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Al Nier's contribution to atomic weights

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After completing his Ph.D. at the University of Minnesota, Al Nier took up a Post-Doctoral Fellowship at Harvard University where he measured the isotopic composition of 19 elements, with such attention to accuracy that his data have invariably stood the test of time. One of those elements was lead, which he measured in a variety of uranium minerals from the Richards-Baxter collection, and showed that they varied in isotopic composition dependent on their age and chemical composition. This led to his long-standing interest in atomic weights. In 1950 Nier produced some isotopically enriched argon, and used this to calibrate a mass spectrometer to provide argon isotope abundances that were absolute, in the sense that they were free from all sources of bias. He used the same spectrometer to measure the "absolute" isotope abundances of nine other elements, assuming that the isotopes of those elements behaved in a similar manner to those of argon. In the early 1950s Nier's interest turned to the measurement of atomic masses. He and his colleagues built a double-focusing mass spectrometer and this was used to measure the atomic masses of numerous elements with high accuracy. He also departed from the accepted mass spectrographic technique for measuring atomic masses by using electronic measuring devices rather than photographic techniques. Atomic masses, together with absolute isotope abundances, are essential parameters in determining atomic weights, and in some cases, fundamental constants. Professor Nier also made a significant contribution to the International Commission on Atomic Weights. He served as a member of the Commission from 1947–1961, and was a key figure in the unification of the "chemical" and "physical" scales of atomic weights using carbon-12 as the common base. (Int J Mass Spectrom 178 (1998) 1–7) © 1998 Elsevier Science B.V.

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Introduction

Atomic weights are one of the most fundamental sets of scientific data because they enable mass to be related to amounts of substance, which is the basis of analytical chemistry. They also serve as a foundation for trade and commerce, as these areas are directly involved with transactions involving amounts of substance. It is therefore not surprising that the measurement of atomic weights, which was one of the major tasks of chemistry in the nineteenth century, continues to play a key role in the progress of science [1]. Atomic weights can now be determined with sufficient precision to enable improvements in the values of such fundamental constants as the universal gas constant R, the Faraday constant F, and the Avogadro number N_A to be made. These data, in turn, can influence the value of other constants that are basic to modern science [2].

The International Committee on Atomic Weights was formally constituted as part of the International Union of Pure and Applied Chemistry (IUPAC) in 1920, although a number of committees concerned with atomic weights had existed since the latter part of

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Dedicated to the memory of Al Nier.

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the last century. In 1921 it was decided to reorganise and enlarge this committee by giving it the responsibility of advising on radioactive and stable isotopes, as well as on atomic weights. It was renamed the Committee on Chemical Elements. Two members of the committee were Francis Aston and Frederick Soddy, both of whom received Nobel Prizes for their work on isotopes. In 1930 the Committee on Chemical Elements was subdivided into three parts, one of which became the Atomic Weights Committee. In 1979 this committee became the Commission on Atomic Weights and Isotopic Abundances (CAWIA), which has the role of evaluating new isotope abundance data and providing the outcomes of such investigations to the scientific community on a regular basis [3].

The basic concept of atomic weights is attributed to the British chemist John Dalton, who in 1805 published a table showing the “relative weights of the ultimate particles of gaseous and other bodies.” He was the first to realize that elements combine in simple numerical ratios of numbers of their atoms. By the beginning of the twentieth century there was tacit agreement to base the atomic weight scale relative to the weight of one atom of oxygen being equal to 16, rather than the weight of one atom of hydrogen being equal to one, as originally suggested by Dalton. As a result, the first International Table of Atomic Weights was published on the $m(\mathrm{O}) = 16$ amu scale [3].

Atomic weights were originally based on precise gravimetric determinations by using chemical stoichiometry. The “Harvard method” for determining chemical atomic weights was pioneered by T.W. Richards of Harvard University, who received the Nobel prize in chemistry for this work in 1914. High-purity chlorides or bromides of the element were prepared, followed by the measurement of their mass ratio to silver or to the corresponding silver halide. Solutions containing nearly equivalent amounts of reactants were mixed, and the point of exact equivalence determined. This was followed by the quantitative collection and weighing of the precipitated silver halide.

Into this sane and ordered development came the discovery of isotopes. Experimental investigations in nuclear physics began to require specialised instruments—one of which was the mass spectrometer. F.W. Aston demonstrated that many elements were polyisotopic. In 1920 A.J. Dempster calculated the atomic weight of Mg by using the relative abundances of the isotopes together with the whole number masses of the isotopes, and shortly afterwards made similar studies of Li, K, Ca, and Zn. Thus began the ultimate demise of chemically determined atomic weights. From this time until the late 1930’s, Aston, Dempster, Bainbridge, Nier, and others determined the isotopic composition of most of the elements, so that the “physical” method of determining atomic weights became a viable alternative to the “chemical” technique and, in the longer term, became the accepted method [1]. This review is concerned with the contribution of Professor A.O.C. Nier to the science of atomic weights. His contribution to the field will be discussed in four parts.

The determination of relative isotopic abundances

The August, 1935 volume of “The Physical Review” contained an article by a young graduate student in Physics at the University of Minnesota entitled: “Evidence for the Existence of an Isotope of Potassium of Mass 40” [4]. This article contained many of the features of Al Nier’s future career in mass spectrometry:

(i) instrumental ingenuity;
(ii) dependability of isotopic measurements. ($^{40}\mathrm{K}/^{39}\mathrm{K} = 1/8600$ as compared to 1/8000 today);
(iii) ability to tackle problems of real value (the discovery of $^{40}\mathrm{K}$ led to the development of the $^{40}\mathrm{K}/^{40}\mathrm{Ar}$ geochronological technique);
(iv) reporting of important results in a concise manner.

This latter characteristic is exemplified by Al’s third published paper entitled: “The Isotopic Constitution of Rubidium, Zinc and Argon,” published in the February 1936 issue of *The Physical Review* [5]. The paper was contained in approximately half a page. In fact, Al Nier's many pioneering papers are models of scientific communication. He was brought up in the tradition in which you used a minimum of words to describe the experiment, and allowed the data to speak for themselves. He found it hard to accept the lengthy journal articles that are the norm today, and complained that one of his manuscripts had actually been returned because the editor wanted him to make it longer.

After completing his Ph.D. at the University of Minnesota, Al Nier gained a National Research Council Fellowship at Harvard University, where he worked under the supervision of Professor K.T. Bainbridge, who had established an outstanding reputation for his mass spectrographic studies of atomic masses and relative abundances of isotopes. The Fellowship was supported by a grant of $5,000—a huge amount of money in those days, which was used to build a bigger and better 180° mass spectrometer than was available at Minnesota.

With this new instrument, Al Nier measured the isotopic composition of 19 elements and discovered four new isotopes, ^{36}S, ^{46}Ca, ^{48}Ca, and ^{184}Os. These results were reported in a series of articles from 1936 to 1938 [6–10]. The 25 elements analyzed by Nier represent the measurement of the isotopic composition of one element every 5–6 weeks. One wonders what Al's reaction must have been when he realised there were only 92 elements of which 30 were monoisotopes. At this rate Al would have put himself out of business by 1945. A cosmochemical "Alexander" with no more elements to measure mass spectrometrically.

However, as important as these isotopic composition measurements were to the evolving "physical" method of determining atomic weights, of far greater importance was that Harvard University was the place where T.W. Richards had determined the value of numerous atomic weights. His successor, G.P. Baxter, was still active in the field in 1937, and quickly made Al Nier's acquaintance. The Chemistry Department had a large collection of minerals that had been used in atomic weight determinations, including a large number of lead minerals.

Baxter was extremely generous in providing and personally converting lead samples from the Harvard Collection to PbI_2, a chemical species that Nier could analyze in his spectrometer. Harvard chemists had measured the atomic weights of most of these lead samples and had always found an atomic weight close to 207.21. This implied that the samples had the same isotopic composition, but Nier found that the isotopic abundances of lead varied considerably, depending on the chemical composition and age of the ores [11].

Baxter found it difficult to believe the mass spectrometric results, but finally became a convert to the "physical" method of atomic weight determinations and assisted Al in preparing numerous samples for analysis. Al jokingly remarked that, as a Post Doctoral Fellow, he had a Harvard full Professor as a research assistant!

There was one other productive aspect of Al Nier's Harvard visit as far as atomic weights were concerned, namely, his acquaintance with Earl Gulbransen from Tufts University. They measured the ^{13}C/^{12}C ratios of fourteen different samples of carbon and found variations of up to 5% in the isotope ratios. These variations in isotopic composition resulted from mass fractionation caused by physio-chemical equilibria reactions. These results showed that natural variations in atomic weight occurred in nature, at least in some elements [12].

The determination of absolute isotope abundances

On his return to the University of Minnesota in 1938, Al Nier was given a faculty position which, naturally enough, curtailed his research to some extent, although one would not suspect this from the number of papers produced. He became interested in using thermal diffusion to enrich ^{13}C and, together with John Bardeen (who later won a Nobel Prize in Physics), was able to enrich the ^{13}C/^{12}C ratio by a factor of ten over that of naturally occurring carbon [13]. This enriched C was used in many biochemical experiments involving gas source mass spectrometry.

Of utmost importance was Nier's revolutionary design of a 60° sector field mass spectrometer that replaced the more complicated 180° versions that had previously been used [14]. This simple design not only reduced the weight and power consumption of the electromagnet, but enabled the ion source and detector to be removed from the influence of the magnetic field. However, of more significance was the fact that the Nier design transformed what was essentially a physics research instrument into a machine that could be used by a wider group of scientists. And this was achieved against the prevailing opinion of the day, as expressed by Francis Aston, who argued that mass spectrometry would die away as an active research field. Subsequent developments in mass spectrometric-related fields are testimony to Al's vision, and of the importance of the two papers in 1940 and 1947 that described the sector field instrument that revolutionised mass spectrometry [14,15].

Furthermore, he was more than happy to share his mass spectrometric trade secrets with others. Nier would not only provide the complete details on how to build a mass spectrometer, but would often provide the tube, source, and collectors to get a research group in another University started. This was an important factor in the development of the field in the late 1940s.

In 1950, two papers of enormous importance to atomic weights were published in "The Physical Review" by Al Nier. The first paper described the use of essentially pure samples of ^{36}Ar and ^{40}Ar, produced by thermal diffusion, to prepare synthetic argon mixtures whose ^{36}Ar/^{40}Ar isotope abundance ratios were accurately determined in two gas source mass spectrometers of the 1947 design [16]. These isotope abundance values could then be used to correct for any mass discrimination in the spectrometers so as to produce absolute isotopic abundances that could be used to determine an atomic weight for argon, free of all instrumental bias. Nier then used his calibrated mass spectrometer to measure the "absolute" isotope abundances of C, N, O_2, and K, assuming that the calibrations determined for argon applied equally as well to the other elements [16]. This enabled Nier to quote the isotope abundance of ^{40}K as 0.0119 ± 0.0001% which compares with the presently accepted value 0.011 67 ± 0.000 04%. The second paper gave the "absolute" abundances of Ne, Kr, Rb, Xe, and Hg by using the argon-calibrated mass spectrometers as before [17].

It is of interest to note that Nier's absolute isotopic values for argon are still accepted as the best values in the literature. Furthermore, Nier's value for the atomic weight of argon is an input parameter to the acoustical method used to determine a value for the universal gas constant R, one of the fundamental constants in science [1].

A major study entitled "The Relative Isotopic Abundances of the Elements" was published by Bainbridge and Nier in 1950 by the National Research Council's Committee on Nuclear Science [18]. This comprehensive analysis lists all the published isotopic data on all the elements up to that time. It served as the primary source of isotopic information for many years.

The determination of atomic masses

The determination of atomic weights of polyisotopic elements requires two input parameters—the absolute isotope abundances and the atomic masses of each isotope. Masses of atoms in their atomic and nuclear ground states are important in many areas in science, and thus the early efforts in mass spectroscopy were directed towards measuring the atomic masses of the isotopes of the elements with increasing accuracy. Aston at the University of Cambridge, and Dempster, at the University of Chicago, were pioneers in this field by using mass spectrographic techniques in which separated ion beams were allowed to impinge on photographic plates. By observing the positions of lines on the developed plates, it was possible to determine atomic masses by the mass doublet technique with respect to the mass of the ^{12}C atom in its nuclear ground state by giving it a mass of 12.000. The use of hydrocarbon atoms, singly or multiply charged, can thus provide a reference to most mass determinations throughout the entire mass spectrum relative to ^{12}C.

Prior to 1950, all atomic mass measurements were determined with mass spectrographs that used the mass doublet method. For example, if one examines the mass spectrum of singly charged ^{12}C and doubly charged ^{24}Mg, one can form a mass doublet in which both peaks appear at mass number 12, where they are slightly displaced with respect to one another by virtue of the one part in 1600 mass difference between them. By carefully measuring the lines recorded on the photographic plate, the exact mass difference can be determined from the doublet spacing.

Atomic masses are measured by high resolution double focusing mass spectrographs comprising an electrostatic analyser together with a magnetic analyser. In 1920, Aston's first mass spectrograph had a resolution of 130, by 1970 the resolution of these mass spectrometers had increased to 150 000 [1]. A departure from the classic double-focusing mass spectrographs occurred in the early 1950's, when a new instrument was constructed at the University of Minnesota. This Nier–Johnson double-focusing mass spectrometer employed an electrostatic analyser symmetrically, and a magnetic analyser asymmetrically, which allows a large divergence angle while maintaining second-order direction focusing. An enlarged version of this instrument, with a resolution of 75 000, proved to be one of the most productive instruments in the study of precise atomic mass measurements.

Nier and Roberts [19] departed from the accepted mass spectrographic technique for measuring atomic masses, by using a mass spectrometer in which the ion currents were measured with a vibrating reed electrometer or electron multiplier. In order to minimise fluctuations in the magnetic field or the ion deflecting voltage of their double-focusing mass spectrometer, a smaller auxiliary mass spectrometer tube was deployed in the same magnetic field as used for the main spectrometer. This tube is similar to ones used for isotope abundance measurements, except that a double collector system was used, coupled to a differential amplifier. This tube is adjusted so that the ion current is split, with half going to each collector plate. Under these conditions there will be no output from the diffential amplifier. However, if the magnet field or accelerating voltage changes, the ion beam will shift, and a signal will appear in the output of the differential amplifier. This signal is fed back to the accelerating voltage in a way that restores the beam to its original position. Because both spectrometer tubes obtain their ion-accelerating and deflection potentials from a common voltage divider, the small tube serves the function of correcting for fluctuations that would normally disturb the paths of ions in the main tube and hence reduce the accuracy of the measured atomic masses. The mass doublet was accurately measured from the chart recorder, which was calibrated against the resistance of the potentiometer controlling the high-voltage supply. Mass differences were accurately determined by measuring the distances on the chart between corresponding half heights of the peaks.

In the case of a photographic recording, the position of the line can only be determined to approximately 1/50 of its width. Thus, if the resolution of the instrument is 20 000, a mass difference can be determined with a precision of approximately one part in one million. However, the location of a peak can be determined to approximately 1/500 of its width by using electrical recording. The two peaks of a doublet are made to appear on an oscilloscope screen on alternate sweeps, and are then brought into coincidence by varying a circuit parameter that is related to the mass difference of the doublet. The peaks are matched by the human eye, or by using the digital memory. In addition to reducing the subjectivity of visual matching, the digital system integrates the signal over a period of time, thus increasing the signal-to-noise ratio [20].

The establishment of the atomic mass scale is one of the success stories of measurement science of the 20th century. This achievement has occurred because of the development of larger and more sophisticated double-focusing mass spectrographs. Professor Al Nier contributed to this field over the period 1951 to 1960 by building a new generation of double-focusing mass spectrometers of innovative design that enabled he and his colleagues to measure the atomic masses of many elements with greatly improved accuracy over what had previously been achieved [21]. He also demonstrated that electronic recording of isotopic data could improve the precision of atomic mass measurements by at least a factor of ten as compared to the photographic techniques used in mass spectrographs. Electronic recording was subsequently adopted as the norm for subsequent atomic mass determinations.

International atomic weights commission

Professor Al Nier served on the Atomic Weights Commission from 1947 to 1961. His measurements of the relative and absolute isotope abundances of elements, his accurate determinations of atomic masses, and his demonstration that atomic weights are not constants in nature, but can vary according to physiochemical mechanisms as well as by radioactive decay, had already made a significant contribution to the deliberations of the Commission, whose membership had included six Nobel Prize winners over the years. However, Al was to play an important role on the Commission because of the seemingly unresolvable conflict between the International Union of Pure and Applied Physics (IUPAP) and the International Union of Pure and Applied Chemistry (IUPAC) over a unified scale of atomic weights.

In the late 1920s it seemed that most of the scientific issues surrounding atomic weights had been resolved. The discovery of isotopes had explained the existence of nonintegral atomic weights, and both chemists and physicists were in agreement that a common scale for atomic weights, $m(\mathrm{O}) = 16$ amu, could be adopted, based on the premise that oxygen was monoisotopic. Furthermore, the Harvard chemical methodology for determining atomic weights could be supplemented by independent physical determinations based on mass spectrometry.

The discovery that oxygen was polyisotopic led to the unsatisfactory state of affairs in which the chemical fraternity continued to use an elemental $m(\mathrm{O}) = 16$ amu scale, whereas the physicists opted for an atomic weight scale based on $m(^{16}\mathrm{O}) = 16$ amu. A conversion factor of 1.000 275 was used to convert the physics-derived values into the chemistry scale, but this was further complicated by the fact that, because the isotopic composition of oxygen varied in nature, the two scales were not even related by a fixed constant, but rather the conversion factor varied from 1.000 268 to 1.000 278 depending on the source of oxygen. Furthermore, there was the necessity for two sets of values for N_A, F, and R, and errors were frequently made in matching mass values with the appropriate constant.

In 1957, A.O. Nier and A. Ölander independently suggested that a $m(^{12}\mathrm{C}) = 12$ amu scale be adopted. IUPAC and IUPAP agreed to unify the two scales on the basis of $m(^{12}\mathrm{C}) = 12$ u (where u stands for the unified atomic mass unit), in 1959 and 1960, respectively. The unit defined in this way was 318 and 42 ppm larger than the previous physical and chemical scales, respectively. So, after 31 years of debate, a single scale for atomic weights was achieved [22].

Al tells the story in the following way: “I was a newly elected member of the International Commission on Atomic Weights when I came up with the idea (in a bar in Amsterdam), of using carbon-12 as the common base for atomic weights. I then went to the Max Planck Institute at Mainz where I convinced the Director, Professor Josef Mattauch, of the idea. Mattauch was so excited about the possibility of uniting the two warring factions, that he set off to Paris to convince his physics colleagues, but forgot his passport and was stopped at the border at Trier. I was duly despatched with the missing passport to rescue Mattauch, and carbon-12 was subsequently adopted as the base for the atomic weights table, and is still in use today.”

The decision to use the $^{12}\mathrm{C}$ scale implied that mass spectrometry had to play an important role in atomic weight determinations, because carbon itself possesses two stable isotopes. A major review was published by the Commission in 1962, in which the existing chemical and physical determinations of the atomic weights of all the elements were examined. This review resulted in a Table of Atomic Weights based on the new reference nuclide $^{12}\mathrm{C}$ [23]. At this time the atomic weights of 47 of the 62 polyisotopic elements were based upon physical measurements. The atomic weight of neon was based upon gas density measurements, while the remaining 14 elements were based entirely on chemical determinations. This was either because there was a lack of agreement between different isotope abundance measurements, or a discrepancy between the physical and chemical values with no compelling evidence to choose one result over the other. The atomic weights of the remaining 30 monoisotopic elements were based entirely on atomic mass values, often to an accuracy of 1 part in 10^8.

In 1954 Al published a paper entitled “The Determination of Isotopic Masses and Abundances by Mass Spectrometry” in which he presented a table showing a comparison between the 1953 International Table of Atomic Weights and atomic weights calculated from mass spectrometric measurements [24]. For the 1955 Report of the Commission, Nier performed a complete evaluation of all physical determinations of atomic weights. This is now the task of the Commission on Atomic Weights and Isotopic Abundances.

Conclusions

The accurate determination of atomic masses, isotope abundances, atomic weights, and fundamental constants has been central to the development of science as we know it today. The 20th century has witnessed the evolution of more sophisticated determinations of these values and a knowledge of the uncertainties which can be associated with them. At the time of the 1961 review of atomic weights, they were still generally regarded as being constants of nature, despite the fact that Nier had shown that the isotope abundances of some elements (e.g., C) undoubtedly varied in nature. This phenomenon is now not only recognised, but is utilised to explore physiochemical mechanisms in nature—a field pioneered by Nier himself.

The mass spectrometer has proved to be a remarkably versatile measuring instrument. Advances in electronics, computing, ion optical design, and vacuum technology have provided the impetus for producing instruments capable of impressive performance. Absolute isotope abundances, together with atomic mass data, has provided accurate values for the atomic weights of most elements, some of which can be combined with other data to determine the values of fundamental constants such as the universal gas constant. Atomic weights are absolutely essential in translating mass determinations or weighings into the mole, the unit for amount of substance. Thus, mass spectrometry is a metrological measurement technique of prime importance to science [1].

The present status of mass spectrometry and, in particular, its use in atomic weight determinations owes much to Al Nier—“Father of Modern Mass Spectrometry.” It is my personal view that Al Nier deserved to win a Nobel Prize, if not for his work on atomic weights, then for his work in nuclear physics, space research, meteoritics, and geophysics. It is therefore entirely appropriate that this “Symposium on Inorganic Mass Spectrometry” recognises the name of one of this century’s great scientists, Alfred Otto Carl Nier.

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