

IS MASS SPECTROMETRY ACCURATE?

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ABSTRACT. Mass spectrometry measures atomic masses giving precision of 10^{-10} , but its accuracy has not been verified - precision and accuracy are two independent aspects. The Lorentz force law underlying mass spectrometry has not been verified. In the 1920's, the atomic masses of some elements measured through the early mass spectrometers showed some discrepancies from the '*whole-number-rule*' of atomic weights. The physics community accepted the discrepancies from whole numbers to be correct; they proposed the concept of '*mass defects*'. This, together with the mass energy equivalence of $E = mc^2$ allowed Arthur Eddington to propose a new 'sub-atomic' energy to account for the source of the energy of the sun to be in line with the 15 billion age of the sun in their theory. They never entertained the other simpler option - that their mass spectrometers were only approximately good. If the atomic masses of nuclides were to be just whole numbers equal to the mass number in atomic mass unit, it would be a confirmation of the law of mass conservation in the atomic and subatomic world. The key to decide the fate of nuclear physics is in sodium fluoride NaF. Sodium and fluorine occur in nature only as single stable isotopes. A chemical analysis of NaF with the current analytical balance to determine the relative atomic mass of Na/F would decide conclusively if mass spectrometry is accurate. The current relative atomic mass of Na/F is : 22.989769/18.998403 or 1.210089; the ratio of the mass number of Na/F is : 23/19 or 1.210526. The accuracy of mass spectrometry would be confirmed if the value is 1.210089 ± 0.000012 . Otherwise, if the value is 1.210526 ± 0.000012 , it would mean a confirmation of the law of conservation of mass. The implications of such a scenario is beyond imagination - the whole world of nuclear physics would collapse.

1. INTRODUCTION

Despite the very great advancement in physics since the time of Newton, there are some basic physical concepts that have not changed. One is the concept of mass - it is still the same '*quantity of matter*' in Newton's '*Principia*'. Even special relativity cannot run away from this concept as when a relativistic mass come to rest, it would still be the

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same invariant mass of Newton. We are here concerned only with mass as quantity of matter.

The measurement of mass is central to physics as mass is one of the basic dimensions of physical nature upon which the science of physics is based on. There cannot be the least of a compromise concerning the measurement of mass if physics is to be sound as a science verifiable through empirical and experimental evidence. The method to measure amount of substance since antiquity is the weighing scale based on the lever principle. Although we now have a formal name for the principle as "*Archimedes' lever principle*", the ancients (not just the Greeks!) just understood that *that* was the way to correctly weigh and measure gold, silver, grains, etc - it was just an obvious empirical principle. So the weighing scale for mass is a direct method to measure quantity of substance and matter. We say it is direct as it is based only on a universally recognized natural principle. The balance scale was so much trusted that the sacred texts of some religions seem to suggest that the scale was so accurate that it could even measure the amount of sins that a man committed while living in the world!

In the early days of chemistry, compounds were analyzed to unravel the compositions of pure elements within a compound. From such analysis, together with the development of molecular theory, the atomic weights of the atoms could be calculated. An English chemist William Prout in 1815 found that the atoms of elements all seemed to have a mass that are whole numbers of the mass of the hydrogen atom - the so called '*whole number rule*' of atomic weights known as Prout's hypothesis. So they have a scale of atomic weights of the elements with the hydrogen atom being 1; in this scale, the atomic weight of oxygen is 16, nitrogen 14. In fact, some of the earlier periodic tables had atomic weights of the elements as whole numbers. This '*whole number rule*' appeared to be discredited when mass spectrometry was invented in the late 1910's; mass spectrometers could sort and isolate ions of nuclides and to weigh them with the new '*scale_of_the_20th_century*' to higher, and ever higher, resolution until they found that the atomic weight of an atom differ slightly from the whole number which is the mass number of the atom - the number of protons and neutrons.

It was with mass spectrometry that the isotopes of elements were discovered; isotopes are different nuclides of the same element with differing atomic weights. With his first spectrograph, J.J. Thomson in 1913 found that neon had two species, the Ne-20 with the usual atomic weight of 20 and another with an estimated weight of 22. This was the start of the discovery that most elements in nature have more than one isotopes. Many have stable non-radioactive isotopes with their abundance distribution being rather fixed for many of the

elements. Following this would be a new age of nuclear physics as the ability to even weigh the mass of nuclides would allow for greater understanding of the atom and its nucleus. In fact, this ability to weigh an atom borders on the miraculous and seems to infringe on a domain that once were reserved for the gods. With this new technique of mass spectrometry, the push was for higher and yet higher resolution. The latest mass spectrometer using the Penning trap has the ability to weigh ions to 1 part in 10^{11} . The physics world only cared for greater resolutions of their new tool. No one stopped to ask the critical question: *Is mass spectrometry accurate?* The main aim of this paper is to answer this question.

2. THE PRINCIPLE BEHIND A BALANCE NEED TO BE VERIFIED

Before we question the accuracy of mass spectrometry, we will first examine the question of reliability of a method for weighing mass. Here we are questioning whether the principle behind the method is accurate.

Take the common scale balance that have been in used since antiquity. Is the principle of such a balance reliable? The answer is a resounding 'Yes'. The scale is based on a universally accepted natural principle. As we have noted earlier, the scale based on the lever principle may even be said to a 'direct' method of weighing mass; it is the only direct method of weighing mass among the available type of weighing balances. All other types of weighing scales may be said to weigh mass 'indirectly' as they have to rely on the properties of some physical phenomena in order to determine the mass of a body. If the physics behind the method is not accurate, then the weighing scale would not be accurate.

Let's examine the simple spring balance. It relies on the extension x of a spring from its equilibrium position where the extension is proportional to the force pulling on the spring: $F = mg = Kx$ where K is the spring constant. The equation simplifies to : $m = (\frac{K}{g})x$. We could just use one calibration of x_1 with a standard weight m_1 and simply use this reference mark to calibrate the spring balance to read a whole range of weights through simple proportionality; every equal division between two markings represent the same change in the mass reading. Is this spring balance reliable? We all know that it is not. The principle behind this balance is approximate as we know the linearity of any spring is only approximate within a range of extension. This shows that any method that weighs mass indirectly has to be verified.

It is always necessary to verify the accuracy of a method to weigh mass if the method is indirect.

The most precise chemical balance today is the analytical balance, the '*force restoration balance*'. When a weight is placed on a scale pan, it will tilt a balance beam. There is a sensor that detects displacement. An electro-magnetic restoring force is applied at the other end through a transducer circuit until the beam's tilt is neutralized. The transducer will record a current needed to produce the restoration force. Such a transducer has been tested for linearity that the force is proportional to the current to a high degree of accuracy. The current would now be translated to a weight measurement. The analytical balances today is capable of an accuracy to weigh one gram to 1 part in 10^5 or 10^7 .

Besides a direct experimental verification of the principle behind a balance type, there are two physical tests that are available that may be used as indirect tests of the principle behind the balance. These two tests could also detect flaws of an individual balance due to design or technical failure.

- (1) Consistency test. The balance may be tested to be consistent with a different but verified weighing method. As an example, the analytical balance can be tested for consistency with a beam balance. We know the beam balance has a much lower precision, but by comparing the two balances to weigh a sample, the analytical balance's reading must be consistent with that of the beam balance's reading in its order of uncertainties. Such a consistency test is fundamental and a balance type should never fail such a test.
- (2) Linearity test. A balance weighs samples A and B separately giving values of m_a and m_b . When it weighs A and B together, the result of the combined masses of A and B must be equal to $m_a + m_b$.

3. GENERAL PRINCIPLES OF MASS SPECTROMETRY

There are many variations of mass spectrometers, but all of them are based on the Lorentz force law : $\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B})$. The earliest usually rely on the deflections of a moving charged particle in a magnetic field. If there is a region of vacuum with a uniform magnetic field \mathbf{B} and a charged particle or ion is injected perpendicular to the magnetic field, the particle will trace a circular path where the plane of the circle is perpendicular to \mathbf{B} . The equation of motion here is:

$$\begin{aligned} F &= qvB = mv^2/r \\ q/m &= v/rB \end{aligned} \tag{1}$$

q, m being the charge and mass of the particle tracing a circular path of radius r . If the quantities on the RHS of the equation are known, then the charge-mass ratio of the particle would be found. In general, the particle traces only part of an arc and then would leave the

magnetic field and travel straight hitting a screen (in the early days, a photographic plate was used). By noting the position that the particle hits the screen, and together with the measured deflection of the particle's direction from its original direction, the radius r could be found. The charge q is usually one electron charge. In this manner, the mass could be found from the equation (1) above.

The 'Penning trap' makes use of the same uniform magnetic field to trap an ion in a circulatory motion in the x-y plane about a z-axis parallel to \mathbf{B} . Such a pure circular motion in the x-y plane cannot be stable. The penning trap makes use of an overlap of a weak static and an alternating voltage across the z-direction to restrain the motion of an ion along this z-axis. In this way, the ion is trapped in a 3D oscillatory motion within a cell space. With proper choices of parameters for the electric and magnetic fields, an ion may be trapped within a cell with a typical dimension of 1cm to 5cm. At present, nearly all nuclidic mass measurements are made with the Penning trap and the resolution may go as high as 1 part in 10^{11} . From the same equation of motion (1), we can arrive at an equation with an angular frequency ω_c instead:

$$m = \frac{qB}{\omega_c} \quad (2)$$

With the same unchanged electric and magnetic fields environment of the trap for two particles, the relative mass of two masses m_2, m_1 with the same electron charge would be:

$$\frac{m_2}{m_1} = \frac{\omega_1}{\omega_2} \quad (3)$$

This equation is only a simplification to show that the relative atomic mass is related to the ratio of characteristic frequencies of trapped ions. The actual relationship is complex. The Penning trap enables a measurement of relative frequencies to arrive at a relative atomic mass of two ions trapped under the same trap parameters. It is the very high resolution with which the frequencies can be measured that the Penning trap can measure relative atomic mass to the current high resolutions.

4. VARIOUS ISSUES WITH MASS SPECTROMETRY

- (1) Lorentz force law unverified. First and foremost, the Lorentz force law has not been experimentally verified directly. Mass spectrometry makes use of $\mathbf{F} = q(\mathbf{v} \times \mathbf{B})$. When used to implement a measuring technique, the precision of the technique cannot be higher than the precision to which the law has been verified experimentally. In order that mass spectrometry can measure atomic mass to 1 part to 10^{11} , the magnetic force law, too, need to be experimentally verified to at least this

Particle	amu	r cm	B Tesla	v/c	γ	γ_1/γ_2
$^{12}\text{C}^+$	12	1	7	0.0018774	1.0000018	1.0002521
$^1\text{H}^+$	1	1	7	0.0225288	1.0002539	
$^{12}\text{C}^+$	12	2	7	0.0037548	1.000007	1.0010096
$^1\text{H}^+$	1	2	7	0.0450577	1.0010166	
$^{12}\text{C}^+$	12	3	7	0.0056322	1.0000159	1.0022759
$^1\text{H}^+$	1	3	7	0.0675865	1.0022918	
$^{12}\text{C}^+$	12	4	7	0.0075096	1.0000282	1.004057
$^1\text{H}^+$	1	4	7	0.0901153	1.0040853	
$^{12}\text{C}^+$	12	5	7	0.009387	1.0000441	1.006361
$^1\text{H}^+$	1	5	7	0.1126441	1.0064054	

TABLE 1. Errors from relativistic effects. γ_1/γ_2 is the estimate of the error factor for a particle pair; it increases with increasing r and B.

order of precision. But the Lorentz force law has never been directly verified through experiments to be correct as a mathematical law expression. In schools, the Lorentz magnetic force law is only demonstrated by showing how a magnet could deflect an electron beam in a discharge tube; but this is not the type of verification that would suffice for the Lorentz magnetic force to be the basis of a technique to weigh atoms. There may also be the claim that the Lorentz magnetic force has been indirectly verified by the force between two current carrying conductors. This too is insufficient. It is not a general verification as we know the drift velocity of electrons within conductor currents is in the order of millimeter per second whereas the velocity of the ions are moving way beyond such velocities and also in vacuum.

If we ponder the question in some depth, we may arrive at the conclusion that there may not be any means to verify the magnetic force law directly. It would require the need to measure a magnetic force acting on an infinitesimally small moving particle in a magnetic field. Just measuring the force itself would present an insurmountable obstacle. Magnetism is founded on the Biot Savart Law; it implies measuring the magnetic field \mathbf{B} of the Biot Savart Law precisely - and without recourse to the Lorentz force law itself! It is unlikely any physicist would be up to such a task. This may be the very reason why no experiment has ever been done to verify the Lorentz force law to any degree of precision. Without the Lorentz force law being verified, other methods have to be found to directly verify the technique of mass spectrometry itself.

Particle	amu	r cm	B Tesla	v/c	γ	γ_1/γ_2
$^{12}\text{C}^+$	12	1	7	0.0018774	1.0000018	0.9999983
Fe-56	56	1	7	0.0004023	1.0000001	
$^{12}\text{C}^+$	12	2	7	0.0037548	1.0000007	0.9999933
$^{56}\text{Fe}^+$	56	2	7	0.0008046	1.0000003	
$^{12}\text{C}^+$	12	3	7	0.0056322	1.0000159	0.9999849
$^{56}\text{Fe}^+$	56	3	7	0.0012069	1.0000007	
$^{12}\text{C}^+$	12	4	7	0.0075096	1.0000282	0.9999731
$^{56}\text{Fe}^+$	56	4	7	0.0016092	1.0000013	
$^{12}\text{C}^+$	12	5	7	0.009387	1.0000441	0.999958
$^{56}\text{Fe}^+$	56	5	7	0.0020115	1.000002	

TABLE 2. Errors from relativistic effects. γ_1/γ_2 is the estimate of the error factor for a particle pair; it increases with increasing r and B.

- (2) The relativistic mass effect. The relative mass between two ions in mass spectrometry is strictly the ratio of two '*relativistic masses*'; there should be a further γ -factor to each of the masses giving the true rest-mass ratio of m_1/m_2 an additional relativistic error proportional to γ_2/γ_1 . The two tables (1) and (2) show the estimates. The simplified formula for the velocity of an ion within a Penning trap is: $v = (q/m)rB$ assuming a small v/c . Increasing magnetic field will allow for cells of smaller sizes; typical values of B ranges from 3 to 9T. The cell dimension ranges from around 1 - 5cm. The γ_1/γ_2 error increases with increasing radius r and B. As seen from the pair C-12/H-1 for r = 5cm and B = 7T, the relativistic error factor is about 6 part in 1000; if such high systemic errors are found in mass spectrometry, then it truly is unreliable. With the typical parameters as in the tables, it is not possible for the Penning trap to determine the mass of the electron if paired with C-12; the very small mass of the electron would need near light speed for it to stay within the Penning trap.

5. ACCURACY OF MASS SPECTROMETRY NOT VERIFIED

Ever since the invention of mass spectrometry, the pursuit was only for higher - and yet higher - resolutions of this new technique. There never was any call to examine if the principle behind mass spectrometry was accurate. It seemed to be just accepted on plain faith - a large dose of it to go with. As we have seen earlier, the physics behind mass spectrometry itself has not been verified. Mass spectrometry may not be an accurate technique to measure atomic masses of elements. Even though the resolving powers and precision of the Penning trap may reach 1 part in 10^{11} , such a precision does not translate to accurate

measured values for atomic masses if the principle behind mass spectrometry itself is inaccurate. It may even be possible that the systemic error of mass spectrometry renders its accuracy to only just about 1 part in 10^4 , *a seven order difference from its precision!* It is conceivable as precision and accuracy are two fundamentally different aspects. As long as mass spectrometry is not verified, its accuracy could be anything.

The accuracy of mass spectrometry is unknown as it has not been verified.

As we have seen earlier, all our balances for weighing macroscopic mass have been validated to be reliable in principle. As to what precision the balances could deliver is a matter of design and technology. On the other hand, atomic mass is now solely determined with mass spectrometry, but its method is unverified. G. Audi [1] described in *'The History of Nuclidic Masses and of their Evaluation'* how, with his improved mass spectrometer, Francis William Aston in 1919 could revive the *'whole-number-rule'* of atomic weights; the only exception seems to be hydrogen with an atomic weight of 1.008 in agreement with the value of the chemist. There was a discrepancy in the weights of helium and hydrogen from the whole number rule - the atomic weight 4 of helium was short of the weight of four hydrogen atoms. A *'mass-defect'* was discovered. It was Arthur Stanley Eddington (who observed the famous solar eclipse of 1919) who accepted the discrepancy of the atomic weights from whole numbers as correct as he proposed the notion of mass-defect with the mass-energy equivalence of $E = mc^2$ to account for the source of the sun's energy. This theory of nuclear energy based on such *'mass defects'* finally won the full support of the physics academia.

There actually was another simpler explanation for the discrepancies of the atomic weights of some elements from the *'whole-number-rule'*, but which no one in the 1920's seemed eager to entertain.

Mass spectrometry was only an approximate technique.

Mass spectrometry may not be an accurate weighing technique. This is not surprising as it was not verified. It is conceivable that if we had weighed atoms using the beam balance, the atomic weights would be just whole numbers equal to the mass number of a nuclide in atomic mass unit! This hypothesis is not outrageous. It is just the *'law of mass conservation'* at work. We know that the free neutron decays into a proton and the electron; with mass conservation, the mass of the neutron is simply the sum of the mass of the proton and the electron; this is also the mass of the hydrogen atom. So with the law of conservation, the mass of a nuclide is just its mass number in atomic mass unit. If the law of mass conservation is found to be correct, the

implications would be unimaginable. There would not be any need for the law of mass-energy conservation, no more mass deficit and the use of the equation $E = mc^2$; there is no more any need to weigh atoms. But one very important theory would be missing - a theory of nuclear energy. We would then have to come out with a new theory to explain the nuclear energy of fission and fusion.

If the law of conservation of mass is correct, it would mean the total collapse of nuclear physics as a theory.

6. SODIUM FLUORIDE HOLDS THE KEY

As we have seen so far, the very fate of physics depends on the answer to just one question: *Is mass spectrometry reliable?* We already have some views on the question. Firstly, the Lorentz magnetic force law underlying mass spectrometry has not been verified. Secondly, mass spectrometry fails the linearity test. The atomic mass of Helium-4 is 4.002603 amu; that of deuterium is 2.014101 amu. We know that Helium-4 has exactly twice the number electrons, protons and neutrons as in deuterium, but the atomic mass of Helium-4 is not exactly twice that of deuterium. But the physics world prefers the concept of mass-deficit and rejects the notion that mass spectrometry weighs atomic masses only approximately. Such is still just an accepted viewpoint without any experimental justification. But there is a way out to resolve this question conclusively - and also very easily. The key is in Sodium Fluoride NaF.

We finally have to do a consistency test for mass spectrometry. Mass spectrometry is not the only technique available to weigh atoms; the chemists of the 19th century already had done that. The atomic weights in chemistry in the earlier centuries are actual chemical analysis of compounds and the weights are determined with the chemical balance - a direct method of weighing mass. They had a value for the relative atomic mass of the pair Na/F. The 1900 value of the atomic weights (of chemistry) of Na is 23.00, that of F is 19.03. This gives the relative atomic mass of Na/F to be 23.00/19.03 or 1.21. This is so because it happens sodium and fluorine both occurs in nature as the only stable isotope. But this figure of 1.21 is of insufficient precision to decide the accuracy of mass spectrometry. The relative atomic mass of Na/F based on the current atomic mass is : 22.989769/18.998403 or 1.210089; this figure may be taken to be without uncertainty as the atomic masses have no uncertainty in the 6th decimal. The ratio of the mass number of Na/F is : 23/19 or 1.210526. So the problem reduces to doing a chemical analysis using our chemical balance to determine the relative atomic mass of Na/F, whether it agrees with 1.210089 or with 1.210526. To conclusively resolve the question of the reliability of mass spectrometry, we need

a figure that is at least accurate to the 4th decimal, i.e. 1 part in 10^4 . Fortunately, our current analytical balance has a precision of 1 part in 10^5 or even higher. With a fresh analysis of NaF today, we could come out with a value of : 1.210089 ± 0.000012 confirming the accuracy of mass spectrometry; or the value may be 1.210526 ± 0.000012 rejecting mass spectrometry and confirming the law of mass conservation - unequivocally.

The question of the accuracy of mass spectrometry could be resolved conclusively by a chemical analysis of Sodium Fluoride to determine the relative atomic mass of Na/F. If the figure is 1.210089 ± 0.000012 , the accuracy of mass spectrometry would be confirmed; if it is 1.210526 ± 0.000012 , it means the law of mass conservation is confirmed bringing with it the total collapse of nuclear physics theory of today.

7. CONCLUSION

Mass spectrometry has achieved a very high precision even reaching 1 part in 10^{11} ; but precision and accuracy are two independent aspects. Until now, there has been no experiment done to verify the accuracy and reliability of the technique to weigh atomic masses. The current accepted masses of nuclides published in the CODATA with precisions reaching 10^{-10} may even be just accurate to only 10^{-4} , off by 6 orders of magnitude. If atoms could be weighed with our verified chemical balances, the atomic masses of nuclides may just be the mass number in unified atomic mass unit. This would mean a confirmation of the law of conservation of mass in the atomic and sub-atomic world. Whether mass spectrometry is consistent with our analytical balances in weighing mass could be tested through a chemical analysis of sodium fluoride NaF to determine the relative atomic mass of Na/F. The accuracy of mass spectrometry would be confirmed if the value is 1.210089 ± 0.000012 . Otherwise, if the value is 1.210526 ± 0.000012 , it would mean mass conservation is upheld. This latter outcome would mean a total collapse of nuclear physics theory; we would then need to develop a new theory of nuclear physics.

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