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1 Atomic weights of the elements: from measurements 2 to the Periodic Table

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Summary. — Atomic weights of the elements are the indicators for what is possible in chemical measurements. With very few exceptions, one cannot perform chemical measurements with more precision than the underlying atomic weights have. While determining the atomic weights and the corresponding isotopic compositions of the elements might seem like research topics from a bygone era, recent efforts in revising the International System of Units illustrate the continued relevance of this topic.

4

5 1. – Historical introduction

6 Chemists have long known that elements display similar properties. In the 1820s, 1
7 however, German chemist Döbereiner also noticed similarities in the atomic weights of
8 such elements [1]. Consider lithium, sodium, and potassium: the atomic weight of sodium
9 (23) is exactly the average of the other two: $\frac{1}{2}(7 + 39) = 23$. The same goes for many
10 other element triads such as Cl-Br-I, Ca-Sr-Ba, or S-Se-Te. This was an early attempt to
11 bring order and clarity to 50+ chemical elements known at the time. Mendeleev seized
12 the idea that the atomic weight of elements, in addition to their chemical properties and
13 similarities, could act as the numerical organizing principle of all chemical elements.

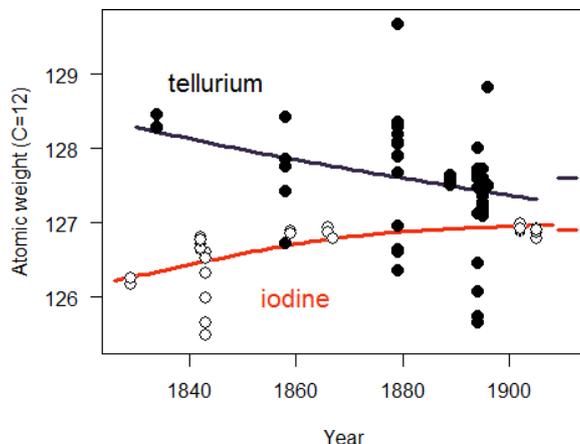


Fig. 1. – *The original inconvenient truth*: 19th century atomic-weight determinations of tellurium and iodine did not favor Mendeleev’s suggestion that $A_r(\text{Te}) < A_r(\text{I})$. Note the temporal trends for the measurement results of $A_r(\text{Te})$ and $A_r(\text{I})$ to gradually conform with Mendeleev’s hypothesis —this is known as the expectation bias [3]. The current standard atomic weights are shown as thick horizontal bars to the right.

The atomic-weight pattern seen from Li-Na-K was put to test for elements whose atomic weights were hard to measure. For example, determination of the atomic weight of titanium was challenging between the 1820s and 1880s with values ranging from 36 to 56. In his 1897 textbook, Mendeleev asserted that the atomic weight of titanium should be 48, the average of its neighboring elements scandium (44) and vanadium (51) [2]. This prediction has stood the test of time.

For most part, the chemical properties and atomic weights did not conflict with one another: when elements were ordered by their chemical similarities, their atomic weights followed suit. But then there was tellurium whose chemical properties required placement under selenium and before iodine whereas the atomic weight order required tellurium to be placed after iodine. To Mendeleev the solution was simple: the atomic weight of an element may sometimes be amended by a knowledge of those of its contiguous elements, he wrote in 1869. Thus, he continued “the atomic weight of tellurium must lie between 123 and 126, and cannot be 128” [2]. Although Mendeleev was not right about tellurium, he raised an awareness about the need for more scrutiny and measurements underlying the atomic weights in general (fig. 1). This need remains to this day as tellurium still lacks a calibrated measurement of its isotopic composition.

2. – Atomic-weight measurements

Many efforts have been taken to determine the atomic weights of the elements throughout the 19th and 20th centuries. This has resulted in improved laboratory techniques and better understanding of how to purify chemicals in general. A culmination of this



Fig. 2. – Dmitri Mendeleev (1834-1907) raised the awareness for more scrutiny of atomic-weight measurements whereas Theodore W. Richards' (1868-1928) work on atomic-weight determinations earned him the first Nobel Prize given for metrology.

35 line of research was the 1914 Nobel Prize in Chemistry which was awarded to Theodore
 36 W. Richards in recognition of his accurate determinations of the atomic weight of a large
 37 number of chemical elements. This was, in fact, the first prize for metrology or “pure
 38 precision work” as it was noted by the Nobel Committee (fig. 2).

39 Precision atomic-weight measurements have played important role in science. Exam-
 40 ples of this nature have been told by many. High-precision nitrogen density measurements
 41 revealed slightly lower values for nitrogen obtained from decomposition of chemical com-
 42 pared to that isolated from air [4]. This led to the discovery of argon and two Nobel
 43 Prizes in 1904. In the late 1920s, the early mass spectrometric measurements of the
 44 atomic weight of hydrogen gave $A_r(\text{H}) = 1.007\,56(14)$ which was slightly lower than the
 45 best measured value from chemical measurements, $A_r(\text{H}) = 1.007\,77(4)$. This small dis-
 46 crepancy led to the discovery of deuterium and in his 1935 Nobel lecture Harold Urey
 47 wrote that “without [this discrepancy], it is probable that we would not have made a
 48 search for it and the discovery of deuterium might been delayed for some time” [5].

49 **2.1. Measuring the atomic weight.** – Atomic weight of an element is the amount-
 50 weighted average mass of its atoms expressed on a scale by assigning carbon-12 to be 12
 51 exactly. Historically, atomic weights were calculated by measuring the masses of various
 52 chemical that combine with each other (equivalent masses). As an example, thermal
 53 decomposition of pure AgI gives iodine and silver with mass ratio $m(\text{I})/m(\text{Ag}) = 1.175$.
 54 Assuming the molecular formula of silver iodide as AgI, the atomic weights of iodine and
 55 silver are related as follows:

$$(1) \quad \frac{A_r(\text{I})}{A_r(\text{Ag})} = \frac{m(\text{I})}{m(\text{Ag})} = 1.175.$$

In addition, many results and methods were available for each element as shown in the example below for silver [6]:

$$\begin{array}{ll} \text{KI} : \text{Ag} = 1.537 & 3\text{O} : \text{AgIO}_3 = 0.171 \\ \text{I} : \text{Ag} = 1.175 & 3\text{O} : \text{KIO}_3 = 0.225 \\ \text{AgI} : \text{Ag} = 2.176 & \text{I} : \text{O} = 7.850 \\ \text{AgI} : \text{AgCl} = 1.637 & \text{O} = 16(\text{exact}). \end{array}$$

These data represent 8 equations (including the scale-defining identity $\text{O} = 16$ which was in effect before the 1960s) and 4 unknown variables (atomic weights of K, I, Cl, and Ag) which can be solved for using nonlinear least squares adjustment in a manner similar to how best estimates of fundamental constants are still obtained [7].

The chemical analysis required high-purity substances and relied on the analysis of as many substances of an element as possible in order to avoid making assumptions regarding the stoichiometry. Today the atomic weights are not measured directly, rather calculated from the isotope ratios of an element which are usually obtained using mass spectrometry. This method of analysis does not require possession of pure chemicals and the atomic weight is calculated from the isotope masses and measured isotope ratios. For silver, we have the following relationship:

$$(2) \quad A_r(\text{Ag}) = \frac{\sum_{i=107,109} A_r({}^i\text{Ag})R_{i/109}}{\sum_{i=107,109} R_{i/109}} = \frac{A_r({}^{107}\text{Ag})R_{107/109}}{R_{107/109} + 1} + \frac{A_r({}^{109}\text{Ag})}{R_{107/109} + 1}.$$

For elements with two isotopes, such as silver, the atomic weight and the single isotope ratio are directly comparable quantities in a sense that it is possible to obtain the value of one of these quantities from the other (much like how the Planck and Avogadro constants can be compared using the Rydberg equation [7]):

$$(3) \quad R_{107/109} = \frac{A_r({}^{109}\text{Ag}) - A_r(\text{Ag})}{A_r(\text{Ag}) - A_r({}^{107}\text{Ag})}.$$

The best chemical measurements in the 1960s yielded $R_{107/109} = 1.073 \pm 0.006$ whereas the best physical measurements gave $R_{107/109} = 1.076 \pm 0.001$ clearing the way for mass spectrometry to become the preferred method of analysis.

The early applications of isotope measurements were limited to radioactive isotopes and they included the solubility determination of highly insoluble substances, total blood volume determination in humans, surface area measurements of crystal powders, or verification of the Nernst equation. Arguably, the most notable early application of isotope ratios was the estimation of the age of the Earth from lead isotope ratio measurements from various minerals using the following measurement model [8]:

$$(4) \quad \frac{R_{207\text{Pb}/204\text{Pb}}(t) - R_{207\text{Pb}/204\text{Pb}}(t=0)}{R_{206\text{Pb}/204\text{Pb}}(t) - R_{206\text{Pb}/204\text{Pb}}(t=0)} = \frac{e^{\lambda({}^{235}\text{U}) \cdot t} - 1}{e^{\lambda({}^{238}\text{U}) \cdot t} - 1} R_{235\text{U}/238\text{U}}(t),$$

80 which can be solved for the age of the Earth (t). Other early applications of isotopes
 81 provided solubility estimates for highly insoluble substances, total blood volume deter-
 82 mination, surface area of crystal powders, and trace metal analysis. Today, isotope ratio
 83 measurements play an important role in science and they reveal useful applications when
 84 high-accuracy and high-precision is reached. As an example, one can distinguish between
 85 the natural and synthetic testosterone from their carbon isotope ratios if they can be
 86 measured to parts-per-thousand precision [9].

87 Even though mass spectrometry was proven reliable from the early days (table I), one
 88 of the best kept secrets of the Periodic Table of chemical elements is that handful of ele-
 89 ments still lack calibrated measurements of their isotopic composition [10]. This includes
 90 elements such as tellurium and oxygen. In addition, many other elements have few inde-
 91 pendent measurements published. As an example, ytterbium has only two independent
 92 measurements of its isotopic composition and they disagree significantly [11].

93 3. – Calibration of isotope ratio measurement results

94 Although mass spectrometry is designed to measure the isotopes of the elements, this
 95 technique is not quite faithful at preserving the isotope ratios because lighter isotopes
 96 travel faster than the heavier ones and their ratios are therefore altered as they go
 97 through the mass spectrometer from the sample introduction inlet to the detector. To
 98 obtain accurate results, a standard with a known isotope ratio is therefore required.
 99 Consider the simplest case of an element with two isotopes. This can be achieved as
 100 follows: 1) obtain pure materials of both isotopes, 2) gravimetrically prepare a mixture
 101 of known isotopic composition from these two standards. The calibration of the mass
 102 spectrometer then consists of comparing the measured isotope ratio in this mixture to
 103 the known (gravimetric) value. Turns out, one can establish the isotope ratios this way
 104 even when the two starting materials of isotopes are not entirely pure but contain small

TABLE I. – *Atomic-weight measurements by classical methods of chemical analysis validate mass spectrometry [12]. The discrepancy in the atomic weights of Kr and Xe by gas density analysis was soon resolved in favor of mass spectrometric values yielding $A_r(\text{Kr}) = 83.7$ and $A_r(\text{Xe}) = 131.3$ [13].*

Element	Classical analysis (1931)	Mass spectrometry (1931)
chromium	52.01	52.011
zinc	65.38	65.380
molybdenum	96.0	95.97
krypton	82.9	83.77
tin	118.70	118.72
xenon	130.2	131.27
mercury	200.61	200.62

amounts of the other isotope. Using silver as an example, the mathematical model for the process of obtaining calibrated isotope ratio measurements proceeds as follows:

(STEP 1) Measure the isotope ratios in both isotope standards, $r_{A,107/109}$ and $r_{B,107/109}$ and note the proportional relationship between the true isotopic composition of these standards, $R_{A,107/109}$ and $R_{B,107/109}$:

$$(5a) \quad R_A = K \cdot r_A,$$

$$(5b) \quad R_B = K \cdot r_B.$$

(STEP 2) Both isotopic silver standards are blended together in a known mass ratio. The measured isotope ratio, r_{AB} , is related to the known value, $R_{AB,107/109}$:

$$(6) \quad R_{AB} = K \cdot r_{AB}.$$

(STEP 3) The isotope ratio R_{AB} can be expressed as a function of R_A and R_B , and masses of the materials A and B used to make the blend AB. This provides the fourth equation:

$$(7) \quad R_{AB} = \frac{R_A m_{A(AB)}(R_B m_{107} + m_{109}) + R_B m_{B(AB)}(R_A m_{107} + m_{109})}{m_{A(AB)}(R_B m_{107} + m_{109}) + m_{B(AB)}(R_A m_{107} + m_{109})}.$$

Here, m_{107} and m_{109} are the atomic masses of silver isotopes. This system of 4 equations and 4 unknown variables (R_A , R_B , R_{AB} , and K) can be solved using linear algebra. Since the 1950s, scientists have used iterative solutions to solve this system of equations and the full analytical solution for the generalized two-isotope system become available only recently largely as a result of the efforts related to the redefinition of the kilogram.

Note that this problem can be generalized by removing the requirement to measure pure isotope materials [14]. Thus, the general model for two-isotope system allows one to measure three distinct mixtures of pure isotopes. Thus, the calibration factor for the isotope amount ratios, K , can be expressed in a single master equation using matrix determinants:

$$(8) \quad K_{107/109} = \frac{m_{109}}{m_{107}} \frac{\begin{vmatrix} r_1 & r_2 & r_3 \\ w_{A1} & w_{A2} & w_{A3} \\ w_{B1} & w_{B2} & w_{B3} \end{vmatrix}}{\begin{vmatrix} r_2 r_3 & r_1 r_3 & r_1 r_2 \\ w_{A1} & w_{A2} & w_{A3} \\ w_{B1} & w_{B2} & w_{B3} \end{vmatrix}}.$$

Here, w_{Ai} and w_{Bi} are the mass fractions of the parent materials A and B in each of the three blends $i = 1 \dots 3$.

The best isotope ratio measurements to date routinely achieve relative uncertainties of few parts in 10^4 , some of which are presented in table II. Note that the high-precision

128 (few parts in 10^8) molar mass of ^{28}Si -enriched silicon in support of the redefinition of
 129 the kilogram and the mole involved rather low-precision isotope ratio measurements with
 130 relative uncertainties of few percent.

131 **3.1. More complex isotope systems.** – The mathematical framework of isotope ratio
 132 measurement calibration has been extended to three isotope system only recently thanks
 133 to the work overseen by International Avogadro Coordination (IAC) in support of the
 134 new International System of Units (SI) [15].

135 A useful feature of gravimetric mixture method for isotope ratio calibration is the
 136 redundancy in mathematical expressions [16]. Consider a case of N -isotope system where
 137 all isotope ratios of N pure materials are measured in addition to $(N - 1)$ unique two-
 138 material mixtures. This is the simplest experimental design of minimal complexity. For
 139 a 2-isotope system such experiment yields a single mathematical solution for the isotope
 140 ratio calibration factor, as shown in the previous section. For a 4-isotope system, however,
 141 we can obtain 16 different mathematical solutions. Although all of these solutions are
 142 algebraically equivalent, they are not equal from metrological standpoint [17].

143 Many prefer having analytical measurement model equations over numerical solu-
 144 tions [18]. However, the mathematical complexity of the analytical solutions for the
 145 isotope ratio calibration factors rises quite fast. The full analytical expression for a sin-
 146 gle isotope ratio calibration factor in a 4-isotope system (lead) consists of nearly one
 147 million terms in its fully expanded form. To appreciate the complexity, one can display
 148 this equation on the screen using standard font size and scroll through the entire equa-
 149 tion. It would take more than ten minutes. Clearly, such equations can only be handled
 150 by computers and it questions the usefulness of analytical expressions of such complexity.

TABLE II. – *A selection of best high-precision isotope ratio measurements to date.*

Year	Element	Relative uncertainty	Instrument	Ref.
1997	silicon	4 parts in 10^5	Sector field gas MS	[19]
2016	magnesium	8 parts in 10^5	MC-ICPMS	[20]
1982	silver	10 parts in 10^5	TIMS	[21]
2019	lead	15 parts in 10^5	MC-ICPMS	[17]
2017	molybdenum	18 parts in 10^5	MC-ICPMS	[22]
2007	cadmium	22 parts in 10^5	TIMS, MC-ICPMS	[23]

151

152 **3.2. Variable transformation.** – Mass spectrometers are ill-suited to measure high-
 153 and low-abundance isotopes simultaneously and clever experimental designs can afford
 154 the ability not to measure certain isotopes —a feature that is crucial when working with
 155 highly-enriched isotopic materials. The kilogram and the mole were redefined in 2019
 156 as a decades-long research effort to measure the Avogadro and Planck constants. This
 157 experiment involved a crystal of silicon-28 isotope with other two isotopes present only at

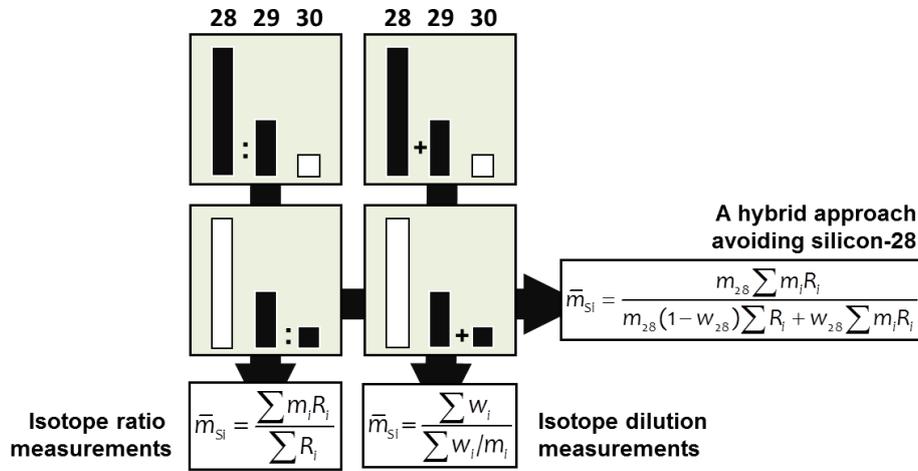


Fig. 3. – Atomic-weight measurements of silicon for redefinition of the kilogram and mole: mathematical variable transformation affords the ability *not* to measure silicon-28 in the sample.

parts-per-million levels. Measuring the atomic weight of silicon in this material therefore required a way to avoid measuring silicon-28 which was done using the experimental design to avoid measuring silicon-28 as shown in fig. 3 [15, 24].

3.3. Mass-bias calibration models. – Isotope ratios undergo changes in mass spectrometers and the instrumental fractionation models allow to calibrate any isotope ratios of an element from a single known isotope ratio. Isotope ratio calibration factors in mass spectrometry are usually modeled using monotonic functions of the mass difference between the isotopes. In the case of silicon, this can be written as

$$(9) \quad K(^A\text{Si}/^{28}\text{Si}) = f(m_A - m_{28}).$$

This is known as the mass-dependent fractionation and more common choices are listed in table III. For many years, the observed isotope ratios were corrected based on simple assumptions regarding the nature of gas flow in various mass spectrometer inlet systems. With the advent of calibrated measurements in the 1950s, however, it was noticed that performing such corrections could produce larger errors than simply accepting observed isotope ratios as is [25]. Today, most commonly used model to correct the instrumental fractionation of isotopes is the exponential law.

Correcting the instrumental fractionation effects is perhaps the most significant aspect of isotope ratio measurements today. Early atomic-weight measurements of natural silicon (1994) for better Avogadro/Planck constant had overlooked a calculation error

TABLE III. – *A selection of isotope ratio fractionation models used in mass spectrometry.*

Model type	Name	Equation
theoretical	effusion	$K_{1/2} = (m_1/m_2)^{1/2}$
empirical	linear	$K_{1/2} = 1 + a \cdot (m_1 - m_2)$
empirical	exponential	$\ln K_{1/2} = a \cdot (m_1 - m_2)$
empirical	Russell	$\ln K_{1/2} = a \cdot (m_1/m_2)$
empirical	generalized	$\ln K_{1/2} = a \cdot (m_1^n - m_2^n)$

176 which had the effect of producing non-monotonic calibration factors

$$\begin{aligned}
 K(^{28}\text{Si}/^{28}\text{Si}) &= 1 \text{ (exact),} \\
 K(^{29}\text{Si}/^{28}\text{Si}) &= 1.0015, \\
 K(^{30}\text{Si}/^{28}\text{Si}) &= 0.9976.
 \end{aligned}$$

177 The error in the correction factor $K(^{29}\text{Si}/^{28}\text{Si})$ was found more than a decade later (its
 178 value has to be below 1) but the lack of full disclosure of the raw data in previous studies
 179 delayed the understanding of the errors inherent in these results [26]. This small error
 180 ultimately had the effect of creating a few parts-per-million disagreement between the
 181 best estimates of Avogadro and Planck constants at the time and even questioned the
 182 validity of two phenomena that led to two physics Nobel Prizes the quantum Hall effect
 183 and the Josephson effect (both CODATA-2002 and CODATA-2006 reports investigated the
 184 exactness of the relations $K_J = 2e/h$ and $R_K = h/e^2$) [10].

185 Much debate exists over the mathematical form of the mass-bias correction model
 186 to correct the observed isotope ratios; whether linear, exponential, or polynomial [27].
 187 However, almost entirely neglected has been the question whether the dependence of the
 188 instrumental correction factors on the isotope masses can be approximated with a single
 189 smooth function altogether. Many isotopes are known to undergo instrumental fractionation
 190 that is markedly different from the neighboring isotopes of the same element. An
 191 example of this is the fractionation of germanium isotopes in MC-ICPMS wherein close to
 192 a half percent bias can be obtained when isotope ratio $^{72}\text{Ge}/^{74}\text{Ge}$ is used to correct for
 193 $^{73}\text{Ge}/^{74}\text{Ge}$ using the Russell law [28].

194 **3.4. Secondary methods of calibration.** – Introduced in the 1960s, the double-spike
 195 method is among the oldest practical means to correct for instrumental fractionation
 196 effects [29] and remains routinely used in geosciences [30]. Double-spike calibration relies
 197 on the fact that isotope ratios of mixtures are linear combinations of their constituent
 198 components. For example, isotope ratios of lead, $R_{i/206}$ ($i = 204, 207, 208$), in sample A,
 199 isotopic standard B, and their mixture (AB) are related as follows:

$$(10) \quad R_{i/206}(\text{AB}) = q \cdot R_{i/206}(\text{A}) + (1 - q) \cdot R_{i/206}(\text{B}),$$

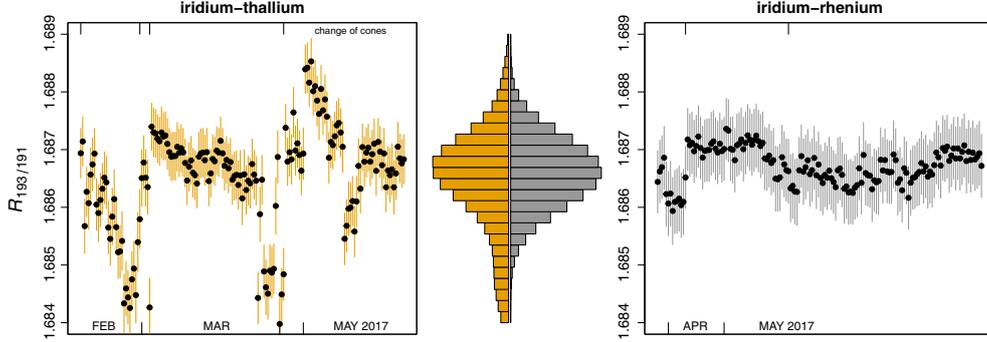


Fig. 4. – MC-ICPMS measurements of iridium isotope ratios using rhenium and thallium standards with the regression method [32].

where q is the mixing-ratio. Measuring all three lead isotope ratios from the sample (A) and the sample-standard mixture (AB) provides sufficient information to calculate the true isotope ratios of lead in the sample if all measured isotope ratios are modeled using the exponential law ($i = 204, 206, 208$):

$$(11a) \quad \ln R_{i/206}(A) = a_A \cdot (m_i - m_{206}) + \ln r_{i/206}(A),$$

$$(11b) \quad \ln R_{i/206}(AB) = a_{AB} \cdot (m_i - m_{206}) + \ln r_{i/206}(AB).$$

In this model we allow for a different instrumental isotopic fractionation when measuring the sample (a_A) and the sample-spike blend (a_{AB}). Together, eqs. (10) and (11) constitute a nonlinear system of 9 equations and 9 unknown parameters ($R_{i/206}(A)$, $R_{i/206}(AB)$, a_A , a_{AB} , and q) with $r_{i/206}(A)$, $r_{i/206}(AB)$, and $R_{i/206}(B)$ as the input data.

Another cost-efficient approach to correct instrumental fractionation takes advantage of the correlated changes of the measured isotope ratios [31]. Consider a sample of lead admixed with isotopic standard of thallium. If the measured isotope ratios $r_{208/206}$ (lead) and $r_{205/203}$ (thallium) from this mixture can be obtained over a certain period of time such that they exhibit strong correlation in a logarithmic scale, *i.e.*,

$$(12) \quad \ln r_{208/206}(t) = a + b \cdot \ln r_{205/203}(t),$$

then it is possible to obtain fractionation-corrected isotope ratio $R_{208/206}$ as follows:

$$(13) \quad \ln R_{208/206} = a + b \cdot \ln R_{205/203}, \quad \text{or} \quad R_{208/206} = e^a \cdot b^{R_{205/203}}.$$

The regression method has been used for several decades with promising results. Figure 4 shows iridium isotope ratio measurements with MC-ICPMS using two different isotope standards —rhenium and thallium— with both measurements yielding same results [32]. Furthermore, the regression method has been shown to provide results identical to the gravimetric mixture method to few parts in 10^4 .

220 **3**'5. *Coherence of isotope ratio measurement results.* – Before the 1960s atomic weights
221 were largely based on classical chemical analysis and not mass spectrometry. A major
222 consequence of this was the inter-connectivity of the various atomic-weight estimates. Be-
223 cause most substances for the atomic-weight determinations were halides whose chemical
224 equivalent was determined from their silver salts, the atomic weights of silver, chlorine,
225 bromine, and iodine would influence the atomic weights of many other elements. Thus,
226 for example, it was noted in the 1925 Report of the Atomic Weights Commission that any
227 changes to the standard atomic weight of silver would affect over 40 other elements [33].
228 Today, this feature is largely lost as mass spectrometric analysis produces results for each
229 element independently. There is, however, a need to compare isotope ratios between ele-
230 ments. Various radiometric dating methods —Rb-Sr, U-Pb, Sm-Nd, or Re-Os to name a
231 few— rely on direct comparison and interpretation of isotope ratios between various el-
232 ements. Recent applications of the regression method with MC-ICPMS has re-established
233 the ability to evaluate the coherence of isotope ratios between various elements. In the
234 last decade, in fact, numerous isotope systems have been successfully compared which
235 include Hg-Tl, Pb-Tl, Ir-Tl, Os-Ir, Re-Os, W-Re, and Hf-Re among others. Given that
236 for most elements there are only few independent measurements of their isotopic compo-
237 sition, the ability to perform additional compatibility tests is key towards strengthening
238 the trust in isotope ratio measurement results.

239 **4. – Isotope ratio measurements and the International System of Units (SI)**

240 Accurate determinations of atomic weights of the elements has a rich legacy of con-
241 tributions in science [34]. The discovery of isotopes has questioned the limits of many SI
242 units at the time. When isotopes of cadmium were discovered in 1920s it became clear
243 that the isotopic wavelength shifts limited the realization of the metre to parts in 10^6
244 using the red cadmium line with interferometry. The atomic weight of silver remained
245 the main source of uncertainty in the Faraday constant until the 1980s, and isotope ratio
246 measurements of argon remained the single largest uncertainty component in the best
247 measurements of the Boltzmann constant before the redefinition of the SI in 2019.

248 Natural variations of the isotopic composition of hydrogen and oxygen limit the real-
249 ization of the water triple point to $100\ \mu\text{K}$ [35]. As a result, the definition of the kelvin
250 was clarified in 2005 to specify the isotopic composition of water. More recently, the
251 isotope ratio measurements of silicon were at the center of uniting two colossal inter-
252 national experiments —the Kibble balance and the Avogadro project— for determining
253 the Planck constant in support of the new definition of the kilogram. These examples
254 illustrate the broad relevance of atomic-weight measurements in science which is unlikely
255 to disappear any time soon [10].

256 Among the most common means of realizing the chemical amount (mole) is from
257 mass measurements of substances through the use of standard atomic weights (or molar
258 masses) provided by IUPAC. For many years now it is well-known that isotopic compo-
259 sition of many elements varies substantially among natural materials —a feature that
260 enables many applications. As an example, isotope ratios of boron vary by 4% in na-

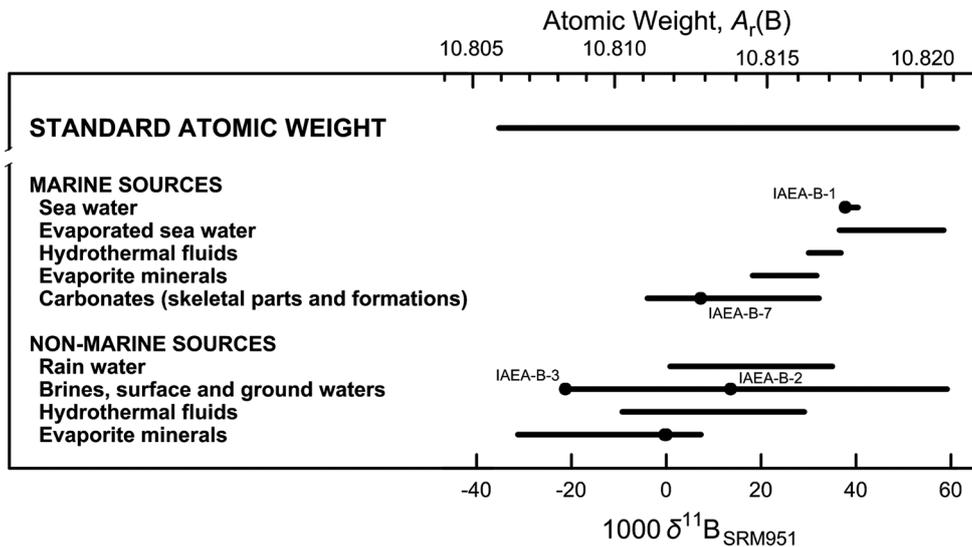


Fig. 5. – Variations of the isotopic composition of boron in nature (modified from [36]).

ture (fig. 5) which limits the accuracy of concentration measurements when “common” isotopic composition is assumed.

5. – Building consensus

Results outside ± 4 standard uncertainties are deemed highly unlikely, yet they occur rather often in science [37]. In the 1990s, as an example, contemporary determinations of Newton’s gravitational constant were in severe disagreement, the half-life estimate of technetium-97 has doubled between the 2003 and 2012, and the only two independent atomic-weight estimates of ytterbium are apart by ten standard uncertainties. A feature common in all these examples is that combining information from diverse sources often requires additional efforts to understand the discrepancies and select mathematical methods suited to combine such data.

Consider Clarke’s 1897 landmark compilation of atomic-weight measurements summarizing published results from diverse methods and researchers (table IV) [6]. Clarke proceeded to combine these results using the weighted mean which yielded a value 126.52 with standard uncertainty 0.01. Clarke utilized the following statistical model:

$$(14) \quad A_r(\text{Te})_i \sim N(\mu_1, u^2(A_r(\text{Te})_i)).$$

Here, the input data are related through a statistical model also known as the observational measurement model [38]. The sole output quantity, μ_1 , is the inverse-variance weighted average of results from all studies.

TABLE IV. – *Summary of 19th century atomic-weight determinations of tellurium* [6].

i	Method of analysis	Result, $A_r(\text{Te})_i$	Uncertainty, $u(A_r(\text{Te})_i)$
1	Te : TeO ₂	127.040	0.017
2	4Ag : TeBr ₄	126.650	0.030
3	K ₂ TeBr ₆ : 6AgBr	126.502	0.143
4	Te : H ₆ TeO ₆	126.303	0.025
5	TeO ₂ : H ₆ TeO ₆	126.209	0.014
6	TeO ₂ : Te	125.960	0.157

279 One can notice that the average difference between the individual estimates of $A_r(\text{Te})$
 280 is much larger than the reported uncertainties. This indicates a significant source of
 281 uncertainty that is not recognized by these methods of analysis. One way to capture this
 282 uncertainty is by the use of a random effects statistical model [39]:

$$(15) \quad A_r(\text{Te})_i \sim N(\mu_2, u^2(A_r(\text{Te})_i) + \tau^2).$$

283 Solving this two-parameter model for μ_2 and τ yields a consensus value $\mu_2 = 126.45$ with
 284 significantly larger uncertainty $u(\mu_2) = 0.20$ compared to $u(\mu_1) = 0.01$. Not only is the
 285 uncertainty of the random-effects consensus value 20 times larger but the best estimate
 286 (μ_1) is also shifted by 8s with respect to the fixed-effects model (μ_2). The parameter τ
 287 in eq. (15), sometimes known as the dark uncertainty, can be estimated using a variety of
 288 statistical methods among the most popular of which is the method-of-moments solution
 289 put forward by DerSimonian and Laird in 1986 [40].

290 6. – Mathematics of isotopic composition and atomic weights

291 Consider a sphere and three parameters that can be used to describe its size: volume
 292 (V), diameter (d), and circumference (l). All of these variables are related through a
 293 common variable —the radius (r). While it is trivial to recognize the mathematical
 294 relationships between these variables, less appreciated is the fact that the uncertainty
 295 estimates are also related:

$$(16) \quad u(V) = 4\pi r^2 \cdot u(r) = 2\pi r^2 \cdot u(d) = 2r^2 \cdot u(l).$$

296 As with the sphere, isotopic composition of the elements can also be described using
 297 several complimentary quantities —isotope ratios (R), isotopic abundances (x), or the
 298 atomic weight (A_r). These quantities and their uncertainty estimates too are mathemat-
 299 ically related [41]. As an example, the following holds true for hydrogen:

$$(17) \quad u^2(A_r(\text{H})) = (m_1 - m_2)^2 \cdot u^2(x_1) + x_1^2 \cdot u^2(m_1) + x_2^2 \cdot u^2(m_2).$$

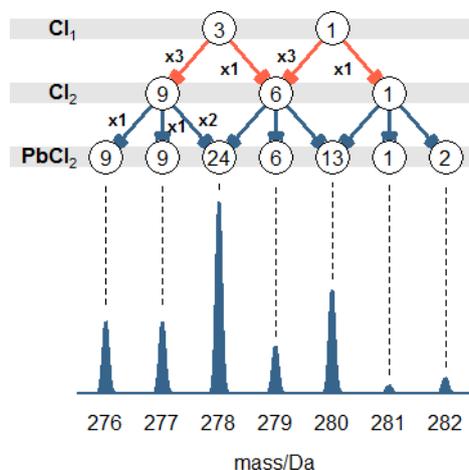


Fig. 6. – Construction of complex isotope patterns using simple cellular automaton [47,48]. For brevity, the minor lead-204 isotope is ignored in this schematic.

Isotopic abundances are constant-sum variables because their sum is constrained to 1 exactly. One of the properties of closed-sum variables is the Chayes rule which states that no isotopic abundance uncertainty can exceed the sum of all others [42]:

$$(18) \quad u(x_j) \leq \sum_{i \neq j} u(x_i).$$

A more trivial property of constant-sum closure is that in two-isotope systems the uncertainties of both isotopic abundances must be equal. Overall, handling correlations between the isotopic abundances or isotope ratios is an important part in evaluating uncertainty of isotopic composition of the elements.

While atomic and molecular weights form the basis for many chemical calculations, isotope patterns are used, for example, to identify substances and to deduce their molecular formula. Calculation of isotopic abundances of molecules involves basic principles of combinatorics and polynomial expansion [43]. Still, isotope patterns of rather complex molecules can be even calculated without resorting to a calculator. This is illustrated in fig. 6 where a cellular automaton is used to construct the isotopic pattern of PbCl_2 .

The uncertainty evaluation of isotopic composition of molecules is a challenging task due to the complexity of the measurement models. As an example, a simple amino acid methionine ($\text{C}_5\text{H}_{11}\text{NO}_2\text{S}$) consists of 2304 different molecules (isotopologues). Traditionally, the polynomial expansion has been used to calculate the isotopic composition of molecules which is a highly-inefficient process from the computational point of view. Hence, efficient mathematical methods are needed to convert the isotopic composition of individual elements into the isotopic composition of molecules. Among such methods are recursive algorithms based on Newton-Girard and Viète formulas [44] or efficient construction of isotope patterns using Fourier transform [45, 46].

322 **7. – Outlook**

323 Isotope ratio measurements have played a crucial role in science for a century now
324 and one expects no less of them in the future. Indeed, the scientific applications of
325 isotopes have come a long way from estimating the water content of the human body in
326 the 1930s [49]. Today, for example, one can use isotopic exchange as thermodynamically-
327 based thermometer and estimate the formation temperature of carbonates by measuring
328 their isotopic composition [50]. In addition, isotope ratio measurements of carbon dioxide
329 play a key role in understanding the fate of our planet [51]. Who knows what new
330 applications will emerge from high-precision analysis of isotopes.

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