

H. G. J. Moseley; the Scientist Who Put the Z in ZAF (and k_{AB}).

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A century ago, a graduate research assistant performed a brilliant series of experiments showing that the wavelengths of emitted X-rays were proportional to Z , the atomic number of the elemental source. Hitherto, from 1869 when Mendeleev first presented his periodic table, the atomic weight, A , was assumed to be the defining characteristic of each element. Ninety-nine years ago on August 10, 1915, that scientist was killed by a sniper's shot to the head during the Gallipoli campaign, an event Isaac Asimov described as "*the most costly single death*" [1] of the ~20 million that occurred in World War I.

That scientist was Henry Gwyn Jeffries Moseley, known to all as Harry. In 1913 he had started his research at the University of Manchester, having first spent time "*teaching elements to idiots*". During his prior undergraduate years at Trinity College, Oxford, "*most of the time Harry spent with Trinity men was on the river and in the debating society*". Perhaps as a consequence he had left Oxford with a second-class degree, which he saw as a "*failure*". However, he was in the right place at the right time, working in Rutherford's group at Manchester, the university founded on the work of Dalton and Joule.

"*We find that an X-ray bulb with a platinum target gives out a sharp line spectrum of the wavelengths*" he wrote to his mother on May 18, 1913. "*Tomorrow we search for the spectra of other elements. There is here a whole new branch of spectroscopy*". How right he was! Similar work was being performed by William Henry Bragg in Leeds and Maurice de Broglie (older brother of Louis) in Paris. The latter two focused attention on the X-rays, not what they revealed about the target. The important difference was that all the work in Manchester was on atomic structure, not on X-ray physics. Rutherford had gathered the dream team including Geiger (whose key experiment with Marsden, then an undergraduate, revealed the importance of the nucleus and the atomic number), Darwin (grandson of Charles and known to the TEM community through the Darwin-Howie-Whelan equations) and Chadwick (later of neutron fame). Late in 1913, Harry decided to measure the K X-rays that were known to gain in hardness (frequency) regularly and almost monotonically throughout the periodic table. Moseley's hypothesis (originally ascribed to Van der Broek, an amateur physicist in Amsterdam) was that "*The element's nuclear charge equaled its serial number*".

So, in October 1913, Moseley built an apparatus with "*several different anticathodes in the same X-ray bulb... so he was not dependent on the lab's (jealousy guarded) vacuum pump for each experiment*" (Figure 1). In four days he obtained cathode-ray induced X-ray spectra from Ti, Cr, Mn, Fe, Co, Ni, Cu and Ag. Two weeks later his first data appeared in Phil Mag. [2] followed by a second paper [3]. Figure 2, his now famous 'step ladder' is Plate V in [2]. Moseley found that the frequency of the $K\alpha$ line was proportional to $(Z-1)^2$. Neils Bohr who spent many months in Manchester said (in 1962): "*The Rutherford work (the nuclear atom) was not taken seriously. The great change came with Moseley*".

Because of Moseley's research, the role of X-rays in physics, chemistry and materials science was extended from probing the possible crystallographic structure to the unequivocal identification of the elements within the specimen. "*He knew in minutes the contents of a sample which a chemist might take years to analyze*". Now of course we know the answer in seconds, down to the individual atom level.

Thus, in a couple of weeks, Moseley facilitated the birth of X-ray microanalysis using electron beams. This technique was not immediately popular. It took 31 more years for Hillier and Baker [4] to combine the techniques of electron scattering and X-ray detection into one instrument. It took almost 40 years for Castaing [5] to develop the quantification technique relating the elemental composition to the X-ray intensity through the ZAF approach. It took over 60 years before Cliff and Lorimer [6] developed the k-factor approach for high-resolution, thin-film quantification by ignoring the A and F in Castaing's equation. The factor $k_{AB} (= Z^{-1})$ is thus a correction for the different Z values of elements A and B in the thin specimen, as described in Williams and Carter [7].

How fitting that the method by which Moseley's X-ray spectroscopy was ultimately applied at the single-atom level was developed in Moseley's own Manchester University.

References

- [1] All quotes from J. L. Heilbron, "H. G. J. Moseley" (University of California Press, Berkeley, CA, 1974). Reproduced Courtesy of The University of California Press.
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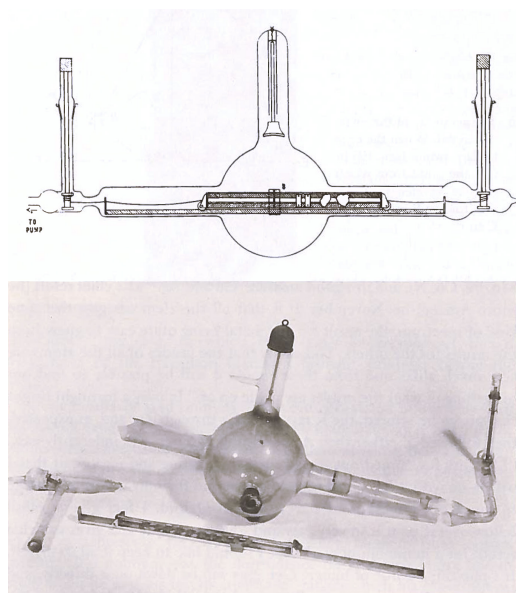


Figure 1. Moseley's definitive apparatus for measuring hard X-rays (a) schematic (b) what remains of the actual apparatus. Courtesy, University of California Press.

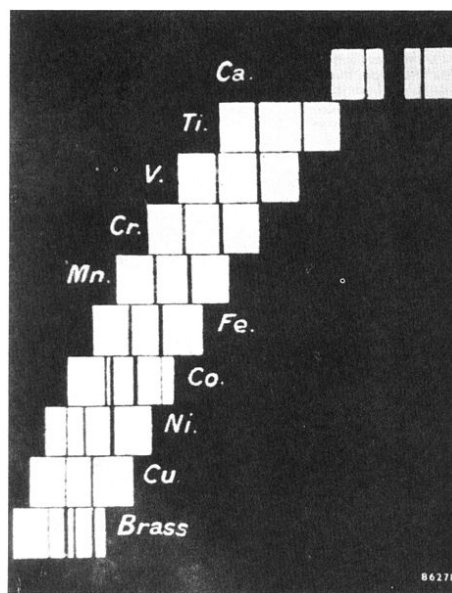


Figure 2. Moseley's 'step ladder' arranged with frequency decreasing from left to right. The darker of the two lines in each spectrum is $K\alpha$ and the other is the $K\beta$. An element is clearly missing between Ca and Ti. Moseley had no Sc sample available. Courtesy, Taylor and Francis.