Determination of Isotopic Masses and Abundances by Mass Spectrometry

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MASS spectroscopy has developed in two principal directions (*1*). On one hand, research has progressed along the lines started by Aston, who, in 1919, completed the first mass spectrograph. Positive ions originating in a high-voltage glow discharge tube are sent through a combination of electric and magnetic fields in such a way they are sorted according to their masses. The separated beams of ions are allowed to impinge upon a photographic plate. From measurements of the positions and intensities of the lines found on the plate after development, one can determine both the masses of the ions and the relative abundances.

In recent years, most mass spectrographic work has been done with three basic types of instruments that were developed, respectively, by Mattauch (*2*), Bainbridge and Jordan (*3*), and Dempster (*4*). All have certain features in common. The unresolved ion beam leaving the ion source is sent through a portion of a cylindrical electrostatic condenser followed by a region in which there exists a magnetic field. With the proper arrangement of this geometry, these instruments can be given the property of focusing to a common point all ions that deviate slightly in energy and diverge slightly in direction. Such an instrument is said to be double focusing. Mass spectrographs have had their greatest usefulness in the field of determination of precise atomic masses.

The mass spectrometer. The other general approach in mass spectroscopy has been that which was originated by Dempster (*5*), who constructed the first mass spectrometer . Mass spectrometers have been simpler in design than mass spectrographs. Figure 1 is a schematic diagram of some essential parts of the type of mass spectrometer (*6*) that has been used extensively in recent years for the measurement of the relative abundances of isotopes or for making gas analyses. A heated tungsten filament F emits electrons that are collimated into a fine beam. The ions produced in the electron beam by collisions with gas or vapor molecules are accelerated by falling through the difference in potential between plates B and C. Because the ions are produced in a region of practically constant potential, all those that leave the ion source have very nearly the same energy. As they pass between the trapezoidal-shaped poles of a magnet, they are bent in circular paths, the radius of curvature depending upon the mass, the strength of the magnetic field, and the energy that the ions acquired in the ion source.

As is shown in Fig. 1, if the ion-source defining slit, the collector slit, and the apex of the effective magnetic field all lie on a straight line, direction focusing is produced. Ions that deviate slightly in direction as they leave the ion source are all focused on the collector slit. Instruments with various geometry have been employed. Dempster's original instrument was of the 180° type; that is, β was 180°, whereas α and γ were each 0°. In the interest of economy of construction, most modern instruments use a smaller angle β. An instrument in common use has α, β, and γ, each equal to 60°. Another instrument employed to some extent uses $\beta = 90°$, with α nd γ each equal to 45°.

The collector current due to the ion beam for a given isotope is relatively steady. Thus, it is convenient to use an electric measuring instrument, such as an electrometer tube amplifier, for measuring ion currents. A mass spectrum may be swept by changing either the accelerating voltage applied to the ions or the magnetic field. For detecting extremely small ion currents, electron multipliers followed by electrometer tube amplifiers are being used. It is common practice to connect the output of the measuring instrument to a strip-chart recorder and record the ion currents automatically as the mass spectrum is swept.

Relative abundance measurements. It is apparent, therefore, that such an instrument lends itself readily to abundance measurements, since it requires simply a measurement of electric current. In contrast, the use of a mass spectrograph for this purpose involves the more serious problem of converting the blackening of a photographic plate into a measure of beam intensity.

For precise measurement of relative abundances, two ion collectors may be employed along with two separate amplifiers. With a suitable electric measuring circuit one may then measure the ratio of the two ion currents. In this manner higher precision can be obtained with the same expenditure of effort that is required when a single collector is employed.

In 1933 almost all known isotope abundances had been measured with mass spectrographs; by 1942, 48 of the 83 naturally occurring elements had been measured by electric means. At the present time, 79 have been so determined.

Most isotope-abundance ratios are known to 1 percent or better, and the regions in the neighborhood of the known isotopes have been carefully explored for possible rare isotopes. It is unlikely that more than a few naturally occurring isotopes remain undiscovered.

The absolute values for most isotope-abundance ratios are known with sufficient accuracy for most practical purposes. Thus, the principal interest in further work lies in the applications of isotope-abundance measurements to other fields. For example, one of the extremely interesting fields today is the study of differences in isotope-abundance ratios resulting from chemical or nuclear effects that take place in nature. There is, of course, the important use of the mass spectrometer as a detecting device when stable isotopes are used as tracers in research in various chemical and biochemical fields.

Figure 2 is a mass spectrum determined with a 180° apparatus for the element mercury. We see here the seven isotopes of mercury, including the very rare one at mass 196. The sensitivity of measurements with an instrument of this kind is such that one can measure the relative abundance of this rare isotope to about the same precision as that of the other isotopes. If an electron multiplier is used as a detector, isotopes whose abundances are as low as 1 part in 1 million can be measured quite readily.

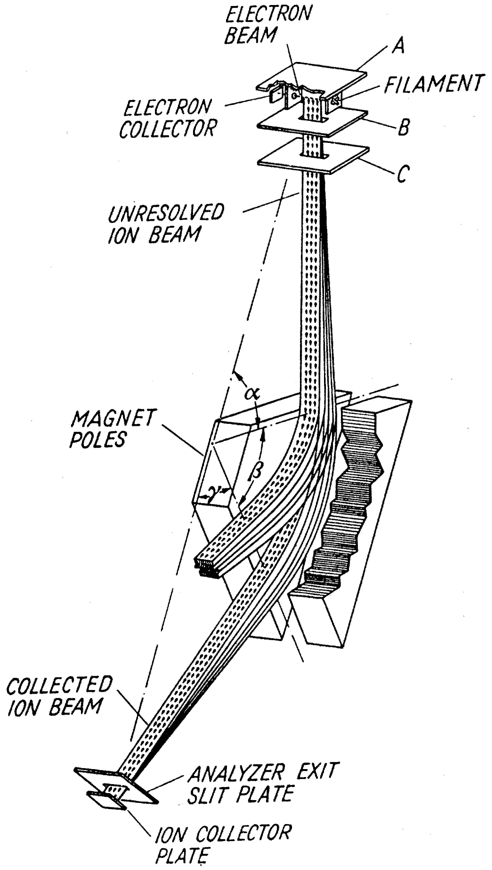

Fig. 1. Schematic drawing of essential parts of a mass-spectrometer tube. Ion source, path of ions, and collector arrangement are enclosed in a suitable envelope that is pumped continuously with a mercury or oil diffusion pump.

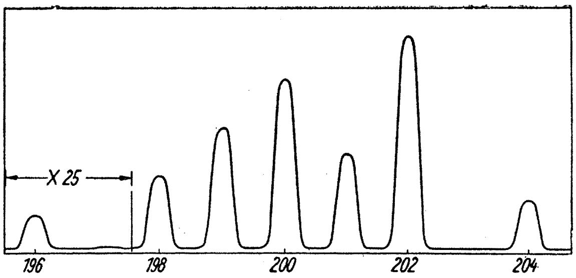

Fig. 2. Mass spectrum showing isotopes of mercury. The sensitivity in the region of Hg^{196} has been increased by a factor of 25 times in order to show the relatively rare isotope. The barely perceptible peak occurring between 196 and 198 is due to a hydrocarbon impurity present during the time this particular spectrum was taken. It is interesting to note that the small peak is slightly closer to the 198 than to the 196 peak. In high-resolution instruments, even those not intended primarily for precision determination of atomic masses, the spectra obtained often show displacements caused by differences in the deviation of masses from whole numbers.

The double-focusing mass spectrometer. Several years ago we became interested in the possibility of using a double-focusing high-resolution mass spectrometer for the precision determination of atomic masses. A properly designed instrument would have certain advantages over conventional mass spectrographs: (i) Inasmuch as the ion currents are detected electrically, data may be taken continuously during the time the apparatus is undergoing adjustment in preparation for taking final measurements. (ii) Because of the high sensitivity it is possible to measure extremely rare isotopes. Consequently it should be possible to make systematic studies and measure isotopic masses for all the isotopes of a given element. (iii) The design and operation of the instrument would in general be sufficiently different from the mass spectrographs already in use, so that systematic errors, if they exist, should be different from those found in other instruments.

Figure 3 is a schematic view of the instrument that we designed. The ion source is similar to that employed in the conventional mass spectrometer. The ion beam is collimated by slits S_1 and S_2 and passes between the plates of a 90° segment of a cylindrical condenser. An energy spectrum is obtained in the plane of slit S_3. For illustrative purposes, ions having two different energies are shown in Fig. 3. The ions continue until they enter the gap between the trapezoidal-shaped poles of the magnetic field, where they are deflected, as in a mass spectrometer. A focus occurs finally at position S_4. When the beam trajectory and the geometric arrangement of both fields are properly (*7*) chosen, double focusing is produced in the same sense as in the mass spectrographs discussed earlier; that is, ions of slightly different energy and diverging slightly in angle as they leave slits S_1 and S_2 will focus at the same point, S_4.

The particular instrument that we have developed has a higher order of angle focusing (*8*) than more conventional instruments, with the result that slit S_2 in the ion source can be considerably wider than S_1

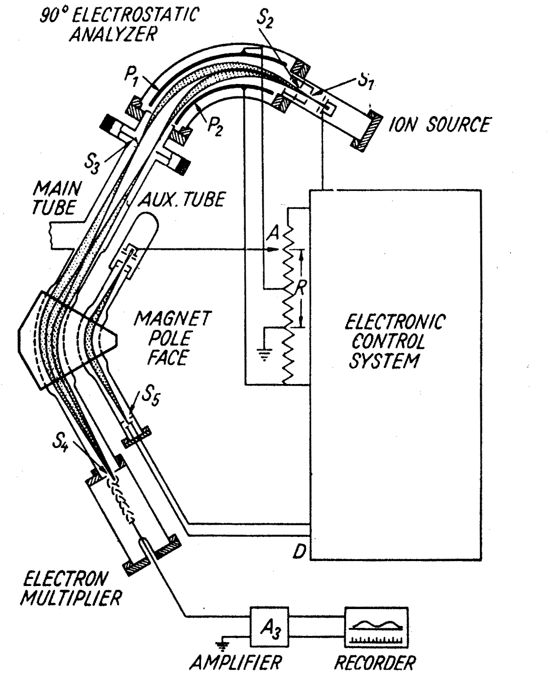

Fig. 3. Schematic drawing of double-focusing mass-spectrometer tube and associated control and measuring circuits.

without a sacrifice of resolution. The use of a larger exit angle at the ion source results, of course, in larger ion currents and consequently higher sensitivity than would be possible otherwise.

A small single-focusing mass spectrometer tube mounted in the same magnetic field is used to compensate for variations in the magnetic field or in the electric field appearing between plates P_1 and P_2 in the electrostatic analyzer. In the interest of simplicity, details of the circuit arrangement are not shown in Fig. 3 and may be found elsewhere (*9*). Suffice to say that a mass spectrum may be swept by changing the position of tap *A* on the resistor shown —that is, by changing the resistance *R* between point *A* and ground. A detailed analysis of this circuit indicates that the mass collected at slit S_4 is exactly proportional to the value of *R*.

The ion current is measured by means of an electron multiplier and amplifier, and the results are recorded on a standard strip-chart recorder.

Atomic mass determinations. Figure 4 shows the mass spectrum in the mass-28 region when a mixture of N_2 and CO are present. Although these two molecules differ in mass by only 1 part in 2500 the ion peaks are clearly resolved. The mass spectrum is swept by a motor that moves the point *A* (Fig. 3) and changes the resistance *R* at a uniform rate.

Actually all atomic masses are measured today by the "doublet" method. That is, one measures the mass difference between two molecules having approximately the same mass. If the mass of one component of the doublet is known, the mass of the other component may then be calculated from a knowledge of the mass difference. In practice, hydrocarbon fragments are generally used as the "known" masses. Because of the many possible combinations of hydrogen, carbon, and oxygen, one can choose a "known" standard for practically every mass-number position.

Physicists have not been able to agree upon the best values for the masses of carbon and hydrogen. Thus, the use of these as standards in computing other masses is unfortunate, although the range of uncertainty is small. Table 1 lists the most recent values for the masses of H^1 and C^{12}.

Figure 5 summarizes our knowledge of the atomic masses of atoms in the range from mass 10 to 210. The packing fraction is defined as $(M-A)/A$, where *M* is the measured mass and *A* is the nearest mass number. Plotted values below mass 32 are obtained from nuclear reactions given by Li (*10*). Those from mass 32 to 136 are based on our own measurements, whereas the heavier masses were obtained by Henry E. Duckworth of McMaster University, Canada, using a Dempster-type spectrograph.

All but a few of the known stable isotopes from mass 32 to 136 have been measured by the Minnesota group, so that it is possible to draw an essentially complete packing-fraction curve to a high order of accuracy in this region. It is seen that all atoms of odd mass number (indicated by *X*) lie on a relatively smooth curve, as is shown by the broken line. On the other hand, even mass isotopes for a given element (indicated by •) fall on a parabola, at least within

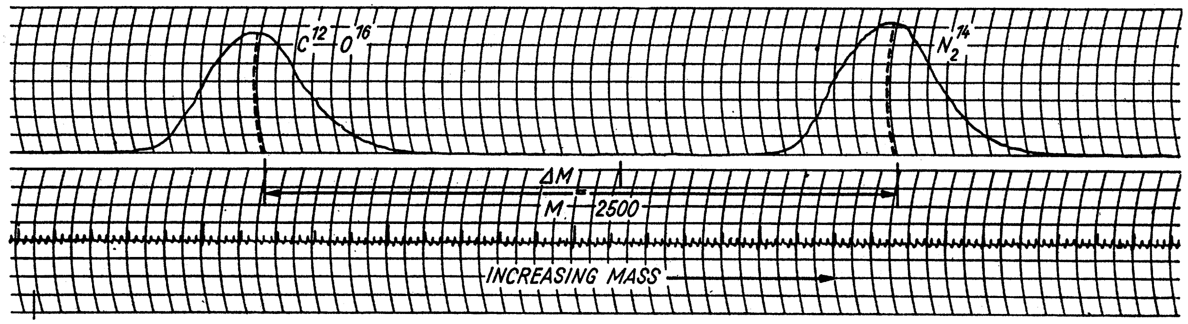

Fig. 4. Mass spectrum in region of mass 28 for a mixture of N_2 and CO. For this spectrum $S_1 = S_4 = 0.0125$ mm, $S_2 = 0.5$ mm, and $S_3 = 3$ mm. For other dimensions in apparatus, see reference 7.

Table 1. Recent values proposed for masses of H^1 and C^{12} (relative to $O^{16} = 16.0000$).

H^1	C^{12}	Method
1.008146 ± 3	12.003842 ± 4	Mass spectrometry*
1.008141 ± 2	12.003807 ± 11	Mass spectrometry†
1.008145 ± 2	12.003844 ± 6	Mass spectrometry‡
1.008142 ± 3	12.003804 ± 17	Nuclear reactions§
1.0081459 ± 5	12.0038231 ± 33	Mass spectrometry‖

* T. L. Collins, A. O. Nier, W. H. Johnson, Jr., *Phys. Rev.* **84**, 717 (1951).

† H. Ewald, *Z. Naturforsch*, pt. 6a, **293** (1951).

‡ K. Ogata and H. Matsuda, *Phys. Rev.* **89**, 27 (1953).

§ C. W. Li *et al.*, *ibid.* **33**, 512 (1951).

‖ J. Mattauch and R. Bieri, *Z. Naturforsch.* **9a**, 303 (1954).

experimental accuracy. An example of such a parabola is shown for the element xenon (Fig. 6), which has seven even mass isotopes. The curve was determined by a least squares fit, and it displays clearly the remarkable parabolic form. Further theoretical work is needed to explain this and other experimentally observed features of the entire packing-fraction curve.

Nevertheless, it is already possible, on the basis of these more accurate measurements, to verify certain theoretical aspects, notably of the "nuclear shell" theory. This theory predicts that the packing-fraction curve should show discontinuities in slope due to sudden changes in binding energy when the number of nuclear particles is one of the so-called "magic numbers"—14, 20, 28, 50, 82, and 126. Examples of such discontinuities are clearly seen at mass 28 (owing to the presence of 14 protons and 14 neutrons, both magic numbers), mass 40 (20 protons and 20 neutrons, also doubly magic), the region of mass 60 (28 protons), and the region below mass 90 (50 neutrons). Other less obvious cases can be seen on closer examination.

Isotope and gas analyses. We have recently become interested in the possibility of employing a double-focusing mass spectrometer for making isotope-abundance measurements as well as gas analyses. Accordingly, the slits in the instrument were widened somewhat in order to obtain better intensity and also to produce flat-topped peaks in the mass spectrum.

Figure 7 shows the mass spectrum over the region of CO_2 when a mixture of CO_2 and C_3H_8 were present. The large amount of C_3H_8 was deliberately chosen so that the peak in the 45-position corresponding to the molecules $C_2{}^{12}C^{13}H_8$ would be larger than the peak $C^{13}O_2{}^{16} + C^{12}O^{16}O^{17}$ that is usually found in CO_2 at mass 45 and is used for determining C^{13}/C^{12} abundance ratios.

It is clear from Fig. 7 that one can readily measure the mass 45/44 abundance ratio in CO_2 in spite of the fact that a very large "impurity" is present. As a matter of fact, the detailed analysis of the mass spectrum indicates that, although the two fragments in the mass-45 position differ in mass by only 1 part in 600, the resolution of the instrument is sufficient that the background of one fragment contributes only 1 part in approximately 1500 to the height of the peak of the other. When a low-resolution mass spectrometer is used for making isotope analyses, overlapping of mass peaks due to impurities can result in appreciable errors. With the higher resolution of a double-focusing mass spectrometer, these errors can be minimized. Of course, the resolution can be adjusted to the desired degree by suitable adjustment of the slitwidths in the instrument.

Instruments of this type will undoubtedly prove useful in the field of gas analyses in the future. Molecules having the same mass numbers but differing in weight by an amount determined only by the difference in binding energies of the nuclear particles can be clearly resolved as in this example. Extension of the use of the instrument to the resolution of heavy hydrocarbons should prove fruitful.

Calculation of atomic weights. Chemists have long been interested in the relative combining weights of elements. Every 2 years a Commission on Atomic Weights, meeting as part of the International Union of Pure and Applied Chemistry, prepares a report on current work and recommends atomic weights for

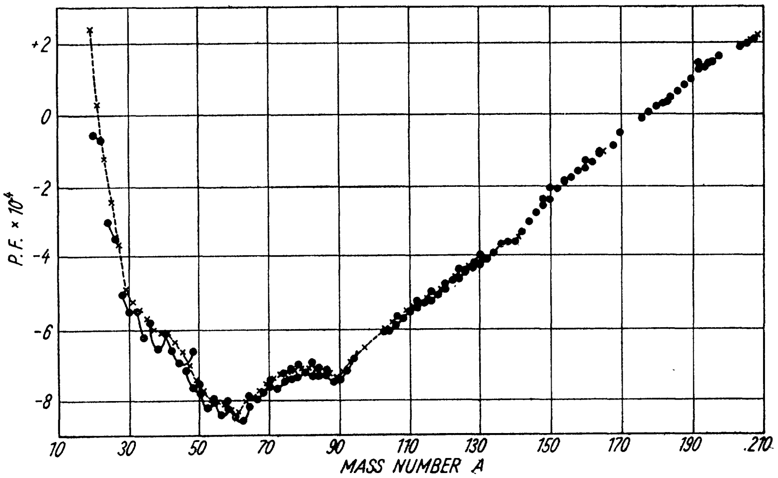

Fig. 5. Packing-fraction curve for stable atoms in mass range 10 to 210. Dashed line is through odd mass atoms; solid lines are through even mass atoms for each element.

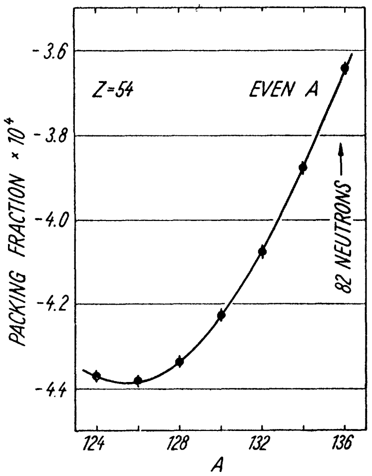

Fig. 6. Packing-fraction curve for even mass isotopes of a typical even atomic number element (xenon in this case). Curve shown is a parabola fitted to the experimental points by the method of least squares.

all the elements. In the 1953 report, 10 changes of atomic weights are recommended—some rather substantial—based on the results of mass spectroscopy and nuclear physics.

That there should have been some reluctance in the past in adopting physically determined values for atomic weights is understandable. Many of the early mass-spectroscopic measurements were in error. However, the art of measurement has so improved in recent years that this is no longer the case.

Masses of the very light elements can be determined either by mass spectroscopy or from nuclear-reaction data. Most of the points shown in Fig. 5 are the results of mass spectroscopy. Isotope abundances have been found by means of density measurements and optical or microwave spectra. However, most of the best values for relative abundances of isotopes are the determinations of mass spectroscopy.

Table 2 gives a comparison between the atomic weights of elements as adopted in 1953 by the International Union of Pure and Applied Chemistry and the values computed from physical measurements alone. The physical values are all based on the results of mass spectroscopy or nuclear physics.

Chemical atomic weights determined from measurements of the masses of individual isotopes and the relative abundances of isotopes can be in error because of four different effects.

1) The conversion factor between physical and chemical scales. Oxygen has three naturally occurring isotopes with mass numbers 16, 17, and 18. On the physical scale of atomic weights, the mass of O^{16} is assumed to be exactly 16.0000. Nuclear reaction data (*10*) give a mass of 17.004533 ± 7 for O^{17} and 18.004857 ± 23 for O^{18}.

The mean atomic weight for oxygen, of course, depends also on the relative abundance of these three isotopes. Unfortunately, there is considerable variation in the composition of samples taken from various sources. For an atmospheric sample, I (*11*) give percentage abundances as follows: O^{16}, 99.759 percent; O^{17}, 0.0374 percent; and O^{18}, 0.2039 percent. The O^{18} content in water and iron ores may be as much as 4 percent lower, and more recent work indicates a possibility of even larger variations in some special cases (*12*).

As a result, the mean atomic weight and, correspondingly, the conversion factor from physical to chemical scales, show some variation. For atmospheric oxygen, the physical weight is 1.0002783 ± 5 times greater than the chemical weight, whereas for oxygen from water, the factor is approximately 1.000268. In Table 2 it was arbitrarily decided to use 1.000275 in conformity with the practice followed by the Commission on Atomic Weights, although the evidence indicates that the mean value of 1.000273 ± 5 might better have been used.

In the few cases where its contribution was important, the associated uncertainty was taken to be 5 parts in 1 million.

2) Accuracy of isotopic mass measurements. Present mass-spectroscopic techniques have been developed to the point where isotopic masses can generally be determined with an uncertainty of not more than 1 part in 200,000, and frequently less. Both spectrographs and spectrometers are in active use, and some instruments now under construction may well improve even this high order of precision.

As is mentioned in preceding paragraphs, many of the lighter masses have also been calculated from accurately known nuclear-reaction data. These yield about the same accuracy, and, although small differences are present, the two methods agree remarkably well (see Table 1).

In cases where no reliable measurements have been

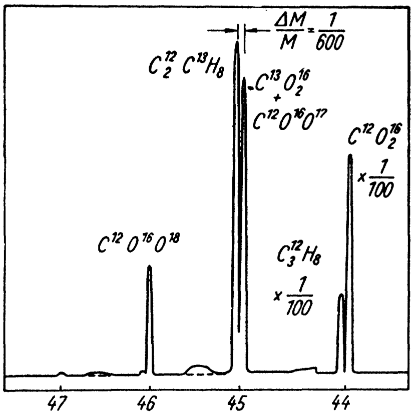

Fig. 7. Mass spectrum in region of CO_2 for a mixture of CO_2 and C_3H_8. In this case the slits in the double-focusing mass spectrometer described in reference 1 have been widened so that the measurement of a relative abundance of ions will be facilitated. Slit widths were $S_1 = 0.125$ mm, $S_2 = 0.5$ mm, $S_3 = 3$ mm, and $S_4 = 0.150$ mm. The broad peaks occurring between masses 46 and 47 and between masses 45 and 46 are artifacts, unexplained at the moment, and probably due to some misadjustment in the apparatus at the time the spectrum was taken.

Table 2. Atomic weights of the elements.

Atomic number	Element	1953 international value*	Computation from physical measurements	References	
				Isotopic mass	Relative isotopic abundance†
1 H	Hydrogen	1.0080	1.00801 ± 5^{a,c}	L-1	†
2 He	Helium	4.003	4.00277 ± 4^{m,c}	L-1	A-1
3 Li	Lithium	6.940	6.941 ± 2^{v}	L-1	†
4 Be	Beryllium	9.013	9.0126 ± 1^{c,m}	L-1	
5 B	Boron	10.82	10.82 ± 1^{v}	L-1	T-1
6 C	Carbon	12.011‡	12.0115 ± 4^{v}	L-1	N-1
7 N	Nitrogen	14.008	14.00733 ± 10^{c,a,m}	L-1	N-1
8 O	Oxygen	**16**			
9 F	Fluorine	19.00	18.9992 ± 2^{m,c}	L-1	
10 Ne	Neon	20.183	20.172 ± 10^{a}	L-2	N-2
11 Na	Sodium	22.991‡	22.9908 ± 2^{m,c}	L-2	
12 Mg	Magnesium	24.32	24.313 ± 7^{a}	L-2	W-1
13 Al	Aluminum	26.98‡	26.9827 ± 2^{m,c}	L-2	
14 Si	Silicon	28.09‡	28.086 ± 1^{a}	L-2	N-8, W-2, I-1
15 P	Phosphorus	30.975‡	30.9750 ± 2^{m,c}	L-2	
16 S	Sulfur	32.066§	32.067 ± 3^{v}	C-1	T-2
17 Cl	Chlorine	35.457	35.462 ± 8^{a}	C-1	N-3
18 A	Argon	39.944	39.949 ± 1^{a}	C-1	N-1
19 K	Potassium	39.100‡	39.103 ± 2^{a}	C-1, J-1	N-1
20 Ca	Calcium	40.08	40.080 ± 1^{a}	C-1, J-1	N-4, W-1
21 Sc	Scandium	44.96‡	44.9577 ± 4^{m,c}	C-1	
22 Ti	Titanium	47.90	47.876 ± 3^{a}	C-2, J-2	N-4
23 V	Vanadium	50.95	50.944 ± 1^{c,m}	C-2, J-2	H-4, L-4
24 Cr	Chromium	52.01	52.000 ± 3^{a}	C-2, J-2	W-1
25 Mn	Manganese	54.94‡	54.9407 ± 5^{m,c}	C-2	
26 Fe	Iron	55.85	55.849 ± 1^{a}	C-2	V-1, W-1, H-6
27 Co	Cobalt	58.94	58.935 ± 1^{m,c}	S-2	
28 Ni	Nickel	58.69	58.712 ± 2^{a}	C-2	W-1
29 Cu	Copper	63.54	63.550 ± 5^{a}	C-2	B-1
30 Zn	Zinc	65.38	65.390 ± 5^{a}	C-2	H-5, L-5
31 Ga	Gallium	69.72	69.725 ± 4^{a}	C-3	I-2
32 Ge	Germanium	72.60	72.632 ± 6^{a}	C-3	I-3
33 As	Arsenic	74.91	74.9251 ± 6^{c,m}	C-3	
34 Se	Selenium	78.96	78.99 ± 1^{a}	C-3	W-1
35 Br	Bromine	79.916	79.910 ± 2^{a}	C-3	W-2
36 Kr	Krypton	83.80‡	83.808 ± 1^{a}	C-3	N-2
37 Rb	Rubidium	85.48	85.472 ± 2^{a}	C-3	N-2
38 Sr	Strontium	87.63	87.621 ± 3^{a}	C-3	N-5
39 Y	Yttrium	88.92	88.910 ± 1^{c,m}	C-3	
40 Zr	Zirconium	91.22	91.228 ± 5^{a}	C-3, G-1	W-1
41 Nb	Niobium	92.91	92.910 ± 1^{c,m}	C-3	
42 Mo	Molybdenum	95.95	95.89 ± 4^{a}	D-1, D-3, D-4, G-1	W-2
43 Tc	Technetium	(99)‖			
44 Ru	Ruthenium	101.1‡	101.07 ± 1^{a}	H-1	F-1
45 Rh	Rhodium	102.91	102.909 ± 2^{m,c}	n	
46 Pd	Palladium	106.7	106.44 ± 3^{a}	H-3	S-3
47 Ag	Silver	107.880	107.88 ± 1^{a}	n	W-1
48 Cd	Cadmium	112.41	112.429 ± 6^{a}	H-3	L-5
49 In	Indium	114.76	114.824 ± 2^{a}	H-3	W-1
50 Sn	Tin	118.70	118.747 ± 13^{a}	H-3	H-6, H-10, W-1
51 Sb	Antimony	121.76	121.76 ± 1^{a}	n	W-1
52 Te	Tellurium	127.61	127.634 ± 5^{a}	H-3	W-1, W-2
53 I	Iodine	126.91‡	126.910 ± 1^{m,c}	H-3	
54 Xe	Xenon	131.3	131.298 ± 2^{a}	H-3	N-2
55 Cs	Cesium	132.91	132.912 ± 3^{m}	Estimated	
56 Ba	Barium	137.36	137.335 ± 7^{a,m}	H-2	N-5
57 La	Lanthanum	138.92	138.911 ± 3^{m}	Estimated	I-4, I-5
58 Ce	Cerium	140.13	140.121 ± 7^{a,m}	D-5, H-2	I-5
59 Pr	Praseodymium	140.92	140.912 ± 2^{m}	H-2	
60 Nd	Neodymium	144.27	144.25 ± 1^{a}	D-5, H-2	I-7

Atomic number	Element	1953 international value*	Computation from physical measurements		References	
					Isotopic mass	Relative isotopic abundance†
61 Pm	Promethium	(145)‖				
62 Sm	Samarium	150.43	150.35	$\pm 2^{a}$	H-2	I-3
63 Eu	Europium	152.0	151.97	$\pm 1^{a}$	Estimated	H-7
64 Gd	Gadolinium	156.9	157.262	$\pm 8^{a}$	H-2	H-7, L-6
65 Tb	Terbium	158.93‡	158.934	$\pm 5^{m}$	Estimated	
66 Dy	Dysprosium	162.46	162.506	$\pm 8^{a,m}$	H-2	I-6
67 Ho	Holmium	164.94	164.937	$\pm 5^{m}$	H-2	
68 Er	Erbium	167.2	167.268	$\pm 6^{a,m}$	H-2	H-8
69 Tm	Thulium	168.94‡	168.94	$\pm 1^{m}$	Estimated	
70 Yb	Ytterbium	173.04	173.044	$\pm 11^{a,m}$	Estimated	H-9, L-6
71 Lu	Lutetium	174.99	174.974	$\pm 7^{a,m}$	Estimated	H-8
72 Hf	Hafnium	178.6	178.50	$\pm 1^{a}$	H-2	H-6
73 Ta	Tantalum	180.95‡	180.947	$\pm 6^{m}$	Estimated	
74 W	Tungsten	183.92	183.856	$\pm 9^{a,m}$	D-2, D-5, G-1	W-2
75 Re	Rhenium	186.31	186.22	$\pm 1^{a,m}$	Estimated	W-1
76 Os	Osmium	190.2	190.25	$\pm 2^{a,m}$	H-2	N-6
77 Ir	Iridium	192.2‡	192.20	$\pm 3^{a,m}$	Estimated	S-1
78 Pt	Platinum	195.23	195.09	$\pm 1^{a,m}$	D-1, D-2, H-2	I-8, L-7
79 Au	Gold	197.0‡	196.975	$\pm 6^{m}$	Estimated	
80 Hg	Mercury	200.61	200.61	$\pm 1^{m,a}$	Estimated	N-2
81 Tl	Thallium	204.39	204.39	$\pm 2^{a,m}$	Estimated	H-6, W-1
82 Pb	Lead	207.21	207.22	$\pm 4^{v}$	H-2	N-7
83 Bi	Bismuth	209.00	208.987	$\pm 7^{m}$	H-2	
90 Th	Thorium	232.05	232.05	$\pm 1^{m}$	S-2	
92 U	Uranium	238.07	238.04	$\pm 1^{m}$	S-2	C-4, G-2

* *Comptes Rendus,* 17th conf., International Union of Pure and Applied Chemistry (1953), p. 93.

† A summary of all work on isotopic abundance through 1950 may be found in Bainbridge and Nier, "Relative Isotopic Abundances of the Elements," Preliminary Report No. 9, National Research Council, Washington, D. C. Wherever possible the references for Table 2 are to the original work on which the present calculations are based. Where more than one of the superscripts a, c, m, and v appear for a given element, they have been set down, whenever possible, in the order of their relative numerical contribution to the total uncertainty. In all cases the quoted uncertainty is intended to represent an estimate of the limit of error. When the original work gave only the probable error, this was, as a general rule, increased by a factor of 3 to 4.

[a] This uncertainty arises chiefly from the measurements of isotopic abundance.

[c] This uncertainty arises chiefly from the conversion factor 1.000275 ± 5 used in changing from the physical to the chemical scale of masses.

[m] This uncertainty arises chiefly from the mass measurements.

[v] This uncertainty arises from the known natural variation of isotopic abundance.

[n] These masses are obtained from unpublished calculations by T. L. Collins of this laboratory and are based on nuclear-reaction data from various published works.

‡ These values have been revised in recent years with consideration given to physical measurements.

§ Because of natural variations in the relative abundance of its isotopes, the atomic weight of sulfur has a range of ± 0.003.

‖ A value given in parentheses denotes the mass number of the isotopes of longest known half-life.

made, it is possible to interpolate the position of the isotope on the packing-fraction curve. Even if such an interpolation is in error by as much as one-half of a packing-fraction unit (which is highly unlikely), the resulting mass error is less than 1 part in the second decimal place (see thulium as an example).

3) Accuracy of relative isotopic abundances. In most cases, this source of uncertainty is by far the most serious. For some elements no measurements have been made since the development of precision techniques, and for others the available work shows sufficient lack of agreement to justify further investigation.

It is clear that these uncertainties do not affect single-isotope elements and have only a small effect on elements consisting of one abundant isotope and a few very rare isotopes. In such cases, mass and conversion-factor uncertainties are the only limitations.

4) Natural variations of isotope abundance. It is now well established that a variation of relative abundance occurs among the isotopes of a few elements, determined by the source from which the sample was taken. Oxygen has already been discussed as an example; sulfur is another and more dramatic case. Clearly, it becomes meaningless to speak of precision atomic weights for these elements, at least without specifying the exact sources from which they are obtained. Mass-spectroscopic techniques here serve only to indicate the range over which the atomic weight may be expected to vary.

In general, the agreement between the chemical and physical weights listed in Table 2 is quite good. Physical techniques clearly provide considerably greater precision whenever the atomic weight does not depend on relative abundance measurements. (Typical cases are single-isotope elements, such as scandium, and a few, such as vanadium, that have one overwhelmingly abundant isotope.) New isotopic mass measurements are being published continuously, and it is to be expected that their accuracy will be even further improved by the instruments currently under construction.

For elements that have more than one abundant isotope, it is considerably more difficult to achieve such accuracy. Mass discrimination can occur both in the sample-handling system and within the instrument, partly because of small fractionation effects. It, therefore, requires the utmost care to reduce systematic errors below 1 percent, and only a few elements have been thus investigated. It should be noted that although much precise work has been done on isotope-abundance variations for a given element, one cannot always rely on their absolute accuracy. Finally, there are still some elements that have not been studied for many years, chlorine being a typical example. It is to be hoped that further work will soon be done along these lines, but for the present the chemical atomic weights are the most reliable in these cases.

References and Notes

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