the discovery of new elements. Berzelius's work on atomic weights, determination and tabulation together with Mendeleev's systematisation of chemistry in his periodic table, among other developments paved the route to understanding the limits of the number of elements to be expected to exist, as well as to making important predictions about "missing elements", which were sought eagerly and finally discovered.

As stated by van Spronsen [28] the perfection of analytical methods in this period was a fundamental cornerstone for the determination of the atomic weights (Berzelius, Stas, Dumas, Avogadro, Marignac, etc.) the knowledge of which was a decisive factor for the process of scientific chemistry both for rationalisation purposes as well as for predictive, induction-based, chemistry. The chemical methodology typical of the "classic chemical analysis" was reinforced stepwise by new physical methodologies suitable for the separation and identification of elements, as the complexity of the problems increased.

Among the main specific factors influencing the discovery of chemical elements the following should be particularly considered [14]:

- Atypical, non chemical discoveries (i.e., platinum)
- Analytical "losses" in gravimetric analysis
- Communication problems and preceding claims of discoveries
- Faulty interpretation of experimental findings leading to spurious discoveries
- Dubious attitude and insecurity vs. the interpretation of new findings
- The dogmatic weight of consecrated "authorities" in chemistry
- Nomenclature problems and controversies vs. the naming of new elements
- Specific objective experimental difficulties (unstable elements, families or pairs of elements of very similar chemical behaviour, scarcity of elements in nature, etc.) leading to frequent confusion
- Rediscovery of elements
- Confusion of oxides and earths with their metals
- Revision of established discoveries as derived from indirect inferences of anomalous elemental behaviour vs. well-established chemical or physical laws
- Overlooking or misinterpretation of experimental findings

Such a long enumeration of potentialities of incidence on the discovery of chemical elements has given rise to a wide acumulation of curiosities, incidences, and anecdotes in the history of element discovery. For illustrative purposes a few interesting facts will be briefly abstracted and recalled here, while others will appear later below:

- the discoveries of Nb and V were seriously hampered by the "authorities" of Wollaston and Berzelius, respectively
- Klaproth thought to have isolated uranium as metal erroneously since he had characterised it as an oxide, Regnault pointed out the deviations exhibited by the "metal" towards Dulong-Petit's law. Peligot revised Klaproth's discovery finding that it was uranium oxide obtaining finally the pure metal by reduction of uranium chloride with potassium (1841)

- Analytical "losses" detected occasionally in the gravimetric analysis of different minerals and ores allowed for the discovery of new elements. Such was the case for Ti (Gregor 1791), Li (Arfwedson 1817) and Ge (Winkler 1886). However, the scientist who detected the analytical "losses" was not always the discoverer of the responsible elements: Vauquelin detected the "Li-loss" in spomudene in 1801 while Plattner observed the "Cs-loss" in 1846 in a sample of polux of Elbe. The glory of identifying such "losses" was reserved however for Arfwedson and Bunsen/Kirchoff (1861), respectively
- The painstaking discovery of hafnium by Coster/Hevesy (1923) mandated the revision of the atomic weight officially established for Zr about one century before because of contamination of Zr by Hf as impurity

Nomenclature problems with the chemical elements

To rationalise systematically the naming of new elements Lavoisier suggested to name new elements based on their most representative and characteristic physical or chemical properties which led to the establishment of an specific commission of nomenclature in Paris. Such suggestion resulted in important errors, especially in the case of oxygen [40]. The establishment of chlorine [41] and iodine [42] as elements as well as some etymological and lexicographic corrections raised against Lavoisier's proposals led to other suggestions. Klaproth was the principal opponent being followed by a great number of chemists, among them Berzelius. More liberal and less compromising criteria were defended by Klaproth which led very quickly to the naming of new chemical elements on a variety of criteria: mineralogical (Be, Ca, Ba, Mo, Zr, Cd, Si, Al, Li), astronomic (Se, Te, U, Ce, Pd), mythologic (Ti, Nb, Ta), localities where minerals were found (Sr, Y, Er, Tb, Yb, Mg), properties of the elements or of their compounds (Cr, Rh, Os, Ir, Br, Cl, I), nations and cities (Sc, Ge, Fr, Ho, Hf, Bk, Cf), continents (Eu).

Of special historical interest is the fact that Berzelius opposed naming elements after persons. This recommendation has been ignored but exclusively for nonliving scientists (Es, Fm, Md, No). At the present time a harsh polemics has been raised on this matter between outstanding national and international institutions of chemistry on the naming of some superactinides after persons, even those still alive.

The nomenclature problem related to nitrogen caused countless controversies and discussions until finally Chaptal suggested in 1790 the actual name. However, "azote" and "azotic acid" (nitric acid) persisted over most of the 19th c. using the Az symbol for nitrogen in the French literature.

Some other historical inconsistencies subsist nowadays (i.e., the symbol of iodine often appears as J in German and Russian literature; W is named as wolframium or tungstene depending on countries; the halogen elements exhibit different terminations in English literature vs. European continental literature, etc.).

Past are the days where anarchical chaos of trivial names directly derived from alchemic habits existed as illustrated in Table 3. However, the nomenclature problem has not been overcome so far as witnessed by the strong controversies of the last few years which seem to be a revival of the historic controversies of the beginning of the 19th century. A number of interesting and curious facts of historical significance have been gathered in Tables 4 and 5 which are related to priorities and naming of chemical elements [43], the formulation of

Table 3 Typical nomenclature related to the discovery of gaseous elements in the pneumatic period of chemistry

Year of discovery	Official discoverer	Element	Denominations
1771	Scheele	Oxygen	"fire air", "igneous air", "vitriolic air" (Scheele); "deflogisticated air" (Priestley); "oxygine", "vital air", "empireal air", "eminently breathable air" (Lavoisier); "fatty acid" (Wenzel); "air nitro" (Hooke); "volatile niter" (Boyle); "nitroaerial spirit", "spirit of the world" (Mayow); "pure air" (Bergman); "elastic fluid" (Bayen); "pirogen" (Chavaneau); "arxikayon" (Arejula); "comburent" (Porcel y Aguirre)
1772	Rutherford	Nitrogen	"fixed, unbreathable, unhealthy, harmful air" (Rutherford); "putrid, filthy air" (Scheele); "mephitic air", "nitric flogisticated acid" (Cavendish); "flogisticated air" (Cavendish, Priestley); "nitrificated air" (Mayow); "foul air" (Bergman); "alcaligen" (Fourcroy); "amoniagen", "nitrigen" (Porcel y Aguirre); "azote", "mofette" (Lavoisier); "septon" (Mitchell); "azoe" (Arejula); "azotikos" (Dirgart, Remy)
1774	Scheele	Chlorine	"deflogisticated muriatic/marine acid" (Scheele); "oxymuriatic acid" (Lavoisier); "oxygenated muriatic acid" (Berthollet); "halogenium" (Schweiges)
1776	Cavendish	Hydrogen	"inflammable, combustible air" (Cavendish); "facticious air" (Boyle); "aqueous inflammable principle" (Lavoisier); "inflammable vapour" (Lomonosov); "hydrogine" (Lavoisier); "hydrium" (Goryanov); "protyle" (Prout)

Table 4 Priorities in the discovery of chemical elements (selected examples)

Year	Element	Official discoverer	Remarks
1669	P	Brand	Appropiation of the discovery was attempted by Kunckel
1751	Ni	Cronstedt	Identity controversies lasted over 20 years
1771	O_2	Scheele	Discovery attributed long time to Priestley who discovered it independently (1774) but published it in 1775, secondly and shortly after Lavoisier while Scheele's publication appeared in 1776
1772	N_2	Rutherford	Obtained independently and about the same time by Scheele, Priestley, Cavendish and Hales
1782	Te	Müller	Published obscurely the discovery was ignored for 16 years, Kitaibel rediscovered it (1789). Klaproth confirmed the discovery, recognized honestly Müller's priority and named the element
1791	Ti	Gregor	The discovery did not transcend. Rediscovered and named by Klaproth in 1795 acknowledging Gregor's priority
1797	Cr	Vauquelin	Discovered independently by Klaproth somewhat later in the same year
(1801)	V	Sefström	Discovered by del Rio in 1801, he retracted shortly afterwards by a number of reasons. Rediscovered in 1831 by Sefström
1801	Nb	Hatchett	Refuted by Wollaston who thought it to be identical with tantalum discovered one year later by Ekeberg. It took several decades to establish the identity of both elements
1803	Ce	Hisinger Berzelius	Discovered independently by Klaproth in the same year
1808	B	Gay-Lussac Thénard	Discovered the same year independently by Davy by a different method, who published it 9 days later than the French chemists
1823	Si	Berzelius	Discovered independently in 1808 by Davy and Gay-Lussac/Thénard who overlooked the discovery
1825	Al	Oersted	Discovery long time credited to Wöhler who rediscovered it in 1827. Oersted's finding did not transcend as derived from its publication in a Danish journal
1826	Br	Balard	First obtained by Liebig who misinterpreted the finding. Löwig obtained it in 1825 but published later than Balard
1907	Lu	Urbain	Obtained by Auer same year but published later than Urbain
1925	Re	Tacke Berg	Identified independently on the same year by Heyrovský/Dolejšek (polarography) and Loring/Druce (X-rays)
1937	Tc	Sergé Perrier	Discovery claimed in 1925 as "masurium" by Noddak, Tacke and Berg in uranium minerals

Table 5 Metaphysical principles and spurious discoveries of elements

1. Theoretical phantasies

1789: Lavoisier postulated the existence of caloric and of the muriatic, fluoric and boracic radicals
1800: Winterl developed a theory of two protoelements, one male ("Andronia"), the other female ("thelyke")
1865: Schoenbein, theory of "murium", theory of "ozone-antiozone"
1887: Crookes, theory of "metaelements" built up from "protyle"
1895: Stoney, theory of the "infraelements"
1897: Rydberg, astral theory assuming the existence of "nebulium or nebularium"
1900: Lockyer, theory of "protometals" such as "archonium", "asterium", "asturium"
1902–1904: Mendeleev, theory of the "chemical ether" (elements "newtonium", "coronium")
1907: Morosov, theory of protoelements ("anodium", "catodium", "archonium")
1912: Wegener, assumption of the existence of "geocoronium"

2. Experimental discoveries of fictitious elements

1781: Bergman, two new elements, "siderium" and "hydrosiderium"
1785: Ruprecht, announced the discovery of "austrium"
1802: Proust, discovery of "silen" (in fact rediscovery of uranium)
1803: Berzelius, discovery of "gahnium" and "thorine"; assumed the existence of the hypothetical radical "nitricium"
1806: Sniadecki, discovery of "vestium" (ruthenium?)
1904: Baskerville, discovery of "carolinium" and "berzelium"

false theories and the announcement of amazing discoveries of new elements [44–47] to end with some intoxications, accidents and death casualties suffered by chemists from laboratory work carried out during the discovery of new elements.

There are but hundreds of similar "findings" the details of which can be found elsewhere [44–47]. Brief mention will be made to the especially productive periods of the discovery of certain elements which posed very great analytical problems related to their separation and identification.

Table 6 Incidences and accidents related to discovery of chemical elements

1) *Intoxications*

Scheele: repeatedly intoxicated by careless work with Hg, As, AsH_3, HF, HCN, H_2S (he used to smell and taste any chemical)

Gay-Lussac, Thénard: intoxicated by HF

Davy: intoxicated by HF, Cl_2, N_2O_3

Woehler: seriously intoxicated by HF was obligated to retire from laboratory work several months this fact preventing him to rediscover vanadium before Sefstroem

Saint-Claire Deville: frequently intoxicated by osmic acid

Moissan: several intoxications by HF, F_2 and CO

Priestley, Woodhouse: seriously intoxicated by CO

Chruickshank: grave intoxications by CO and phosgene

G. Knox: obliged to retire from laboratory 3 years (HF, F_2 intoxications)

2) *Serious accidents*

Dulong: Lost an eye and suffered grave hand damage by explosion (NCl_3)

Davy: Endured grave vision and hand damage by explosion (NCl_3)

Ekeberg: lost and eye by explosion of a matrass held in his hands

Gay-Lussac: nearly lost his vision from an explosion

Bunsen: escaped barely to death loosing an eye by explosion investigating cacodyl cyanide

Aartovara: suffered serious sight damage by explosion while investigating on francium

Demarçay: lost an eye by explosion of an iron vessel while investigating nitrogen sulphides under high pressure

3) *Death causalities*

J. G. Lehmann: died by the explosion of a retort heating arsenic while investigating chromium minerals

T. Knox, P. Louyet, J. Nickless: died from HF and F_2 intoxications

4) *Radiation damage*

M. Curie, I. Joliot-Curie, Perey: developed fatal cancers from excess radiation exposure

Remarks: No reliable records are available on damage by X-ray and radioactive expositions at the beginning of the century which presumably affected to a greater or lesser extent to a number of physicists and chemist working on the discovery of new chemical elements

Such was the case with the platinum group, although ironically platinum itself, introduced by 1848 by Ulloa from South America did not pose any analytical problem at all in its discovery but only afterwards in connection with its purification and mechanization. Brief mention will be made only about some of the many spurious discoveries related to new elements of the platinum group [45] such as “vestium, vestalium, polinium, pluranium, davyum, ilmenium, neptunium, amarillium, canadium, nigrium, norium, nipponium, jargonium ...”.

It went much worse with the rare-earths, today humoristically considered neither rare nor earths, and the lanthanide elements were first characterized as their oxides or “earths”, not as metals. Among the profusion of exotic names devoted to the discovery of new elements of this family the following may be quoted [46, 47]: “monium, victorium, delta, gamma, zeta, omega, philippium, rogerium, welsium, wasmium, denebium, dubium, euxenium, glaucodimium, incognitum, decipium, demonium, mosandrium, russium, metacerium, damarium, lutium, carolinium, berzelium...”. A humoristic touch into such an anarchy of discoveries and impressive denominations was expressed by Kosmann who ridiculed such a trend of incontinency by announcing the discovery of two new elements, “kosmium and new-kosmium” directly associated with his own name within the best satiricals spirit to commemorate “Fool’s day” in 1896 [48].

Highlights in the discovery of the elements

A summary of the chronological evolution of the number of elements discovered is presented in Table 7 under consideration of significant years of special interest for the history of chemistry.

Some important aspects and curious incidences related to the discovery of missing elements in the period 1913–1925 are summed up in Tables 8 and 9 while Table 10 details the actual controversy for the naming of transactinide elements. The problems related to the nomenclature of new chemical elements as well as possible criteria to deal properly with the matter have deserved a lot of attention, especially after the discovery of the transuranium elements [49, 50] as well as at the present time in connection with the controversies for the naming of the superheavy elements, beginning with element 104 and going up to element 109. In the meantime two new elements, 110 and 111, have been claimed to be discovered by the Darmstadt group working on high-energy physics. The different suggestions for the naming of these elements are reproduced in Table 10.

The year 1913 presented the availability of a new identification tool by introduction of X-rays together with Moseley’s law which proved extremely useful in connection with Bohr’s atomic model both for the organization and completion of Mendeleev’s empiric periodic system.

Table 7 Highlights in the historical evolution of the discovery of elements

Year	Remarks
1669	Accidental discovery of phosphorous by Brand. First element associated with a known discoverer. So far 14 elements known from antiquity and Middle Age had been commonly used
1735	Discovery of cobalt by Brandt
1748	Platinum is introduced in Europe by Ulloa. First element discovered in America
1751	Discovery of nickel by Cronstedt. Controversies extended over two decades until the identity of the new element was finally confirmed by Bergman in 1775
1789	Lavoisier's tabulation of 33 simple bodies, 23 of them were true elements (Zr, Hf discovered the same year were omitted)
1815	Berzelius tabulated the atomic weights of 43 elements from a total of 48 known at the time
1869	First Periodical Table by Mendeleev including 64 elements
1900	82 elements known including 6 nobles gases and 4 radioactive elements (Ra, Po, Rn, Ac)
1913	Moseley's law. 85 known elements. 7 missing elements in Mendeleev's periodical system (Nrs. 43, 61, 72, 75, 85, 87, 91)
1925	Completion – after the discovery of Re and Hf – of the natural stable elements. 4 elements were still missing
1950	98 elements known. Some of them unstable, obtained by nuclear synthesis artificially. Mendeleev's table became extended after the discovery of Np and Pu in 1940 and 1941, respectively
1995	The discovery of element 111 is announced by the GSI group (Darmstadt)

Table 8 Some aspects related to the discovery of the three last natural elements

Atomic number	Element	Discoverer(s)	Year	Remarks
91	Pa	Hahn/ Meitner	1918	Mendeleev's "Eka-Ta". Fajans and Göring characterized "UX_2" or "brevium" which corresponds to $^{234m}_{91}$Pa. Soddy and Craston discovered Pa independently from Hahn and Meitner. Suggested denominations: "lisonium", "lisotium"
72	Hf	Coster/ Hevesy	1923	Element search orientated by Bohr in Zr-minerals. Urbain claim in 1911 for this element as "celtium" was demonstrated by Moseley to be unfounded (X-ray identification). Instead Urbain had rediscovered Lu, discovered by himself in 1907 just before Auer. Spurious discoveries: "jargonium", "nigrum", "norium", "nipponium" "Tm-II"
75	Re	Noddack/ Tacke/Berg	1925	Mendeleev's tri-, dvi-Mn. Discovered independently the same year by Heyrovsky, Dolejšek (polarography) and Loring, Drude (X-rays). Spurious discoveries: "pragium", "neotungsten", "uralium", "canadium", "josephinite"

Table 9 Some aspects related to the discovery of the four missing elements

Atomic number	Element	Discoverer(s)	Year	Remarks
43	Tc	Ségre/Perrier	1937	First artificially man-made element. Mendeleev's "Eka-Mn". Spurious discoveries as "ilmenium", "lutium", "masurium", "davyum", "nipponium"
87	Fr	Perey	1939	Mendeleev's "Dvi-Cs". Meyer, Hess and Panneth claimed its discovery in 1914 but the outburst of 1st World War hindered its verification. Allison and Murphy claimed its discovery as "virginium". Papish and Wainer obtained spectroscopic evidence of the element in 1931. Spurious discoveries as: "alcalinium", "moldavium", "russium". The element was first named by its discoverer as "Ac-K" who attempted to coin the name "catium", as the most electropositive element
85	At	Corson/MacKenzie/ Segré	1940	Mendeleev's "Eka-I". Spurious discoveries as "alabamium", "anglo-helvetium", "austrium", "dacinum", "helvetium", "leptine"
61	Pm	Marinsky/Glendenin/ Coryell	1945	Corresponds to "Eka-Nd". Spurious discoveries as "cyclonium", "illinium", "rigium", "florentium"

Table 10 Nomenclature situation on the transactinide elements

Element	Proposed names	Symbol	Suggested compromise [64]
104	Rutherfordium (US)	Rf	
	Kurchatovium (Russia)	Ku	
	Unnilquadium	Unq	
	Dubnium (US)	Db	Dubnium
105	Hahnium (US)	Ha	
	Nielsbohrium (Russia)		
	Unnilpentium	Unp	
	Joliotium (IUPAC)[a, b]	Jl	Joliotium
106	Seaborgium (US)	Sg	Seaborgium
	Unnilhexium	Unh	
	Rutherfordium (IUPAC)	Rf	
107	Nielsbohrium (Germany, US)	Ns	Nielsbohrium
	Unnilseptium	Uns	
	Bohrium (IUPAC)	Bh	
108	Hassium (Germany, US)	Hs	
	Unniloctium	Uno	
	Hahnium (IUPAC)	Hn	Hahnium
109	Meitnerium (Germany, US)	Mt	Meitnerium
	Unnilenium	Une	
	Meitnerium (IUPAC)	Mt	
110	Ununnilium	Uun	
111	Unununium	Uuu	

[a] This denomination is used alternatively by russian scientists for nobelium

[b] The IUPAC recommendations are still provisional

Three new elements were discovered in the 1913–1925 period from the seven ones still missing to complete the periodical system. Such new discoveries were bound to considerable experimental difficulties which resulted in rediscoveries, false discoveries and priority questions as summed up briefly in Table 8.

A few additional comments can be made about Table 8. By 1925 came the end of the “heroic epoch” of pure chemical analysis when all the natural elements were finally identified. A lot of difficult analytical work involving very tedious separations and problematic identifications of chemically very akin elements (Zr–Hf, rare-earths group) or of elements lacking specific minerals and of scarce abundance was done as was the case with rhenium. There remained 4 voids in the periodical system which could not be filled by chemical means exclusively. Hypothesis and predictions were made both to justify the absence in the earth of such elements as well as to account for the means to find them some way. After 1913 a new powerful means was available through Moseley’s law and the generalization of X-ray spectroscopy for identification purposes which were decisive for the discovery of Hf and Re.

The chemical stalemate was overcome in the following years by the development of ultramicroanalysis. However, many pitfalls had to be circumvented to discover the four missing elements as seen by the abundance of false discoveries and proposals of curious nomenclature as summed up briefly in Table 9.

The first historical problem of accomodation of a series of elements into Mendeleev’s periodic system was posed by the rare-earth-group [28, 47, 50]. A similar problem appeared several decades afterwards which was brilliantly solved by Seaborg for the transuranium elements [51–54]. The actual problems related to the transactinide, superactinide or superheavy elements are quite great as derived from their difficult nuclear synthesis, their equally difficult identification and finally their nomenclature. In addition to many individual points of view the actual controversies involve the IUPAC, ACS, GSI and Russian Dubna teams and institutions [55–63]. The result is an international group of chemists is producing a compromise on element names [64]. The actual situation of the question is detailed in Table 10.

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