Lead kindly light: spectroscopy and the periodic table

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Spectroscopy, in the visible as well as X-ray regions, played a significant role in putting the periodic table on a firm footing. This article provides a few glimpses of this aspect.

Introduction

THE first part of the title that I have chosen is actually the title of a well-known poem from the 19th century poet John Newman. Its Kannada version by the erudite professor, B. M. Srikantaiah, is quite popular too. In fact, it is light, rather the wavelength discrimination of light or spectroscopy, which helped greatly in discovering an entire group of elements as well as identify the proper parameter to form the basis for the periodic table. This article looks at a few champions who contributed significantly to deploy spectroscopy for the identification of elements.

Bunsen and Kirchoff

The spectacular colours in fireworks are a matter of chemistry. A judicious and carefully chosen combination of elements and compounds used, and incandescence, which is a function of temperature, is responsible for the vivid colours. There are documented records, which clearly indicate that at least by 14th century, mankind, specifically the Chinese, had a good knowledge of the recipes of chemicals needed to be added to gunpowder to realize a whole span of colours. For example, strontium and lithium salts produce red, while copper compounds are responsible for the blue colour. Of course, in the modern world we certainly have extremely well developed correlation between the metal and the colour. Alkalies and alkaline earths are among the strong favourites.

Better understanding of the correlation is due to the work by Robert Bunsen, of the Bunsen burner fame, and Gustav Kirchoff. Bunsen's primary research aim was to study the colour emitted by different elements when heated to high temperatures, and establish photometric standards. However, his observation was that the burners prevalent then were giving a sooty flame burning yellow or orange, which makes them not suitable for the purpose at hand, as the yellow incandescence from the carbon atoms heated to a high temperature, would mask all other effects. Thus, there was a need for a flame with very little soot. The solution was to provide the system with copious amounts of oxygen by having a controllable vent. The design by Bunsen and the mechanic at University of Heidelberg, Peter Desaga, created an essentially colourless, non-sooty flicker-free flame[1], producing temperatures as high as 1500°C. Bunsen used the new burner quite effectively to be considered as the first person to systematically study the emission spectra of elements. Detecting an unknown blue spectral line produced by mineral water he isolated the then unknown caesium (Latin, for deep blue), after distilling 40 tonnes of water to get 17 grams of the new element[2]. His contributions[3], important but qualitative, were given a new dimension through the collaborative effort brought by his colleague Gustav Kirchhoff[4] through experimentation in the form of a new scientific field of analytical spectroscopy, and concepts in the form of the three laws of spectroscopy, which consider three cases (see Figure 1) as in the following.

Case 1: A luminous solid, liquid or dense gas emits light of all wavelengths (a continuous spectrum).

Case 2: A low density, hot gas in a cooler background produces a bright-line or emission line spectrum.

Case 3: If this low-pressure cool gas in front of a hotter source emits a continuous spectrum then it produces dark line or absorption line spectrum located at the same wavelengths, which would be bright lines in case 2 mentioned above.

The interesting point to note is that the wavelength of the emission or absorption lines depends on atomic/ molecular composition of the gas and its temperature. Applying the three empirical laws to the celestial situation of a cooler gas surrounding the Sun, and observing a continuous spectrum interspersed with dark lines, a feature that Fraunhofer had earlier seen, Kirchoff concluded that the spectrum is due to the presence of the element sodium. This became an important turning point in observation astronomy to establish with confidence the composition of celestial objects and clouds of gas millions of light years away[5].

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Ramsay and Rayleigh

This story is about the efforts that went in to establish what used to be referred to as inert gases. At least in Mendeleev's times identification of an element was tough. A practical way of going about it was to look for the chemical reactivity of the suspected element. Thus, imagine the plight of someone trying to identify an element, which does not react at all. Two people get the credit for this: Sir William Ramsay and Lord Rayleigh, who shared the Nobel Prize in 1904 for their work. The story seems to have begun on an innocuous note. On 19 April 1894, Ramsay attends a lecture at the Royal Society. John William Strutt, better known as Lord Rayleigh, would be speaking on the composition of air. Concluding the talk, Rayleigh quotes a recent publication of his[6] and concludes, 'I am much puzzled by some recent results as to the density of nitrogen, and invite suggestions as to the cause'. The puzzle that he was talking about was about the substantial difference in the density of nitrogen synthesized in the lab and that isolated from air. The difference was small, 0.1%, but being a good experimenter he was confident that it was beyond the errors, and suspected it be due to a lighter impurity in the synthesized sample. Ramsay who was in the audience, and would have studied notes of Cavendish on similar experiments conducted a century ago, makes a cryptic remark that it could be the opposite as well that the atmospheric sample contains a heavier impurity. They decided to work together. Indeed, with single-minded determination within four months Ramsay proved his point by isolating a new and heavier gas from the atmospheric sample. In a letter to Rayleigh[7] on 4 August 1894, he said, 'I have isolated the gas. Its density is 19.075, and it is not absorbed by magnesium ...'. Two days later Rayleigh replied, 'I too have isolated the gas, though in miserably small quantities'. Within a week, they announced to the British Association for the Advancement of Science meeting in Oxford, the existence of the new gas. H. G. Madan, a chemist present in the meeting suggested[8] naming it Argon, from the Greek word *αεργον*, to mean idle, indicating its predominantly non-reactive character.

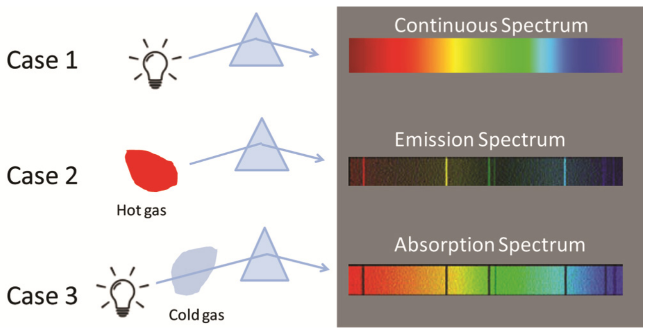

Figure 1. Schematic illustration of the Kirchoff's laws of spectroscopy. The three cases are described in the text.

Much later, gases such as Argon come to be known as Noble gases. However, as would happen to many a discovery, there were sceptics including the Master, Mendeleev, as argon did not fit into any of the columns of his table arranged as per the automatic weights and identified by chemical reactivity. Spectroscopy again comes to the rescue, in the form of help from Sir William Crooks providing the undeniable proof that Ramsay and team were looking for. As a mark of confirmation of their observations, on 31 January 1895 Ramsay gave a talk to the Royal Society with the interesting title, 'Argon, a new constituent of the atmosphere'[9]. Nevertheless, Mendeleev was unconvinced and remained so for another seven years.

Ramsay continued working in this field and discovered four other noble gases. The first such was also the first alien element, i.e. found first not on earth, but in space. The developments in this regard have an Indian connection, although in a tangential way. Funded by the French Government, and in his quest to unravel the chemical composition of the universe, Pierre Janssen, a French astronomer did investigations during eclipses, and thus came all the way with his spectroscope to Guntur in India, for the total solar eclipse of 18 August 1868. He detected a bright yellow line (the D3 line, to distinguish it from the D1 and D2 lines of sodium) in the spectrum of the solar chromosphere whose wavelength did not match with any known element, and had no corresponding Fraunhofer line. Although the spectrum was quite similar to that for sodium, it was markedly distinct enough to be considered as from a new element. Around the same time, an English astronomer, Norman Lockyer, also reported a similar observation and even named it Helium, Helios meaning Sun. Interestingly, Luigi Palmieri, a professor at the University of Naples, while analysing, using a Bunsen burner, the lava material collected from the volcanic site of Vesuvius which erupted in 1881, found the same D3 line. Despite these, and numerous other attempts, it finally comes to our chemist hero, Ramsay, to put his stamp of authority after isolating it from the mineral clèveite, and again with the spectroscopy evidence from Crooks. The event is well summed up by Lockyer in his Presidential Address to the Vesey Club on 12 November 1895 published a year later in *Nature*[10]: '…[T]he twenty-six-year-old helium had at last been run to earth. D3 was at last visible in a laboratory.' A second Indian connection to the story of Helium came in the form of a news item in *Journal of Chemical Education* titled 'Production of helium from monazite', mentioning the source of the mineral as the sands of Kerala[11]. An exhaustive and well-told account of the folklore and reality unfolding the discovery of helium, is given by Biman Nath[12]. It is worth emphasizing that this entire effort was possible primarily due to the spectroscope of Kirchoff.

Ramsay's team was working at an amazing pace, and were already a name owing to Argon and Helium. In fact, while the discovery of a new element is a rare event, in a matter of four months (June–September 1898) this team added three more elements – neon, krypton and xenon – to their basket. It is as if a matter of courtesy they left radon, the last one to make this group of naturally occurring noble elements to Friedrich Dorn. What must be emphasized is the discovery of each of these Group 8 (now Group 18) elements was an uphill task: These are all inert (or at best, weakly reacting) gases, becoming liquid or solid at extremely low temperatures, colourless, odourless, tasteless, and most importantly, having an extremely small content in air[13], from which most of them were isolated. It may be relevant to recall that throughout this work on noble gases, Ramsay's team gained significantly owing to the tenacity of an young researcher – Morris William Travers – who in 1906, on the recommendation of Ramsay, gets appointed as the first Director of the Indian Institute of Science.

Henry Moseley

Comparison of the periodic table prepared by Mendeleev and the modern one brings out a primary difference: the parameter used for the classification itself is different. This story is about a young man who was responsible for that.

When this young man, Henry Moseley, entered the field, X-rays and their interaction with matter had just become a hot topic: Laue's diffraction of X-rays by inorganic compounds, Reflection of X-rays by crystals, The Bragg's law, etc. A parallel development took place by Barkla and Rutherford showing nuclear charge is approximately equal to 1/2 the atomic weight of the element, which was then the basis for the arrangement of the periodic table. When Moseley joins the group of Rutherford teeming with young talents (Geiger, Darwin, Chadwick ...), he was assigned a research project on radioactivity. Even though Moseley was more interested to work on X-rays, Rutherford would not relent. Finally, the young man gets a break when William Henry Bragg invites him to the University of Leeds where he was taught the nitty-gritty details of working with X-rays. Several things happened around the time, which help Moseley in his work. He received a suggestion from Niels Bohr, that the degree of scattering of X-rays might be proportional to atomic charge rather than to the atomic weight. A second piece of information came from an unexpected corner, in the form of Dutch economist and amateur scientist, Anton van den Broek, who proposed (i) a new fundamental particle, Alphon, charge +1, mass of two units, (ii) arranging PT not on the basis of atomic weight, but by Alphon, (iii) each element to differ from the preceding one by +1 charge[14]. Employing atomic weight as the basis also gave rise to the problem of *pair reversals*: The first element in the pairs of Ar and K, Co and Ni, Te and I, has its atomic weights higher than those of their pairs. However, if one is guided by the chemical properties, their place in the Table had to be flipped.

With this background, Moseley started his experiments by making important modifications to the X-ray spectrometer designed by Bragg. Figure 2 shows a schematic representation of his apparatus[14], in which a potassium ferrocyanide crystal grating takes the place of the prism in an optical spectrometer. As his interest was to study a number of elements, the earlier design of the apparatus posed a problem. The vacuum of the glass bulb had to be broken every time a new sample had to be placed. Since vacuum pumps were time shared, this method was a handicap, which made Moseley come up with a brilliant design of a sample train so that by operating bobbins at the two ends of the train he could conduct experiments on several samples without the need for breaking the vacuum. The experiment involved bombarding the sample contained in the glass vacuum tube with electrons, and capturing the emitted X-ray photons on a photographic film placed outside the vacuum tube, to obtain spectral lines, similar to the Kirchoff spectral lines, characteristic of the target employed. In this pioneering usage of combining his new technique with Bragg's law, Moseley analysed, in a matter of a few months, the X-ray spectra associated with as many as 45 elements spanning from aluminium to gold[15]. The analysis led him to discover a simple but astounding correlation, a law that now carries his name. He found that the square root of the frequency of the reflected X-rays was proportional to $Z - 1$, with Z being an integer representing the charge on the nucleus of the atoms in the element used as the target. Thus, in one stroke, the charge on the nucleus, or more specifically the number of protons or atomic number got its status changed from an inconsequential serial number in a table to one that should be – instead of the atomic weight – indeed the metric for the classification. The modern periodic table was born. Besides this achievement of fundamental importance, Moseley's law also solved many puzzles of the Mendeleev's version, including pair reversals, the existence of Group 18 for noble gases. It also enabled Moseley to identify precisely the gaps in the periodic table, anticipating the presence of

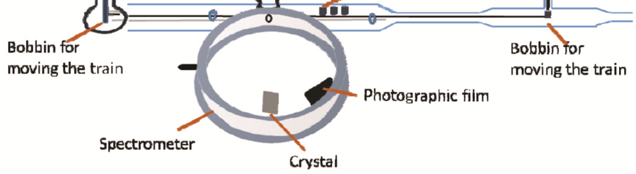

Figure 2. Schematic representation of the X-ray spectrometer used by Moseley (redrawn from ref. 9).

elements with atomic numbers 43, 61, 72 and 75. The power of the analysis is amply demonstrated in the fact that the prediction has come true with the subsequent discovery of technetium, promethium, hafnium and rhenium. The importance of his contributions can be judged from the fact that there have been speculations that Moseley would have got the Nobel Prize in 1916. Alas, tragedy struck in the form of the First World War. Moseley, volunteered to join the army (Royal Engineers), got posted to the Turkish front of Gallipoli, where he took a bullet in his head to breathe his last at a young age of 27 years. Truly, it is a loss, not only for his family, country, but also to the scientific world as a whole.

Postscript

Spectroscopy has made many more advances since these phenomenal efforts. For example, energy-dispersive X-ray spectroscopy (EDS or EDX) is specifically appreciated by the pharma industry and practitioners of nanoscience serving as an inseparable part of the characterization methods. A nagging question about the periodic table has been whether there is an upper limit to the number of elements. Richard Feynman is supposed to have put forward an argument that an element with an atomic number of 137 should be the last[16]. Viewed together, the Bohr's model and Einstein's theory of relativity also support this. However, the last word on this is yet to be out[17,18]. Certainly spectroscopy would be playing an important role in the identification of such elements.

I would like to end on a sober note: Nature has been expertly playing this correlation between the element and the colour emitted. The spectacular display of colours that occurs at the north and south poles, referred to as Aurora Borealis and Aurora Australis respectively, is caused by the particles discharged from the Sun travelling towards Earth before drawn overwhelmingly toward the magnetic poles. While passing through the Earth's magnetic shield, they mix primarily with oxygen and nitrogen lighting up the sky with different shades and hues of colour. While interactions with oxygen give out yellow and green, with nitrogen red, violet, and occasionally blue are produced.

1. Bunsen, R. and Roscoe, H. E., *Poggendorff's Ann. Chem. Phys.*, 1857, **100**, 43. An interesting account of the story behind the creation of this burner is given in W. B. Jensen. *J. Chem. Ed.*, 2005, **82**, 518.
2. It may be mentioned owing to its long half-life (~30 years), the radioactive isotope caesium-137 caused much concern during nuclear disasters like the one that occurred in Chernobyl in 1986.
3. Apart from discovery of Caesium and Rubidium, he also found that addition of iron oxide hydrate to a solution having arsenic dissolved precipitates the poison, rendering it harmless. This serves as an antidote for arsenic poisoning even in modern times. As a token of appreciation of Robert Bunsen's contributions, Google ran a doodle on his 200th birthday, 31 March 2011, in which the Burner found a prominent place.
4. The electrical engineers know him better for his laws of circuit analysis. It is amazing that he came up with this quite profound analysis when, as a student, he was asked to give a seminar. In fact, his laws of thermochemistry are also well known.
5. Kirchhoff coined the term *black body* to describe a hypothetical perfect radiator that absorbs the entire incident light and emits all of that light when maintained at a constant temperature.
6. Rayleigh, Density of nitrogen. *Nature*, 1892, **46**, 512.
7. A detailed account of the life and works of Sir William Ramsay can be found in A. G. Davies, *Science Progress*, 2012, **95**, 23; doi:10.3184/003685012X13307058213813.
8. Williams, R., Lord Rayleigh and the Discovery of Argon: 13 August 1894; This Month in Physics History. *APS News*, 2013, **22**(8).
9. Lord Rayleigh and Ramsay, W., Argon, a new constituent of the atmosphere. *Philos. Trans. R. Soc. London*, 1895, **186**, 187.
10. Lockyer, J. N., The story of helium: chapter II. *Nature*, 1896, **53**, 321; 342.
11. Production of helium from monazite. *J. Chem. Edu.*, 1930, **7**, 1596; doi:org/10.1021/ed007p1596
12. Biman Nath, *The Story of Helium and the Birth of Astrophysics*, Springer, 2013.
13. The content in air of these elements are, Ar: 0.93%, He: 5 ppm, Ne: 18 ppm, Kr: 1 ppm, and Xe: 0.09 ppm.
14. A well illustrated diagram of Moseley's apparatus is given by Jim and Rhoda Morris in http://www.scitechantiques.com/Mosley_atomic_number/; also see Scerri, E., 'Master of Missing Elements' *Am. Sci.*, 2014, **102**, 358; doi:10.1511/2014.110.358; a documentary video 'The Mystery of Matter' https://www.youtube.com/watch?v=GWQZE0HPoAY.
15. Moseley, H. G. J., The high frequency of spectra of the elements. *Philos. Mag.*, 2013, **26**, 1024; https://web.lemoyne.edu/~giunta/Moseley-article.html
16. Kutzleman, T., The Search for the Final Element. https://www.chemedx.org/blog/search-final-element
17. Nazarewicz, W., The limits of nuclear mass and charge. *Nature Physics*, 2018, **14**, 537; doi:10.1038/s41567-018-0163-3.
18. Ball, P., Extreme chemistry: experiments at the edge of the periodic table. *Nature*, 2019, **565**, 552; doi:10.1038/d41586-019-00285-9.

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