

Atomic Masses of H^1 , D^2 , C^{12} , and S^{32} †*

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The large double-focusing mass spectrometer recently developed has been used to measure a series of 25 mass doublets. This instrument features a new peak-matching method of measurement which involves the presentation of a portion of the mass spectrum upon an oscilloscope. A group of consistency tests has been performed to prove the correctness of the mass dispersion formula used in calculating mass differences.

The measured doublets are sufficient to calculate the mass of C^{12} by five different cycles and to also calculate the masses of H^1 , D^2 , and S^{32} . The resulting mass values are $H^1=1.0081442\pm 2$, $D^2=2.0147406\pm 6$, $C^{12}=12.0038167\pm 8$, and $S^{32}=31.9822401\pm 9$ amu, where the errors shown include the statistical standard error and the resistance calibration uncertainty. A discrepancy exists between the mass values determined here and some of those derived from nuclear reaction energy data.

INTRODUCTION

THE physical table of atomic masses has as its standard O^{16} which is assigned a mass of exactly 16 atomic mass units (amu). Since most isotopes cannot be compared directly with O^{16} , secondary mass standards are required. The most useful of these are H^1 , D^2 , and C^{12} because of the extensive number of hydrocarbons which provide reference peaks at almost all mass numbers. In addition S^{32} is a useful standard.

The masses of these secondary standards, particularly that of C^{12} , have been measured mass spectroscopically by numerous investigators.¹ Because of its proximity to O^{16} , a precise value for the mass of C^{12} can also be obtained from nuclear reaction energies. Unfortunately there exists a considerable lack of agreement between the various measurements, particularly as regards C^{12} and S^{32} . This discrepancy exists not only between the various mass spectroscopic values and the Q -value results, but also among the mass spectroscopic measurements themselves.

We have devoted considerable effort to the measurement of these secondary standards, particularly C^{12} , not only in an attempt to resolve these discrepancies, but also to establish reliable values for these standards for use in future work at this laboratory.

APPARATUS

The large double-focusing mass spectrometer recently constructed at this laboratory² has been used in this investigation. The combination of spectrometer elements employed, shown in Fig. 1, provides first- and second-order angle focusing as well as first-order energy focusing. That is, ions of a given mass are focused

independent of kinetic energy deviation (to first order) and of entrance angle (to first and second order) in the plane of dispersion.

Ions formed by electron impact are accelerated by falling through a potential difference of approximately 40 kv and are focused on the object slit S_1 . These ions pass through the image slit S_4 and the ion current (10^{-12} – 10^{-9} amp) is detected by an electron multiplier. All slits are externally adjustable to facilitate focusing.

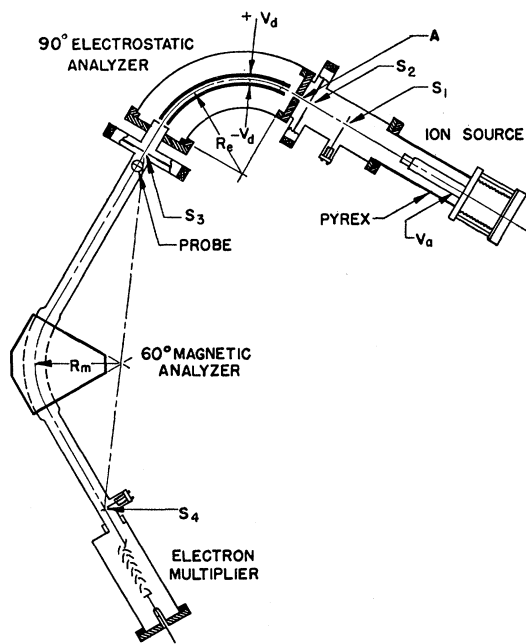


FIG. 1. Schematic diagram of the large double-focusing mass spectrometer. $R_e=20$ inches. $R_m=16$ inches. The beam defining slits are adjustable from outside the vacuum. Slits systems S_2 and S_3 are adjustable in position in the dispersion plane and in width. Slits S_1 and S_4 are adjustable in position in all directions and in rotation. S_4 may also be adjusted in width. Typical dimensions for these slits are $S_1=S_4=0.0005$ in., $S_2=0.007$ in., and $S_3=0.015$ in. The potential $V_d=\pm 1500$ v and $V_a=38\,000$ v. Pyrex pipe is used for the source vacuum housing to provide the necessary high voltage insulation. A probe beyond S_3 detects a portion of the ion beam to facilitate operation and adjustment of the V_d/V_a ratio. Ion detection is by means of a 10-stage silver-magnesium alloy electron multiplier.

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¹ For a summary of earlier work, see Duckworth, Hogg, and Pennington, *Revs. Modern Phys.* **26**, 463 (1954).

² Scolman, Quisenberry, Collins, Giese, and Nier (to be published, 1956).

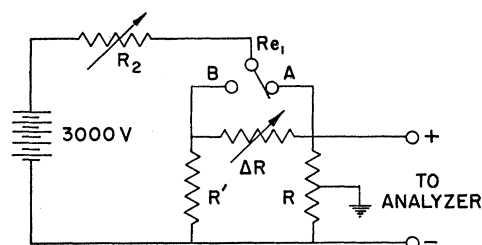


FIG. 2. Schematic diagram of the electrostatic analyzer potential control circuit. All resistances, except R_2 , are wound using Manganin wire. They are enclosed in a box whose atmosphere is temperature controlled. Resistance $R=3\,371\,630\pm 65$ ohms and R' matches R to within 0.01%. ΔR is variable from zero to 100 000 ohms, with the ratio $\Delta R/R$ known to at least $1/50\,000$ for any value. Leakage current to ground is less than 10^{-9} amp. Re_1 is a sealed, fast acting relay with mercury contacts. Variable resistance R_2 is used to compensate for the slow voltage drift of the 3000-v battery stack.

An important feature of this instrument is the display of a portion of the mass spectrum on an oscilloscope. This is accomplished by using the oscilloscope's horizontal sweep sawtooth to modulate the magnetic field. This sweeps the ion beam across the image slit S_4 . The ion current signal drives the vertical amplifier of the oscilloscope so that a small portion (usually about 2 peak widths) of the mass spectrum is displayed. This instantaneous display of the mass peaks greatly facilitates focusing the mass spectrometer.

METHOD OF MEASUREMENT

The application of a mass spectrometer to the measurement of atomic mass depends upon the fact: If, for any configuration of electromagnetic fields, all electric potentials are changed by a factor A ; then the mass of ions which, starting from rest, can follow a particular

trajectory changes by a factor $1/A$. The mass difference between the two members of a doublet is measured by determining precisely the voltage change required to alter the spectrometer focus from one member to the other. The distinguishing feature of the peak-matching method, which this instrument utilizes, is the determination of this voltage change using a visual presentation of these two peaks.

The voltages applied to the electrostatic analyzer are provided by the circuit shown in Fig. 2. ΔR is adjusted so that one member of the doublet is collected with the relay Re_1 in position A and the other member collected in position B . This relay is then switched after each sweep of the oscilloscope so that one sees a simultaneous display of the two members of the mass doublet. The potential change, derived from ΔR , is then adjusted until the two peaks exactly coincide. The mass difference ΔM is then determined from the dispersion formula

$$\Delta M/M = \Delta R/R, \quad (1)$$

where M is the mass of the lighter member of the doublet. A second synchronized relay switches the ion accelerating voltage V_a the appropriate amount (i.e., $\Delta V_a/V_a = \Delta R/R$).

This system requires that there be no significant drift in the interval between the collection of the two kinds of ions. Since the display frequency is rather high (usually about 30 cycles/sec), the power supplies must be hum- and noise-free, but long-term stability is not required. Very slow drifts can be tolerated, and hence batteries are ideally suited for use as power sources.

The usable resolving power is limited by the high display frequency which makes it necessary that the ion currents be rather large if the mass peaks are not to be excessively noisy. For this reason, resolving powers of from 30 000 to 60 000 are customarily employed although values as high as 75 000 have been used. Resolving powers in this range are sufficiently high to resolve almost all contaminants whose masses are close to that of the desired ion peak. This removes the necessity of making corrections for C^{13} satellites on the hydrocarbon reference peaks at virtually all mass numbers.

TREATMENT OF DATA

A number of runs (always 10 or more) were recorded for each mass doublet, with the data being collected over a period of at least three days. Each run consists of 20 superpositions of the two peaks taken in four different ways to minimize possible systematic errors in the method of measurement. The unweighted average of the 20 superpositions is taken as the result for the run. No statistical analysis is made for the data within the run and the averages of the runs are used with equal weight as the basic input data for all further calculations.

Each quoted error is the square root of the sum of the squares of the statistical standard error of the mean

TABLE I. Doublet consistency checks.

	Mass no.	Doublet	ΔM (mMU) ^a
(1)	16	CH ₄ -O	36.3931±9
	28	C ₂ H ₄ -CO	36.3934±8
	44	$\frac{1}{2}$ (C ₃ H ₈ -CO ₂)	36.3935±8
	Av		36.3933±5
(2)	16	NH ₂ -O	23.8164±5
	17	NH ₃ -OH	23.8159±6
	Av		23.8162±5
(3)	14	CH ₂ -N	12.5803±4
	16	CH ₄ -NH ₂	12.5804±5
	28	$\frac{1}{2}$ (C ₂ H ₄ -N ₂)	12.5793±3
	Av		12.5800±3
(4)	18	H ₂ O-DO	1.5476±5
	17	NH ₃ -NDH	1.5478±4
	Av		1.5477±4

^a Errors quoted are statistical standard error plus the resistance calibration uncertainty. Limit-of-error is about three times the quoted value.

associated with the group of run averages and the error reflecting the resistance calibration uncertainty. The limit of error is about three times the values shown.

CONSISTENCY CHECKS

To check the resistance calibration and the performance of the spectrometer, several consistency tests were performed.

An obvious test is to measure a mass doublet regularly, with the measurements spaced over a wide time interval. This has been done for several doublets, notably O₂-S and C₂H₄-CO,³ with several months elapsing between the initial and final runs. No appreciable change of result was observed.

A second test is to measure the same mass difference using doublets of different mass number. A comparison of the results so obtained is a test of the linearity of the mass scale and also of the correctness of the calibra-

TABLE II. Triplet cycle consistency checks.

Mass	Doublet	ΔM (mMU)
16	CH ₄ -O	36.3931± 9
	-(CH ₄ -NH ₂)	-12.5803± 4
	-(NH ₂ -O)	-23.8164± 5
	Sum	- 0.0036±11
20	D ₂ O-Ne ²⁰	30.6872± 7
	-(D ₂ O-H ₂ O ¹⁸)	- 8.3102± 4
	-(H ₂ O ¹⁸ -Ne ²⁰)	-22.3770± 6
	Sum	0.0000±10
28	C ₂ H ₄ -CO	36.3934± 8
	-(C ₂ H ₄ -N ₂)	-25.1585± 6
	-(N ₂ -CO)	-11.2353± 7
	Sum	0.0004±12

tion of part of the resistance network. This has been done for four mass differences and, as is shown in Table I, the agreement between the results is satisfactory.

Another consistency test is to measure the three possible doublets of a mass triplet. One then arithmetically checks the triplet cycle for closure. This was done at masses 16, 20, and 28 and the results, shown in Table II, confirm the satisfactory operation of the instrument. Errors are calculated as before. The closure error at mass 16 is slightly outside this limit, but the cycle is considered satisfactory.

A sensitive test of the exactness of the mass dispersion formula used in calculating mass differences is the direct measurement of a hydrogen mass unit. This is done using a doublet whose heavier member contains one more hydrogen than the lighter member, and whose members are otherwise identical. At present this has been done at only one mass, using the doublet C₄H₈O₂

³ Throughout this paper H, C, N, O, and S refer to the abundant isotopes of these elements, namely H¹, C¹², N¹⁴, O¹⁶, and S³².

TABLE III. Doublet results used in the mass calculations.

No.	Doublet	ΔM (mMU)
<i>a</i>	C ₄ -SO	33.0269±13
<i>b</i>	O ₂ -S	17.7599± 9
<i>b'</i>	O ₂ - $\frac{1}{2}$ Zn ⁶⁴	25.2633±26
	SO ₂ -Zn ⁶⁴	
<i>c</i>	$\frac{1}{2}$ C ₄ H ₈ O-H ₂ S	25.3926± 9
<i>d</i>	$\frac{1}{2}$ C ₄ H ₈ O-O ¹⁶ O ¹⁸	19.0367± 8
<i>e</i>	H ₂ O-O ¹⁸	11.4033±21
<i>f</i>	D ₂ O-H ₂ O ¹⁸	8.3102± 4
<i>g</i>	C ₃ -A ³⁶	32.4729±20
<i>h</i>	H ₂ O- $\frac{1}{2}$ A ³⁶	26.7937± 6
<i>j</i>	CH ₄ -O (av)	36.3933± 5
<i>k</i>	H ₂ -D (av)	1.5477± 4
<i>l</i>	C ₃ H ₄ -A ⁴⁰	68.9344±13
<i>m</i>	D ₂ O- $\frac{1}{2}$ A ⁴⁰	41.9390±13

-C₄H₇O₂. The mass difference obtained, 1.00816±2 amu, agrees with the measured H¹ mass, 1.0081442±2, to 1 part in 50 000. This agreement suggests strongly that our inclusion of an uncertainty of this magnitude in the resistance ratio $\Delta R/R$ in the quoted errors is sufficient to allow for possible errors in both the mass dispersion formula and the resistance calibration.

SECONDARY STANDARD MASSES

The experimental results for the doublets necessary in the calculations that follow are listed in Table III together with their associated errors. In any case where more than one doublet giving the same mass difference has been measured, the value in Table III is the unweighted average of all such measurements.

Carbon

Because of the interest in this mass value, considerable effort has been devoted to its determination. As is shown in Table IV, five different doublet cycles have been used to obtain the C¹² mass. The letters in the equations refer to the doublets listed in Table III.

Cycle I

This set of doublets was first used by Nier,⁴ and later by Collins *et al.*⁵ and Ogata and Matsuda⁶ to obtain

TABLE IV. Doublet cycles used to calculate the C¹² mass.

Cycle	Equation	Result (amu)
I	C ¹² =12+ $\frac{1}{2}(a-b)$	12.0038168±4
II	C ¹² =12+ $\frac{1}{2}(c-b)$	12.0038164±6
III	C ¹² =12+ $\frac{1}{4}(2d-e-f-2k)$	12.0038161±7
IV	C ¹² =12+ $\frac{1}{4}(g+j-2h)$	12.0038197±6
V	C ¹² =12+ $\frac{1}{4}(l+j-2m-4k)$	12.0038147±8
	Unweighted average	C ¹² =12.0038167±8
	Weighted average	12.0038168±3

⁴ A. O. Nier, Phys. Rev. **81**, 624 (1951).

⁵ Collins, Nier, and Johnson, Phys. Rev. **84**, 717 (1951).

⁶ K. Ogata and H. Matsuda, Phys. Rev. **89**, 27 (1953).

TABLE V. The mass of C^{12} determined from previous investigations.

Investigator	Result (amu)	Reference
Ewald (1951)	12.003807 \pm 11	a
Collins <i>et al.</i> (1951)	12.003842 \pm 4	b
Ogata and Matsuda (1953)		c
C_4 -SO cycle (I)	12.003849 \pm 6	
A^{40} cycle (V)	12.003827 \pm 15	
Mattauch and Bieri (1954)	12.0038231 \pm 33	d
Kettner (1955)		e
O^{18} cycle (III)	12.003817 \pm 7	
O^{17} cycle	12.003811 \pm 5	
Smith (1955)		f
Synchrometer	12.0038212 \pm 38	
Nuclear calculation		
Li <i>et al.</i> (1951)	12.003804 \pm 17	g
Wapstra (1955)	12.003803 \pm 5	h

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

^b See reference 5.

^c See reference 6.

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

^e See reference 8.

^f L. G. Smith, Third Annual Meeting, Committee E-14, American Society for Testing Materials, 1955 (unpublished).

^g C. W. Li *et al.*, Phys. Rev. **83**, 512 (1951).

^h See reference 10.

the C^{12} mass. As is seen from the summary of Table V, this cycle led to a C^{12} mass higher than that obtained by any other method and gave rise to a large discrepancy with the nuclear value. Recent investigation of the C_4 -SO doublet by Giese⁷ at this laboratory, using a spectrometer with resolving power of about 15 000, disclosed a close-lying contaminant near the C_4 ion peak. Subsequent investigation and mass measurement led to the conclusion that the satellite is caused by the presence of methyl mercaptan, CH_3SH , in the butadiene source of C_4 ions. This previously unresolved impurity is present with intensity just sufficient to explain the earlier high result from this laboratory, and correction for it brings these results into agreement with those from other cycles. Nevertheless, a discrepancy between mass spectroscopic and nuclear results remains. This is discussed in a following section. The present measurements of this doublet were made with a resolving power of about 40 000, thus eliminating any problem due to the impurity.

The other doublet used in this cycle, O_2 -S, is believed correct for several reasons. The measured doublet difference has remained constant over a data recording period of eight months, and the O_2 -S value obtained using the Zn^{64} doublet measurements (Table III) is seen to be in excellent agreement with the directly measured result.

Cycle II

Recently introduced by Kettner,⁸ this cycle uses doubly charged C_4H_2O ions obtained from the organic compound Furan. Since this cycle also depends upon the O_2 -S result, any change in that doublet will affect both cycle results in the same direction. However its

⁷ C. F. Giese (private communication, 1954).

⁸ M. E. Kettner, preceding paper [Phys. Rev. **102**, 1065 (1956)].

TABLE VI. Final masses of the secondary standards and these same values derived from nuclear reaction energy data.

	Atomic mass (amu)		
	Spectrometric	Reference	Nuclear calculation ^e
H^1	1.0081442 \pm 2	a	1.0081452 \pm 15
D^2	2.0147406 \pm 6	b	2.0147403 \pm 28
C^{12}	12.0038167 \pm 8	c	12.003803 \pm 5
S^{32}	31.9822401 \pm 9	d	31.982196 \pm 26

^a Based on doublet (*j*), CH_4 -O.

^b Based on doublet (*k*), H_2 -D.

^c Unweighted average of five cycles.

^d Based on doublet (*b*), O_2 -S.

^e Based on the calculation of Wapstra, reference 10.

effect here is twice as great as in the case of Cycle I. In comparing these two cycles, one can combine doublets *a* and *c* to obtain for the O_2 -S difference 17.7583 \pm 22 mMU, a result in good agreement with the directly measured doublet.

Cycle III

This is another cycle originated by Kettner,⁸ and the value obtained here agrees well with his result. Some trouble was experienced with the H_2O - O^{18} doublet because of low O^{18} ion intensity. This led to the alternate method of obtaining this mass difference, using doublets *f* and *k*, as is shown in Table IV. This addition introduces the H_2 -D doublet *k* and removes the independence of Cycle III from other cycles, but the error reduction of the mass difference makes the C^{12} result more dependable.

Cycle IV

This doublet cycle gives that C^{12} mass which deviates most from the average, being 3 μ MU high. The deviation is probably caused by the C_3 - A^{36} doublet *g* since considerable difficulty was experienced obtaining sufficient C_3 ion intensity. Also the doublets entering here are relatively wide, and any error proportional to doublet width will exert a greater absolute influence. Although the consistency of the present results is improved over that of previous investigations, small deviations remain, as this cycle result demonstrates.

Cycle V

First introduced by Roberts,⁹ this cycle was used by him (and later by Ogata and Matsuda⁶) in an early spectrometric measurement of the C^{12} mass. It is similar to Cycle IV, except for requiring one more doublet. In searching for sources of this deviation, one notes that the CH_4 -O doublet enters both Cycles IV and V in the same manner. Since the Cycle IV result is high, and that from Cycle V is low, any change in CH_4 -O would improve one result at the expense of the other. Because of this, and because of the excellent agreement in the CH_4 -O consistency check, it is felt

⁹ T. R. Roberts, Phys. Rev. **81**, 624 (1951).

that the source of deviation in these cycles lies elsewhere.

Final C^{12} Mass

Having solved this set of mass doublets for the C^{12} mass through the expedient of doublet cycles, there remains the problem of obtaining the final C^{12} mass. The result of each cycle is shown in Table IV together with the error derived from the doublet errors. Also shown are the weighted and unweighted averages of these results. Because the results from Cycles IV and V are farther from the average than their errors allow for a consistent set, the unweighted average is chosen as the adopted result. When more doublets are measured and combined with those reported here, it may be desirable to perform a detailed statistical fitting of the data.

Other Secondary Standards

For the other secondary standard masses, a cyclic process has not been used. Instead, the C^{12} value determined above was combined with doublet results in which we have particular confidence to obtain the masses. In Table VI, the doublets used are listed together with the resulting mass values.

COMPARISON WITH NUCLEAR VALUES

The mass values for these secondary standards calculated from nuclear reaction energy data by Wapstra¹⁰ are also shown in Table VI. The agreement between the two sets of results is excellent for H^1 and D^2 , but a definite discrepancy exists in the case of C^{12} and S^{32} . The results presented here, together with other mass spectroscopic determinations (Table V), suggest some error in the nuclear mass of C^{12} . A detailed analysis mass spectroscopically of the masses of all stable isotopes from carbon to sulfur might shed light upon this problem and suggest certain nuclear reactions for re-examination.

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¹⁰ A. H. Wapstra, *Physica* **21**, 367 (1955).