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

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The Minnesota 16-inch double-focusing mass spectrometer has been used to measure a series of mass doublets which enable one to calculate the atomic masses of H^1, C^{12}, and S^{32}. The doublet $\frac{1}{2}C_4H_4O-H_2O_2$ is used to relate the C^{12} mass directly to that of the O^{16} standard. Recent tests of the instrument and its calibration give confidence in the reliability of the present results. The resulting mass values are $H^1=1.008\,1451\pm2$, $C^{12}=12.003\,8156\pm4$, and $S^{32}=31.982\,2388\pm9$ amu. These values differ from the previously reported results by more than the published errors might lead one to predict. However, in no cases do the changes reflect a significant change in previously published atomic masses.

INTRODUCTION

BECAUSE knowledge of the masses of the secondary standards H^1, C^{12}, and S^{32} is essential in the measurement of atomic masses by the doublet method, these masses have been the subject of numerous investigations.[1] In particular, the C^{12} mass has been measured using a variety of mass-doublet combinations in an effort to resolve previous inconsistencies. Most investigators now agree upon the essential correctness of the recently published result.[2]

These secondary standard masses were among the first measured using the Minnesota 16-inch double-focusing mass spectrometer. In the nearly two years that has elapsed since these results were obtained, the instrument has been used to determine the atomic masses of all isotopes of all elements from boron to zinc.[3–5] During this period improvements have been made in the technique of instrument calibration and on the spectrometer focusing procedure.

Therefore, to test the long-term reproducibility of our results and to examine the effect of the various improvements upon the mass values, we have remeasured certain doublets and measured a new one which enable us to calculate new values for the atomic masses of H^1, C^{12}, and S^{32}. It is somewhat encouraging to note that these new values deviate only slightly from the earlier results, and that in no case does the change reflect a significant change in previously published atomic masses.

INSTRUMENT CALIBRATION

The technique used with our mass spectrometer reduces the measurement of a mass difference to the determination of a resistance ratio.[2] The exact dispersion relation is

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

where ΔM is the mass difference, M is the mass of the lighter of the two doublet members, R is the resistance in the circuit when the instrument is focused on mass M, and ΔR is the resistance change required to shift the focus to the heavier doublet member. An accident early in 1956 destroyed several of the precision resistors used in ΔR and their replacement stimulated considerable improvement in both the physical construction of the resistance unit and in the calibration technique employed.

All the precision resistors are now mounted inside a Lucite box, through which temperature-controlled air is circulated. The air system is closed so that the temperature controller holds the air temperature to ±0.05°C at the more important resistors. All parts are mounted to eliminate (as far as can be detected) harmful leakage resistance.

The sensitivity of the calibration has been improved to the point where the ratio between two individual resistances can be reproduced to within 1 ppm. In the over-all combination, however, uncertainties do enter, and we estimate the ratio $\Delta R/R$ is calibrated to an accuracy of 10 ppm or better for any ratio in the range used.

CALIBRATION TESTS

Perhaps the most sensitive test of the exactness of the instrument dispersion relation, Eq. (1), is the direct measurement of the H^1 mass. This is done by using a "doublet" whose heavier member differs from the lighter member only by containing one additional hydrogen atom. Thus, such a doublet involves ions of two adjacent mass numbers. This test has been applied periodically during the past nine months and the average of 24 runs gives $H^1=1.008\,1443\pm13$. (Throughout this paper each error listed refers to the last significant figure of the particular result.) The error given is the statistical standard error only and does not include the resistance calibration uncertainty. It should be mentioned that, because of the interrelation between the way the resistors are combined in the resistance-

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

[2] Quisenberry, Scolman, and Nier, Phys. Rev. **102**, 1071 (1956).

[3] Scolman, Quisenberry, and Nier, Phys. Rev. **102**, 1076 (1956).

[4] Quisenberry, Scolman, and Nier, Phys. Rev. **104**, 461 (1956).

[5] C. F. Giese, Ph.D. thesis, University of Minnesota, Minneapolis, Minnesota, 1957 (unpublished).

calibration procedure and in these wide-doublet measurements, certain calibration errors cancel. Hence, the over-all resistance calibration uncertainty for these wide-doublet measurements is reduced to about 5 ppm. It is interesting to note that the relativistic correction to these measurements is +1 ppm. This correction has been included in the result stated above.

The good agreement between the value obtained and our final H^1 mass of 1.008 1451±2 amu suggests that the dispersion relation is correct to at least 2 ppm. However, the uncertainties present in the over-all resistance calibration force the inclusion of the calibration uncertainty error, 10 ppm, as part of the error associated with the results for all ordinary mass doublets.

Another test of the calibration is to compare the results of different doublets that give the same mass difference. This test was applied previously to this spectrometer,[2] and is repeated here using the mass difference CH_4-O.[6] The results of both the present and previous tests are listed in Table I. The doublet CH_4-O was not remeasured because the spectrometer was never operated in the mass-16 region during this test, and because of the good internal consistency between the other three measurements.

The internal consistency seems to be excellent for both sets of data. However, the discrepancy between the two sets is difficult to explain. Since this test measures the correctness of the calibration of ΔR only, it may be that the discrepancy lies in the calibration of R in one or both of the cases. Unfortunately the loss of the precision resistors previously used in ΔR prevents any meaningful investigation of this difference. Therefore we adopt, in light of the present excellent hydrogen-mass test results, the newer value as the correct one.

QUOTED ERRORS

The errors quoted for the doublet and mass results are based on the assumption that all observed deviations contributing to the uncertainty in the results are of a statistical nature. That this is not strictly true has been suggested previously,[7] and evidence seems to indicate that our errors are a factor of 2 or 3 smaller than they should be to explain all data inconsistencies as statistical fluctuations. We use the statistical approximation only because we have no better method with which an estimate of error may be obtained from the raw data.

TABLE I. Results of the CH_4-O mass difference measurements.

Doublet[a]	Mass	Mass difference in mMU Previous[b]	Present
CH_4-O	16	36.3931±9	. . .
C_2H_4-CO	28	36.3934±8	36.3960± 5
CH_3OH-O_2	32	. . .	36.3958±12
$\frac{1}{2}(C_3H_8-CO_2)$	44	36.3935±8	36.3966± 8
	Average	36.3933±5	36.3961± 5[c]

[a] See reference 6.
[b] See reference 2.
[c] Adopted as the final result. See text for discussion.

TABLE II. Doublet results used in the mass calculations.

Code	Doublet[a]	ΔM in mMU Previous[b]	Present
a	C_4-SO	33.0269±13	c
b	O_2-S	17.7599± 9	17.7623±11[d]
c	$\frac{1}{2}C_4H_4O-H_2S$	25.3926± 9	c
d	$\frac{1}{2}C_4H_4O-O^{18}O$	19.0367± 8	c
e	H_2O-O^{18}	11.4033±21	c
f	$D_2O-H_2O^{18}$	8.3102± 4	c
g	C_3-A^{36}	32.4729±20	unreliable[e]
h	$H_2O-\frac{1}{2}A^{36}$	26.7937± 6	unreliable[e]
j	CH_4-O (av)	36.3933± 5	36.3961± 5[d]
k	H_2-D (av)	1.5477± 4	c
l	$C_3H_4-A^{40}$	68.9344±13	68.9346±11
m	$D_2O-\frac{1}{2}A^{40}$	41.9390±13	c

[a] See reference 6.
[b] Taken from reference 2.
[c] Not remeasured in the present investigation.
[d] For the final value of this mass difference, see text.
[e] Remeasured and found to be unreliable. Previous values are also considered to be untrustworthy. See text and reference 5 for discussion.

Each doublet result is calculated from the average of 10 or more runs, where a run consists of 20 separate determinations of the ratio $\Delta R/R$ for the doublet, taken in 4 ways to minimize systematic effects due to the operator and the instrument. To obtain the final error the statistical standard error of the mean of these runs is combined with the values representing the resistance-calibration uncertainty. These are combined by taking the square root of the sum of the squares of the individual error components.

Because the resistance-calibration uncertainty is an estimated standard error, the final error values are only approximately standard errors. Experience shows, however, that a realistic limit of error may be obtained by multiplying the quoted error by a factor of 3 to 4, and we suggest strongly that this be done before comparing these mass results with other data where limit of error is used. Such an arbitrary factor has not been included in any errors given here.

C^{12}

All previous determinations of the C^{12} mass have involved results from two or more mass-doublet measurements. Five different doublet combinations were used to obtain the mass of C^{12} reported recently from this laboratory.[2] Remeasurement of several of the doublets used in this previous calculation stimulated a further examination of the earlier data, with several changes resulting from the analysis. In Table II the mass doublets necessary for the various cycle calculations are listed together with their measured results, both previous and present.

Doublet cycles yielding the C^{12} mass are summarized in Table III together with the cycle results obtained using both the older and the more recent doublet

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[6] Throughout this paper H, C, O, and S refer to the isotopes H^1, C^{12}, O^{16}, and S^{32}, respectively.

[7] A. H. Wapstra, Physica **21**, 367 (1955).

Table III. Doublet cycles yielding the C^{12} mass.

Cycle	Equation[a]	C^{12} mass in amu Previous[b]	 Present[c]
I	$C^{12}=12+\frac{1}{4}(a-b)$	12.003 8168±4	12.003 8162±4
II	$C^{12}=12+\frac{1}{2}(c-b)$	3 8164±6	omitted[d]
IIA	$C^{12}=12+\frac{1}{2}(a-c)$	not used[d]	omitted[d]
III	$C^{12}=12+\frac{1}{4}(2d-e-f-2k)$	3 8161±7	3 8161±7
IV	$C^{12}=12+\frac{1}{4}(g+j-2h)$	3 8197±6	omitted[d]
V	$C^{12}=12+\frac{1}{4}(l+j-2m-4k)$	3 8147±8	3 8155±8
	Average	12.003 8167±8	12.003 8159±4

[a] Lower case letters in the equations refer to doublets listed in Table II.
[b] Calculated from previous doublet values, Table II.
[c] Calculated from present doublet values, Table II, wherever possible.
[d] See text for discussion.

results listed in Table II. One change introduced by the new measurements is caused by the change in the CH_4-O mass difference. This affects Cycle V, raising the result.

In recent measurements involving the argon isotopes, the doublets C_3-A^{36} and $H_2O-\frac{1}{2}A^{36}$ were found to be unreliable and are therefore rejected in the present work (*g* and *h*, Table II).[5] This eliminates Cycle IV from present consideration.

Further, it was observed that Cycle IIA can be formed from the doublets C_4-SO and $\frac{1}{2}C_4H_4O-H_2S$ (*a* and *c*, Table II) to yield the C^{12} mass. This cycle was not included in the earlier analysis. When it is included in an unweighted average it combines with Cycle II, eliminating doublet *c* and leaving Cycle I. Because Cycle I is already included and because we will adopt the unweighted average as our final result, we reject Cycles II and IIA.

This leaves Cycles I, III, and V. Cycle I is changed by the new O_2-S measurement (doublet *b*). Cycle III is unchanged since no doublets involved in it were remeasured. The new cycle average gives a C^{12} mass of 12.003 8159±4, a value 0.8 μMU lower than the previous result. The major cause of the change is the rejection of Cycle IV, one which looked high previously but for which no reason for its rejection could then be found.

A better approach to the C^{12} mass was suggested by Kettner who proposed the doublet $\frac{1}{2}C_4H_4O-H_2O_2$. This doublet connects the C^{12} mass directly to the O^{16} standard with one measurement.[8] It has the advantages that both ions are molecular, thus eliminating the possibility of break-up energy complications; and that its separation is only 1 part in 4000 in mass. Such a narrow doublet demands less in the way of accuracy from the dispersion relation for a given final mass accuracy.

The singly charged H_2O_2 ions are obtained from hydrogen peroxide which, owing to its extreme reactivity, is difficult to pass into the spectrometer. Commercial hydrogen peroxide solution (30% H_2O_2) was concentrated by pumping away vapor from a sample until only about 10% of the original volume remained. Vapor from this concentrate was admitted to the spectrometer ion source through $\frac{1}{4}$-inch diameter aluminum tubing. The adjustable leak was simply a pinched-off portion of the tubing with an adjustable clamp. The doubly charged C_4H_4O ions are obtained from the organic chemical Furan.

The final result for this doublet is $\frac{1}{2}C_4H_4O-H_2O_2=7.6312\pm8$ mMU, yielding a C^{12} mass of 12.003 8156 ±4 amu. Data for this doublet were obtained over a period of about one year, the final result being the average of 32 runs.

The resultant value for C^{12} is in good agreement with the new cycle result of 12.003 8159±4, given in Table III. Because of the several reasons given above, we consider the result derived from the peroxide measurement to be more reliable than that from the cycles. We consider the cycle result to be an excellent confirmation of the over-all consistency of the doublet set. Because some doublets used in the cycles were not remeasured, and because cycle results introduce more potential sources of error, we adopt the peroxide-doublet result as the sole source for our final C^{12} mass. This chosen final value is listed in Table IV where it is compared with the earlier value. The mass value decreases slightly more than one error, an amount not surprising in view of the consistently small quoted errors.

H^1

The H^1 mass is determined, as it was previously, from the adopted C^{12} mass and the average result for the CH_4-O mass difference. The value obtained, $H^1=1.008\ 1451\pm2$ amu, is compared to the previous value in Table IV. The change in result is caused primarily by the change in the CH_4-O mass difference discussed above.

S^{32}

The S^{32} mass was determined previously using only the O_2-S doublet (*b*, Table II). The presently adopted value is calculated from an unweighted average of both the present and previous O_2-S doublet results together with the O_2-S mass difference obtained by substituting the derived C^{12} mass into the $\frac{1}{2}C_4H_4O-H_2S$ doublet (c, Table II). This doublet is the one eliminated by the rejection of the C^{12} cycles II and IIA. The average of the three values is $O_2-S=17.7612\pm9$ mMU, giving a S^{32} mass of 31.982 2388±9 amu. This value is adopted as the final result for S^{32} and is listed in Table IV.

Table IV. Masses of the secondary standards H^1, C^{12}, and S^{32}.

Isotope	Mass in amu Previous[a]	 Present[b]
H^1	1.008 1442±2	1.008 1451±2
C^{12}	12.003 8167±8	12.003 8156±4
S^{32}	31.982 2401±9	31.982 2388±9

[a] See reference 2.
[b] These adopted values are recommended for use in all calculations of atomic masses from mass-doublet data. Errors are standard error. Limit of error is estimated to be about three times the value shown. See text for error discussion.

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[8] M. E. Kettner, Phys. Rev. **102**, 1066 (1956).

CONCLUSIONS

The changes in these secondary masses, though larger than might first be expected from the magnitude of the quoted errors, are small when reflected into calculated atomic masses. Changes of the order of magnitude observed here have no significant effect on either the atomic masses derived from doublets measured on our instrument or the various conclusions drawn from the mass data.

The recent work of Smith gives a value for the C^{12} mass of 12.003 814 58±11 amu.[9] This value is in disagreement with our value by more than two errors, yet using either of the two together with the published doublet results to obtain atomic masses leads to the same conclusions regarding neutron and proton separation energies and pairing energies.

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[9] L. G. Smith, Bull. Am. Phys. Soc. Ser. II, 2, 223 (1957).

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Search for Monopole Pairs from the Second Excited State of C^{12}

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A thorough search for monopole pairs from the second excited state in C^{12} is described. No pairs could be detected and it is concluded that the question of the angular momentum and parity of this state cannot yet be considered as solved.

INTRODUCTION

THE second excited state of C^{12} at 7.68-Mev decays primarily by α emission leading to the ground state of Be^8 [1]; a cascade γ transition through the first excited state of C^{12} at 4.43 Mev has also been reported.[2,3] No direct γ transition to the ground state of C^{12} has been observed and an upper limit for the high-energy radiation is put at 4×10^{-4} of the cascade transitions.[2] In addition evidence was found[4] for electron-positron pair emission in a direct transition from the 7.68-Mev level to the ground state. The author investigated internally converted pairs from the 4.43-Mev level excited in the $Be^9(\alpha_{Po},n)C^{12}$ reaction[5] in a cloud chamber, and together with 70 pairs from the 4.43-Mev transition he found 7 pairs of about 6 Mev which he interpreted as pair radiation from the 7.68-Mev level. From the upper limit for γ emission in this transition as quoted above, the pair conversion coefficient would have to be of the order of unity or bigger to account for those pairs. This can only be the case if the transition is of the monopole type (the conversion coefficient would then be ∞). The 7.68-Mev state was therefore assigned zero angular momentum and even parity—the same as the ground state.

This is the only definite information one has, to date, on the angular momentum and parity of this state and the evidence in this work could not be considered conclusive. It was therefore thought desirable to look for these high-energy pairs with a counter system which could be expected to give a much greater yield of pairs than the cloud chamber procedure. An experiment of this nature is reported in this paper. The main results of this investigation have been presented at a meeting of the Israel Physical Society.[6]

APPARATUS AND EXPERIMENTAL PROCEDURE

In order not to complicate the apparatus unduly, it was decided to look just for electron (or positron) emissions, and not more specifically for pairs of given total energy.

The experimental arrangement is shown in Fig. 1. The source consisted of 50 mC of Po deposited on a Pt foil of 7 mg/cm², facing a piece of Be of 23 mg/cm². The energy of the electrons was measured in a NaI crystal which was covered by an Al foil 0.09 mm thick. The height of the pulses from the crystal was measured in a single-channel pulse-height analyzer and the output of the analyzer was gated by pulses from a thin-walled G.M. counter which was placed between the source and the crystal. In this way counts due to electrons produced inside the crystal were largely eliminated. A 0.05-mm brass absorber had to be placed in front of the counter to reduce the intense x-ray radiation from the source.

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[1] Miller, Rasmussen, and Sampson, Phys. Rev. 95, 649 (1954).

[2] Beghian, Halban, Husain, and Sanders, Phys. Rev. 90, 1129 (1953).

[3] R. G. Uebergang, Australian J. Phys. 7, 279 (1954).

[4] G. Harries, Proc. Phys. Soc. (London) A67, 153 (1954).

[5] α_{Po} indicates α particles from a Po source, i.e., at energy 5.3 Mev.

[6] Goldring, Wiener, and Wolfson, Bull. Research Council Israel 5A, No. 1, 87 (1955).